

COLL 1

Rationally designed peptoids insert into edge and face of bicelle structure

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The study of membrane-affiliated interactions is significant to the understanding of cell function, detecting biomarkers to diagnose disease, and testing the efficiency of new therapeutic targets. The amphiphilic character of membrane proteins makes them difficult to work with due to low stability. Model membrane systems can be used to stabilize membrane protein structure and maintain native activity. The model membrane system of focus in this study are bicelles, disc-shaped lipid bilayers created by combining long- and short-chain phospholipid pairs. We have developed a protocol to modify the chemistry at the edges and at the planar region of bicelles by incorporating peptoids, non-natural protein mimics. Peptoids are ideal for this application since a large diversity of side chains can be easily incorporated in a sequence-specific manner. In these preliminary studies two sequence of peptoids were designed to contain a lipophilic side chain at the C-terminus for interactions with the short and long-chain lipid tail groups to for the edge and planar modification, respectively as well as thiol groups at the N-terminus for characterization. Peptoid-bicelles were prepared by two methods: (1) peptoid added during bicelle formation and (2) peptoid added after bicelle formation. Method one produced the desired incorporation of peptoids into the edges of the bicelles while method two resulted in incorporation of peptoids into both the faces and edges of bicelle structure with no preference. Peptoid-bicelles were imaged using transmission electron microscopy and size analysis was performed by dynamic light scattering. The presence of peptoids in the edges and planar regions of the bicelles was confirmed by attachment of gold nanoparticles to the thiol groups within the peptoid sequence. Our results show that the designed peptoids incorporate preferentially into the edges and planar regions of the bicelles, respectively as expected. Further studies will be performed to analyze the surface using AFM and XRD.

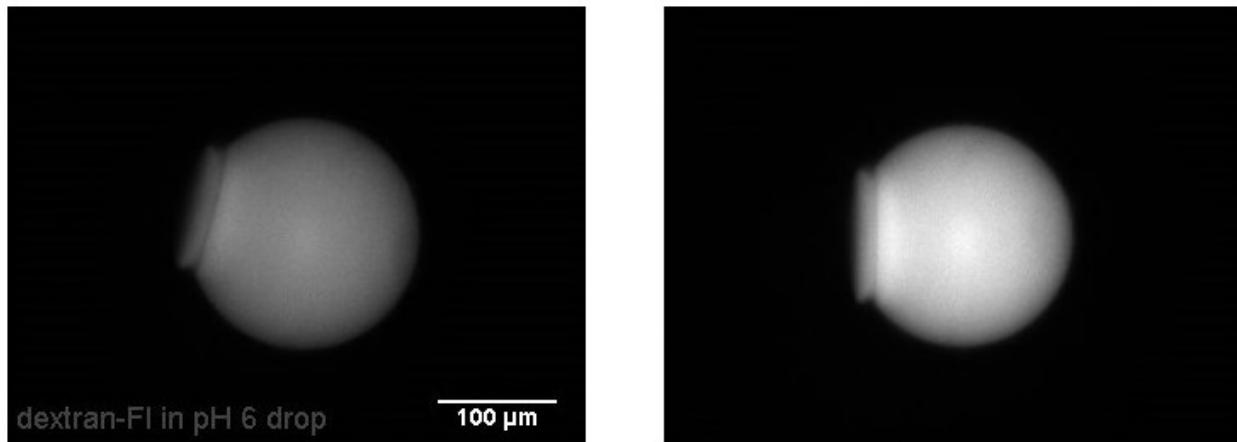
COLL 2

Transport across droplet interface lipid bilayers via a pH gradient

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The formation of lipid bilayers at the interface of adhering aqueous droplets in an oil matrix offers a unique route to study the biophysical properties of lipid bilayers and proteins associated with bilayers. In this presentation, we demonstrate an all optical platform to study the transport of protons across gramicidin pores in droplet interface bilayers (DIBs) via pH gradients. Several pH dependent fluorescent reporters are used.

Temporal plots of fluorescence signal using a ratiometric dye indicate a counterion effect on proton transport across these bilayers. We measure a rate constant for proton transport across such DIBs that is found to be dependent on the gramicidin concentration in the vesicles that were used to form the DIBs.



Detection of proton transport across droplet interface bilayers using dextran-fluorescein dye. An increase in the fluorescence signal of the pH 6 drop indicates proton transport from the pH 8 drop that is part of the droplet bilayer system but is not visible in the image since it does not incorporate a fluorescent indicator dye.

COLL 3

Second harmonic generation studies of water-soluble peptoids adsorbed to phospholipid membranes

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Peptoids (or N-substituted glycine oligomers) are a unique class of organic compounds that have exhibited pharmaceutical properties. Peptoids may promote or inhibit the activities of important protein receptors found in the plasma membrane. Unlike proteins and peptides, which have also been commercially used as drugs, peptoids are less susceptible to protease degradation and may exhibit enhanced biostability. A molecular-level understanding of how peptoids interact with phospholipids, the major component of cell membranes, will allow us to gain a better understanding of the physical interactions between peptoids and plasma membranes. We monitored the adsorption of a water-soluble peptoid, which contains five naphthalene substituents, to supported lipid bilayers composed of either saturated or unsaturated phospholipids using second harmonic generation (SHG). We discovered that adsorption of peptoids to lipid bilayers varies with temperature and quantified thermodynamic forces that drive peptoid adsorption to artificial cell membranes.

COLL 4

Lipid structure, lateral order and inter-membrane forces

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Using solution x-ray scattering and advanced analysis tools, developed in our lab, we are investigating the high-resolution structure of charged and dipolar lipids under various aqueous solution conditions. These conditions include, different salt solutions containing monovalent, multivalent, or polyvalent ions, as well as ionic liquids. We determine the electron density profile along the normal to the membrane plane and the spacing between bilayers when lamellar phases form.

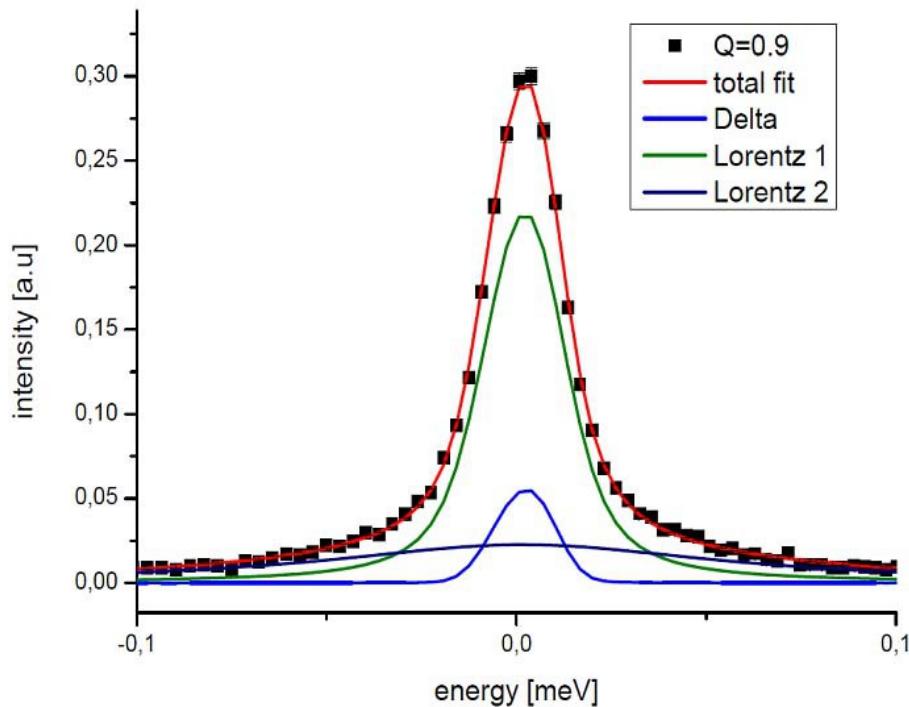
Using the osmotic stress method, we are determining the forces between these bilayers under different conditions and compare with the predicted interactions based on thermal fluctuations and a modified Poisson Boltzmann theory. This comparison reveals the extent of ion dissociation, entropic effects, membrane elastic properties, and the non electrostatic interactions between the ions and the lipid membranes. We are also revealing the lateral order within the bilayers, using solution wide angle x-ray scattering experiments and our advanced analysis tools.

COLL 5

Probing model membrane local dynamics

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Local dynamics of phospholipids are effected by various parameters as temperature, pressure, hydration or additives. In recent years neutron scattering has probed this dynamics at various time and length scales in the nano- to picosecond time range. We will show the influence of small molecules as short chain alcohols and cholesterol on the phospholipid local dynamics as probed by elastic and inelastic neutron scattering. By these methods local diffusion coefficients and motions are derived as well as thermodynamic parameters.



QENS data of lipid/alcohol mixture.

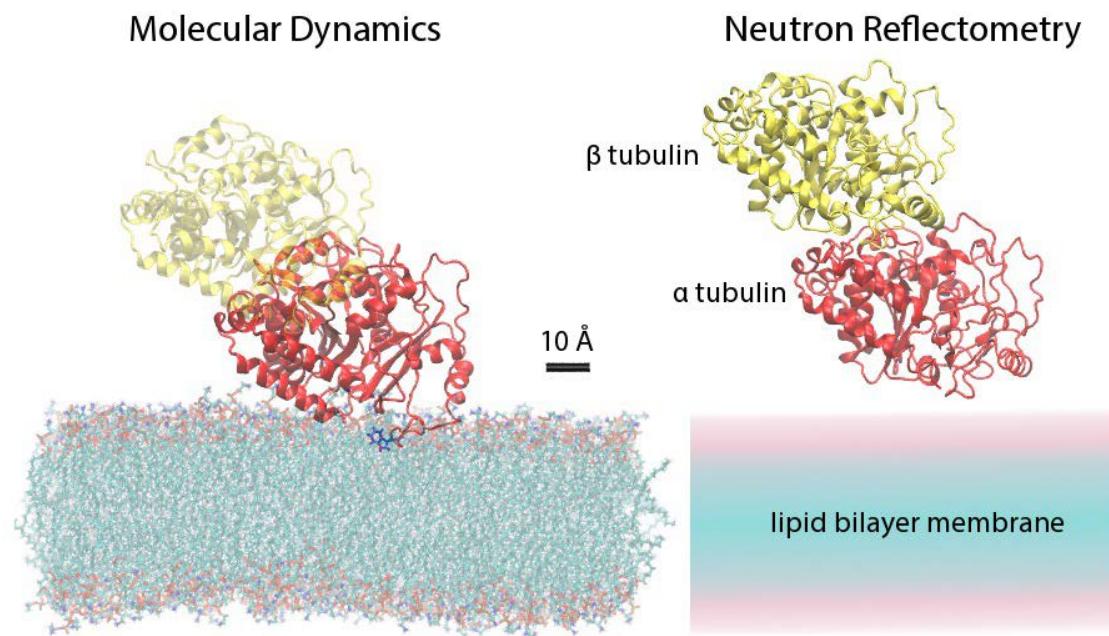
COLL 6

Tubulin on biomimetic mitochondrial membranes: Structural features and identification of lipid binding domain

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Dimeric tubulin, an abundant cytosolic water-soluble protein, has emerged as an important regulatory factor of the permeability of the voltage-dependent anion channel (VDAC) in the mitochondrial outer membrane, with implications for mitochondrial energetics as well as the Warburg effect observed in cancer cells. A wealth of recent *in vitro* and *in vivo* evidence points to a mechanism of this regulation in which a charged C-terminal tail of tubulin occupies the water-filled VDAC pore, thus blocking metabolite fluxes through this passive transport channel. The membrane-binding properties of tubulin have proven difficult to ascertain, as early work generated contradictory results regarding the tubulin-membrane association, including whether it was integral or peripheral in nature. Here we report on a comprehensive biophysical study of tubulin

binding to biomimetic lipid membranes with compositions that mimic the mitochondrial outer membrane. A combination of surface plasmon resonance, bilayer overtone (second harmonics) analysis, and single-channel recordings show that tubulin distinguishes between lamellar and non-lamellar lipid components of the membrane. A multisite binding model captures the essential features of the lipid-dependent binding and allows an estimation of the free energy of binding. To obtain the structural features of the tubulin heterodimer on the membrane surface, we have employed neutron reflectometry (NR) of tubulin on a tethered bilayer lipid membrane platform. The NR results definitively show that tubulin binds peripherally, and in combination with molecular dynamics (MD) simulations suggest the binding domain to be a highly conserved amphipathic α -helix on α -tubulin. Thus tubulin joins a short but growing list of amphitropic proteins that target cell and organelle membranes by sensing lipid packing defects via amphipathic α -helices, suggesting a pathway by which lipid homeostasis regulates mitochondrial function.



COLL 7

Cell-free expression of biologically active integral membrane protein

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Integral membrane proteins (IMPs) are becoming increasingly important therapeutic targets. Despite their significant role in the drug discovery process, it's extremely challenging to express, purify, and *in vitro* stabilize IMPs. Cell-free transcription-translation system (TX-TL) has emerged as a promising alternative for producing complex proteins, but they are still not a viable option for expressing IMPs due to

improper post-translational folding of these proteins. We are studying key factors influencing *in vitro* folding of TX-TL-expressed IMPs, particularly oligomeric proteins (*i.e.*, ion channel). Using a chimeric ion channel, KcsA-Kv1.3 (K-K), as a model IMP, we have investigated several physiochemical determinants including artificial bilayer environment (*i.e.*, lipid, detergent) for K-K *in vitro* stabilization. Our results indicate that anionic lipids (*i.e.*, DMPG), are required for correct folding of TX-TL-expressed monomeric K-K into tetramer, underscoring the importance of lipid-protein interaction in maintaining structural-functional integrity of ion channels. Additionally, we have observed that fusion of ‘superfolder’ green fluorescent protein (sfGFP) to K-K as a protein expression reporter, not only improves the protein yield, but surprisingly facilitates the K-K tetramer formation probably by enhancing the solubility of monomeric K-K.

COLL 8

Determining the mRNA nanoparticle structure using SANS and SAXS

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Messenger RNA (mRNA) is pioneering the development of an entirely new class of drugs which shows much promise in biotherapeutics. This novel drug platform builds on the discovery that modified mRNA can direct the body’s cellular machinery to produce nearly any protein of interest. Once delivered, modified mRNA can direct ribosomes to express proteins or antibodies within targeted tissues, thereby harnessing the body’s own cellular machinery to produce the broadest possible array of therapeutics across diverse therapeutic areas and across numerous routes of administration for serious diseases that are not treatable today. In order for mRNA to reach the cellular apparatus, it must be protected from degradation mechanisms that rapidly inactivate mRNA, such as enzymatic degradation by RNases that are ubiquitous in the environment and body. To overcome these degradation pathways, we have chosen to physically encapsulate the mRNA in nanoparticles so that the mRNA payload can safely reach its cellular target. The overall structure of these nanoparticles is obtained through the simultaneous model fitting of small angle neutron scattering (SANS) data collected by varying neutron scattering length density (NSLD) of the solvent (*e.g.* different ratios of H₂O to D₂O). In addition, small angle x-ray scattering (SAXS) further validates the SANS results, providing insights into the mRNA structure within the nanoparticle.

COLL 9

How is the metal precursor reduced during a synthesis of colloidal nanocrystals?

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A typical synthesis of colloidal metal nanocrystals involves the reduction of a salt precursor. Despite the remarkable progress in recent years, it is still unclear how the precursor is reduced to atoms for their evolution into nuclei, seeds, and then nanocrystals. It has been challenging to resolve such a process due to the lack of characterization tools. In general, the precursor can be reduced to atoms in the solution phase, followed by their deposition on the surface of a growing nanocrystal.

Alternatively, the precursor can adsorb onto the surface of a growing nanocrystal, followed by reduction through an autocatalytic surface growth process. With Pd as a typical example, we have designed a set of kinetic experiments to resolve on the reduction pathway undertaken by a salt precursor during the growth of metal nanocrystals. Based on the quantitative analysis, we found that the pathway has a strong dependence on the reduction kinetics involved. Specifically, the precursor was reduced on the surface of a growing nanocrystal under a slow kinetic whereas it was reduced in the reaction solution at faster reaction rates. We also demonstrated the switching of reduction pathway by manipulating the reaction parameters such as the type of precursor used and the reaction temperature, to modulate the reaction kinetics.

COLL 10

Crystal phase-controlled synthesis of novel noble metal nanomaterials

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In this talk, I will summarize the recent research on the crystal phase-controlled synthesis of novel noble metal nanomaterials in my group. It includes the first-time synthesis of hexagonal-close packed (*hcp*) Au nanosheets (AuSSs) on graphene oxide, surface-induced phase transformation of AuSSs from *hcp* to face-centered cubic (*fcc*) structures, alternating *hcp/fcc* Au square-like plates from AuSSs, ultrathin Au nanowires containing *hcp* phase, synthesis of ultrathin *fcc* Au@Pt and Au@Pd rhombic nanoplates through the epitaxial growth of Pt and Pd on the *hcp* AuSSs, respectively, the first-time synthesis of 4H hexagonal phase Au nanoribbons (NRBs) and their phase transformation to *fcc* Au RNBs, the epitaxial growth of Ag, Pt, Pd, PtAg, PdAg, PtPdAg, Rh, Ir, Ru, Os and Cu on 4H Au NRBs to form the 4H/*fcc* Au@metal core–shell NRBs, and the synthesis of 4H/*fcc*-Au@metal sulfide core–shell NRB heterostructures. Currently, my group focuses on the crystal phase-based applications in catalysis, surface enhanced Raman scattering, waveguide, photothermal therapy, etc., which we believe are unique. Importantly, the concept of crystal-phase noble metal heterostructures is proposed.

COLL 11

Synthesis of branched and polyhedral Pd-Cu nanostructures by seed-mediated co-reduction

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Metal nanoparticles (NPs) are of great interest for applications in catalysis, electronics, and chemical sensing. Their utility is dictated by compositional and physical parameters such as particle size, particle shape, composition, and overall architecture (e.g., hollow vs. solid). Interestingly, the addition of a second metal to create bimetallic NPs adds promising multifunctionality, with new emergent properties. However, reliably synthesizing bimetallic NPs remains a great challenge. One synthetic pathway to architecturally controlled bimetallic NPs is seed mediated co-reduction (SMCR) in which two metal precursors are simultaneously co-reduced to deposit metal onto shape-controlled metal seeds. Previously demonstrated using a Au-Pd system, here SMCR is applied to a system with a larger lattice mismatch between the depositing metals: Pd and Cu (7% mismatch for Pd-Cu vs. 4% for Au-Pd). Through manipulation of precursor reduction kinetics, the morphology and bimetallic distribution were tuned to achieve 8-branched Pd-Cu NPs with Cu localized at the tips and Pd-Cu alloy nanostructures. Significantly, the symmetry of the seeds can be transferred to the final nanostructures. By expanding the compositional range for bimetallic deposition, the synthesis of new structurally defined nanostructures should be possible and allow for the composition-dependent properties of these materials to be studied and applied.

COLL 12

Solvent effect on ligand-metal interactions in Pd nanoparticle synthesis

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Metal nanoparticles have been attracting considerable attention over the past decades, because of their unique electronic, catalytic and optical properties that are found highly dependent on the size and shape. To minimize trial and error and realize controlled synthesis with desired nanoparticle morphologies and specific properties, we need a better understanding of the interactions between the metal, ligands and solvent system and their effects on the synthesis mechanism and kinetics. We will present our study on investigating the effect of solvents on ligand-metal interactions and how the solvent can be used to control the synthesis of Pd nanoparticles of specific sizes. By combining in-situ small-angle X-ray scattering (SAXS), X-ray absorption fine structure spectroscopy (XAFS) and nuclear magnetic resonance (NMR) techniques, we show that the

coordinating ability of solvents affects the ligand-Pd interactions, resulting in different nucleation and growth kinetics and final sizes (4.2 nm in pyridine, a coordinating solvent, and 1.3 nm in toluene, a non-coordinating solvent). Furthermore, using these insights, we systematically varied the solvent properties to synthesize Pd nanoparticles of sizes ranging from around 1 nm to 5 nm with low polydispersity (~10-15%). We will show the correlation between the solvent properties and ligand-metal interactions, and how they can affect the kinetics and final size. The results provide a better understanding of the critical solvent and ligand effects on the synthesis kinetics and show the potential for tailoring the solvent-ligand-metal interactions to realize controlled synthesis of metal colloidal nanoparticles without trial and error.

COLL 13

Colloidal synthesis of anisotropic noble metal nanostructures

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Over the past decades, colloidal synthesis of various nanostructures with controllable morphology and desired properties has attracted much attention. Although much efforts has been devoted to understanding the synthetic mechanism of diverse nanostructures, it is still a big challenge to find a universal mechanism that can be applied to various systems. In this presentation, we will present our recent efforts in the colloidal synthesis and mechanistic study on noble metal nanostructures, including gold and silver. An oxidative etching has been used to prepare noble metal nanostrctures with designed shape and surface plamon resonance (SPR) properties. The application of such nanostructures in many fields, including catalysis, SERS, and phototherapy, will be introduced.

COLL 14

Salt-triggered deposition of polymer-coated noble metal nanoparticles on solid surfaces

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We report on a simple, generally applicable method for depositing gold and silver nanoparticles on a wide variety of solid surfaces under all aqueous conditions. Noble-metal nanoparticles obtained by citrate reduction followed by coating with thermoresponsive polymers spontaneously form a monolayer-like structure on a wide variety of substrates in presence of sodium chloride whereas this phenomenon does not occur in salt-free medium. Interestingly, this phenomenon occurs below the cloud point temperature of the polymers and we hypothesize that salt ion-induced screening of electrostatic charges on the nanoparticle surface entropically favors hydrophobic association between the polymer-coated nanoparticles and a hydrophobic substrate.

COLL 15

Exotic syntheses of supported metal nanoparticles via metal-in-Li solutions

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Metal nanoparticles (NPs) have generated a wide range of new research disciplines in heterogeneous catalysis, plasmonic optics, drug carrier, and sensors etc. According to the phase diagrams of Li with other metals, all main group metals, all precious metals and some other transition metals can be dissolved in molten Li at temperature not too much above the melting point (m.p.=183 °C) of Li. Using this method, we demonstrated the synthesis of catalytic Pt NPs by dissolving bulk Pt (m.p.=1768 °C) in molten Li at 220 °C. After cooling down the Pt-in-Li solid solution and converting the metal Li to LiOH in air, Pt NPs of ~2 nm are formed. Then, by mixing the Pt-containing LiOH with any water-insoluble support materials, such as carbon black, the Pt NPs can be collected onto the desired support material via leaching off the LiOH with water under ambience. Often, atomically intermixed metal nanoalloys are desired for tailored selectivity and/or enhanced activity in catalysis and tenability in plasmonics. Our method can also be extended to synthesizing supported atomically intermixed nanoalloys by directly dissolving the bulk alloys such as Pd₃Ag nanoalloys in molten lithium, followed by the aforementioned processes. Furthermore, the versatility of this method is further extended by dissolving two different bulk metals, e.g. Pd and Pt, in molten lithium to obtain their corresponding supported PdPt nanoalloy. The method is further pushed to call a combination of a precious metal with a non-precious metal with large redox potential difference, such as Pd and Zn, atomically intermixed PdZn nanoalloy can be synthesized via their solution in molten lithium.

This metal solution-based method circumvents the chemical complications in the synthesis of precursory metal ions, and avoid the use of organic solvents, surfactants, and reducing agents. LiOH, as the only by-product can be sustainably recycled as it is exactly the raw material in Li production industry. The method provide more flexible selection on support materials and is capable of producing true atomically intermixed nanoalloys (not core-shelled) with compositional metals having large difference in their standard reduction potentials so as to bypass the complications in make such nanoalloys based on conventional ion-reduction methods e.g additional tuning of the precursors, surface charge of support, annealing etc.

COLL 16

Seeded growth of catalytically active copper-based nanostructures

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Seeded growth is a robust approach to synthesize bimetallic and multi-metal nanostructures. Different configurations of nanostructures could be controlled by the

geometry of the seeds and the growth rate of the secondary components. While numerous studies have shown the success in tailoring the morphology of bimetallic noble metals using the seed-mediated method, applications of this method involving $3d$ transition metals are limited. In this talk, seeded growth of copper-based nanostructures will be presented involving both the use of noble metal and copper nanoparticles as seeds. By tuning the reaction rate, the deposition of the second metals could site-selectively occur on specific facets of the seeds. In addition, the diffusion rate of the dissimilar metals increases with increased temperature, thereby dictating the conversion between core-shell/heterostructures and alloy/intermetallics. *In situ* heating and cooling electron microscopy study on individual nanostructures will also be discussed. These copper-based nanostructures are catalytically active for methanol electro-oxidation. A comparison study of structure and composition effects on the electrocatalytic activities will also be presented. The electron coupling effects on the oxidation states of the different components in the copper-based nanostructures will be discussed to provide some guideline for rational design of next-generation electrocatalysts.

COLL 17

Designer noble metal nanostructures: Controlled synthesis and beyond

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Metal nanostructures have been studied quite extensively in the research area of heterogeneous catalysis long before the introduction of the concept of nanoscience and nanotechnology. The significant progress achieved in the past twenty years in chemical synthesis has enabled exquisite control over not only the size but also the shape of the metal nanostructures, and therefore attracted intense interest not only in catalysis but also optoelectronics due to the well-known effect of localized surface plasmon resonance. The main challenges in the field are now beyond synthesis. In this presentation, I will introduce our recent progress in the stabilization, assembly, and functionalization of the metal nanostructures. I will first focus on reviewing our efforts in synthesis of metal nanostructures and their stabilization by alloying, physical confinement, and surface modification, along with their excellent performance in sensing and catalysis. Then I will report the assembly and disassembly of plasmonic metal nanostructures and the associated opportunities in the development of novel optical devices such as stress-responsive colorimetric sensors that can memorize the stress that the system has experienced. Finally, I will introduce the dynamic optical control enabled by the orientational dependence of surface plasmon resonance of anisotropic nanostructures.

COLL 18

Surface science meets homogeneous catalysis: Cooperative properties of electrophilic organometallic ensembles

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When chemisorbed upon certain metal oxide surfaces, the reactivity of many types of organometallic molecules is dramatically enhanced. High activities for a variety of catalytic olefin reactions are illustrative consequences of this altered reactivity. This lecture focuses on intricate non-covalent and covalent multi-center interactions that modulate these catalytic processes, focusing primarily on olefin polymerization. Specific interrelated topics include: 1) Catalytic chemistry of mononuclear and multinuclear group 4 catalysts anchored on/activated by surfaces versus those in homogeneous solution, 2) Catalytic chemistry and cooperativity effects in multinuclear group 4 catalysts in homogeneous solution, 3) Catalytic chemistry and cooperativity effects in multinuclear groups 4 and 6 catalysts in homogeneous solution, 4) Definitive structural characterization of these catalysts on “super-acidic” surfaces, and the scope of their catalytic properties. It will be seen that the information obtained from these studies leads to design rules for next-generation homogeneous and supported catalysts, and for novel and useful polymerization and hydrogenation processes.

COLL 19

First-principles, microkinetic modeling, and experiments for reaction mechanisms and improved catalysts

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Using a combination of first-principles calculations, microkinetic modeling, and reactivity experiments, we establish a rigorous framework for developing a fundamental mechanistic understanding of chemical reactions catalyzed by heterogeneous catalysts. First, and through an iterative process between these three components of our research, we demonstrate unique insights derived on the nature of the active site. Then, based on that understanding, and insights derived for the importance of atomic-scale structure sensitivity, we show how we can provide guidance to inorganic synthesis for preparing shape- and composition-selected alloys which are predicted to hold promise for improved activity and selectivity for the reactions of interest. Examples may cover vapor phase catalysis and/or electrocatalysis.

COLL 20

Sum frequency generation microscopy of surfaces

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Sum frequency generation spectroscopy (SFG) is a useful technique to study molecular properties of surfaces. As a second-order technique it is uniquely sensitive to the average organization of molecules at the surface. However, as most surfaces are

spatially heterogeneous, it is difficult to interpret the spectrum as single domain. The development of SFG into a microscopy has allow a more detailed and accurate analysis of the spatio-spectro-temporal evolution of the surface chemistry. The SFG microscope development will be presented, as well as the use of compressive sensing and the application toward corrosion inhibition and self-assembled monolayers.

COLL 21

Surface spectroscopy and surface microscopy of catalytic processes: From model to technological materials, from UHV to *operando* conditions

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Our group's philosophy is to study catalytic surface reactions on heterogeneous catalysts *via a two-fold approach*, employing both *surface science based planar model catalysts* as well as *industrial-grade catalysts*. For both, the focus is on examining *active functioning catalysts* under *operando* conditions, at (near) atmospheric pressure and at elevated temperature.

In particular for ultrahigh vacuum (UHV) based model catalysts that has been a challenge, requiring application of *in situ surface spectroscopy*, such as sum frequency generation (SFG) laser spectroscopy, polarization-modulation infrared reflection absorption spectroscopy (PM-IRAS) and near atmospheric pressure x-ray photoelectron spectroscopy (NAP-XPS). To image ("see") ongoing surface reactions by *in situ surface microscopy*, photoemission electron microscopy (PEEM) was applied to polycrystalline samples. For technological catalysts, analogous *operando* studies were performed by Fourier transform infrared spectroscopy (FTIR), X-ray absorption spectroscopy (XAS), NAP-XPS, and X-ray diffraction (XRD). Most of the *operando* studies were performed at synchrotron sources (BESSY (DE), MaxLab (SE), SLS (CH)), and in lock-step with theory.

This two-fold approach yields a more "holistic" view of the catalytically relevant atomic and electronic surface structure of catalysts, as well as of molecular details that steer reaction activity and, even more important, reaction selectivity. Comparing surface science based single crystals with nanoparticle model catalysts elucidates the *materials gap*, and comparing UHV to ambient pressure studies reveals the *pressure gap*. In particular, synergisms between studies on model and technological catalysts often provide access to atomistic details.

Among the systems studied are

- i) CO oxidation and H₂/CO/O₂ reaction (PROX) on supported and unsupported noble metals, Co₃O₄ and CoO thin films UHV-grown on Ir(100), and commercial cobalt oxides,
- ii) methane reforming on Ni-ZrO₂ and CuNi-ZrO₂, employing an ultrathin ZrO₂ trilayer (O-Zr-O) film on Pt₃Zr(0001) as well as commercial ZrO₂ as support.

For all, the *operando* studies identify the relevant surface processes, providing further atomistic insight on dynamics, such as changes of the surface and bulk oxidation state

(oxygen vacancy formation), metal-support interface effects, reaction-induced surface segregation, surface hydroxylation, adsorbed species, and others.

COLL 22

Vinyl acetate formation pathways and selectivity on model metal and alloy catalyst surfaces

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Surface reaction pathways are explored on model single crystal catalyst surfaces using a combination of surface science experiments in ultrahigh vacuum, in-situ monitoring of the surface intermediates during reaction, and by using density functional theory (DFT) calculations. This approach enables detailed reaction pathways to be obtained and is illustrated using palladium- and palladium-gold alloy catalyzed synthesis of vinyl acetate monomer (VAM) from a reaction between adsorbed acetate and gas-phase ethylene. It is shown that vinyl acetate is formed on a Pd(111) model catalyst via the so-called Samanos pathway, where reaction is initiated by coupling between ethylene and surface acetate species to form an acetoxyethyl intermediate that decomposes by a rate-limiting β -hydride elimination step to form VAM. The way in which the adsorbate coverage controls both reactivity and selectivity is also discussed. Gold-palladium alloys are found to improve the selectivity of the commercial catalyst. The origins of the catalytic selectivity and activity of the alloys are also investigated by exploring reactions on well-characterized Au/Pd(111) and Au/Pd(100) model alloys as a function of the gold coverage in the alloy. In particular, a change in the rate-limiting step in the Samanos pathway from the β -hydride elimination step being rate limiting to the coupling step being rate limiting is found as the gold coverage increases and is ascribed to a combination of electronic, geometric and coverage effects.

COLL 23

Surface science for the 21st century

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Over the past century the science of surfaces has undergone an enormous progress. The atomic and electronic structure, reactivity, and dynamics of many material surfaces have been uncovered. Several Nobel prizes have marked the great accomplishments of our predecessors, from I. Langmuir in 1932 to G. Ertl in 2007. This progress has been fostered and propelled by the continuous development of powerful techniques that have provided atomic and molecular level details of surfaces, adsorption and desorption phenomena, vibration and electronic spectra, electron diffraction and real space imaging by the Scanning Tunneling Microscope. The nature of many techniques has constrained Surface Science to ultra-high vacuum environments, and often under

cryogenic temperature to achieve measurable coverage of weakly bound adsorbates. And yet practical surfaces are surrounded by gases and liquids at ambient conditions of pressure and temperature. Under these conditions the surfaces are covered with dense layers of adsorbed molecules in equilibrium with the gas phase, while the relevant ambient temperature unlocks many kinetic processes that are frozen at low temperatures. I will review the physics and chemistry of surfaces with dense layers of adsorbates and show new phenomena that derive from this, including the effect of reactant gases such as C₂H₄, CO, and CO₂ on the structure of Pt and Cu surfaces. Prospects for similar studies of the solid-liquid interface, a new frontier in the field, and their impact in environmental science, electrochemistry and energy storage will be discussed.

COLL 24

Lowering friction while saving the world: New approaches to lubrication

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The number of possibilities for enhancing the tribological properties of lubricating oils has expanded significantly over the last decade. On the one hand, the drive to reduce sulfur, phosphorus, and metals in oils (in order to protect emission-control catalysts) has intensified, and a number of options are being explored, including the use of metal-free additives and the introduction of additives based on boron. On the other hand, radically new approaches have been examined, including the addition of ionic liquids to oil blends and the coating of sliding surfaces with polymer brushes. While both the latter approaches appear promising, they bring with them their own challenges, including the effects of water on ionic-liquid performance, and the need to protect brush systems from wear.

COLL 25

Thermal and shear effects in boundary film formation

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The formation of a boundary films by reaction with a gas-phase lubricant or lubricant additive occurs in several steps that involve the initial reaction of the lubricant molecule on the surface, followed by shear-induced decomposition and formation of the boundary film. Fully understanding this sequence of steps will enable the structure of the additive molecule to be related to the nature of the resulting boundary lubricating film. Systems are studied for which the interface is at thermodynamic equilibrium to allow kinetic models to be applied.

The first regime for which the system is in thermodynamics equilibrium is when the

interfacial temperatures are high (~1000 K), so-called extreme-pressure (EP) lubrication. Here, the film formation pathways are dominated by thermal reactions at the surface and is illustrated for small chlorinated hydrocarbons reacting with iron.

The second regime occurs under mild sliding conditions where the temperature rise is small. The tribochemistry in this regime investigated by carrying out friction measurements in ultrahigh vacuum, by analyzing the composition in the wear track region using Auger spectroscopy and by detecting gas-phase products evolved during sliding and is illustrated by the gas-phase lubrication of copper by dialkyl disulfides. They initially form thiolate species and shear causes sulfur and some carbon to penetrate the substrate to form a boundary film that reduces friction. The reaction rate constants for these elementary step reactions can be measured for a monolayer of methyl thiolate species on the surface. It is assumed that similar reactions occur during gas-phase lubrication where the clean surface produced by rubbing is replenished with thiolate species by reaction with the gas-phase lubricant. The kinetic equation for this process are solved analytically to predict the variation in friction coefficient as a function of the number of sliding passes that is in excellent agreement with experiment.

COLL 26

Measuring atomic wear of graphene using local stress and heat

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Here we investigate the chemical dynamics of local graphene oxide reduction through the application of local temperature and stress using a heated atomic force microscope (AFM) tip. A Si AFM cantilever with an embedded Joule heater applies local stress and heat to chemically functionalized graphene during sliding. The friction of the graphene sheet depends linearly on percent chemical group surface concentration, so monitoring friction force during chemical reduction provides an *in situ* measure of chemical functionality on the surface over time. We first demonstrate bond cleavage of oxygen, fluorine, and hydrogen from graphene using solely force from the AFM tip. We then investigate the application of local temperature and force during tip sliding on graphene oxide. Monitoring friction over time for tip temperatures between 310–355°C and loads <40 nN provides the kinetics of the reduction process. Calculating reaction rate as a function of temperature assuming a first order reaction provided an activation energy for bond scission of 0.7 ± 0.3 eV, where measurement noise contributed significantly to error and precluded determination of reaction order. In an effort to reduce measurement time and error, friction was measured as a function of load during linear temperature ramps of the tip heater. Such a measurement is analogous to thermogravimetric analysis or temperature programmed desorption (TPD), resulting in an activation energy of 0.62 ± 0.07 eV and a reaction order $n \sim 1$. It was further shown that applied force non-linearly reduces the observed activation barrier, at odds with the prevailing models of

atomic scale wear. Quantitatively, the results conflict with TPD experiments where graphene oxide reduces via a 2nd order recombination reaction with activation energies significantly exceeding 1 eV. We propose an alternative reduction mechanism where the temperature rise at the tip promotes diffusion of molecules. This mechanism is physically intuitive, as adsorbed species can no longer contribute to friction once excited above the diffusion energy barrier. Thus, we showed that heated AFM tips can simultaneously drive and measure chemical reactions on 2D surfaces, provide quantitative measures of the kinetics of those reactions, and induce reactions which would otherwise not be possible during bulk processing. Such exquisite thermomechanical control over local surface chemistry will impact nanofabrication efforts and fundamental studies of surface chemistry.

COLL 27

Tribochemistry of GaN, a surprisingly wear resistant semiconductor

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Surface chemistry of GaN has been studied for decades; however, most of these studies are based on static chemical/physical interactions. The act of sliding on GaN results in unexpectedly low wear (approaching wear rate of diamond) and triggers equally surprising reaction products and pathways. This study focuses on (1) how sliding interaction affects surface chemistry and (2) wear mechanism of GaN. Experiments revealed that, the wear rate of GaN spans orders of magnitude depending on environment. Several state-of-the-art characterization techniques, including XPS, scan Auger, SEM and TEM, were employed to analyze the surface after wear test and link the surface reaction to environment dependence.

COLL 28

Optimization of a ReaxFF reactive force field for modeling tribocatalytic reactions of Cu-S and Cu-thiol/ alkoxy systems

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We have optimized a new ReaxFF reactive force field parametrization for Cu-S, Cu-thiol and Cu-alkoxy to enable molecular dynamics simulations of the thermal and shear-induced reaction kinetics of OCH₃ and SCH₃ on copper surfaces. Based on previously-developed Cu-water ReaxFF parameters, Cu-S bond, valence angle, and torsional

parameters were added and parameterized in order to reproduce accurate energy barriers for surface and sub-surface adsorption, heat of formation, and the crystal structure properties of CuS, CuS₂, and Cu₂S phases. In addition, the parameters for binding energy, adsorption and desorption, and decomposition of thiol and alkoxy molecules on the copper surfaces were included and optimized using density functional theory. This new force field has been used to study the tribochemistry of adsorbed thiolate and alkoxy species in a sliding copper interface. The reaction pathways for molecular decomposition and dissociation were followed to explore the shear-induced reactions.

COLL 29

Tribochemical aspects of mechanical mixing in tribological contacts

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During sliding of surfaces the near surfaces undergo significant changes in terms of topography, composition and microstructure and a so-called “third body” or “tribomaterial” forms which is largely different from the bulk material in terms of topography, composition and microstructure. The third-body formation strongly influences the frictional and wear behavior of the system. By using in-situ tribometry and surface analytical techniques such as XPS, Focused Ion Beam Analysis and nanoindentation we gained insight into the third body formation of tungsten sliding against diamond-like carbon coatings and diamond.

COLL 30

Effect of hydrogen and oxygen partial pressure on the tribochemistry of silicon oxide-containing hydrogenated amorphous carbon

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Among the variants of diamond-like carbon films developed for the ever-increasing performance and durability requirements of tribo-mechanical applications, silicon oxide-containing hydrogenated amorphous carbon (a-C:H:Si:O) is of interest as it exhibits good tribological performance across a broader range of environments compared to hydrogenated amorphous carbon, and higher thermo-oxidative stability. However, the scientific basis for this improved behavior is not established. In this work, we develop a fundamental understanding of the structural transformations occurring in a-C:H:Si:O when sliding against steel in different environments (from high vacuum to controlled hydrogen and oxygen pressures). The results of tribological experiments revealed that upon increasing the oxygen pressure in the experimental chamber from 10 mbar to 1000 mbar, the coefficient of friction increased from 0.02 ± 0.01 to 0.06 ± 0.01 , whereas upon increasing the hydrogen pressure from 50 mbar to 2000 mbar, the coefficient of friction decreased from 0.08 ± 0.01 to 0.02 ± 0.01 . The subsequent near edge X-ray absorption fine structure (NEXAFS) spectroscopic measurements and X-ray photoelectron spectroscopy (XPS) analyses provided insights into the structural transformations and chemical reactions occurring in a-C:H:Si:O upon sliding. Independently of the gas, a stress-induced conversion from sp^3 - to sp^2 -bonded (disordered) C-C bonds occurs. When sliding in hydrogen, the newly-generated, strained sp^2 carbon layer reacts with hydrogen molecules to form a hydrogenated amorphous carbon interfacial material. Upon increasing the hydrogen pressure, the fraction of C-H bonds increases in the near-surface region of the wear tracks formed on a-C:H:Si:O. This is proposed to progressively lower the shear strength of the material at the sliding interface, thus resulting in a decrease of friction with hydrogen pressure. When sliding in oxygen, the dissociative reaction of oxygen molecules with strained sp^2 C-C bonds leads to the formation of C=O groups. Additionally, increasing the oxygen pressure during tribological testing leads to an increase in oxygen concentration in the near-surface region of a-C:H:Si:O together with an increase in the fraction of Si atoms in high oxidation states. These surface chemical changes and structural transformations are proposed to increase friction with oxygen pressure by progressively increasing the shear strength of the material generated at the sliding interface.

COLL 31

Wear mechanisms and regime transitions for self-mated silicon nitride lubricated by ionic liquid/water mixtures

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In this work, the wear mechanism of self-mated silicon nitride lubricated with ionic liquids (ILs), or water/ILs mixtures, was investigated under different speed and load conditions.

The analysis of topography and chemical composition of the samples lubricated with water-containing ILs suggests that a tribochemical mode of wear dominates during

sliding, leading to preferential removal of material at asperity peaks.

The situation is reminiscent of the mechanism observed in the case of silicon nitride lubricated with water, and indeed the dominance of a tribochemical mechanism involving the formation of a sacrificial layer in the case of silicon-based materials lubricated with a hydrophilic ionic liquid exposed to humid air has been already evidenced.

In particular, similarly to the case of water, in the case ILs/water mixtures it was possible to observe transitions from a boundary/mixed to a full-fluid film regime of lubrication as a result of smoothening and increase of contact area due to tribochemical wear.

Nonetheless, the higher viscosity of the ILs and, possibly, a certain ability of adsorbed ions to prevent asperity-asperity contacts, resulted in a lower and more stable friction at very low speeds as compared with the case of water, leading to better tribological performance for applications requiring slow speeds or intermittent motion.

COLL 32

Mechanochemistry at sliding interfaces – Tribo-polymerization of adsorbed molecules upon mechanical shear

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Mechanochemical reactions initiated by a mechanical force or action are ubiquitous in nature and engineering systems. The most obvious example would be chemical reactions induced by frictional heat at sliding interfaces. There are numerous chemical reactions occurring at mechanical interfaces where frictional heat generation is negligible. In such cases, chemical reactions must be initiated or driven by directly channeling mechanical force or energy into chemical reaction coordinates, which leads to chemical reactions that usually do not occur in thermal, photochemical, or electrochemical conditions. This talk will address how mechanical actions alter or control reaction dynamics or mechanisms. The system studied here is tribochemical polymerizations of adsorbed molecules (bicyclic terpenes and allyl alcohol) occurring at the sliding interface of solids (stainless steel, silicon oxide, etc.) Experimental and computational studies found that the distortion of molecules is a prerequisite for shear-induced chemical reactions and such distortion is facilitated when molecules are anchored to one of the solid surfaces via chemisorption.

COLL 33

RNA-based complex coacervates

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Biological cells are highly organized with numerous subcellular compartments, many of which lack membranous boundaries such as those that surround organelles. We are

developing simple experimental models for these membraneless organelles based on liquid-liquid phase separation, which is a common phenomenon in aqueous solutions of macromolecules. Liquidlike compartments inside living cells are often dynamic, for example appearing and disappearing at different points in the cell cycle. In this presentation, the charge-mediated interaction, or complex coacervation, of RNAs with biological polycations such as spermine or arginine-containing peptides will be described as a means to generate simple model liquid organelles capable of reversibly compartmentalizing biomolecules. Formation and dissolution of RNA/peptide liquid bodies was controlled by changes in peptide phosphorylation state using a kinase/phosphatase enzyme pair. RNA/spermine coacervates could be reversibly formed by changes in temperature that impacted RNA secondary structure. When the RNA-rich coacervate phase is present, solutes such as peptides or nucleic acids can be locally concentrated in a sequence and structure-dependent manner. We have also observed self-assembly of submicrometer lipid vesicles at the aqueous/aqueous interface around the RNA-rich droplet phase; this interfacial layer does not impede solute transport across the interface.

COLL 34

Spanning length scales in polymeric complex coacervate self-assembly

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Charge interactions are a powerful way to drive polymer self-assembly. One such motif in polymer materials design are *complex coacervates*, which are solutions of oppositely charged polyelectrolytes that can undergo associative phase separation. Coacervates form transient gels in aqueous solution, and are thus useful in a wide range of applications such as food and personal care products, delivery vehicles for hydrophilic drugs, and bio-mimicking adhesives. Despite widespread use and a long history in academic research, the theory of coacervates has yet to be settled. Our work demonstrates the challenges in doing so, with many length scales playing an important role in the phase behavior of complex coacervates. A combination of theory and simulation demonstrates how features such as charge spacing, charge patterning, and molecular size have a profound effect on the phase behavior of complex coacervates. Neglect of even one of these features can prevent even qualitative matching of phase behaviors observed in these materials. We introduce new multi-scale methods designed to address the challenge posed by self-assembling coacervates; a combination of Monte Carlo simulation and polymer field theory is capable of capturing the salient features on both monomeric and morphological length scales. This can lead to surprising results, such as salt-induced ordering transitions and morphological coexistence, which arise due to the complex interplay between the various species. We demonstrate comparison to experiment, including qualitative and near-quantitative matching given reasonable choice of molecular parameters.

COLL 35

Sequence-encoded phase behavior of intrinsically disordered proteins

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This talk will present results from recent efforts to uncover the relationships between amino acid sequence the phase behavior of intrinsically disordered proteins.

COLL 36

Asymmetric segregation of P-granules by position dependent phase separation

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An important question in Cell Biology is to understand the mechanisms by which molecular components are positioned and distributed in cells. During asymmetric cell division in the *Caenorhabditis elegans* embryo, liquid compartments called P-granules are segregated asymmetrically and targeted to only one daughter cell. This segregation is achieved via a position dependent regulation of phase separation of components in the cell cytoplasm that can lead to the formation of liquid droplets. The position dependence is determined with the help of a protein concentration gradient. I will discuss the dynamics of droplets in such a concentration gradient and highlight an RNA competition mechanism that is responsible to locally regulate phase separation.

COLL 37

Intra- and intermolecular electrostatic complexes of cationic antimicrobial peptides with their anionic propeptides

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Eukaryotic cells that produce cationic antimicrobial peptides (AMPs) often do so as fusions with anionic propeptides. Sometimes, they are even produced as multiblock copolymers in which cationic AMPs alternate with anionic propeptides. It is thought that electrostatic complexation of the anionic prodomains neutralizes the activity of the antimicrobial peptides, thus protecting the cells from the potentially toxic effects of the AMPs. So far, very little work has been done on characterizing the putative electrostatic complexes of antimicrobial peptides with their pro-domains, and on characterizing the relationship between the electrostatic complexation and the biological activity of the AMPs. We have started to explore this topic using as a model AMP a short but highly

active fragment from the rattle snake venom AMP crotalicidin. As a model anionic propeptide we use E₁₀, and as a control fusion partner we use (GS)₄. Surprisingly we find that crotalicidin forms insoluble intermolecular complexes when mixed with E₁₀, but only forms soluble intramolecular complexes when E₁₀ is fused to the crotalicidin on the N-terminal side. Both when E₁₀ is mixed and when it is fused to the crotalicidin fragment, the antimicrobial activity of the latter is abolished, while N-terminal fusions with the (GS)₄ control peptide retain full activity. Preliminary Circular Dichroism measurements show that the intramolecular complexation in the fusion with the E₁₀ propeptide leads to the formation of alpha-helical secondary structure, and this may be a first clue as to why for the fusion there is no intermolecular, but only intramolecular complexation.

COLL 38

Intrinsic disorder and overcrowding

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The interior of an eukaryotic cell represents a highly inhomogeneous and crowded milieu where in addition to the high content of various biological macromolecules, numerous proteinaceous membrane-less organelles (PMLOs) are present, which are condensed liquid droplets created by the reversible and highly controlled liquid-liquid phase transitions. Since protein and nucleic acid concentrations inside these cellular bodies are noticeably higher than those of the crowded cytoplasm and nucleoplasm, PMLOs can be considered as overcrowded liquid entities. Although PMLOs are different in size, shape, and composition, they almost invariably contain intrinsically disordered proteins. This suggests that the formation of these phase-separated droplets is dependent on intrinsic disorder. The goal of this presentation is to introduce the protein intrinsic disorder phenomenon and to show why intrinsic disorder might be crucial for the biological liquid-liquid phase transitions and for the formation of PMLOs.

COLL 39

Composite porous colloids for SERS-based biosensing

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Surface enhanced Raman scattering (SERS) has become a popular ultrasensitive analytical tool, even for the identification of biological substances. One of the potential threats in this connection is the selectivity, in connection with the presence of a large number of substances in biofluids. In this context, the use of porous materials has been proposed, which can combine the required electric field enhancement by metal nanoparticles with a molecular sieving effect. Porous nanoparticles additionally offer the possibility to implement molecular gates that can selectively open or close the pore

entrances, in the presence/absence of a certain (bio)analyte. Even more complex colloidal architectures can be built by infiltration of the pores with molecularly imprinted polymers (MIPs), so as to enhance selectivity in biodetection.

In this talk we shall present several examples of the combination of plasmonic nanoparticles with porous nanomaterials, toward improving the selectivity in SERS-based biodetection.

COLL 40

Functionalizing various metallic nanostructures with highly effective multi-coordinating polymers

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We introduce a new set of multi-coordinating and multifunctional polymers that are optimally adapted for capping a variety of inorganic nanocrystals and promote their integration within biological media. The ligand design relies on the introduction of multiple anchoring groups, hydrophilic moieties and reactive functionalities into a single polymer chain, via a one-step nucleophilic addition reaction. We have shown that, in addition to luminescent quantum dots, these ligands can be applied to surface functionalize Au nanoparticles, Au nanorods, Au nano-shells and Au nano-stars alike. This surface-functionalization strategy yields inorganic platforms that exhibit long-term colloidal stability over a broad range of biological conditions. For instance, this polymer capping prevents corona formation on Au nanostructures in biological media. We have also used the resulting hydrophilic platforms to develop a range of applications, which include biosensor design based on energy and/or charge transfer interactions and imaging of live cells.

COLL 41

Towards SERS-enabled diagnostics: Quantitative detection of glucose and other biomarkers

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Plasmonic nanostructures provide an ideal platform for low-volume sample detection and identification using surface-enhanced Raman spectroscopy (SERS).

Yet, overcoming inherent limitations – either from the SERS substrate itself (e.g., distance dependence of the SERS signal) or the lack of affinity for some analytes to adsorb onto bare metal surfaces – requires careful experimental design of the metal-organic interface to enable SERS biosensing.

In this talk I will present recent work on SERS sensors for the qualitative and quantitative detection of glucose. By developing capture layers for the specific capture of glucose, it is possible to directly (i.e. without the need for an external label) this

analyte in the physiological range (1-10 mM). I will also describe how such SERS sensors can be used towards the detection of human stress biomarkers.

COLL 42

In-situ SERS detection at picoliter scale using substrate-less Ag nanoparticle-based liquid marbles

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Current microscale tracking of chemical kinetics is limited to destructive ex-situ methods, which are also unable to provide real-time reaction monitoring at a molecular level. In this talk, I will discuss our group's development using highly flexible plasmonic liquid marbles as pico-liter analytical sensors. By using the ultrasensitive surface-enhanced Raman scattering (SERS) capability imparted by the plasmonic shell of the Ag nanoparticles of the liquid marbles, the liquid marbles are capable of quantitative examination of multiple analyte(s), even at trace level. Simultaneous two-phase analyte detection at the interfacial of aqueous and organic solvents can also be achieved using our marble. Recently, we extend the usage of our flexible liquid marbles as picoreactor, which is also capable of providing in-situ identification of reaction dynamics in their native reaction environment and at molecular level. One unique property of the liquid marbles is that they can be submerged at liquid–liquid interface. We exploit the interfacial property to monitor the interfacial reaction of dimethyl yellow (*p*-dimethylamino-azobenzene (DY)) across aqueous and organic phases. Using this soft plasmonic platform, we have successfully resolved the presence of two isomeric products with very similar physical properties, which would otherwise be indiscernible by other analytical methods. Ultimately, our ability to precisely decipher molecular-level reaction dynamics sketches new horizons to develop more efficient processes in synthetic chemistry and nanotechnology.

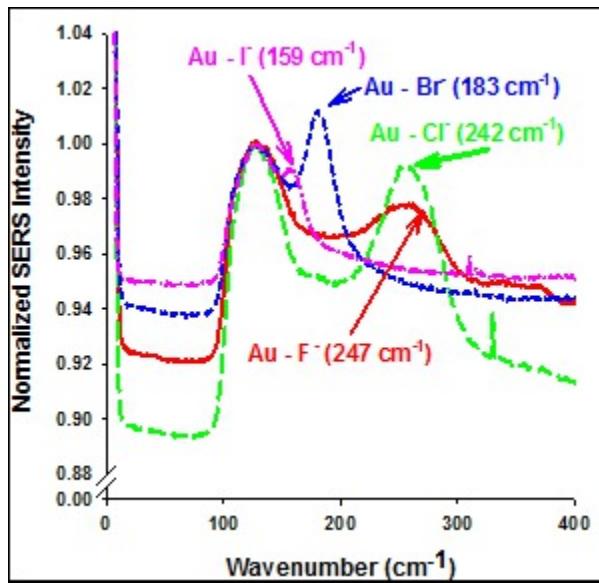
COLL 43

Low frequency vibrational mode surface enhanced Raman spectroscopy characterization of gold interactions with aqueous halides

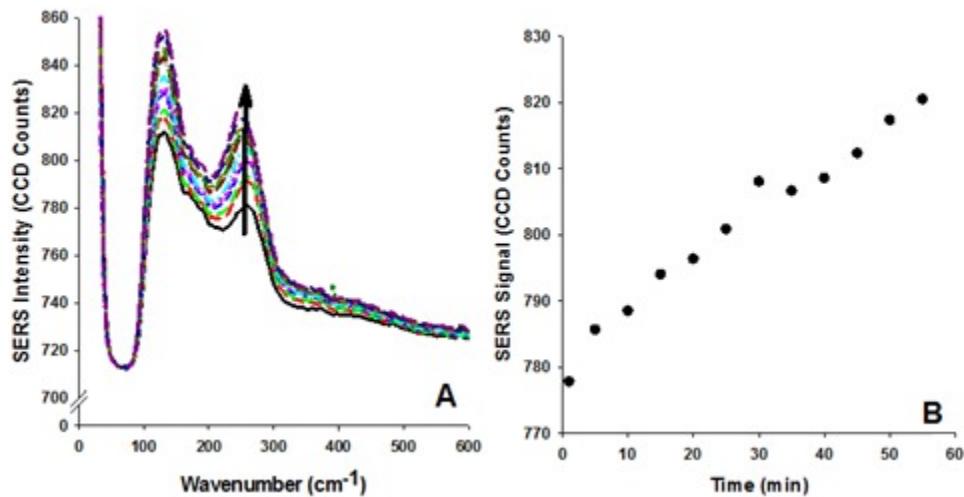
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Low frequency vibrational interactions between gold surfaces and dissolved halide were investigated by surface enhanced Raman spectroscopy (SERS). Experiments were conducted with NaF, NaCl, NaBr, and NaI salts with commercial gold SERS substrates as well as with citrate-coated gold nanoparticles (cit-AuNP). The Raman active gold-halide interactions were isolated with the aid of signal enhancement from nanoscale surface features present on the aggregates formed by cit-AuNP in the presence of salt (Figure 1). The Raman shift trends of the Au-X⁻ SERS bands corroborate with the

corresponding covalent interaction strength as estimated by force constant calculations. Time-resolved superpositioned SERS spectra indicate that the Au-X⁻ signal increases with time and this trend is concomitant with AuNP aggregate formation (Figure 2). This SERS-detectable interaction provides new routes for aqueous halide sensing.



SERS shift band of the various Au-X⁻ interactions. Experiment conducted with 15 nm citrate-coated gold nanoparticles.



A: Superimposed SERS spectra of Au-Cl⁻ interaction between dissolved NaCl and 15 nm citrate-coated gold nanoparticles. Arrow indicated time progression. B: Time-resolved Au-Cl⁻ SERS band intensity of the same experiment in A.

COLL 44

High throughput optofluidic Surface-Enhanced Raman Spectroscopy (SERS) interrogation: Proof of concept via lectin detection of cancerous cells

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This paper presents the first application of label-based surface enhanced Raman spectroscopy (SERS) in combination with droplet microfluidics for whole-cell disambiguation from a mix culture. We propose a non-invasive surface labeling approach to distinguishing cell types that also keeps individual cells intact for standard pathology studies and further omic analysis.

Droplet microfluidics is ideally suited for single-cell analysis from sample limited sources, such as cancer biopsies, where, after sample processing, between 100,000 and a few million cells are typically removed from a patient. However, rapidly distinguishing the cell types in the sample remains elusive. SERS provides an excellent method for such a study because, compared with fluorescence, there is minimal photo-bleaching, extensive multiplexing capabilities, and spatially defined detection. At present SERS, as an analytical technique for biomolecular systems, is often plagued by a lack of quantification and reproducibility due to colloidal variation and the length of time required for individual sample analysis. To overcome these issues droplet microfluidics has been employed in conjunction with SERS.

Specifically, the N-acetyl neuraminic (sialic) acid residue overexpressed on cancerous prostate cells (PC3) in comparison to non-cancerous prostate cells (PNT2) was targeted with wheat germ agglutinin (WGA) functionalized gold nanoparticles. We developed a device where cell containing droplets are stored and locked into position, thus enabling the SERS screening of nearly one thousand droplets in less than 10 minutes with the ability to return to locations (cells of interest) and track spatial and temporal variation of individual cells. As well, nanoprobes can be introduced to the cell samples on-chip to minimize sample contamination and maximize the homogeneity of the nanoprobe distribution. In-house algorithms were developed in Matlab to rapidly and automatically baseline correct and normalize SERS data and re-render SERS intensity maps. The results from these live 3D experiments demonstrated that previous fixed cell experiments underestimated the needed sample size for a representative population. Moreover, we demonstrated that across multiple nanoparticle batches, probe syntheses, cell passages, and instruments that WGA functionalized nanoprobes could not selectively distinguish cancerous cells from non-cancerous prostate cells.

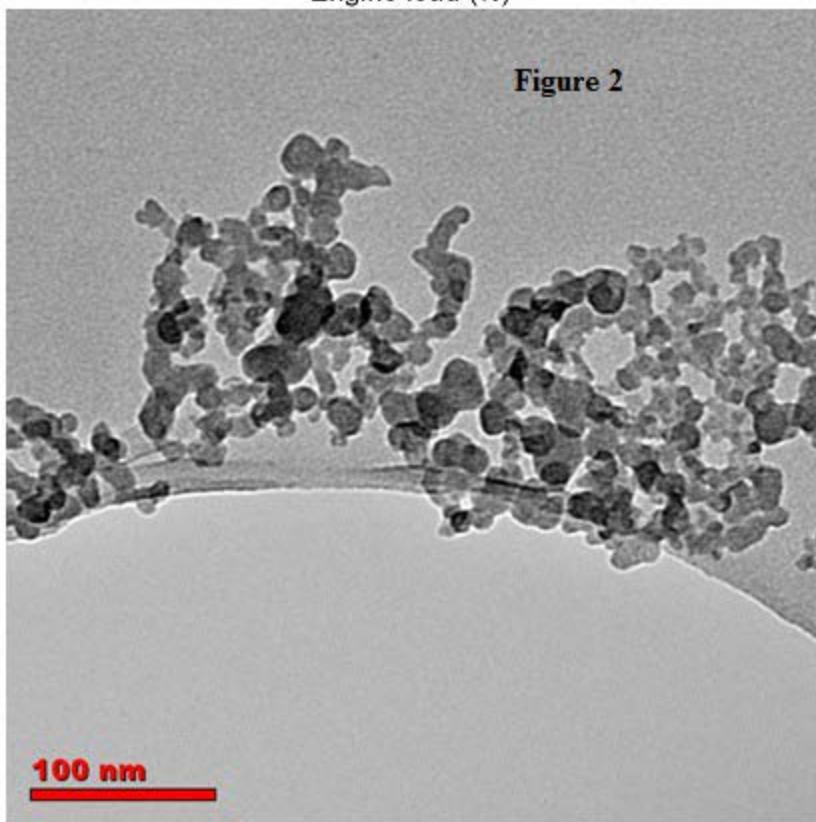
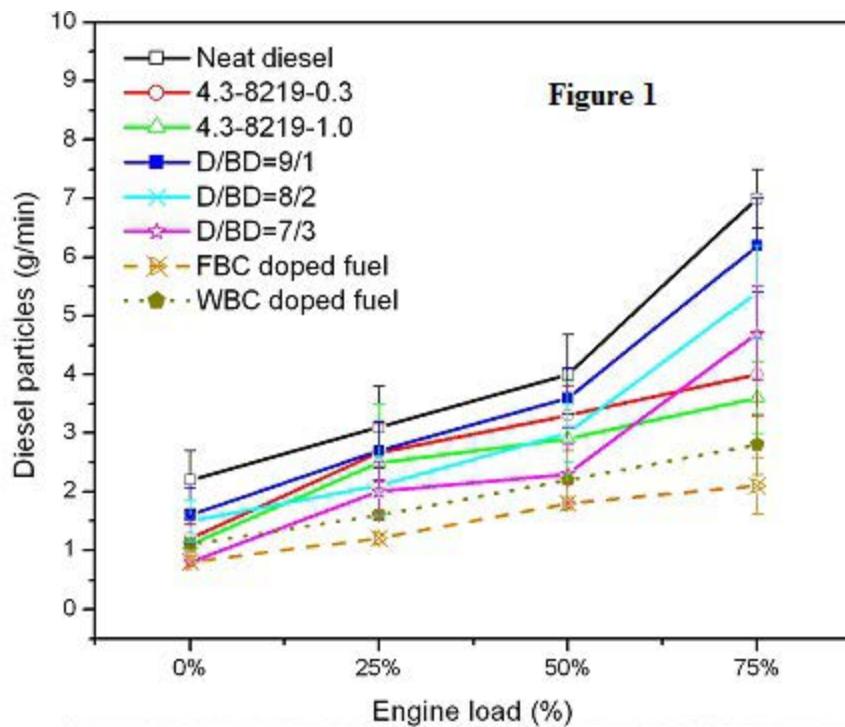
COLL 45

Nanoengineering water-in-diesel/biodiesel microemulsion interfaces to minimise particulate and NOx emissions from diesel engines to minimise atmospheric pollution

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Stable water-in-oil microemulsions of diesel (D) and biodiesel (BD) fuels were produced from Span 80, sucrose esters and cosurfactants. They were defined by HLB-(D/(surfactant+cosurfactant))-(surfactant/cosurfactant)-wt% H₂O values. As the water content increased so the droplet size increased. To some were added water-borne catalysts (WBC: Ce(NO₃)₂) and fuel-borne catalysts (FBC: Ce(acac)₄). Figure 1 shows that particulate emissions from engines operating on these fuels (especially at higher loads) decreased from those seen with neat D. The same was true for NOx emission. Figure 2 shows the types of finely-dispersed and fractal particulates emitted. When WBC and FBC catalysts were incorporated in the fuels these were seen by TEM-EELS in the emitted particles.

We have analysed particulate types and concentrations over a period of time in the atmosphere of San Diego, CA; such levels can be decreased by the type of microemulsion fuels described here.



COLL 46

Uloborus walckenaerius bioinspired attachable, self-standing, nanofibrous membrane for versatile use in oil–water separation

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Oil pollution in water is a universal problem, causing long-term effects on the health of livings and the environment, whereas high-purity oil is an important energy resource on which humans depend to maintain their current lifestyle. Thus, devices to separate oil-water mixture such as separation filter, oil absorbents, and oil collector are getting much attention.

Recent approaches to oil–water separation are based on the selective wetting of oils, chemicals and water onto 2D or 3D porous materials. Although the development of selective-wetting materials enabled highly effective separation, there are still challenges of practical use in terms of cost, scale and material dimension limiting the strategy (*i.e.* Oil absorbents requires 3D material whereas filter and collector need 2D materials). Our strategy was to design a self-standing sheet for oil–water separation that could be attached to various materials to provide this function to both 2D and 3D materials. The conventional approach to this requires chemical interaction or physical cross-linking between the supporting material and the functional material; however, such type of versatile attachment is difficult.

Here, *Uloborus walckenaerius* spider webs provided the inspiration for attachable, self-standing nanfiber sheets (NF-S) via electrospinning the easily chargeable fluorine polymer of poly(vinylidene fluoride-co-hexafluoropropylene) mixture (Structure is shown in **Figure A and B**). The developed product adds selective wettability against oil–water mixtures to both 2D and 3D materials by attaching or covering them, leading to successful separation including emulsion (**Figure C**) through a facile, scalable and low-cost process.

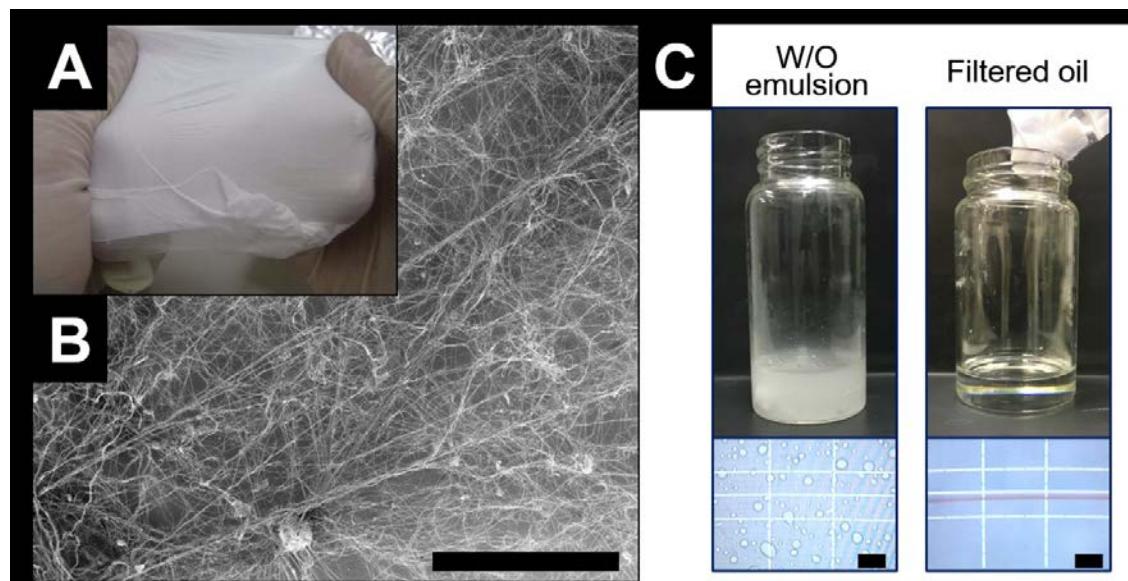


Figure. (A) Photograph and (B) SEM image of a *Uloborus walckenaerius* bioinspired nanofiber sheet. The scale bar is 200 μm . The nanofiber sheet can self-stand to attach various materials by electrostatic *van der Waals*. (C) Photographs and optical microscopy images of before and after emulsion through nanofiber sheet filtration. The scale bar is 5 μm .

COLL 47

Interfacial interactions of granular particles with floating crude oil under different granular flow regimes

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Flow regimes of granular particles are well studied and classified as solid, liquid, and gaseous types. Besides the behavior of particles is very different in each flow regime, the interaction of granular particles with floating hydrophobic liquid-water interface presents new phenomena that have not been reported in the scientific literature. Understanding the interaction of particles with oil-water interface opens up the possibilities of development of new technologies for oil spills capture, submergence, and floating oil mobility control.

Experiments were conducted with South Louisiana crude oil (MC 252), and pure quartz sand with two different particle sizes (0.15-0.42 mm and 0.60-0.85 mm). The application rates of sand varied in order to represent different granular flow regimes and were controlled by an opening size in a funnel.

Sand particles, reaching the floating hydrophobic layer, initiated instantaneous aggregation of the floating oil and various submergence patterns occurred.

Submergence patterns were described for each application rate of particles and the critical oil thickness was defined in relation to the observed submergence phenomena. The interaction patterns we observed can be used for granular enforcement of liquid-liquid interfaces, rapid transfer of the floating oil to the submerged state, and phase transformation of light hydrophobic liquids.

COLL 48

Fabricating reservoir micromodels by *in situ* grown calcium carbonate nanocrystals in microfluidic channels

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Microfluidic channels have been widely used as reservoir micromodels to mimic the underground oil-reservoir environment for multi-phase flow studies, enhanced oil recovery, and reservoir network mapping. However, most of the micromodels usually built by glass or polymer materials cannot replicate the length scales and geochemistry of carbonate because of their material limitations. Here we introduce a simple method to create calcium carbonate (CaCO_3) micromodels composed of *in situ* grown thin layer of CaCO_3 nanocrystals. The surface of microfluidic channels was first chemically functionalized by carboxylate groups and nanosized CaCO_3 seeds were generated, and then CaCO_3 nanocrystal layers were grown *in situ* from these seeds via supplying Ca^{2+} and CO_3^{2-} ions in solutions. This approach enables us to fabricate synthetic CaCO_3 reservoir micromodels with controllable dimension and geometries of microfluidic

channels. Using this new method, we have demonstrated an immiscible fluid displacement process used in real oil field applications to visualize pore-scale fluid–carbonate interactions in real time by Raman imaging technique.

COLL 49

Effects of confinement and composition on oil/water interface in nanopore environment

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Controlling interfacial phenomena at the oil/water interface is relevant in many practical applications. For example, to achieve enhanced oil recovery from nanopores of oil reservoir rocks, it is essential to increase the mobility of the oil phase present in these nanopores. In the present study, we use molecular dynamics (MD) simulations to examine structure and behavior of oil/water mixtures and interfaces in calcite nanopores, in dependence of two parameters: 1) nanopore size; and 2) oil/water composition. We determine that oil/water mixtures exist in two different phases, in which oil assumes either the droplet form or the bulk mobile form. Phase transformations, from oil droplet to mobile oil, occur when nanopore sizes are decreased, while oil/water mixtures have larger fractions of oil where thin layer of water is formed on the calcite surface.

COLL 50

Impact of microemulsions on mobilization, emulsification, and solubilization of oil in heterogeneous rocks

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Conventional reservoirs with high residual oil saturation are often targets for chemical flooding during enhanced oil recovery processes designed to mobilize and solubilize oil. Chemical additives (such as surfactants) are usually added to brine to decrease the interfacial tension (IFT) and contact angle, thereby reducing the capillary drawdown inside the pores. The decrease in oil/brine IFT allows the spontaneous emulsification and mobilization of bulk oil whereas solubilization of adsorbed oil results in wettability reversal. Recent studies suggested that putting surfactants into a micro-emulsified state prior to injection might improve their performance. Most of these studies proved that microemulsion (ME) efficiency depends on test conditions and the proper selection of their chemical formulations and brine chemistry. However, the impact of rock characteristics (such as mineralogy, roughness, and wettability state) on the complex fluid-rock interactions is still unclear, especially in heterogeneous rocks. The goal of this study was to examine the effect of MEs on oil recovery from three different aged rocks

(Berea, Edwards, and Tensleep) and identify the test conditions in which MEs outperform surfactants alone. The effectiveness of an environmentally friendly ME formulation was evaluated from different sets of spontaneous imbibition tests and petrographic analyses. Two ME solutions containing low and high concentrations of a nonionic surfactant were used and compared to surfactant solutions at the same concentrations. Several mechanisms such as IFT reduction, oil emulsification, and wettability alteration were responsible for the improved recovery. Both surfactant and ME lowered the IFT from 12 mN/m to less than 1 mN/m. However, high ME concentration was able to decrease the size of oil droplets by one order of magnitude, significantly enhancing oil mobilization in all three rocks. The solubilization capability of MEs was superior in Tensleep rock due to the unique ability of ME components to penetrate certain types of minerals and alter their wettability.

COLL 51

Nanoengineering at the oil-water interface to maximize hydrocarbon production

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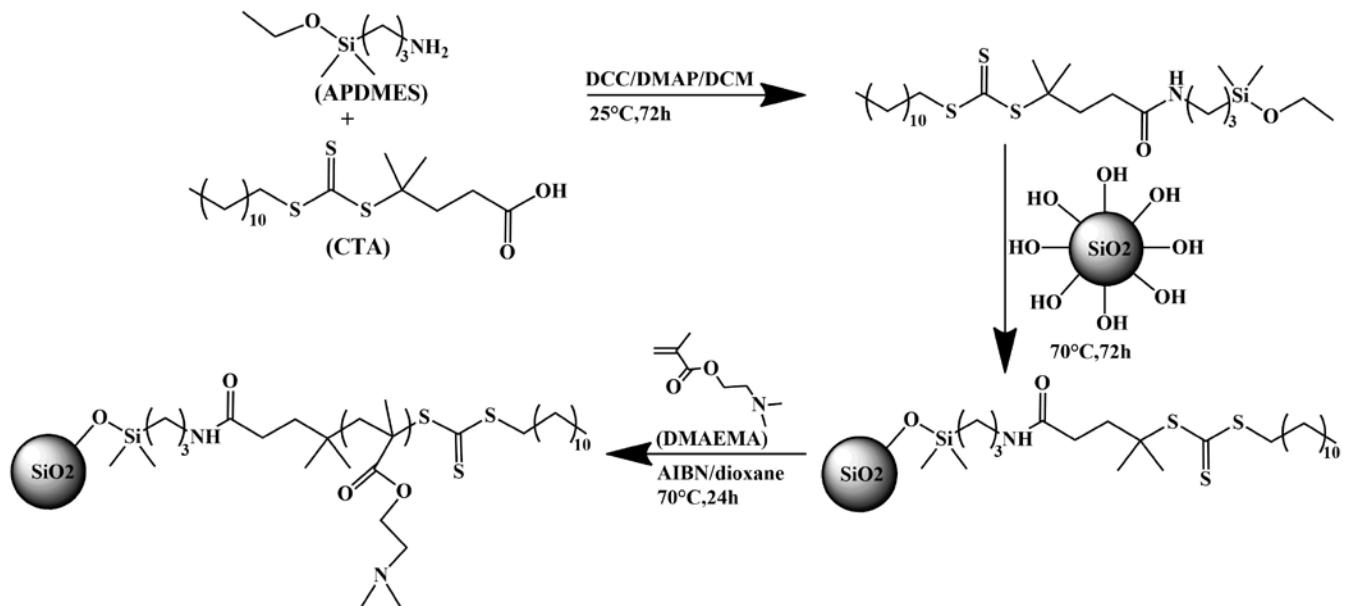
Biogenic oil and gas was formed in water bodies devoid of oxygen where biomass accumulates biomass. Oil/gas migrate into structural traps with anhydrite/salt/shale caps alongside formation water (FW) in sandstone or limestone reservoirs. They are to be found in networks of pores above ambient temperature (e.g. 350 K) and pressure (700 bar). Total world proved oil reserves reached 1687.9 billion barrels at the end of 2013 and are sufficient to meet 53.3 years of global production at present levels of consumption. Fracking has impacted on hydrocarbon production. Nanoengineering relates to maximising hydrocarbon production/stabilising of prices via (i) enhanced hydrocarbon recovery through surface tension/viscosity and (ii) minimised scaling when sulphate-rich waters are injected into Ba²⁺-rich FWs. Here we use two oil fields as examples of such nanoengineering at the oil-water interface: the Clair field 75km west of Shetland in Jurassic/Devonian-Carboniferous sandstone at 150m below the sea surface on the UK continental shelf that contains 410 million metric tons of oil in a sandstone matrix that is 1500m thick and North Dome/South Pars gas and oil fields in Cretaceous Aptian carbonate reservoir in the Shu'aiba formation at the Qatar/Iranian border.

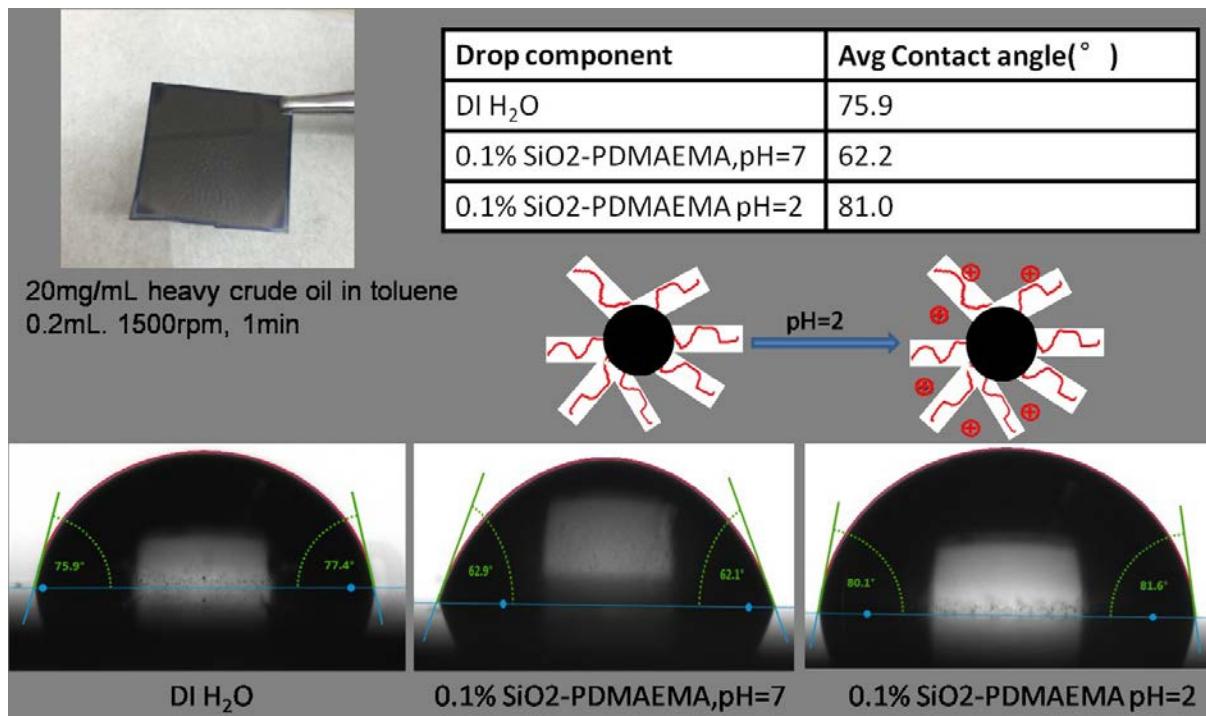
COLL 52

pH-responsive polymer coated nanoparticles for controlled emulsification of heavy oil

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Heavy crude oil has lower solubility and higher density than that of light crude oil, and it mostly comes in the form of natural bitumen from oil sand. Therefore, there are significant challenges in both the production and transportation of heavy oil. Oil-in-water emulsions are commonly used to reduce the viscosity, but subsequent demulsification can be challenging. Here, we investigate pH-responsive polymer coated nanoparticles (PNPs) that are interfacially active and can be used to either stabilize or break oil/water emulsions by varying pH. Silica particles with dimethyl ethyl acrylamide (DMAEMA) chains covalently grafted to the surface are prepared though a reversible addition fragmentation chain transfer (RAFT) grafting-through technique. TGA, DLS, and TEM are used to confirm the attachment of the polymer coating, and the resulting polymer-coated nanoparticles contain 60 wt % polymer. We show that DMAEMA PNPs can be used to stabilize emulsions of high viscosity Venezuela heavy oil at additive concentration as low as 0.1 wt % and at a neutral pH. The performance of the PNPs exceeds that of pure DMAEMA homopolymer additive or of just water with no additive, and approximately 10mg crude oil is stabilized for each 10 mg of PNP used. By changing the pH of the aqueous solution, the interfacial activity of the DMAEMA decreases, and the emulsion is destabilized. Surface energy measurements show a 20 degree difference in contact angle on a crude oil coated substrate for a DMAEMA PNP drop at pH=7 and pH=2. Finally, we perform sandpack flooding using PNPs as additives to mobilize heavy oil. The PNPs penetrate the sandpack and are able to recover more than 25 wt % of the crude oil in place. This work demonstrates the applicability of polymer-coated nanoparticles as surface active materials for EOR processes and for heavy oil transportation.





COLL 53

Surfactant Enhanced Oil Recovery (EOR): Role of reservoir wettability and oil-water interfacial tension in designing efficient surfactant systems

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The recovery of crude oil using surfactant-based EOR technologies depends strongly on the ability of a surfactant to favorably change the properties of the oil-water-solid interfaces encountered in a reservoir. In particular, the wettability of the rock surface and the oil-water interfacial tension must be judiciously managed for efficient mobilization of oil trapped in tight pores by capillary forces. The use of surfactants that can change rock surface wettability has been extensively investigated as a method to enhance water imbibition into tight pores to displace trapped oil and hence improve oil recovery operations. This process is driven by changes in capillary pressure, which depends on the wettability of the rock surface (defined by the contact angle of fluids on the rock surface) and the oil-water interfacial tension. Therefore, the application of this technology relies on the ability to design a surfactant or surfactant formulation that provides the optimal balance between wettability alteration and oil-water interfacial tension reduction. Moreover, the surfactant system must be tailored for a particular reservoir, since the physical and chemical properties of rock surfaces and crude oil can vary significantly for different reservoirs. In this presentation, we will describe our approach to design surfactant systems to optimize wettability and interfacial tension to modify the relative permeability of fluids and improve oil recovery and reservoir

performance. In addition, we will review some of the main challenges encountered when designing and implementing surfactant-based technologies to improve oil production operations, which include heterogeneous reservoir wettability and permeability, surfactant solubility at reservoir conditions, and surfactant adsorption to rock surfaces.

COLL 54

Formulation and utility of microemulsions in cleaning applications

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Microemulsions are thermodynamically stable dispersions of oil and water that consist of distinct oil and water phases and may be oil, water or bi-continuous. Due to the ability to tune the inherent cleaning performance of both the aqueous and oil phase and control the overall microemulsion phase behavior they are very useful in a variety of cleaning applications ranging from dilute aqueous hard surface cleaners to heavy duty degreasers to cleaning products for fine art restoration. In order to generate commercially useful microemulsions it is necessary to optimize the surfactant and optional co-surfactant packages to minimize surfactant levels and maintain stability over the typical use or storage conditions. In this talk we will describe the strategies for formulating microemulsion based cleaning products, as well as unique high throughput approaches to develop high performance products which maximize stability and performance.

COLL 55

Biodegradable and biocompatible regular nanopatterned surfaces for selective cell enrichment

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Cell behavior can be influenced by biomolecular and topographical cues in the natural microenvironment. Cancer stem cells are speculated to have the capability of self-renewal and re-establishment of tumor heterogeneity, possibly involved in the potential relapse of cancer. EpCAM⁺, CD24⁺, ALDH1A1⁺ cells have been reported to possess tumorigenic properties, and these biomarkers are thought to be highly expressed in ovarian cancer stem cells.

We hypothesized that different cell populations in ovarian cancer tissue exhibit different

adhesion characteristics on substrates with nanotopography.

Adhesion characterizations were performed using human ovarian epithelial cancer cells (Ovcar3) on nanopatterned poly(lactic-co-glycolic acid) (PLGA) films. Hemispherical protrusion shaped templates were manufactured by spin coating polystyrene (PS) particles with diameters of 77, 170, 280, and 460 nm on silicon wafers. The PS templates were used to form a negative relief in polydimethylsiloxane (PDMS) moulds against which PLGA was solvent cast. Topography demonstrated a significant effect on ovarian cancer cell adhesion, and the effect was cell type dependent.

Immunofluorescence histochemistry and flow cytometry analysis showed that the EpCAM+CD24+ALDH1A1 + subpopulation in Ovcar3 adhered preferentially to the 170-nm topography.

These results pave the way towards the development of a label-free method employing the differences in cell adhesion to isolate cancer stem cells, as well as different cell populations from cancer tissue.

COLL 56

Tailoring 5–10 nm chemically orthogonal surface patterns on layered materials using sitting phases of polymerizable amphiphiles

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(2) Biomedical Engineering, Purdue University, West Lafayette, Indiana, United States

Chemically orthogonal surface patterns at scales (5–10 nm) approaching the molecular scale are required for emerging applications in a range of fields including nanostructured electronic and organic optoelectronic materials. However, synthetic material designers encounter an array of significant challenges in this regard. For instance, ionizable functional groups represent one of the strongest local modulators of surface chemistry; however, at polar–nonpolar interfaces, ionizable functional groups undergo substantial pKa shifts (in some cases, >5 units) that substantially limit their ability to ionize. Drawing lessons from biology to design noncovalent surface chemistry for modern technological materials such as graphene, we have demonstrated that polymerizable phospholipids can be assembled into ‘sitting’ phases that expose alternating stripes of hydrophilic and hydrophobic surface chemistry, and that the phospholipid headgroup architecture negates interfacial pKa shifts for the terminal functional group, by providing a locally polar environment even when assembled on a nonpolar interface. Building on this idea, we demonstrate that sitting phases may be assembled through Langmuir-Schaefer transfer, enabling modulators in the aqueous subphase to be used to tune orthogonal surface patterning; the use of such patterns to direct further nanoscopic assembly at the interface will also be discussed.

COLL 57

Artificial membranes composed of fluid and polymerizable lipids: Fractional polymerization produces nanoscale domains with retained fluidity and enhanced stability

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Fluid phospholipid bilayers have been frequently used as biocompatible structures in receptor-based sensors and arrays, however their structural integrity may be compromised by chemical and mechanical instability. For example, long-term monitoring of the activity of an ion channel receptor reconstituted into a suspended membrane composed of fluid lipids may be limited by the susceptibility of the membrane to mechanical rupture. In this type of construct, the lipids are self-associated via a network of relatively weak intermolecular forces and, as a consequence, membrane rupture frequently occurs within a few hours after formation. This limitation can be addressed by cross-linking polymerization of synthetic lipid monomers substituted with reactive groups. However this strategy may inactivate the receptor if a high degree of membrane fluidity is required to maintain its activity. We have been investigating mixed bilayers composed of dienoyl-functionalized lipids, which can be polymerized to form linear or cross-linked polymers, and nonpolymerizable fluid lipids. Polymerization of the mixed bilayer induces phase segregation, producing a membrane composed of poly(lipid) domains and fluid domains with sub- μm lateral dimensions. This presentation will describe the structural and functional properties of these mixed bilayers, including morphology, fluidity, mechanical properties, and the activity of incorporated proteins.

COLL 58

Chemical lift-off lithography and sensors

Wei-Ssu Liao, wsliaochem@ntu.edu.tw. *Chemistry, National Taiwan University, Taipei, Taiwan*

Chemical lift-off lithography (CLL) can selectively remove alkanethiol molecules from self-assembled monolayers (SAMs) on gold surfaces with high pattern fidelity. This “subtractive” process avoids lateral diffusion problems which restrict the feature resolution that can be achieved through conventional stamping related techniques. By the use of soft-materials, e.g., polydimethylsiloxane (PDMS), feature patterning and material transferring over a large area is achievable. Notably, surface molecule density and interfacial environment can be regulated by stamping conditions during chemical lift-off processes. This unique surface molecular environment control provides an exceptional opportunity for high-throughput bio-recognition array and sensor fabrication. Incorporated with image analysis and device construction, the chemical lift-off process treated surface delivers the potential substrates for practical sensing platforms.

COLL 59

Patterning arrays of geometrically complex nanostructures on planar surfaces

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This talk will describe the use of a combination of colloidal lithography, reactive ion etching, capillary force lithography, and wet etching techniques to create unique arrays of features at the nanoscale. Architectures can be created from soft materials as well as metals and employed in plasmonic or surface enhanced Raman spectroscopy. An important feature of this methodology is that it relies on multiple, simple serial steps to create libraries of patterns. By varying the details of these steps, one can create a library of complex shapes and features that would be difficult to create by other methods. Indeed, the types of features that can be formed grow exponentially with the number of steps involved. The alternative is to employ electron beam lithography, which is slower and only capable of patterning a small area. By contrast, this new stepwise approach can create patterns quickly, cheaply, and easily over areas on the order of square centimeters.

COLL 60

Self-assembly of proteins into periodic nanostructures through spatially-confined nanofluids

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The versatility of biomolecules can be used to rationally design new molecular architectures with specific structures and functionalities unseen in nature. However, it is challenging to organize biomolecules into well-controlled assemblies. Here, we present a facile patterning method that uses spatially-confined nanofluids formed between flat substrate and nanospheres/nanochannels to guide self-assembly of proteins into highly ordered and periodic arrays of nanostructures. During the evaporation process, the solution can be localized inside the spatial confinement on surfaces to form various nanofluids, such as circular water meniscus, water bridge or water nanoline. As the solvent further evaporates, capillary forces enforce protein molecules to concentrate within nanofluids, which induce protein molecules to self-assemble into well-defined nanostructures. The morphology of the protein nanostructures can be tuned by selecting the shapes of nanofluids and drying conditions. Well-defined nanopatterned protein surfaces may be suitable for multiplex biosensing and for nanoscale investigations of protein binding interactions.

COLL 61

Modified soft lithographic approach for Surface-Enhanced Infrared Spectroscopy (SEIRA) substrates and their application to live cell monitoring

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A versatile and reliable method for patterning gold nanostructures of varying shapes is presented in this work. It begins with a close-packed array of polystyrene nanospheres, which are shaped through simple plasma etching. The vapor-deposition of nickel shadowed over the shaped masks creates the possibility of forming a wide range of gold nanostructures. This is an easy, powerful, and straightforward method that offers several degrees of freedom to precisely control the shape and size of nanostructures. We made a library of nanostructures including gold nanocrescents, double crescents, nanorings, and nanodisks with dimensions in the range of 150 to 650 nm. The fabricated nanostructures are highly packed (up to $8 \times 10^8 \text{ cm}^{-2}$) and uniformly cover the centimeter scale substrate. The optical properties of these metallic nanostructures were studied by a combination of UV-Vis-NIR and Fourier transform infrared (FTIR) spectroscopies, and the features agreed well with predicted optical responses. The materials are highly sensitive surface enhanced infrared absorption (SEIRA) substrates as was demonstrated with gold nanocrescent arrays. Gold nanocrescent arrays exhibited highly tunable plasmon resonance to cover desired molecular vibrational bands and exhibited three orders of magnitude enhancement of IR signal over the entire substrate and up to 10^5 SEIRA enhancement factors on hot-spot areas. These substrates are biocompatible for growth, adhesion, and proliferation of human dermal fibroblast cells. Leveraging the capability of gold nanocrescent arrays to enhance IR signals, we developed a real time SEIRA spectroscopic technique for label-free biological cell analysis. The performance of proposed method was assessed by in-situ tracking the SEIRA signal of human dermal fibroblast cells cultured on gold nanocrescent arrays.

COLL 62

Characterizing and manipulating mercaptoalkanoic acid molecular ruler multilayers using scanning probe lithography

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Complex surface structures with molecular-scale organization and chemical functionalities have garnered tremendous attention in recent years. Multicomponent alkanethiol-based chemical films assembled onto noble metal surfaces are commonly utilized due to their rich and well-characterized structures and chemistries. However, the

patterning of these films is typically limited to two-dimensional structures due to the reliance on the assembly of monolayers and the limited library of molecules. Therefore, we have assembled, characterized, and manipulated mercaptoalkanoic acid "molecular ruler" multilayers as a potential strategy to generate three-dimensional chemical films. These "molecular ruler" multilayers are assembled through the sequential deposition of mercaptoalkanoic acid molecules and coordinated metal ions where the overall film thickness of the multilayers is governed by the number of iterations in the deposition process. By combining this multilayer assembly strategy with the scanning probe lithography, we can manipulate the local structure of these multilayer films. We explore the ability to remove various components of the multilayer film as means to gain insight into the assembly process and to generate complex three-dimensional chemical patterns.

COLL 63

Counterion-specific counterion condensation

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Conuterion condensation is indirectly monitored via the effcetive charge of polyelectrolytes, which is determined in a combination of electrophoresis and diffusion NMR. The hydrodynamic friction is erived from the diffusion coefficient determined in PFG NMR, while electrophoresis NMR yields the electrophoretic mobility. Both are determined with chemical shift resoultion, which means tehy can be attributed to specific functional groups or structures. Thus organic counterions can be isnvvestigated simultaneously.

Poly(styrene sulfonate) has been titrated with hydroxides of different cations. to generated teh respective salts. While littel effect has been observed for monovalent counterions, there significantly stronger binding for bivalent counterions and strong differences with Ca showing strongest binding
Higher valence of counterions has been established using small organic molecules. This in addition has the advantage, that the counterion is observed directly providing an additional cross check. Larger counterions establish the rtransition to the formation of polyelectrolyte complexes. In the present study primary complexes can be investigated selectively showing the electrostatic nature of the complex formation.

COLL 64

Carbonate rock wettability investigated with finer spatial resolution

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The success of water flooding in EOR techniques requires knowledge and understanding of pore wetting. However, till date a conclusive study about the fundamental chemical understanding of all the factors affecting the reservoir wettability remains elusive. This is due to the absence of techniques with higher spatial resolution for investigating pores. Conventionally pore wetting has been estimated using the macroscopic method i.e., Static Contact Angle (SCA) measurements.

We have macroscopically and nanoscopically investigated the wettability of atomically flat calcite crystal which is a representative of a carbonate reservoir. Freshly cleaved calcite undergoes a wettability transition from being super hydrophilic to hydrophobic nature on being exposed to ambient atmosphere. When investigated under an AFM, it was observed that the dangling bonds of freshly cleaved calcite are balanced by hydrolyzed water which causes the wettability transition. Calcite transitions from being super hydrophilic to hydrophilic when aged in DI water. The samples underwent dissolution with time which was observed with AFM, FTIR and ICP MS. The macroscopic studies were carried out by drying the sample with Nitrogen and then measuring the SCA. However, when probed under an AFM it was observed that there is always a layer of water present on top of the sample surface. When the droplet from contact angle goniometer is put on top of the sample surface, it will interact with water layers present at the nanoscale and thus alter the contact angle results; thereby putting the macroscopic wettability results into question.

These observations hint that macroscopic measurements alone are not sufficient to understand the cause for the observed time dependent wettability transition of calcite and call for the use of higher spatial resolution techniques. Our work has shown that SCA results of calcite when aged in liquid environments like DI water cannot be taken to be the true measurement of the sample wettability.

COLL 65

Light scattered by hedgehog particles

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Sensitive to even a small perturbation in its construct, particles provide versatile and compact platforms with which to design electromagnetic responses. With great advances in the nanofabrication, diverse particle types exhibiting unique and useful scattered radiation patterns have been realized or theoretically predicted. In particular, particles exhibiting broadband scattering with flexibility to suppress backscattering and enhance forward scattering hold promises in a diverse array of photonics devices servicing photodetectors, antennas and photovoltaics. Recently, we have reported the 'hedgehog' particles whose high aspect-ratio surface roughness, composed of ZnO nanospikes, on a polymeric microsphere elicits anomalous dispersion behavior that

breaks the well-known “similarity rule”. The ‘hedgehog’ particles represent a novel class of “rough” particles comprised of all dielectric components that lies within the Mie scattering regime due to wavelength comparable dimensions. It should be noted that such types of particles are barren in previous endeavors, both experimentally and theoretically. In this research, in addition to deviation in the interaction potential as reported previously, we will show that high aspect ratio nano-topography also modifies electromagnetic responses from what is predicted by Mie theory for smooth dielectric particles. In detail, the high aspect-ratio interfacial nano-corrugation 1) educes broadband scattering at the visible spectrum, 2) suppresses resonant modes within the ‘hedgehog’ particles despite its sizes and constitutive properties and 3) creates near-field profiles that elicits broadband suppression of backscattering and enhancement of forward scattering at two spectral regions inclusive to telecommunication range and mid-infrared. Addition to a library of electromagnetic responses of diverse particle types is expected further enrich scientific foundation and engineering of photonic devices.

COLL 66

Cross-linked cationic diblock copolymer worms are superflocculants for micrometer-sized silica particles

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A series of linear cationic diblock copolymer nanoparticles are prepared by polymerization-induced self-assembly (PISA) *via* reversible addition–fragmentation chain transfer (RAFT) aqueous dispersion polymerization of 2-hydroxypropyl methacrylate (HPMA) using a binary mixture of non-ionic and cationic macromolecular RAFT agents, namely poly(ethylene oxide) (PEO₁₁₃, $M_n = 4400 \text{ g mol}^{-1}$; $M_w/M_n = 1.08$) and poly([2-(methacryloyloxy)ethyl]trimethylammonium chloride) (PQDMA₁₂₅, $M_n = 31800 \text{ g mol}^{-1}$, $M_w/M_n = 1.19$). A detailed phase diagram was constructed to determine the maximum amount of PQDMA₁₂₅ stabilizer block that could be incorporated while still allowing access to a pure worm copolymer morphology. Aqueous electrophoresis studies indicated that zeta potentials of +35 mV could be achieved for such cationic worms over a wide pH range. Core cross-linked worms were prepared *via* statistical copolymerization of glycidyl methacrylate (GlyMA) with HPMA using a slightly modified PISA formulation, followed by reacting the epoxy groups of the GlyMA residues located within the worm cores with 3-aminopropyl triethoxysilane (APTES), and concomitant hydrolysis/condensation of the pendent silanol groups with the secondary alcohol on the HPMA residues. Transmission electron microscopy and dynamic light scattering studies confirmed that such core cross-linked cationic worms remained colloidally stable when challenged with either excess methanol or a cationic surfactant. These cross-linked cationic worms are shown to be much more effective bridging flocculants for 1.0 μm silica particles at pH 9 than the corresponding linear cationic worms (and also various commercial high molecular weight water-soluble polymers.). Laser diffraction studies

indicated silica aggregates of around 25–28 µm diameter when using the former worms but only 3–5 µm diameter when employing the latter worms. Moreover, SEM studies confirmed that the cross-linked worms remained intact after their adsorption onto the silica particles, whereas the much more delicate linear worms underwent fragmentation under the same conditions. Similar results were obtained with 4 µm silica particles.

COLL 67

Spray coating of colloidal and organic layers

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Spray deposition is a versatile, rapid coating method, compatible with roll-to-roll (R2R) technology. It allows for layer-by-layer assembly (LbL) of functional layers, for fabricating hybrid materials as well as conformal and nanostructured coatings of three dimensional objects. Spray deposition itself is a complex fluidic process, which can be described as a deposition of nanolitre droplets. In order to tailor the structure-function relationship starting from the nanoscopic level to mesoscopic domains, it is thus mandatory to study the thin film formation *in situ* and real time. Therefore, we first combined colloidal solution spraying with microbeam grazing incidence small-angle x-ray scattering. This allows for following the rapid structural build-up *during* spraying on solid substrates on multiple length scales. We show that the parameter temperature of the substrate is crucial to obtain tailored morphologies of the thin colloidal film and extract quantitatively the detailed thin film formation kinetics. Secondly, we investigated the LbL formation of enzymatic cellulose / silver nanoparticle (Ag NP) sandwich structures. The latter work reveals that spray deposition of Ag NP leads to a fine distribution of the Ag NP on the cellulose layer by suppression of the coffee ring effects. The final capping with an additional cellulose layer for protective reason does not alter the underlying layer morphology, which is crucial with respect to advance, bio-inspired and cellulose based organic electronics.

COLL 68

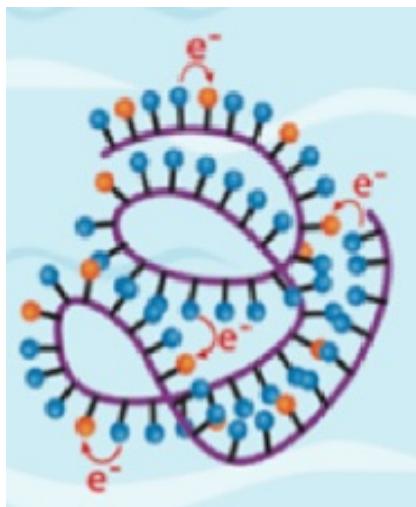
Elucidating the reactivity and solution dynamics of redox active polymers and colloids

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Redox active polymers (RAPs) and Redox Active Colloids (RACs) are emerging as attractive charge storage medium for applications in novel non-aqueous size-excluding flow batteries. Our group demonstrated in 2014 that RAPs can store charge reversibly and be effectively excluded from crossing over a simple nanoporous separator. While increasing the size of the polymer, accessed synthetically in particles ranging from ~4 nm to ~800 nm, should enhance the size exclusion effect for better performing batteries, it also places important constraints on electron transfer. We will discuss on the impact of size and electrolyte interactions on the electrochemistry of RAPs and RACs.

In contrast to the large body of literature existing on polymer films, detailed studies linking polymer structure and dynamics in solution to electrode reactivity are still incipient. Understanding the relationship between solution dynamics and their electrochemical signatures would enable to identify the rate limiting steps in the charge/discharge process in order to design better-performing devices. It is known that ionic electrolyte interactions with charged redox species can dramatically influence the reduction potential and electrochemical kinetics. We have found that ionic interactions, size of electrolyte ions, and the ionic strength can be tuned to systematically enhance the reactivity of poly-nitrostyrene RAPs. Additionally, we will discuss the impact of pendant-to-pendant proximity, colloid size, and electrostatic effects on the transient and steady-state electrochemical behavior of a wide range of polymers in solution and dispersion. Unlike monomers, the electrochemical reactivity of solution-phase polymers is strongly modulated by the properties of both surface confined and freely diffusing polymers in the electrolytes used for size-selective non-aqueous redox flow batteries.



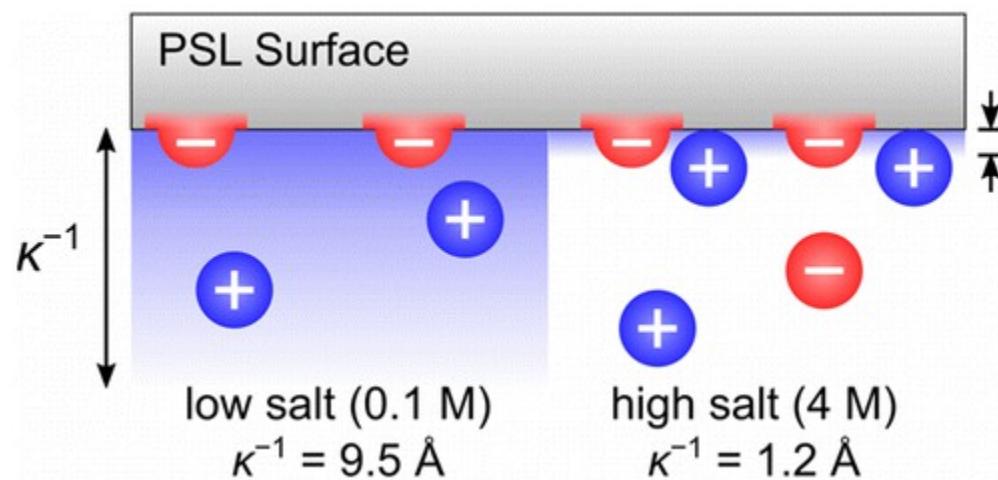
COLL 69

Particle zeta potentials remain finite in saturated salt solutions

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The zeta potential of a particle characterizes its motion in an electric field and is often thought to be negligible at high ionic strength (several moles per liter) due to thinning of the electrical double layer (EDL) to less than a nanometer. Here, we describe zeta potential measurements on polystyrene latex (PSL) particles at monovalent salt concentrations up to saturation (~ 5 M NaCl) using electrophoresis in sinusoidal electric fields and high-speed video microscopy. Our measurements reveal that the zeta potential remains finite at even the highest concentrations. Moreover, we find that the zeta potentials of sulfated PSL particles continue to obey the classical Gouy–Chapman model up to saturation despite significant violations in the model's underlying assumptions. By contrast, amidine-functionalized PSL particles exhibit qualitatively different behaviors such as zero zeta potentials at high concentrations of NaCl and KCl and even charge inversion in KBr solutions. The experimental results are reproduced and explained by Monte Carlo simulations of a simple lattice model of the EDL that accounts for effects due to ion size and ion–ion correlations. At high salt conditions, the model suggests that quantitative changes in the magnitude of surface charge can result in qualitative changes in the zeta potential—most notably, charge inversion of highly charged surfaces. These findings have important implications for electrokinetic phenomena such as diffusiophoresis within salty environments such as oceans, geological reservoirs, and living organisms.



COLL 70

Issue of interchangeable use of reactivity assessment assays for nanoparticle colloids in liquid solution

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Nanomaterials are actively involved in enormous novel technologies and industrial products. Surface reactivity of nanomaterials are underlined to not only cases where the reactivity is utilized for benefits, e.g., nano-catalyst or nano-antibiotics, but also cases where nanomaterials undergo undesirable reactions once they are released from products, e.g., causing oxidative stress to cells or damaging cell membranes, and pose potential risks to the environmental and human health. Many assays were used to assess surface reactivity of nanoparticle (NP) colloids in liquid solution. They are often fulfilled by setting the NPs of interest as a reactant in a reaction, whose procession can be analyzed by a instrument, such as absorbance or fluorescence microscopy, due to the sensitive signal response of the other reactant or product under the analysis. In many cases, a single assay was applied; yet under few circumstances is fully examined whether the applied reactivity assay is sufficiently representative to the material's intrinsic property that is truly relevant to what is studied. Consequently different assays were often interchangeably used and interpreted, and whether they imply the same intrinsic property of the material was not carefully inspected.

In this study, we choose four commonly adopted reactivity assessment assays, namely methylene-blue reduction catalyzing assay (MRCA), ferric reducing assay (FRA), XTT superoxide detecting assay (XTT assay), and reactive oxygen species detection by EPR (ROS-EPR assay), and apply them to typical metal and oxide NP colloids, including Au, Ag, SiO₂ and CeO₂. Under each assay, we analyze the four NP colloids and rank the obtained reactivity magnitude of them by the specific assay. We contrast the reactivity magnitude pattern across the four NP colloids given by different assays. Overall, we conclude that the experimentally assessed surface reactivity information of NP colloids in liquid solution is dependent on the assay that is applied, arguing that we should be extremely careful about interchangeably using or interpreting reactivity of the same NP colloids obtained by different assays. We further propose that, for NP colloids in solution, a selected assay mechanistically assesses the intrinsic material property of redox activity or catalytic activity, the discrimination of which is critical to effective comparisons of NP colloids' surface reactivity.

COLL 71

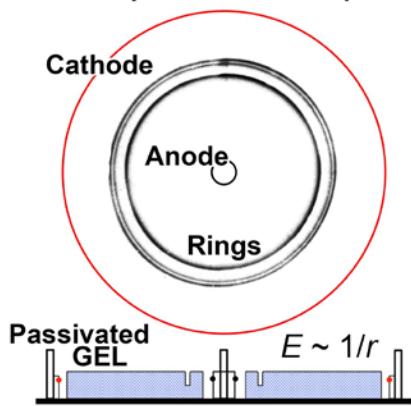
Propagation and separation of charged colloids by cylindrical gel electrophoresis

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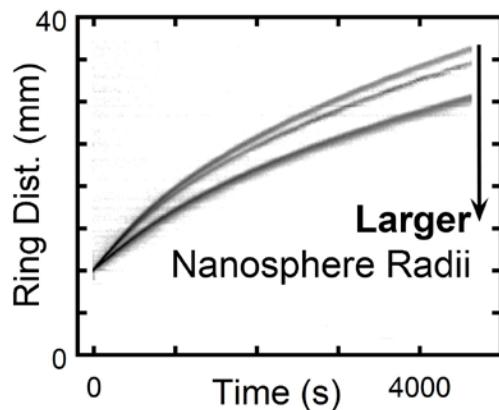
California, United States (2) Department of Physics and Astronomy, University of California - Los Angeles, Los Angeles, California, United States

We construct a full-ring cylindrical electrophoresis chamber and explore the electrophoretic propagation of anionically stabilized polystyrene spheres of various sizes and surface charge densities. This radial electric field, in contrast to traditional Cartesian gel-electrophoresis geometries, causes particles to propagate outward from a center ring-well more rapidly at first before slowing over time as the ring-like front of charged particles moves further away from the axis. By taking movies of light scattered by the propagating nanospheres undergoing electrophoresis, we demonstrate that ring-like fronts of monodisperse nanospheres propagate stably in PEG-passivated agarose gels. The ring radius as a function of time agrees with a simple model incorporating the electric field of the cylindrical geometry. Moreover, a cylindrical geometry offers the potential for improved separations of objects of widely different size: smaller spheres can be retained in the cylindrical gel for the duration of longer run times needed to separate larger objects.

Stable Propagating Rings of Monodisperse Nanospheres



Nonlinear Radial Distance vs Time



COLL 72

Morphology and properties of fibers obtained by emulsion electrospinning

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High Internal Phase Emulsions (HIPE) are known for the excessive usage of aqueous disperse phase volume fraction over 0.74. An effort was made to study the transformation process of restructuring a HIPE into electrospun fiber morphology. Various factors affecting the emulsion properties like polymer concentration, volume fraction of dispersed phase, emulsifier positioning and its channelization into uniform electrospun fibers were studied in detail. Thermal behaviour of the electrospun fibers were evaluated and were related to original HIPE morphology. The novelty of this process is to produce electrospun fibers even from hydrophobic polymers with

minimised usage of toxic organic solvents. Pickering emulsion electrospinning process is another innovative technique for production of hybrid composite fibers. The major advantage of Pickering emulsion electrospinning is no emulsifier and/or template polymer usage reducing the leaching tendency of these materials on exposure to a humid or aqueous environment. Thus the mechanical properties of these fibers are unaffected under aqueous environment. Usage of solid Pickering stabilizer instead of emulsifier has an added advantage of introducing functionality into the electrospun fibers. Various factors affecting emulsion stability and electrospun fiber morphology were studied. Electrospun matrices produced from advanced emulsions with minimum organic solvent and enhanced functionality have potential applications in the field of tissue engineering, filtration, gas adsorption and others.

COLL 73

New strategies for selective deposition of nanoscale materials

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With the growing need for fabrication of nanostructures, selective deposition is likely to become an important process to achieve pattern features at the ~10 nm length scale. Both two-dimensional planar geometries and three-dimensional structures will benefit from selective deposition processes, with bottom-up growth strategies providing advantages in reduced process complexity and improved pattern fidelity. In this presentation, we will describe area selective deposition based on atomic layer deposition (ALD). ALD is a good choice for selective deposition because its chemical specificity provides a means to achieve selectivity on a spatially patterned substrate. In this work, self-assembled monolayers (SAMs) are used to passivate the surface, using SAMs in the regions where deposition is not desired. We will show that the process provides good selectivity for thin deposited films. However, a major challenge is that after a certain amount of material is deposited, the ALD process may begin to nucleate on the part of the surface covered with the SAM. We will describe new strategies to overcome the growth on the SAM and achieve significantly higher selectivity in area selective ALD. In one approach, to improve the blocking properties of the SAM on copper surfaces, the SAM is repaired between ALD cycles with the purpose of recovering the SAM's properties. Results show that the resulting selectivity can be retained for much thicker deposited films. In a second approach, a "self-correcting" process is developed in which selective deposition is combined with selective etching, greatly improving the final selectivity. These strategies may open up the possibility for new applications of nanostructures.

COLL 74

Using surface chemistry to direct the morphology of thin films and nanoobjects of energy materials

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We describe recent progress in our laboratory to build robust complex metal oxide and chalcogenide - molecular nanocomposites. This work has important applications in photovoltaics, molecular and organic electronics, sensing, photonics and other technologies. Several recent developments will be discussed including the atomic layer deposition of ZnO and ZnS and the formation of semiconducting nanowires and other nanostructures on micron-scale patterned surfaces. Optimization and further development of these techniques requires a detailed understanding of the reaction pathways involved in the interaction of organic thin films with organometallic compounds, ions, and other compounds in both solution and gas phases.

COLL 75

Laser-assisted focused electron beam induced synthesis: Photothermal enhancements to athermal electron beam induced reactions

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Electron beam induced synthesis is a direct-write nanoscale synthesis approach in which a focused electron beam induces a scission event of a precursor molecule adsorbed on a substrate surface which either condenses (deposition) or reacts to form a volatile species with the substrate (etching). Strategic scanning of the focused electron beam can thus conveniently deposit nanoscale 2D and 3D objects. The main limitation is the fact that most of the synthesis is performed at room temperature and thus residual precursor ligands are incorporated into the deposits. To this end, we have developed a laser-assisted electron beam induced processing technique which couples a pulsed laser source to the electron beam/precursor region and thus enables a photothermal assist to the otherwise athermal electron stimulated chemical reactions. In this presentation we will briefly overview the laser delivery system and demonstrate regimes (power, pulse width and frequency) in which the laser assist can enhance the deposit purity by facilitating by-product removal. Additionally, a pseudo atomic layer deposition or layer-by-layer approach will be shown in which one half reaction is stimulated by the electron beam induced reactions and a subsequent half reaction is a photothermal step in which residual water vapor reduces the residual carbon in the deposit. Finally, we will demonstrate our recent work developing scanning strategies which enable nanoscale 3D objects to be written and preliminary results comparing ex situ purification strategies to the in situ laser-assisted strategy.

COLL 76

Time is of the essence: Using a fourth dimension to improve chemical vapor deposition

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The term chemical vapor deposition (CVD) summarizes a broad class of deposition techniques, many of which are well-established in several industrial areas. Although CVD is in many aspects a mature technique, it is evolving in order to meet higher and higher demands on thin films: uniform deposition on more complex geometries, with narrow trenches and complicated topologies, on temperature sensitive substrates, and onto underlying films, which requires lower deposition temperatures.

One of the most important evolutions of CVD, atomic layer deposition (ALD), is a time-resolved CVD technique where the precursors are introduced in a time-resolved sequential manner. The precursor supply enables a self-limiting surface chemistry rendering the very high degree of surface control which is the hallmark of ALD. But also time-resolved precursor supply without a self-limiting surface chemistry is an important evolution of CVD as it can be used for growing semiconducting nanowires on a patterned surface without the need for a catalyst or to deposit ternary or quaternary materials in some materials systems.

CVD can also be made time-resolved by controlling the amount of energy available to the process over time. While this is difficult to do with a thermally activated CVD process, a process driven by the energy provided in a plasma discharge can easily be time-resolved in energy. This has allowed self-limiting processes with constant flow of precursors and an enhanced ability to use ionic species for film deposition.

This presentation will discuss some of the possibilities available when CVD is done in a time-resolved rather than continuous manner. Using examples both from literature and my own recent research, I will point to how both low temperature, kinetics and surface control are accessible when controlling the time dimension of CVD.

COLL 77

Real-time XPS monitoring of atomic layer deposition of HfO₂ on Si surfaces

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Atomic layer deposition (ALD) is one of the main techniques for thin layer growth in, e.g., materials science, catalysis, and solar photovoltaics. The self-limiting nature of the growth in ALD deviates strongly from the ideal scheme and the ALD surface chemistry remains largely unknown, not least due to the lack of possibilities for true *in situ* and *operando* studies. In order to address this shortcoming we carried out Ambient pressure

x-ray photoelectron spectroscopy (APXPS) to study the ALD growth of HfO_2 on the clean, oxidized, and native Si(111) surfaces. Tetrakis(dimethylamido)hafnium (TDMAHf) and water were used as precursors. Both half cycles were monitored during the dosing and pumping stages. The results were combined with a post mortem investigation by transmission electron microscopy (TEM) and atomic force microscopy (AFM).

We carried out APXPS at high temporal resolution and identified surface species that occur in the ALD half-cycles (figure 1). Cyclic shifts in binding energy are seen to occur between the TDMAHf and water pulses. The ALD layer grows faster on the SiO_2 surfaces in comparison to the clean one. Interestingly, the oxide layer was not removed during the initial TDMAHf half-cycle exposure, which is in contrast to the ALD of HfO_2 on InAs and which can be explained by the higher stability of the SiO_2 layer in comparison to the HfO_2 layer.

AFM, carried out on the samples from the APXPS experiments, illustrates that the ALD process carried out in the APXPS instruments results in films similar to those produced in real ALD reactors. Clear differences are observed between the films grown on the oxidized, clean, and native Si(111) surfaces. The TEM analysis of sample cross sections confirms the differences in reaction speed between the surfaces which results in differences in thickness and structures of the layer.

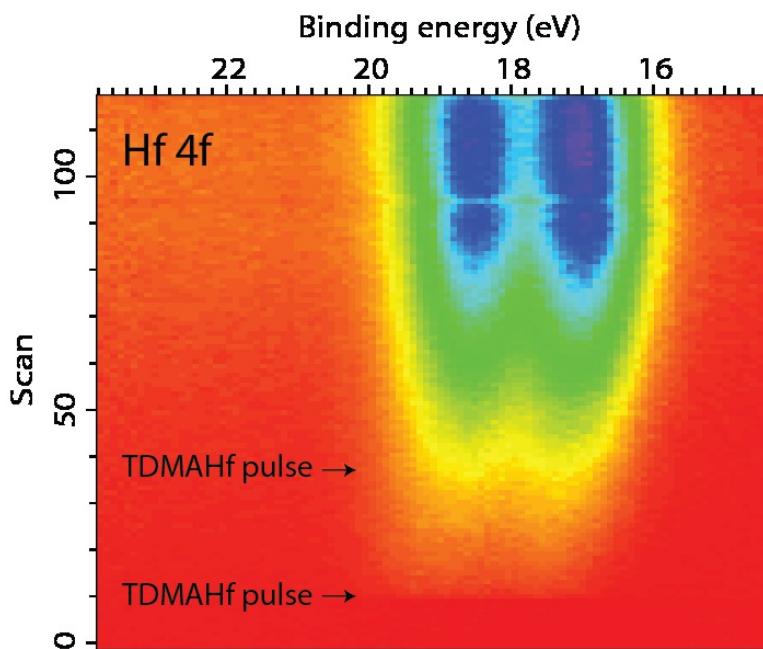


Figure 1. Ambipolar pressure x-ray photoelectron spectroscopy data during the first TDMAHf half-cycle of ALD on the oxidized Si (111) surface.

COLL 78

Directed deposition and etching of functional nanostructures using electron beam and plasma irradiation

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Electron beam induced deposition and etching (EBID and EBIE) are direct-write nanofabrication techniques in which an electron beam is used to dissociate surface-adsorbed precursor molecules to achieve nanostructure etching or deposition inside an environmental scanning electron microscope. Here, we will discuss recent experimental work on directed deposition and etching of fluorescent diamond nanoparticles and the two-dimensional semiconductor hexagonal boron nitride.

First, we use an ammonia plasma to functionalize the surfaces of EBID-fabricated nanoscale carbon seeds (Fig. 1a) with amine groups. Covalent bonding of nanostructures such as nanodiamonds and gold colloids to the amine-functionalized seeds is then achieved by carbodiimide coupling chemistry. To ascertain the nanodiamond attachment yield and selectivity of the technique, we employ confocal microscopy to obtain photoluminescence maps and spectra of the fabricated arrays. The bright fluorescent spots in Fig. 1b correspond to the emission (Fig. 1c) from nitrogen vacancy defects in the nanodiamonds, demonstrating successful attachment.

Our attachment process is applicable to a wide variety of substrates and offers unprecedented stability, which we demonstrate by subjecting the fabricated nanodiamond arrays to up to 12 hours sonication. We demonstrate the utility of our process by assembling fluorescent nanodiamonds into large area arrays that can be utilized as magnetic field sensors.

We also demonstrate high resolution EBIE of the two dimensional semiconductor hexagonal boron nitride in a background atmosphere of water vapour. The hBN undergoes denitrogenation under electron beam induced etching in H₂O, forming volatile NO and NO₂ and resulting in highly localized, clean etching of the hBN. Raman analysis demonstrates that the surrounding hBN material is not damaged by the etch process, enabling damage-free fabrication of well-defined hBN nanoribbons, holes and other geometries.

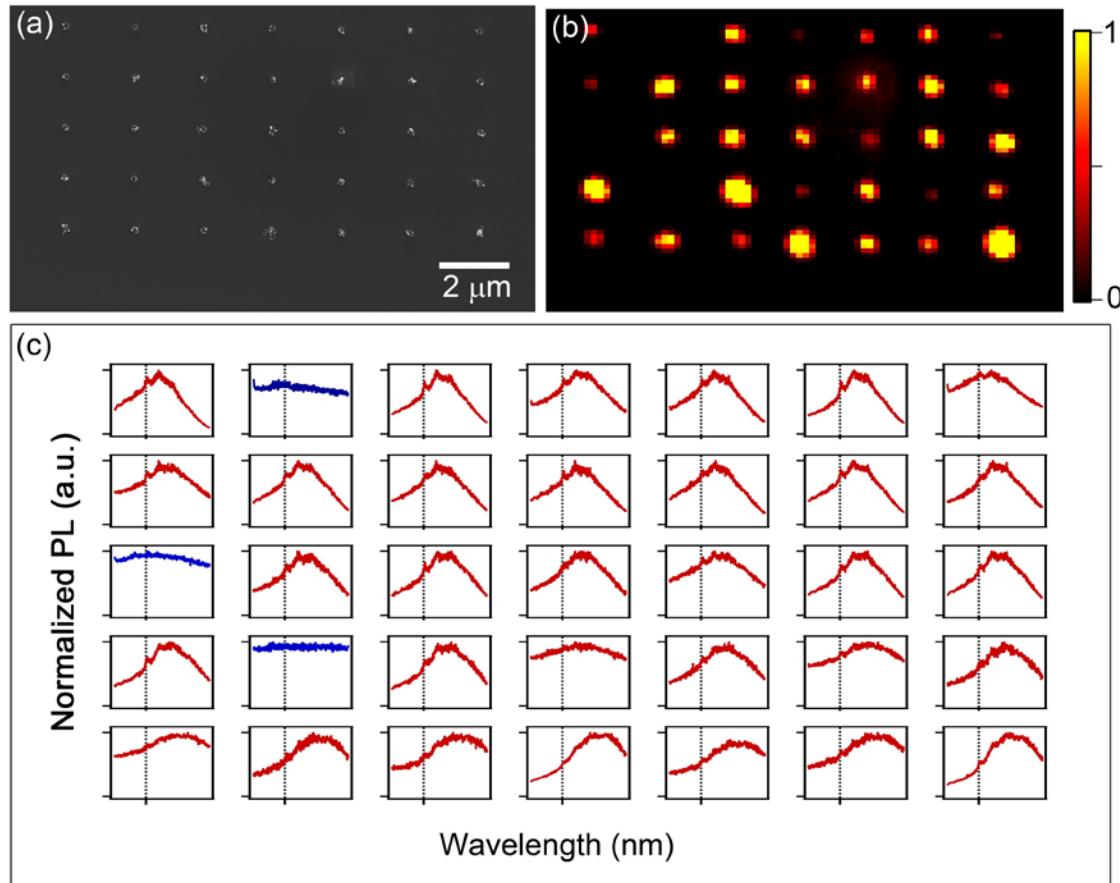


Fig. 1. Characterization of attachment yield and selectivity.

COLL 79

Lipid non-lamellar phases at the solid/liquid interface - structure and dynamics

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Non-lamellar lipid based self-assembly structures have been increasingly recognized as important for living systems. Understanding the biological implication as well as the application of such interfaces, for e.g. drug delivery and other biomedical application, requires the development of well-defined model system. We will discuss how to provide lipid based biofunctional surface films beyond supported bilayers, where the structural changes of deposited lipid can be controlled. We have previously demonstrated the

formation of highly curved, fluid supported bilayers on vertical gallium phosphide nanowire (NW) forests using self-assembly from lipid vesicular dispersions. The formation of non-lamellar lipid liquid crystalline surface layers prepared by spin-coating the constituting lipids followed by hydration of the lipid layer will be demonstrated. We will show that we can form non-lamellar liquid crystalline surfaces of different phases on the surface. The structure and dynamics in these nano-structures films formed by mixtures of soy phosphatidylcholine (s-PC) and glycerol dioleate (GDO) at the silicon-aqueous interface were studied by grazing incidence neutron spin echo spectroscopy (GINSES), specular and off-specular neutron reflectometry and small angle x-ray diffraction (SAXD). Neutron reflectometry measurements and SAXD showed that reverse hexagonal (H_{\parallel}) and micellar cubic phase ($Fd3m$) layers at the solid/liquid interface can be formed by changing the lipid composition. For the cylindrical hexagonal phase only orientation of the liquid crystalline phase was identified. The size of the liquid crystalline domains was 100 nm as estimated from the width of the diffraction peaks. GINSES revealed that both phases form rather rigid films. In comparison the H_{\parallel} film was more flexible, appearing as a modified undulation spectrum of the cylinders due to the interaction with the substrate.

COLL 80

Stimulus-responsive behavior of giant vesicles consisting of amphiphilic diblock copolymers

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Micro-sized giant vesicles formed by the self-assembly of amphiphilic block copolymers are artificial models of biomembranes for cells and organelles based on the similarities in their size and structure. This paper describes the stimulus-responsive behavior of the giant vesicles to temperature, pH, and salt concentration. The thermosensitive behavior of the giant vesicles consisting of poly(methacrylic acid)-block-poly(methyl methacrylate-random-methacrylic acid) was explored in an aqueous methanol solution. The spherical vesicles at 25°C were partly fused at 35°C and further changed into sheet-like morphology at 50°C. The sheet-like morphology reverted to spherical vesicles via network structure and worm-like vesicles by decreasing the temperature to 25°C. The pH-responsive behavior of the giant vesicles was investigated in water. The spherical vesicles at pH = 7.1 were rapidly disrupted over pH 11 and finally dissociated into micelles at pH 12.8. As a result of decreasing the pH to 7.5, the micelles were transformed into a sheet-like morphology due to the interaggregation in the presence of NaCl generated during the neutralization of the basic NaOH solution by HCl. The spherical vesicles were reconstructed from the sheet-like morphology when placed in an aqueous methanol solution. The reconstructed vesicles included budding and hand-shaped vesicles, indicating that spherical vesicles were formed by the budding separation and by way of a bilayer-rod transition. The salt-responsiveness was investigated using poly(allylamine hydrochloride) (PAH) for the vesicles containing 1 mol% of the 3-sulfopropyl methacrylate potassium salt (SpMA) units incorporated in the

poly(methacrylic acid) block. The spherical vesicles were soaked in PAH solutions of different concentrations. The vesicles were disrupted into a nonspecific form at a low PAH concentration. On the other hand, no disruption took place at the high concentration with the exception of partial fusion of the vesicles. It was considered that PAH at the low concentration disordered the copolymers forming a vesicle due to too short interval between the allylamine hydrochloride units interacting with the SpMA units, whereas PAH at the high concentration held the intervals long enough to retain the arrangement of the copolymers in the vesicle.

COLL 81

Selective blood vessel deletion using liposomes: Studying the effect of liposome composition on *in vivo* behavior

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In recent years we developed a drug delivery method based on the fusion of liposomes with live cells and this process was controlled by a complementary pair of lipopeptides. While this method is successful in an *in vitro* environment, achieving selectivity *in vivo* is still a challenge.

More general, cell-type specific targeting is a common goal in nanoparticle drug delivery, yet for most cell types, *in vivo* targeting efficiencies remain less than 1%. Here we use a zebrafish model to dynamically assess nanoparticle fate *in vivo* and uncover targeting specificities of various liposomes composed of naturally occurring phospholipids alone. We identify formulations highly selective for a subset of endothelial cells and through encapsulation of clodronic acid, a cytotoxic and membrane impermeable drug, demonstrate selective deletion of a single blood vessel type *in vivo*. Mechanistically, we identify endothelial scavenger receptor *stabilin-2* as mediator of liposome targeting, extending the function of these receptors to the recognition of neutral nanoparticles. Our findings establish the zebrafish as a powerful model organism for understanding and optimising liposomal drug delivery, reveal a critical importance of lipid composition to *in vivo* liposome fate and identify a novel drug formulation with potential application in anti-angiogenic therapy.

COLL 82

Physical clotting of blood cells using associating biopolymers as the connective glue: An investigation into the mechanism using optical microscopy

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Amphiphilic biopolymers such as hydrophobically modified chitosan (hmC) have been shown to convert liquid blood as well as solutions of vesicles/liposomes into elastic gels.

This interesting property could make hmC useful as a hemostatic agent in treating severe bleeding. The mechanism for blood gelling by hmC is believed to involve polymer-cell self-assembly, i.e., the insertion of hydrophobic side-chains from the polymer into the lipid membranes of blood cells, thereby creating a network of cells bridged by hmC. Here, we probe the above mechanism by studying dilute mixtures of blood cells and hmC *in situ* using optical microscopy. Our results show that the presence of hydrophobic side-chains on hmC induces significant clustering of blood cells. The extent of clustering was quantified from the images in terms of the area occupied by the largest clusters. Clustering increased as the fraction of hydrophobic side-chains increased; conversely, clustering was negligible in the case of the parent chitosan that had no hydrophobes. Moreover, the longer the hydrophobic side-chains, the greater the clustering (i.e., C12 > C10 > C8). Clustering was negligible at low hmC concentrations, but became substantial above a certain threshold. Finally, clustering due to hmC could be reversed by adding the supramolecule alpha-cyclodextrin, which is known to capture hydrophobes in its binding pocket. Overall, the results from this work are broadly consistent with the earlier mechanism, albeit with a few modifications.

COLL 83

Elastic and viscous properties of lipid bilayers: Application of neutron spin echo spectroscopy

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Motions of molecules and their assemblies are fundamental to biological functions. The hierarchical lipid membrane motions span individual molecular movements to undulations of micron-sized patches and vary with the degree of complexity of the membranes. Over this wide space and time range dynamics on the nanometer scale remain largely unexplored due to experimental challenges in accessing the appropriate length and time scales. Over the past several years our group has used neutron spin echo (NSE) spectroscopy to provide unique insights into these elusive dynamics in model lipid bilayers. NSE measures collective motions of membranes on the nanometer and nanosecond scales, such as undulation and thickness fluctuations. These thermal fluctuations of lipid molecules are controlled by the elastic and viscous properties of the membranes and provide a basis for understanding the biomembrane's mechanical properties. Undulation fluctuations have long been studied to understand membrane elasticity as the fluctuations are characterized by the membrane bending modulus, κ , and are damped by the solvent viscosity, η . Thickness fluctuations, on the other hand, have been more challenging to observe experimentally. Our group showed that NSE experiments can capture the thickness fluctuation dynamics and provide a measure of the fluctuation amplitude, Δh , and time scale, τ . Statistical mechanics predicts a relation between the area compressibility modulus, K_A , and the fractional change in thickness,

$\Delta h/h$, under the volume conservation condition. This relationship allows us to estimate K_A values from the experimental Δh measurements. Moreover, recent theoretical developments by Bingham and colleagues suggest that τ is characterized by K_A and the membrane viscosity, μ . We have applied the above discussion to the analysis of the thickness fluctuations dynamics, and it is now possible to determine μ as the only fit parameter to the experimental data. We will explain the method and review some of the results in phospholipid membranes with and without small molecule and peptide additives.

COLL 84

Kinetic pathways of self-assembled systems by time-resolved small-angle scattering techniques

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Self-assembled systems are generally highly dynamic structures characterized by continuous exchange of molecules and fluctuations that may lead to structural transitions upon external influence. Examples include micelles formed by synthetic surfactants and block copolymers as well as lipid membranes and protein complexes found in nature. Despite their importance in technological and biomedical applications, the kinetic pathways associated with the formation and molecular transport of such self-assembled nanostructures are generally poorly understood. Time-resolved small-angle X-ray/neutron scattering (TR-SAXS/SANS) is powerful technique that allow non-equilibrium kinetic processes such as nucleation processes and morphological transitions to be followed with structural resolution over time scales starting from a few milliseconds. Neutrons have the additional advantage of facile contrast variation through H/D substitution schemes, which also allow equilibrium processes such as molecular exchange and diffusion to be studied without perturbation.

In this presentation we will address the basic molecular mechanisms behind kinetic processes found in surfactant and block copolymer micelles. We will address both equilibrium and non-equilibrium kinetics and argue that the understanding of kinetic pathways can be utilized to manipulate and design the physical properties of self-assembled systems. Furthermore, we shall discuss the role of confinement and crystallinity on the stability and molecular transport processes in micelles and discuss the relevance to biological systems and biomedical applications.

COLL 85

Neutron and x-ray scattering approaches for interdisciplinary structural biology

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Neutron and X-ray scattering are unique and highly complementary probes for the study of biological structure and dynamics. Both approaches are at their most powerful when used alongside other techniques (eg NMR, electron microscopy, mass spectrometry) that complement and extend the scope of scattering observations. While synchrotron X-ray studies provide high resolution images of molecular structure, only neutron diffraction can identify the details of protein-water interactions and protonation states – factors that of major importance in (for example) the functioning of redox proteins or in protein-ligand interactions. At lower resolution, small-angle neutron and X-ray methods, used in combination with suitable deuteration regimes, allow macromolecular interactions relevant to protein function to be studied. These types of combined applications will be described and illustrated with examples.

COLL 86

Opening the SANS toolbox for studying mRNA nanoparticle structure

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Modified messenger RNA, which can encode for virtually any known protein in target tissues and organs, is a new paradigm for the design of next generation biotherapeutics. Once the mRNA is delivered inside of the cell, like native mRNA in healthy individuals, the modified mRNA can direct transient dose-dependent expression of protein drug modalities including, but not limited to, intracellular proteins, cell-surface bound proteins, and secreted proteins such as antibodies. Each mRNA molecule has the power to catalyze the expression of hundreds to thousands of proteins or antibodies, making mRNA therapeutics a key technology for tackling un-druggable intracellular pathways, regenerative medicine, and vaccines. The question must then be asked on how to deliver mRNA into the body. One approach which has shown much promise is by embedding the mRNA within nanoparticles which protects the mRNA from chemical degradation mechanisms or attack by natural enzymes such as RNases. In order to characterize these RNA containing nanoparticles, we employed small angle neutron scattering (SANS). SANS is an excellent technique for studying colloids and biological molecules because the neutron wavelength is on the length scale of interactions of molecules within the nanoparticles, and because neutrons are non-destructive yet highly penetrating. Our employment of SANS has allowed for structure–composition correlations which are unattainable by any other means. In this talk we will discuss the role of mRNA in the formation of lipid nanoparticles, and how we use the SANS contrast match method to identify the location of each lipid in the mRNA and non-mRNA containing lipid nanoparticles. The goal of these experiments are to correlate structure, lipid organization, and function of the lipid nanoparticles containing mRNA.

COLL 87

Silicon nanocrystal assemblies

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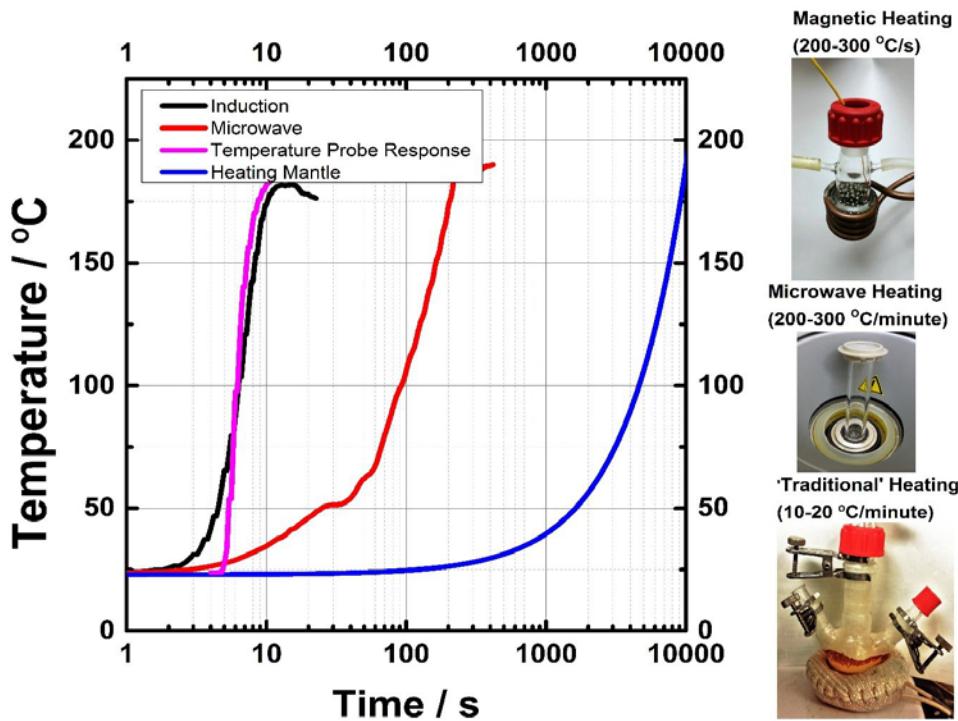
Silicon nanocrystals can now be made with a high degree of uniformity and assembled into a variety of structures. For example, uniform silicon (Si) nanocrystals with cuboctahedral shape, passivated with 1-dodecene capping ligands assemble into face-centered cubic (FCC) superlattices with orientational order. Transmission electron microscopy (TEM), electron diffraction and grazing incidence wide angle and small angle X-ray scattering (GISAXS and GIWAXS) show that the preferred orientation of these soft cuboctahedra depends on the orientation of the superlattices on the substrate, indicating that the interactions with the substrate and assembly kinetics can influence the orientation of faceted nanocrystals in superlattices. These superlattices exhibit structure-dependent solid-solid phase transitions of the Si nanocrystals under pressure. Application of a quasi-uniaxial pressure was found to induce the formation of a new Si phase with diatomic body-centered cubic (BCC) structure and a lattice constant of 4.08 Å at 9.5 GPa. We have also used Si nanocrystals to create substrate-free self-supporting bubble assemblies, which can be used to study optical phenomena in the absence of solvent and substrate effects.

COLL 88

Induction and microwave heating in syntheses of CdSe quantum dots: Effects of extreme high heating rate on their nucleation and growth kinetics

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In colloidal synthesis of inorganic nanoparticles, reliable control of their size and size distribution is one of the most critical aspects of fine-tuning their various properties. The ability to manufacture sub 2-nm ultra-small particles is of particular interest. Here we present a novel induction heating method to provide rapid heating rate for its synthesis, as comparison to the more widely reported microwave heating. We show that with induction heating, mono-dispersed ultra-small nanoparticles can be prepared in a fast and simple manner, with ability to fine-tune its size. With results compared to that of the microwave heating, we also show how extreme high heating rate, precursor reaction mechanism, solvent viscosity and other factors affect the nucleation and growth kinetics of the synthesis.



COLL 89

Enhanced emission of nanocrystal solids featuring slowly diffusive excitons

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Solution processing of semiconductor nanocrystal (NC) solids represents an attractive platform for the development of next-generation optoelectronic devices. In search for enhanced light-emitting performance, NC solids are typically designed to have large interparticle gaps that minimize exciton diffusion to dissociative sites. This strategy, however, reduces an electrical coupling between nanoparticles in a film, making the injection of charges inefficient. Here, we demonstrate that bright emission from nanocrystal solids can be achieved without compromising their electrical conductivity. Our study shows that solids featuring a low absorption-emission spectral overlap (J) exhibit intrinsically slower exciton diffusion to recombination centers, promoting longer exciton lifetimes. As a result, enhanced emission is achieved despite a strong electronic coupling. The observed phenomenon was found consistent with a decreased resonant energy transfer in films exhibiting a reduced J value. The positive correlation between film luminescence and J was revealed through a comparative analysis of CdSe/CdS and ZnSe/CdS solids and further confirmed in two control systems (ZnTe/CdSe and Mn²⁺-doped ZnCdSe/ZnS). Exceptionally slow exciton diffusion (~ 0.3 ms) and high brightness were observed for Mn²⁺-doped Zn_{1-x}Cd_xSe/ZnS NC films exhibiting a nearly vanishing J parameter. We expect that the demonstrated combination of electrical

coupling and bright emission in nanocrystal solids featuring low J can benefit the development of nanocrystal light-emitting technologies.

COLL 90

Detecting material state change in surface coated tensile samples using ultrasmall CdSe quantum dots

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This research focuses on the development of a material state change detection system by incorporating an internal sensor. To accomplish this goal, ultrasmall Cadmium Selenide quantum dots (CdSe QDs) are encapsulated in a biphenyl-perfluorocyclobutyl (BP-PFCB) and coated onto metal and composite tensile samples, such as aluminum and fiberglass. Ultrasmall CdSe QDs are a unique material that emits broad spectrum white light due to multiple surface-related emitting states. These surface states are highly sensitive due to the physical structure of the QD, and minute changes in the surrounding environment can result in observed changes in the emission spectrum. In this research, tensile loadings are applied to samples coated with encapsulated CdSe QDs and the corresponding change in emission spectra is subsequently recorded with increasing levels of load. By analyzing the difference in emission spectra between each load case and unloaded test samples, the effectiveness of using ultrasmall CdSe QDs as an alternative internal sensor for damage detection applications is herein evaluated.

COLL 91

Ligand-induced freeze of gold nanostars and their SERS activities

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Nanomaterials have attracted increasing interest due to their tunable morphologies, unique properties, and broad applications. Gold nanostars are one of the most popularly studied plasmonic nanomaterials because of the highly branched nanostructures. Precise control of the nanoscale branches on gold nanostars is extremely important. Here we developed a facile *in-situ* UV-Vis spectroscopic method and studied the reaction kinetics on seed-mediated growth of gold nanostars. The impacts of ligand concentration and seed amount on the formation of gold nanostars were systematically explored. In addition, an atomic rearrangement model was proposed to explain the morphology evolution during the synthetic process. A new approach of sudden addition

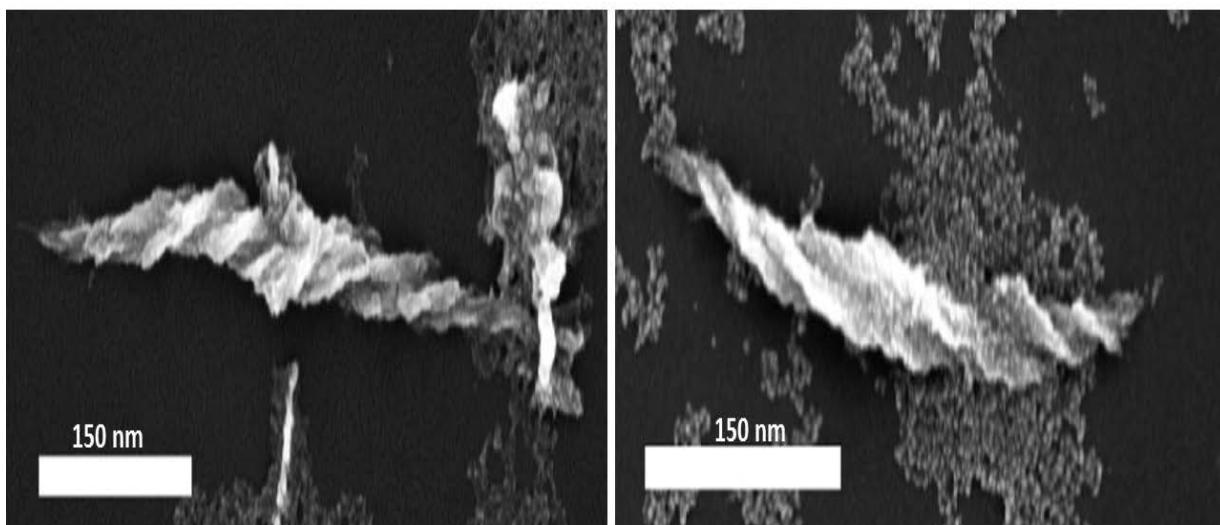
of capping ligands was developed to synthesize gold nanostars with designed morphology. This “ligand freeze” method can significantly advance the syntheses of gold nanostars and might be expanded to other metallic nanomaterials. We will also present our recent work on the impact of morphology evolution on the SERS activities of gold nanostars.

COLL 92

Chiral inorganic nanostructures

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Chiral inorganic nanostructures discovered over the last two decades include individual nanoparticles, their assemblies in dispersions and surfaces, as well as 2D/3D lithographic patterns. For many of them exceptionally strong polarization rotation in many of inorganic nanoscale systems was observed. In this presentation three types of chiral inorganic nanostructures will be considered: individual nanoparticles; their spontaneously formed organized superstructures, and DNA-bridged assemblies. The data linking origin of life and ability of NPs to form complex and dynamic superstructures will be discussed. Recent data on the preparation and properties of chiral graphene quantum dots and chiral ceramic nanoparticles will be presented.



Example of left and right helices assembled from *L*- and *D*-cysteine modified CdTe 5 nm nanoparticles.

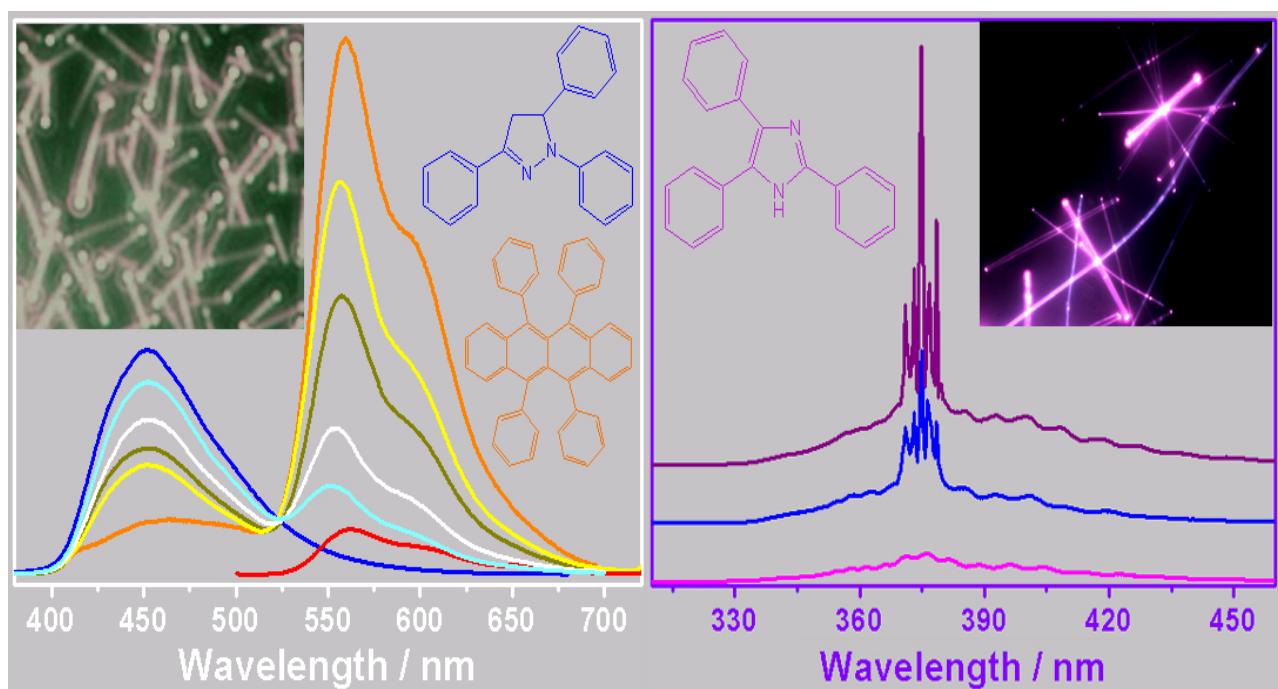
COLL 93

Organic nanophotonic materials and devices

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One-dimensional (1D) nanomaterials based on functional organic molecules have captured more and more interests in the past couple of years. Besides the strikingly different optoelectronic properties from those of their inorganic counterparts, organic nanomaterials also have some advantages in good doping property, high reaction activity, good processability, high photoluminescence (PL) efficiency, etc, which make them complementary to the inorganic materials.

The recent progress in unique photonic properties of organic 1D nanostructures will be introduced in this talk. A series of crystalline nanoscaled organic materials have been synthesized. With these materials, we achieved red-green-blue (RGB) multicolor emission, color tunable emission, and white emission, and applied them as sub-wavelength optical waveguide and miniaturized lasers as shown in Figure 1.



COLL 94

Study of Au nanoparticles self-assembly by in-situ transmission electron microscopy

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The self-assembly of nanoparticles (NPs) attracts great attention for its potential application in the design of hybrid composites with collective properties from different types of materials. Here, the in-situ liquid TEM with liquid cell made from a pair of SiN

membranes was employed to study the self-assembly of Au NPs with positively charged cetyltrimethylammonium ions (CTA⁺) and negatively charged citrate ions surfactants in aqueous in order to unravel the mechanism of NPs self-assembly. Under electron illumination in TEM, the solvated electrons will neutralize the positive charge on CTA⁺ coated NPs to reduce the repulsive electrostatic forces among them, resulting in the assembly of individual NPs into quasi one dimensional chains. The individual particles show a preference to on-axis attachment with the existing dimers, trimers to form trimer and tetramer. The anisotropic forces from dipolar interaction (long distance) and Van der Waals interactions (short distance) are the major driving factors for the anisotropic attachment. We found that positively charged Au NPs self-assembled only when the electron beam intensity exceeds a threshold, while negatively charged particles do not move due to the charging effect from high energy electron beam interaction with insulator SiN membranes.

We further use the in-situ liquid TEM technique to study the self-assembly of Au nanoparticles under biased/current flow conditions in aqueous. At biased condition, once there is liquid suspension with CTA⁺ coated Au nanoparticles across between the electrodes, there can be current through the NPs suspension. We adjusted the beam intensity lower than the threshold to trigger the nanoparticle movement. Under this condition, all the particles are steady without bias voltage applied. Then the different biased voltage was applied to the NPs suspension. It was found that the nanoparticles movement took place. By statistics, we found the nanoparticle displacement is roughly the same under different biased voltage from 0V to 3V. But there were more NPs start moving along with higher biased voltage/bigger current. Over all, the self-assembly dynamics under biased condition is the same as the non-biased condition.

COLL 95

Synthesis and assembly of plasmonic metal oxide nanocrystals

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Semiconductors can be rendered plasmonic by doping to create high concentrations of free carriers. Degenerately doped wide band gap metal oxides are commonly used as transparent conductive thin films in optoelectronic devices, and these same materials exhibit localized surface plasmon resonance (LSPR) when synthesized as discrete colloidal nanocrystals. I will describe our recent efforts to control the shape of plasmonic metal oxide nanocrystals by tuning synthetic conditions. Highly faceted nanocrystals exhibit distinctive LSPR modes that are evident in their absorption spectra. When assembled into close packed clusters or films, hot spots with amplified near field enhancement factors can result in the spaces between these nanocrystals. These hot spots, which can be predicted by electromagnetic simulations and observed by electron energy loss spectroscopy, facilitate resonant coupling with other oscillators.

COLL 96

Dynamic evolution of catalytic surfaces

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The evolution of surface structure under reaction conditions is key to understanding heterogeneous catalysis. We have investigated the structure and activity of nanoporous Au catalysts under reaction conditions using a combination of environmental transmission electron microscopy, ambient pressure X-ray photoelectron spectroscopy, and flow reactor kinetics. We demonstrate that nanoparticles with Ag and Au form under reaction conditions that yield the active site for the critical O₂ dissociation and ensuing selective oxidation of methanol and other alcohols. The results of these studies will be generalized in the context of catalyst design.

COLL 97

Metal nanoparticle catalysts based on classically immiscible and metastable alloys

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Randomly alloyed noble metal nanoparticles with unusual compositions may be prepared as 'stable' entities on the nanoscale using microwave-assisted solution synthesis. Bimetallic and ternary alloys of classically immiscible metals (e.g., RhAg, RhAu and IrAg) and metastable alloys (e.g., RhPd and RhPdAu) have been prepared, and their catalytic properties studied as a result of relative composition. Complimentary theoretical studies help to explain the relationship between surface structure and reactivity in alkene hydrogenation chemistry. Using the tools-of-the-trade taught to us by Prof. Gabor Somorjai, we present some new and unexpected results.

COLL 98

Catalysis on singly dispersed bimetallic sites

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A catalytic site typically consists of one or more atoms of a catalyst surface which arrange into a configuration offering a specific electronic structure for adsorbing or dissociating reactant molecules and its following elemental steps. Catalysis on a bimetallic nanoparticle consisting of continuously packed bimetallic sites at a metallic state has been well studied. An isolated bimetallic site supported on a non-metallic surface could exhibit a distinctly different catalytic performance due to its cationic state of the singly dispersed bimetallic site and the minimized choices of binding

configurations of a reactant molecule compared to these continuously packed bimetallic sites. One example of the singly dispersed bimetallic sites is Rh_1Co_3 which exhibits a distinctly different catalytic performance in reduction of nitric oxide with carbon monoxide at a low temperature, resulting from strong adsorption of two NO molecules on the Co-Rh-Co bridge of Rh_1Co_3 site and N_2O intermediate on Rh_1Co_3 site and a following low activation barrier in dissociation of strongly adsorbed N_2O to N_2 and O atom. The distinctly different catalytic performance between the singly dispersed bimetallic sites and continuously packed bimetallic sites suggests a method to develop new catalysts toward high selectivity.

COLL 99

Ordered bimetallic catalysts for selective hydrogenation and dehydrogenation reactions

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Intermetallic compounds are special alloys that have ordered crystal structures. The formation of the ordered structure is driven by thermodynamic, which means intermetallic compounds are structurally more stable than random alloys. Intermetallic compounds have been used as heterogeneous catalysts and often lead to significantly enhanced selectivity and stability. There are more than 10,000 reported intermetallic compounds of different compositions and structures, while only a very small portion of them have been studied for application in heterogeneous catalysis. Recently, intermetallic compounds also show the promising potential to replace precious metals that are heavily used in heterogeneous catalysis. We recently discovered that intermetallic NaAu_2 is catalytically active for CO oxidation at room temperature. With a newly developed ship-in-a-bottle strategy, we were able to synthesize monodisperse mesoporous silica-encapsulated intermetallic nanoparticles of different compositions. The mesoporous silica encapsulation prevents the aggregation of the intermetallic nanoparticles during high-temperature annealing that is often required for the formation of the ordered intermetallic phase. Meanwhile, the mesoporous silica shell does not prevent reactant molecules from accessing the intermetallic surface. Therefore, these mesoporous silica-encapsulated intermetallic nanoparticles provide a robust platform to study different catalytic reactions in a broad temperature regime.

COLL 100

Ideal catalysts beyond single crystals: MOFs with metal oxide-like nodes

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The nodes of some MOFs closely resemble small pieces of metal oxides, exemplified by the Zr₆ nodes of UiO-66, UiO-67, and NU-1000. Understanding the precise structures of the nodes, including their vacancies and surface sites, is crucial for the application of MOFs as catalyst supports. Structural defect sites of UiO-66/67 and NU-1000 have been inferred on the basis of IR spectra and density functional theory (DFT) to consist of pairs of terminal OH and OH₂ groups (called **site 1**). An open challenge is to tune these sites as a basis for tuning the catalytic properties of metal complexes bonded to them. We developed a treatment process to convert **site 1** into a new proton topology incorporating methoxy groups. IR and DFT results led to the identification of an intermediate methoxy-Zr structure incorporating structural vacancies on the node surface which facilitated the conversion of **site 1** to a new dehydro-monohydroxo site, which provides new opportunities for anchoring of metal-containing catalytic groups to the MOFs. The results show how the combination of DFT calculations and IR spectra can be used to determine the identity and chemistry of the functional groups on the defect sites on MOF nodes. We investigated species formed by chemisorption of Rh(C₂H₄)₂(acac), I, (acac is acetylacetone) on the MOF nodes as catalysts. Bonding of the rhodium to three separate sites gave species identified by IR, EXAFS, and DFT results as mononuclear Rh(C₂H₄)₂ complexes. Conversion of these to rhodium *gem*-dicarbonyls resulted from reaction with CO; the v_{CO} values distinguish electron-donor properties of the support sites and thereby provide a basis for comparison of various MOFs as catalyst supports. The catalytic activity and selectivity of the species initially present as Rh(C₂H₄)₂ for ethylene hydrogenation and dimerization were investigated experimentally and computationally, and the results show that the catalyst performance is strongly influenced by the node sites.

COLL 101

Catalyst synthesis by atomic layer deposition

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Atomic Layer Deposition (ALD) has enormous potential for the synthesis of advanced heterogeneous catalysts with control of composition and structure at the atomic scale. ALD can achieve highly uniform catalytically active metal and oxide phases with (sub-)nanometer dimensions. This lecture will provide examples from our laboratory of ALD used to synthesize oxide supports, catalytic oxide overlayers, and metal nanoparticles. These materials have been characterized by SEM, XRF, ICP, UV-Vis absorption spectroscopy, Raman spectroscopy and evaluated for catalysis of oxidative and non-oxidative alkane dehydrogenation, and combustion. We have focused on the synthesis of supported metal nanoparticles and developed a procedure in which the metal and support materials are grown sequentially in each ALD cycle. This method makes possible the synthesis of exceptionally small particles, ca. 0.5 nm. Using additional ALD

support layers at the conclusion of the growth, a process we call overcoating, the metal particles can be stabilized against sintering and leaching while still remaining active under harsh conditions in both gas and liquid phase reactions. Through proper annealing procedures the overcoating oxide develops porosity, thus ALD becomes a method for introducing and controlling pore structures.

COLL 102

New nanostructures for increased selectivity and stability in catalysis

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We report on our progress in several projects from our laboratory based on the use of novel nanotechnology to design new selective catalysts. Platinum-based catalysts were prepared for the selective trans-to-cis conversion of olefins based on early surface-science work with model surfaces and quantum mechanical calculations that indicated a particular preference for (111) facets in promoting the formation of the cis isomers. New metal@TiO₂ yolk-shell nanomaterials were conceived for both regular and photo-induced catalytic applications. The encapsulation of metal nanoparticles in dendrimer and SAMs organic frameworks has been used to improve on size distribution and to add enantioselectivity. The use of silica coatings and yolk-shell nanostructures has been explored as a way to minimize metal sintering. "Click" chemistry has been used to tether molecular functionality on porous solid materials and design tandem catalysts.

COLL 103

Scale dependence of friction and contact of nanometer to millimeter radius tips

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This talk will explore the interplay of structure and elasticity in determining contact area A and friction F between a nominally spherical tip of radius R and a clean, flat elastic substrate. An efficient Greens function technique allows study of R up to ~mm and reveals new behavior as the contact radius a increases from nm to μm scales. When elasticity is neglected, most bare tips are predicted to exhibit superlubricity: $F \propto A^x$ with $x \leq 0.5$. Friction and area are only proportional ($x=1$) in the rare case of commensurate surfaces with the same period and orientation. We find that interfacial dislocations lead to quantitative deviations from these rigid results when a is greater than the dislocation core width b , which scales inversely with the shear modulus. For $a > b$, the ratio F/A for commensurate surfaces drops, while F/A rises for incommensurate surfaces. In the limit of large a , all crystalline surfaces have F/A near the Peierls stress for dislocation

motion. Dislocations do not form for amorphous tips but there is still a crossover to linear scaling of F with A for compliant surfaces. The talk will conclude with a study of tips with locally self-affine surfaces. For small R and high loads the contact area follows predictions for single-asperity contacts. For large R and low loads, contact is described by theories for flat rough surfaces and contact area is proportional to load. Simple analytic formulae capture the crossover between these regimes for nonadhesive and adhesive contacts.

COLL 104

Limits of Lifshitz theory

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Dispersion interactions between surfaces have been modelled widely using Lifshitz theory, based on consideration of the dielectric properties of the medium in which they occur. Here we describe measurements on hydrocarbon surfaces using friction force microscopy and force spectroscopy, which show that Lifshitz theory yields inaccurate predictions of works of adhesion in many organic liquids, and in liquid mixtures. The work of adhesion in a large number of liquid media has been calculated using Lifshitz theory, which predicts that a wide range of works of adhesion should be measured. In contrast, the adhesion was predicted to be comparatively invariant when calculated in the same liquids using a first-principles approach, (Hunter's model) in which the electrostatic potential across a molecular surface is mapped using density functional theory to yield parameters that may be used to predict the free energy of association in liquid phases. In water, both Lifshitz theory and Hunter's model predict that the interaction energy will be large, and large adhesion forces are measured by force spectroscopy. A non-linear friction-load relationship is observed, indicating that significant energy is dissipated in shearing, consistent with strong tip-sample adhesion. However, in benzyl alcohol, for which Lifshitz theory predicts strong adhesion, a small pull-off force was measured, together with a linear friction-load plot, commensurate with energy dissipation predominantly through "molecular ploughing". This is consistent with the predictions of Hunter's model. Selected liquids, that yield strong and weak adhesion using Lifshitz theory, were found to yield similar, small adhesive forces consistent with the predictions of Hunter's model. In mixtures of benzyl alcohol and methanol, Lifshitz theory predicts that the adhesion force will be large in both liquids. However, Hunter's model predicts accurately that the free energy of interaction will be large in methanol and small in benzyl alcohol, as observed experimentally, and the form of the dependence of ΔG on the composition of the liquid medium is also predicted accurately. We have earlier demonstrated that Hunter's model, based on consideration of chemical equilibria in the solvent medium, yields more realistic values for interaction energies for hydrogen bonding surfaces; these new data suggest that the method applies more

generally, including systems that interact largely through dispersion or solvophobic forces.

COLL 105

Effect of load on current across gold-graphite nanocontacts

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The size of a nanoscale contact between materials is often correlated with electrical resistance at the interface. Application and removal of a load, which might occur during operation of a nanodevice, can affect both contact size and resistance. However, the atomic-scale origin of this relationship is not fully understood. In this work, we explore the effect of loading conditions on current flow across the nanocontact which is formed between a gold-coated atomic force microscope tip and highly oriented pyrolytic graphite substrate. Reactive molecular dynamics simulation with a recently-developed electrochemical dynamics model is employed to calculate the electrical current across the interface. The simulation provides information about both the current and the contact size, enabling analysis of current density and its variation with load. The results are compared with experimental findings to provide an atomic-level understanding of nanoscale contacts.

COLL 106

Examination of DLC adhesion and wear using MD and in-situ nanoindentation

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Adhesion between DLC tips and diamond counterfaces was examined using a nanoindenter coupled to TEM and molecular dynamics (MD). Strong interactions between the surfaces in vacuum led to gradual nanoscale wear of the DLC. Force-separation curves show an approximate correlation between pull-off force and applied load for various contact points, while pull-in force was fairly constant for all contact points and independent of applied load. MD simulations were designed to replicate experiment as closely as possible and used the AIREBO and the REBO+S potentials. DLC tips with the same general shape (which often deviated from the assumed paraboloidal tip geometry due to wear) were brought into contact with diamond surfaces. MD results demonstrate that pull-off force is correlated with bonds formed during contact, providing an explanation of the trends observed in the TEM data. The effects of contact point and hydrogen-termination on pull-off and pull-in forces will also be discussed.

COLL 107

Nonequilibrium molecular dynamics simulations of organic friction modifiers

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The successful development and application of lubricant additives requires a full understanding of their nanoscale structure and tribological behavior, but this is difficult to obtain experimentally. We use nonequilibrium molecular dynamics (NEMD) simulations to examine the structure and friction of organic friction modifier (OFM) films adsorbed on different surfaces. Specifically, carboxylic acid, amide, and glyceride OFMs, with saturated and Z-unsaturated hydrocarbon tail groups, are simulated at various surface coverages, pressures, and sliding velocities. The differences in films adsorbed on iron and iron oxide surfaces with and without nanoscale roughness are also investigated. At low and medium coverage, OFMs form liquidlike and amorphous monolayers, respectively, which are heavily interdigitated, resulting in high friction coefficients. At high coverage, solidlike monolayers are formed for all of the OFMs, which, during sliding, results in slip planes between well-defined OFM layers, yielding lower friction coefficients. Glyceride OFMs gave significantly lower friction coefficients than amides and particularly carboxylic acids. The friction coefficient always increases linearly with the logarithm of sliding velocity; however, the gradient of this increase depends on the coverage. The structure and friction details obtained from these simulations agree well with experimental results and also shed light on the relative tribological performance of these OFMs through nanoscale structural variations. This has important implications in terms of the applicability of NEMD to aid the development of new formulations to control friction.

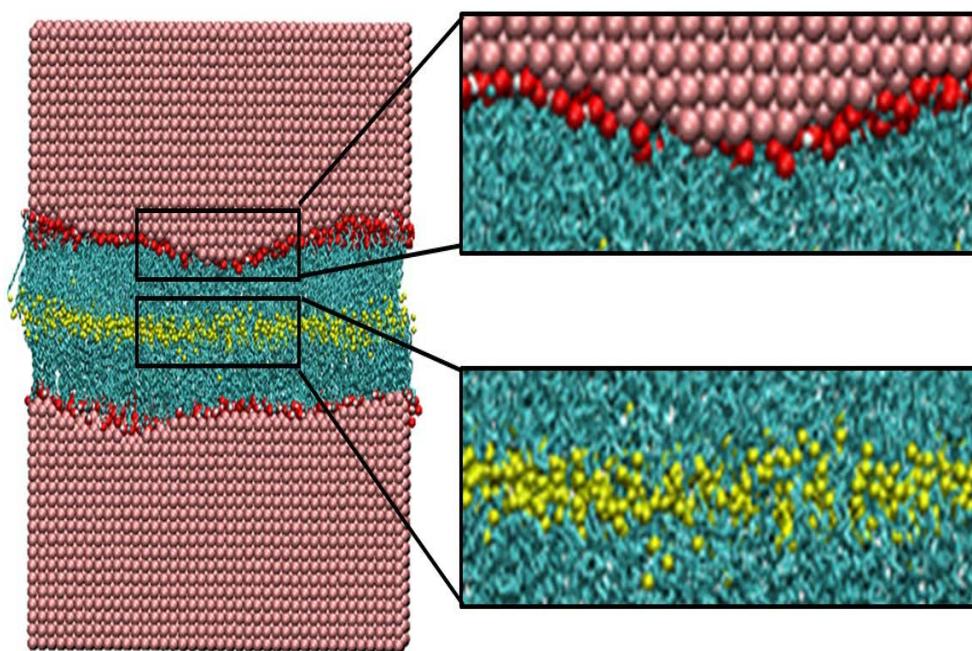


Fig 1. High coverage stearic acid films adsorbed on iron surfaces with nanoscale roughness, compressed to 1.0 GPa

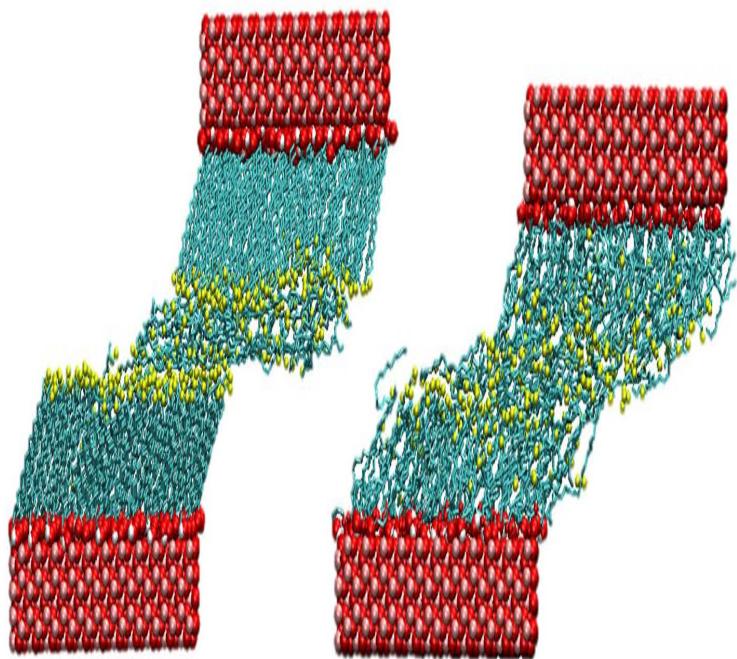


Fig 2. High and medium coverage stearic acid films adsorbed on atomically smooth iron oxide surfaces, compressed to 0.5 GPa and sheared at 10 m/s

COLL 108

Molecular dynamics simulations of multiply alkylated cyclopentane-based lubricant oils

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Lubricant oils composed of multiply alkylated cyclopentane (MAC) fluids have become the dominant lubricant used in moving mechanical assemblies onboard spacecraft. MAC molecules, with a chemical structure unique among lubricant oils, possess many of the physicochemical properties required to help ensure adequate system life in space. Despite the widespread use of MAC lubricants, there is little information on how its chemical structure influences its tribological performance. The use of molecular dynamics simulations to provide molecular-level insight into lubricant performance has been widely reported. Non-equilibrium molecular dynamics (NEMD) simulations of bulk and confined MAC systems will be described; Results will include an investigation into the role of dynamics (e.g., rotational, conformational, etc.) and nanoscale interfacial structure into the observed rheological behavior of this industrially relevant tribological system. Results from NEMD simulations with traditional lubricant oils will be provided for comparison to discern qualitative trends in structure-function relationship of lubricant oils.

COLL 109

Dynamics and thermodynamics of lubricants in flow: A molecular and tribological approach

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While lubricants have been used for a long time to reducing friction and wear of rubbing surfaces, little is known about the local properties of lubricants in tribological contacts. The high pressure, high shear occur in tribological contacts mean fluids in tribological contacts very often exhibit different properties as compared to its bulk properties. This is supported by recent experimental observations that the local flow and local viscosity of lubricants in tribological contact is heterogeneous. Yet it remains unclear the underline physics of these observations. This work investigates the origins of these peculiar observations with molecular dynamic (MD) simulations. The structure of a model lubricant in the contact both at equilibrium with stationary walls and at steady state with shearing walls are examined. The thermodynamics properties of the lubricant will be tabulated. How local viscosity of the lubricant and friction of the system will be explored. The results with local viscosity measurements, friction measurements and MD simulations will be compared.

COLL 110

Adhesive wear mechanisms at the asperity level: Gradual smoothing versus debris formation

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The study of material loss at sliding surfaces, known as wear, has over two centuries of history. Adhesive wear is an important type of wear, which commonly occurs during sliding contacts between materials with comparable hardness in the presence of a strong adhesive force. Despite the critical importance of the adhesive wear process in all engineering applications, it is still described via the classical, yet fully empirical Archard's model, as the microscopic principles have not been yet understood. Single-asperity atomistic wear simulations and recent AFM wear experiments challenge the origins of the adhesive wear process by reporting a gradual asperity smoothing, without formation of debris particles, that are commonly observed in macroscopic wear experiments. This observation poses a fundamental question: when does an asperity collision lead to the formation of a wear debris particle?

In this presentation, using novel coarse-grained atomistic simulations, we for the first time capture the debris formation during the adhesive collision between surface asperities. A systematic set of atomistic simulations reveals a characteristic length scale that controls the adhesive wear mechanisms (i.e. asperity smoothing versus debris formation) at the asperity level. This length scale provides a critical adhesive junction size where bigger junctions produce wear debris by fracture while smaller ones smooth out plastically. This finding explains why wear debris has not been observed in previous atomistic simulations of adhesive wear, where the junction is too small and/or weak to form debris by fracture. Based on this observation, we formulate a simple analytical model that predicts the transition in the asperity-level adhesive wear mechanisms in both the simulation results and atomic force microscope (AFM) wear experiments. We show that the proposed framework opens up a new research path to implicitly model and explore the wear process and revisit classical models.

COLL 111

Entropy the assembler (of polyelectrolytes)

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At first glance, interactions between oppositely-charged repeat units on polymers (polyelectrolytes) appear to be well set up for electrostatic attraction. However, it has been known for several decades that polyelectrolyte complexation is largely athermal. The driving force for assembly must therefore be entropic as opposed to Coulombic attraction (electrostatic). The release of counterions and water molecules is the source

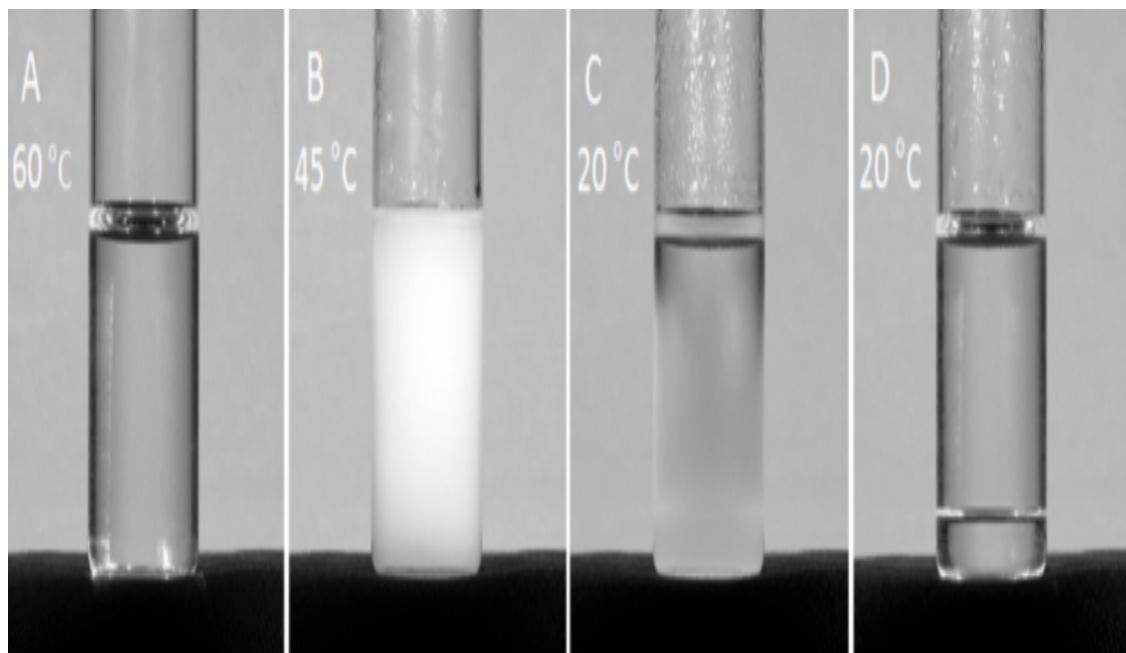
of the required entropy increase. With the advent of more sensitive thermal analysis techniques, such as isothermal calorimetry, small heats of association have been observed, which provide renewed support for the role of Coulombic interactions in polyelectrolyte complexation. This talk will describe how entropy can be used to assemble or disassemble polyelectrolytes taking them through various morphologies such as tough complexes to liquid-like coacervates. The source of the small enthalpies of association will be identified

COLL 112

Simple coacervation of polyguanidiniums and organic polyphosphates

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Simple coacervation is the liquid-liquid phase separation (LLPS) of a single water-soluble polyelectrolyte solution into two aqueous phases, in contrast to complex coacervation, which is the LLPS of two or more oppositely charged water soluble polyelectrolytes. Protamines are small, arginine(R)-rich proteins that replace histones during spermatogenesis to compact chromatin into the sperm heads of fish, birds, and mammals. Salmine, a protamine isolated from salmon sperm, comprises 32 amino acid residues of which 21 are R, with positively charged guanidinium sidechains (guan^+). There are no other ionizable or aromatic sidechains. Salmine sulfate solutions (50 mg/ml salmine, 200 mM Na_2SO_4) separate into two aqueous liquid phases with an upper critical solution temperature (UCST) of 45°C. The coacervate phase comprises 50 wt% water and 600 mg/ml salmine with a sulfate to guan^+ stoichiometry of 1:2. Chloride ions suppress salmine sulfate coacervation. However, in 2M NaCl salmine (50 mg/ml) coacervated in 100% yield with an UCST of 40°C. A set of five synthetic salmine analogs, poly(3-guanidinopropyl methacrylamide-co-acrylamide), were polymerized with the mol% guanidinium sidechains varying from 10% to 65%. The UCST varied linearly with guan^+ mol% from 10-55°C. The counterion dependence was the same as salmine; coacervation occurred with a 1:2 ratio of sulfate to guan^+ , or at $[\text{NaCl}]$ greater than 1.5 M. Coacervation of synthetic polyguan $^+$ demonstrated that coacervation of salmine was driven entirely by cation-cation pairing of the guan^+ sidechains of the R residues. The chirality of the polypeptide backbone or the other amino acid sidechains had little if any effect on coacervation. Simple coacervation of an organic polyphosphate, poly(methacryloyloxyethylphosphate-co-hydroxyethylmethacrylamide) with 80 mol% phosphoester sidechains (pMOEP80) will also be described. pMOEP forms solid precipitates or gels with most multivalent metal ions. However, pMOEP/ Mg^{2+} undergoes LLPS to form transparent coacervates within a narrow range of temperature and pH.



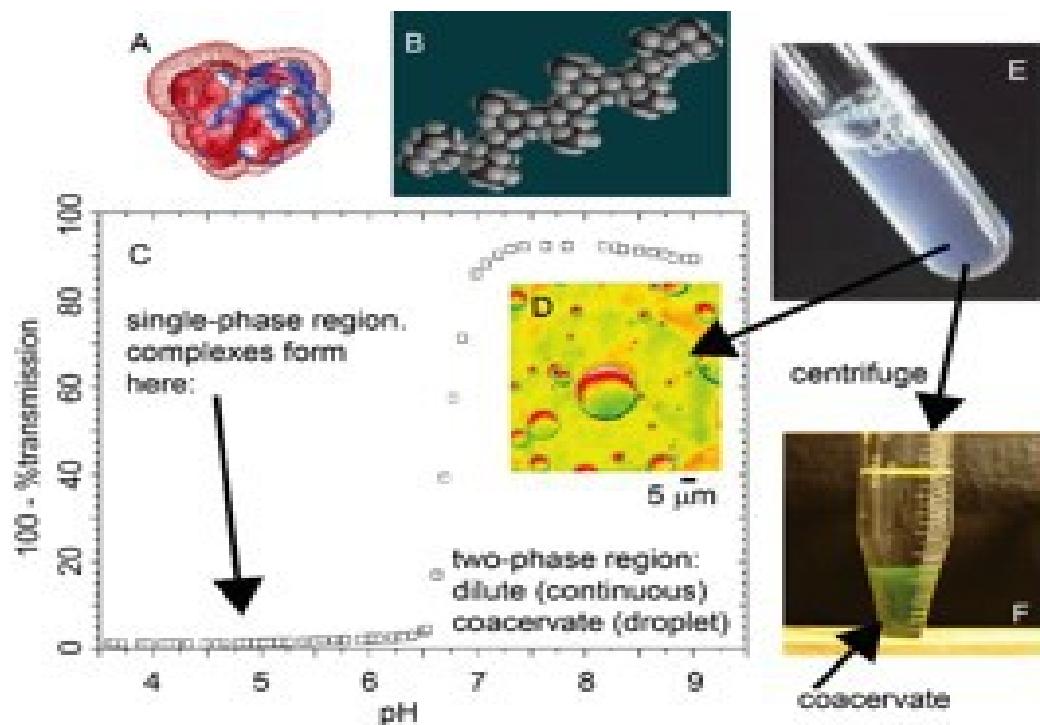
Temperature dependent coacervation of salmine sulfate.

COLL 113

Exploring the coacervation/precipitation interface

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Applications of complex coacervation now include enzyme immobilization, protein purification, protein drug delivery, and phase manipulation in food science and personal care products, all of which involve colloid-polyelectrolyte (PE) interactions. But precipitation (L-S separation), detrimental in all these applications, often appears to accompany (L-L) coacervation. Precipitation might be considered a natural consequence of enhanced inter-macroionic forces, in which PE-colloid ion-pairing replaces counterion-macroion pairing and the expulsion of those counterions leads to desolvation. However, it is unclear if coacervate literally transforms to precipitate, or if the two processes are concurrent. Motivated in part by the coacervation/precipitation overlap for protein-polysaccharide systems, we turn to surfactant micelles as protein surrogates because of their more isotropic shape and charge distribution. More importantly, the exquisite temperature dependence of the PE-micelle system leads to greater differentiation of L-L and L-S phase boundaries, and thence to methods for manipulating them.



COLL 114

Material dynamics in complex coacervates

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Rheology is a powerful method for materials characterization that can provide detailed information about the self-assembly, structure, and intermolecular interactions present in a material. While rheological methods have long been used for the characterization of complex coacervate-based materials, it remains a challenge to predict the dynamics for a new system of materials. Furthermore, most work reports only qualitative trends exist as to how parameters such as charge stoichiometry, ionic strength, and polymer chain length impact self-assembly and material dynamics. There is a tremendous need to link thermodynamic studies of coacervation phase behavior with material dynamics through a carefully-controlled, systematic study of coacervate rheology for different polymer chemistries. We utilize the time-salt superposition methods developed first by Spruijt and coworkers to establish a more mechanistic strategy for comparing the linear viscoelasticity of different polymer-based coacervate systems.

COLL 115

Complex coacervation as a dynamic reservoir of intrinsically disordered proteins

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The liquid-liquid phase separation to form droplets from intrinsically disordered proteins (IDPs) is driven in many cases by the complexation of oppositely charged polyelectrolytes, followed by the further association of these polyelectrolyte complexes into extended assemblies that are held together by weak electrostatic interactions. This process known as complex coacervation in the biomaterials community has been suggested to facilitate bio-inspired coating and wet adhesion, and to be dominantly entropy-driven as facilitated by the release of salt and water from the IDP surface. A consensus property of the complex coacervate phase is high fluid dynamics, rooted in low cohesive energy between the polyelectrolyte complexes and weakly bound water constituting the fluid. This in turn is consistent with the low interfacial tension typically found between the complex coacervate fluid and water, and the tendency for the complex coacervate droplets to fuse and coalesce, as well as engulf exogenous molecules or surfaces. The question we ask is what are the molecular-level consequences for the polyelectrolytes undergoing complex coacervation? Based on electron paramagnetic resonance (EPR) and Overhauser dynamic nuclear polarization (ODNP) measurements using polyelectrolyte-tethered spin labels, we interrogate the conformational and dynamic state of the IDP constituents within the highly condensed and fluidic complex coacervate phase, and find that the IDP is dynamic, fully hydrated and populates a conformational ensemble resembling a dilute solution. We will discuss the potential functional role of the droplet state for IDPs.

COLL 116

Coacervates from biopolymers for cartilage tissue regeneration

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Hyaluronic acid and chitosan are biopolyelectrolytes, which are anionic and cationic, respectively. Coacervation of hyaluronic acid with chitosan was employed to encapsulate bone marrow stem cells. Live/dead assays showed that cells could survive within the coacervates. In addition, we could observe proliferation and spreading of the cells. Chondrogenic differentiation of the encapsulated cells was confirmed by staining Collagen type 2, Aggrecan, and nucleus. Scaffolds formed from coacervates degraded up to 70% in two weeks.

COLL 117

Plasmonic supercrystals for SERS detection

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Metallic nanoparticles are in the focus of interest because of their potential use in microelectronics, optical devices, biomedical and sensing applications, or to develop

new metamaterial properties. Their individual electromagnetic response is highly dependent on the specific size, shape, and surrounding environment of the particles.

Nowadays, there are different methods which allow us to fine tune the control over these parameters and thus, the materials properties. However, the control over the plasmonic intercoupling between particles and thus, their collective behavior rely on the ability to form reproducible organized structures either at the nano, micro or macro scales. Being still a very important challenge to solve for their incorporation into new technological devices. Therefore, it is clear that their controlled organization is of key importance.

COLL 118

Nanoparticles and stem cells, a powerful combination?

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In the last decade there has been significant advance in the synthesis of new nanomaterials. Nanomaterials have been for example suggested as delivery systems for pharmaceutical compounds. One drawback hereby is, similar to conventional pharmaceutical formulations, the problem of targeted delivery, i.e. controlled biodistribution. Biodistribution of nanomaterials after systemic administration has been analyzed with different techniques, predominantly demonstrated unwanted accumulation in the liver. Controlled surface modifications of the nanomaterials may help to improve targeting. On the other hand, stem cells are known for their homing capacity. In this way stem cells might be used as vehicle for targeted delivery of nanomaterials, which will be discussed.

COLL 119

Control of primary particle spacing in gold nanoparticle clusters for both high NIR extinction and full reversibility

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In biomedical imaging, there is particular interest in assembling NIR active gold nanoparticle clusters that can reversibly dissociate back to sub-6nm primary particles that can be cleared via the kidneys. Reversible NIR-active nanoparticle clusters with controlled size from 20 to 100 nm were assembled from 5nm gold nanoparticles (Au NP), with either citrate (CIT) or various binary ligands on the surface, by tuning the electrostatic repulsion via pH. The nanoclusters were bound together only by vdW

forces and dissociated to primary nanoparticles over a period of 20 days at pH 5. Although reversible nanoclusters could be formed with high levels of citrate ligands on the primary particle surfaces, the NIR extinction was only modest. However, the primary particle spacings could be tuned by optimizing the ratio of binary ligands of either cysteine (CYS), glutathione (GSH) or thioctic acid zwitterion (TAZ) with citrate to achieve an NIR extinction ($E_{1000/525}$) ratio of up to ~0.4, while maintaining full reversibility to primary particles. This optimum ligand ratio decreased with increasing length of the secondary ligand (1.5/1 for CYS/CIT, 0.75/1 for GSH/CIT and 0.5/1 for TAZ/CIT) in order to maintain a sufficient interparticle spacing for dissociation. Interestingly, the zeta potential and the first order rate constant for nanocluster dissociation were similar for all three systems at the optimum ligand ratio. After incubation in 10 mM GSH solution (intracellular concentration), only the TAZ/CIT primary particles were resistant to protein opsonization in 100% fetal bovine serum, as the bidentate binding and zwitterion tips of TAZ resisted GSH exchange and protein opsonization, respectively.

COLL 120

Modeling of degradation of virus and amyloid fibril by pre-designed nanoparticles

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In collaboration with experimentalists, we use MD simulations to model a selective multivalent binding of nanoparticles (NPs) and virus capsid. The experiments show that NPs with ligands that mimic heparan sulfate can destroy viruses (HPV, dengue) which recognize the heparan sulfate through their receptors. Our simulations show that the NPs effectively deform the capsid proteins and potentially modify the capsid structure. Similarly, we model selective multivalent coupling of NPs with A β -amyloid fibrils. We have designed few NPs which can deform the fibrils and potentially prevent their further growth. The extent of the deformation of the fibril strongly depends on the terminal functional groups of the NPs and the NPs sizes.

COLL 121

Spectroscopic quantification of surface groups on micro- and nanoparticles with conventional and cleavable reporter

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Nanometer- and micrometer-sized particles are of increasing importance for a wide range of applications in the material and life sciences. This includes carriers for, e.g., drugs as well as dye molecules for use as multichromophoric reporters for signal enhancement in optical assays, platforms for DNA sequencing, and the fabrication of nanosensors and targeted probes for bioimaging studies.

Application-relevant properties of such particles include their size (and size distribution), shape, colloidal stability, biocompatibility, and ease of subsequent functionalization, e.g., with linkers, sensor molecules, and targeting ligands. The latter requires knowledge of the number of groups effectively accessible for subsequent coupling reactions and hence, selective and sensitive methods of analysis, which can be ideally employed for the characterization of a broad variety of particle systems independent of their optical properties, i.e., scattering or the presence of encoding dyes. For product control, robust, reliable and fast methods performable with inexpensive equipment are preferred.

In this respect, we studied a variety of conventional labels for optical readout, utilizing changes in intensity and/or color of absorption and/or emission. In addition, we developed a platform of cleavable and multimodal labels for optical assays which consist of a cleavable linker and an optically active reporter moiety. In contrast to conventional reporters measured directly at the particle surface, which are prone to signal distortions by scattering and encoding dyes, these cleavable labels can be detected colorimetrically or fluorometrically both bound at the particle surface and after quantitative cleavage of the linker in the transparent supernatant. Moreover, they enable straightforward validation by method comparison with elemental analysis, ICP-OES or ICP-MS.

Here, we present representative examples of newly synthesized cleavable labels and their application for the quantification of amino, thiol and carboxy surface groups on different nanomaterials and compare these results with measurements using conventional optical labels.

COLL 122

In vivo biomolecule corona onto clinically-used blood-circulating liposomes

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Nanoparticles (NPs) are instantly modified once injected in the bloodstream because of their interaction with the blood components. The spontaneous self-assembly of proteins onto NP surfaces once in contact with biological fluids, has been termed the ‘protein corona’ and it is considered to be a determinant factor of the pharmacological, toxicological and therapeutic profiles of nanoscale medicines. The dynamic process of protein adsorption onto the NP surface has been evaluated extensively by the incubation of NPs with various plasma-containing media. However, the extrapolation of such *in vitro* studies to predict the fate of NPs *in vivo* remains mainly speculative and largely untested.

Our aim was to study *in vivo* the dynamic protein corona formation onto three different types of clinically tested liposome systems (bare, PEGylated and antibody-conjugated). The formation of *in vivo* protein corona was determined after the recovery of tail-vein injected liposomes from the blood circulation of CD-1 mice, 10 min post-injection. In

comparison, *in vitro* protein corona was formed by the incubation of liposomes in CD-1 mouse plasma. *In vivo* and *in vitro* formed protein coronas were compared in terms of morphology, composition and cellular internalisation. Overall, even though the total amount of protein adsorbed onto circulating liposomes *in vivo* was comparable with that observed from *in vitro* incubations, the protein species that self-assembled onto the liposomes *in vivo* were considerably more, leading to a molecularly ‘richer’ protein corona.

We then investigated how protein exposure time influenced the composition of the self-assembled protein corona, to elucidate the dynamics of protein interactions under *in vivo* conditions. Results of a time-resolved, *in vivo* protein corona study of PEGylated liposomal doxorubicin, identical to the clinical product Doxil® will be shown.

COLL 123

Continuous fabrication of hierarchical and asymmetric bijel structures via Solvent Transfer-Induced Phase Separation (STRIPS)

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In collaboration with Drs. Martin Haase and Daeyeon Lee, we have identified a versatile new route to form bicontinuous interfacially jammed emulsions (Bijels). Bijels are a recently discovered soft material with potential applications in areas ranging from healthcare, cosmetics, and food to energy and diverse chemical technologies. Termed a new phase of matter, bijels comprise interpenetrating bicontinuous channels of one fluid phase in another, formed by spinodal decomposition. Particles trapped at the interfaces as the fluids phase separate form jammed structures that arrest these structures, trapping and stabilizing the interconnected phases.

Typically, bijel fabrication has been achieved in batch processes using mixtures of two fluids that decompose when thermally quenched, and suffers from the relative scarcity of these systems and the narrow temperature windows over which the spinodal quenching occurs. Typical bicontinuous domain sizes are tens of micrometers, and fabrication is inefficient due to its batch-wise nature and expensive starting materials. We have developed an alternative strategy to form bijels by a method Solvent Transfer-Induced Phase Separation (STRIPS). We exploit ternary fluid mixtures, e.g. an oil, an aqueous phase, and a solvent-and, via solvent extraction, force the system to spinodally decompose. Nanoparticles originally in suspension adsorb and stabilize the system. Strategies to functionalize and prepare nanoparticles *in situ* are also developed. What emerges is a robust, versatile method to make bijels from a broadly expanded set of fluids. The method is scalable, and permits continuous formation of bijel fibers and membranes with controllable morphologies and domain sizes down to only a few hundreds of nanometers. Confocal and electron microscopy reveal hierarchical fiber architectures remarkably similar to polymer membranes formed via non-solvent induced phase inversion. However, unlike their polymeric counterparts, bijel fibers remain entirely liquid throughout their volume. This unique feature combined with the

hierarchical morphology opens avenues to new applications such as bijel microfluidics or interfacial catalysis.

COLL 124

Molecular structure and bonding at nanoemulsion and planar oil/water interfaces

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Nanoemulsions have attracted considerable attention in recent years due to their unique potential applications in drug delivery, oil recovery, and as nanoreactors for producing polymers and nanomaterials. They are also predicted to be increasingly important commercially since significantly less emulsion stabilizing surfactant is required for their function. The focus of this presentation will be on our measurements of the molecular structure and assembly of several surfactants and the oil and water solvents examined at the surface of regular and reverse nanoemulsions. How this assembly and structure varies as these surfactants adsorb to the planar oil/water interface will also be presented and compared. The studies involve measuring the vibrational spectroscopy at the nanoemulsion and planar interface using vibrational sum frequency spectroscopy in a scattering and total internal reflection geometry respectively. Surface tension, light scattering, zeta potential and computational methods are used to complement the spectroscopic studies.

COLL 125

Molecular structures of polymer surfaces in different chemical environments

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It is difficult to study molecular surface structures of polymer materials in different environments such as different liquid environments because most surface sensitive techniques require high vacuum to operate. Sum frequency generation (SFG) vibrational spectroscopy has been developed into a powerful tool to probe different interfaces including solid/liquid interfaces. We successfully applied SFG to study molecular surface structures of a variety of polymer materials in different environments. We showed that SFG can be used to elucidate surface crystallization of polymer materials in water, aggregation of plasticizers on polymer surfaces in different environments, and surface structures of layer-by-layer deposited polymers in water and air for oil/water separation.

COLL 126

Molecular studies of the assembly of co-surfactants at the oil-water interface

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It is well known that surfactant molecules within an aqueous solution self-assemble into a wide variety of three-dimensional structures such as micelles, vesicles, and liposomes. The structure formed is dependent upon additional factors such as temperature, salt concentration, and co-surfactants present. In particular it has been shown that an alcohol co-surfactant paired with CTAB, the most prevalent cationic surfactant, can result in drastic changes to the microstructure formed. Yet a fully detailed understanding of various co-surfactant compositions and headgroup interactions directly at the oil-water interface is not yet well understood. This presentation will focus on our results from the use of a powerful surface selective technique, vibrational sum-frequency (VSF) spectroscopy to extract molecular orientation and behavior information about the competitive and cooperative effects that occur between co-surfactants at the oil-water interface.

COLL 127

Mass transfer of lipid-based amphiphiles to water-triglyceride interfaces

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In chemical and physical processes such as emulsification, oil/water interfaces are created very rapidly. Mass transfer mechanisms determine rates of surfactant adsorption and subsequent interfacial tension reduction, with important implications for the final product structure and formulation. However, for hydrophobic fatty acid esters commonly used to form food emulsions, these mechanisms have not been explored in depth. Therefore, the objective of our research was to investigate the transport kinetics of lipid-based amphiphiles with poor water solubility, including free fatty acids and monoglycerides, using a drop profile tensiometer.

Monocaprylin or caprylic acid dissolved in tricaprylin transferred rapidly to a pendant water droplet interface, steeply decreasing the interfacial tension in a diffusion-limited process. However, surfactant adsorption from inside an oil drop was complicated by oil-water partitioning and transport through multiple phases, behavior that can be understood with the aid of mass transfer theory. In commercial corn oil the behavior was still more complex. Purchased corn oil contained native components that promoted a substantial and time-dependent decrease in the interfacial tension. Fatty acid addition at low concentrations actually increased the tension, due to apparent interactions between native amphiphiles and the fatty acid. Purification using magnesium silicate removed the native amphiphiles, yielding a much higher and time-independent interfacial tension. This tension was now reduced at all concentrations by addition of the fatty acid. For the monoglyceride, possible roles of self-assembled structures in the triglyceride were also probed.

The complex kinetics seen in our research can be harnessed to improve processes such as oil uptake, wetting, nucleation, emulsification and detergency. Our results are of particular significance in the utilization of lipid-based amphiphiles, including those that are natural and unrestricted for their addition to food.

COLL 128

Investigating mass transfer and microstructures formation at liquid/liquid interfaces using FT-IR imaging spectroscopy

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Spontaneous emulsification is an intriguing phenomenon; whose understanding is of much scientific interest. Substantial research work has been reported on it but the mechanisms of this process are not yet fully understood. Current applications in drug-delivery systems and petroleum industry require deeper understanding of spontaneous emulsification. In the present work, FT-IR imaging spectroscopy with a Focal Plane Array (FPA) detector has been used. This analytical technique has the advantage to allow the identification of chemical compounds in the complete field of view (FOV). But, it requires the use of IR transparent solvents for larger optical path length.

We observed the spontaneous emulsification at water/CCl₄ interfaces in the presence of a lipophilic surfactant Span 80. When the concentration of Span 80 in CCl₄ is large (higher than its c.m.c.), reverse micelles are known to be formed in low dielectric solvent like CCl₄. Reverse micelles at the interface tend to swell over time before detaching from the interface, which are then transported into the organic phase and contribute to the increased opaqueness. FTIR studies showed the appearance and evolution of the depth of O-H stretching band (3200-3500 cm⁻¹) over time in the CCl₄ phase. It is the signature of the transport of water into the Span 80/CCl₄ solution under study. Experiments were performed for different surfactant concentrations to study the kinetics of the transport process. Figure 1 illustrates that the kinetics of the water transport process becomes faster with the increase in concentration of Span 80.

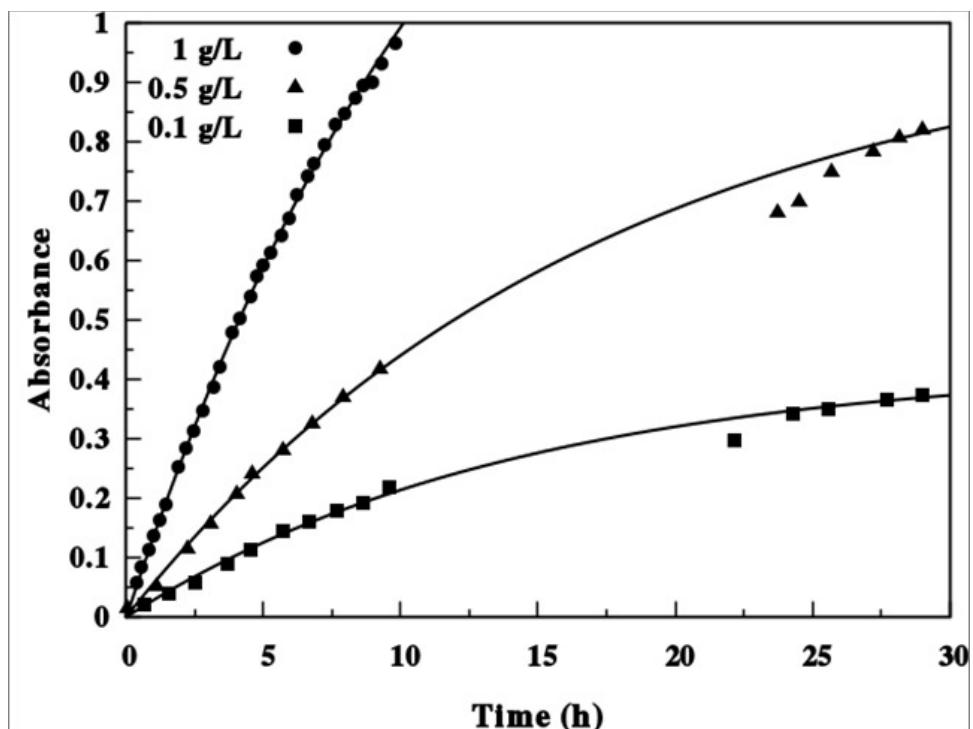


Figure 1: Evolution of the average absorbance (over full FOV) of the Span 80/CCl₄ solution as a function of time for Span 80 concentrations of 1 g/L, 0.5 g/L and 0.1 g/L.

COLL 129

Specific anion effects on caffeine partitioning between aqueous and cyclohexane phases

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Specific ion effects influence a variety of aqueous processes such as micelle formation, polymer aggregation, and protein solubility and follow the Hofmeister series. We studied the effects of eleven anions on the thermodynamics of caffeine partitioning between aqueous and cyclohexane phases. Well-hydrated anions such as CO₃²⁻ and SO₄²⁻ decrease the standard Gibbs free energy for caffeine transfer from the aqueous to cyclohexane phase and promote the transfer process. On the other hand, weakly hydrated anions such as ClO₄⁻ and SCN⁻ salt caffeine into the aqueous phase and hinder the caffeine transfer. Moreover, the enthalpy and entropy of caffeine transfer in the presence of salts were obtained. Caffeine transfer from the aqueous to cyclohexane phase is an endothermic process driven by the entropy change for caffeine transfer. The anion-caffeine interactions are further investigated by using ¹³C and ¹H NMR and ATR-FTIR spectroscopy. The mechanisms for how anions interact with caffeine and affect its partitioning will be discussed.

COLL 130

Protein mixture segregation at coffee ring: Real-time imaging of protein ring precipitation by mid-FTIR spectromicroscopy

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“Coffee ring effects” is one of notable non-equilibrium processes in thermodynamics. Nonetheless, this study has heavily relied upon conventional imaging technologies such as visible light or fluorescent microscopy. In this work, we studied the drying, and precipitation processes of model proteins (Bovine Serum Albumin, γ -Globulin and Fibrinogen) by utilizing FT-IR imaging technology, and we report the real-time observation of coffee ring formation, presenting the different kinetic profiles for the three samples on hydrophobic and hydrophilic surfaces. The analysis of two and three component mixtures also allow to observe the segregation of globular proteins in different layers of the ring. To provide account for the discovery, we established a straight-forward, thermodynamic model to interpret protein transport in an evaporating droplet of medium.

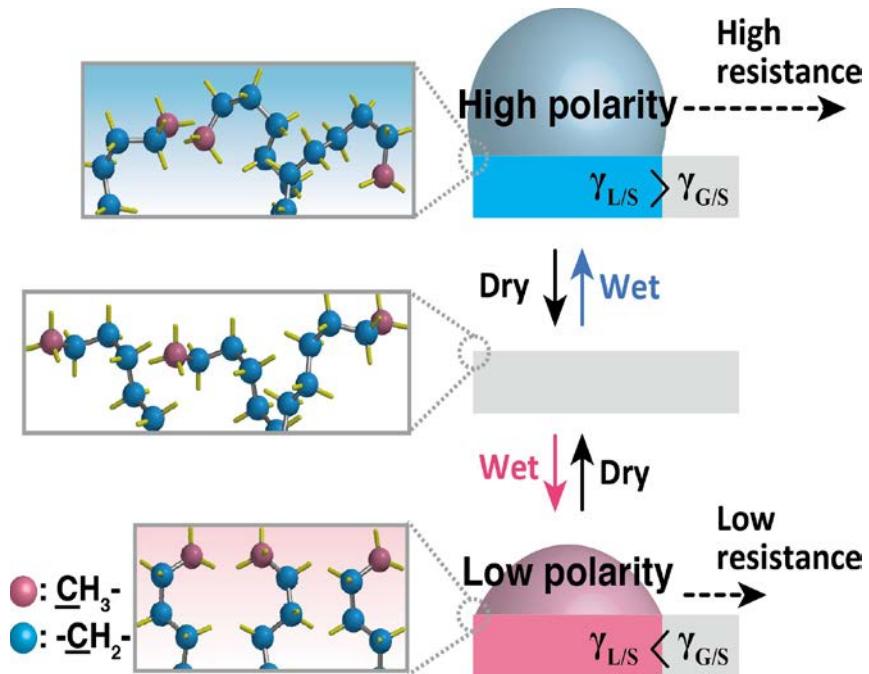
COLL 131

Surface and interfacial exploration of a smooth liquids repellent sol-gel coating

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Correlations between conformational change of surface alkyl chains of alkyl-terminated sol-gel coating in contact with probe liquids (polar and nonpolar, with high and low surface tensions) and liquid repellency were rationally investigated. First, the liquids repellency of the coating against 17 probe liquids with several physico-chemical properties (surface tension, molecular weight, polarity (dielectric constant), density, and viscosity) was estimated using contact angle (CA) hysteresis and substrate tilt angle (TA) measurements. We found that liquids repellency of the coating significantly depended not on the surface tensions which are widely use for contact angle analysis, but on the dielectric constants of the probe liquids, showing easier droplet movement with decreasing dielectric constant ($\epsilon < 30$). Surface and interfacial analysis using the sum-frequency generation (SFG) vibrational spectroscopy then revealed that the conformation of surface-tethered alkyl chains was transformed before and after contact with the different types of probe liquids. When the liquids with low dielectric constants were in contact with the coating, methyl (CH_3) groups were favorably migrated at the solid/liquid interface, leading to a reduction in surface energy. Because of such local conformational change induced surface energy differences at the three-phase contact line of the probe liquid, the contact line can move continuously from low surface energy (solid/liquid) areas to surrounding high surface energy (solid/air) areas without pinning

(Figure). Subsequently, the liquids with low dielectric constants can move easily when only slightly tilted, independent of the magnitude of static contact angles.



COLL 132

Self-assembly in confined spaces: Using defects to advantage

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We have developed and used a number of chemical patterning methods that take advantage of native and engineered defects in self-assembled monolayers. These methods enable stochastic patterning of functional small molecules at scales not otherwise possible. When combined with soft lithography or microfluidics, substrates patterned with small molecules have been shown to recognize and to capture antibodies, native membrane-associated receptor proteins, and nucleic acid aptamers with high selectivity and specificity. Moreover, when patterned with single-stranded DNA, these substrates enable unprecedented hybridization with complementary DNA. We have used quartz crystal microbalance gravimetry, X-ray photoelectron

spectroscopy, scanning probe microscopies, and fluorescence microscopy to characterize these substrates and molecular recognition enabled by them. Moreover, we developed thin-film fluorescence spectroscopy to measure biomolecule binding. Together, this suite of methods enable powerful and flexible avenues for patterning functional substrates over scales ranging from single molecules to clusters of molecules and nanometers to centimeters.

COLL 133

Controlling biomolecular structure and function at the bio/abio interface

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Integrating biomolecular function into abiological devices for sensing, chemical catalysis, and biofuel generation would profoundly expand and change these traditional fields. This goal requires that the biomolecule of interest be effectively integrated with inorganic materials in a controlled and oriented manner without altering its three-dimensional fold or compromising function. In the research described here, we chemically functionalize gold surfaces with peptides of known secondary structure. Through a variety of characterization methods, we demonstrate that correctly functionalized surfaces can induce desired secondary structures in peptides that are disordered in solution. We demonstrate molecular-level control over both helical and fibril-forming peptide strands. This is an important advance in preparing robust biologically mimetic surfaces and is expected to lead to an entirely new mechanism through which biological and inorganic materials can be coaxed to interact.

COLL 134

Probing nano-environments with high-throughput single-molecule tracking

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Surfaces, interfaces, and other low-dimensional environments (such as porous media) may exhibit spatial heterogeneity for many reasons, including chemical or structural inhomogeneity, or topographical effects. We have developed an approach to obtain spatial maps of these heterogeneities based on the premise that “probe” molecules or nanoparticles exhibit varied dynamic behavior that is distinctively related to the local chemistry and topology. For example, the characteristic adsorption rate, retention time, and local molecular mobility (i.e. surface diffusion coefficient) are often exquisitely sensitive to the details of the local environment. Thus, information about molecular dynamics/transport and material structure/topography/topology is obtained simultaneously.

By choosing an appropriate probe molecule (or more than one molecule) and

accumulating large numbers of trajectories (generally several million are analyzed), the dynamic molecular behavior can be spatially partitioned and used to prepare spatial maps. Having identified chemically- or physically-distinct surface regions, the behavior of molecules of interest can be partitioned by region. For example, the retention time and folding/unfolding dynamics of proteins can be measured simultaneously on materials with heterogeneous surface chemistry allowing one to identify anomalously strong binding or denaturing sites, and to determine the influence of these sites on fouling, retention, and/or separation efficiency. Moreover, trajectories with nanoporous materials can be analyzed to understand the impact of topology on transport and retention.

COLL 135

Stable by design: Understanding the role of monomer architecture in stabilizing noncovalent monolayers toward thermal and solvent processing of layered materials

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Many important applications, such as organic photovoltaics, nanoscale electronics and study of transmembrane proteins rely on creating chemically orthogonal patterns (e.g. hydrophobic/hydrophilic or metal/oxide) at length scales <10 nm. Recent work in our group has realized wetting-orthogonal patterns with a 5-6 nm periodicity using noncovalently adsorbed lying down or sitting phases of diacetylene fatty acids and phospholipids on graphitic interfaces. While noncovalent functionalization is both important for preserving the electronic structure of layered materials and convenient for creating monolayers of sub-nm patterned thickness, stability toward environmental perturbations such as temperature and solvent remain a major challenge. Topochemical photopolymerization of the diyne represents a significant step toward increasing monolayer robustness; however, monomer structure also plays a critical role in determining monolayer stability. Utilizing a combination of PM-IRRAS and AFM imaging, we demonstrate the impact of alkyl tail length, dual chain architecture, and head group interactions on the thermal stability of such interfaces. Additionally, we employ molecular dynamics simulations to explore monolayer structural changes in the presence of solvents (including pH changes) and increasing temperature. Broader implications for noncovalent interface design of layered materials will be discussed in the context of these findings.

COLL 136

Optically directed assembly of colloidal particles

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We explore versatile manipulations of colloidal particles using light-controlled temperature field and develop new optical technologies towards LEGO-like construction of superstructures, metamaterials and devices. Herein, I will present our recent developments and applications of two types of the optically directed assembly techniques: bubble-pen lithography (BPL) and opto-thermophoretic tweezers (OTTs). BPL has been developed to pattern a variety of colloidal particles on plasmonic substrates and two-dimensional atomic-layer materials in an arbitrary manner. The laser-directed microbubble on substrates captures and immobilizes nanoparticles through coordinated actions of Marangoni convection, surface tension, gas pressure, and substrate adhesion. OTTs exploit colloid and surface chemistry to precisely control the trapping, manipulation, and bonding of the colloidal particles with the light-controlled temperature field. We have applied OTTs to dynamically manipulate colloidal particles in arbitrary patterns, to create reversibly controllable nanoparticle assemblies, and to carry out LEGO-like construction of colloidal superstructures at low optical power. Properties and applications of the colloidal superstructures and metamaterials will also be discussed.

COLL 137

Laser directed crystallization and patterning of methylammonium lead halide perovskites from solution

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We present a method to crystalize organo-lead halide perovskites from solution in microscale geometries via laser. The process takes advantage of the inverse dependence between perovskite solubility and temperature to induce localized temperature rises and thus crystallization from solution. With this, we demonstrate arbitrary pattern formation of crystalline CH₃NH₃PbBr₃ on a range of substrates and fabricate and characterize a microscale photodetector. This solution-derived methodology provides a facile path forward for the prototyping and production of perovskite-based devices.

COLL 138

Tarnishing silver into semiconducting hybrid chalcogenides

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Silver has long been prized for its luster and reflectivity. This luster is lost on exposure to air and atmospheric sulfur, a result of the formation of tarnish. The reaction corrodes the metal surface, leaving a black deposit of silver sulfide. The removal of this tarnish or prevention of its formation is a topic of interest to preservationists, but the spontaneity of the chemical reaction presents opportunities for producing semiconducting hybrid chalcogenides directly from the metal. Here, we report a method to hijack the spontaneous chemical formation of tarnish to drive instead the formation of semiconducting hybrid chalcogenides containing a 2D silver chalcogenide nanostructure insulated by a supramolecular assembly of organic ligands. These hybrid materials combine organic and inorganic constituents in a crystalline assembly, wherein the organic ligands serve as a structural element and insulating dielectric. The direct conversion of silver into low-dimensional insulated semiconducting nanostructures presents opportunities for the corrosion-assisted patterning of low-dimensional materials into functional semiconducting devices.

COLL 139

Bottom-up preparation of ordered Rh(I) diisocyanide coordination polymers on gold surfaces and their conductivity and electrochemical stability

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The development of highly ordered, conductive, porous materials bound to an electrode surface is desirable for application to problems in molecular electronics, sensors, and catalysis. We are investigating electrode-attached, conductive Rh(I) diisocyanide coordination polymers grown from gold surfaces in a bottom-up procedure. We use a seed layer of an aryl diisocyanide on the gold electrode to template growth of the coordination polymer with Rh(I) centers joining a variety of possible diisocyanide linkers in a square planar geometry. The coordination polymer is prepared via layer-by-layer solution-phase deposition. The structure is comprised of 2-D sheets perpendicular to the gold surface, while Rh-Rh bonding between sheets occurs, improving the conductivity. Prior work with this coordination polymer has only reported preparation of a powder whose conductivity is affected by grain boundaries and disorder. Characterization of our ordered film by IR, XPS, ellipsometry, SEM, UV-vis, and XRD indicates layer-by-layer control and Rh-Rh interaction. Characterization of conductivity by JV-curve analysis and of electrochemical stability by voltammetry explores relevance to electrochemical applications. Our ongoing efforts involve integration of electrochemical catalysts for CO₂ reduction in the structure, which could improve upon the present state of the art in molecular catalysis by providing approaches to stabilizing catalysts against degradation, improving recyclability, and making separation of products more facile.

COLL 140

Investigation of charge-transfer complexes between TCNQ and indium phosphide quantum dots

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With the increasing need for sustainable energy sources comes an increasing need for cost-effective materials. One important type of system being investigated is a system in which semiconductor nanocrystals (NCs) act as energy/charge donors and acceptors with other nanoparticles, proteins, or molecules. These charge-transfer systems have important implications in producing several energy-pertinent technologies such as organic-inorganic hybrid solar cells, NC-sensitized solar cells, and high-efficiency LEDs. In this project, we investigated charge transfer of tetracyanoquinodimethane (TCNQ) with indium phosphide NCs using electronic and vibrational absorption spectroscopy. Charge transfer with TCNQ has been observed with materials such as cadmium selenide and lead sulfide [CITATION?], but InP is a preferred material due to its more covalent nature and smaller relative toxicity than cadmium- and lead-containing materials. Microwave synthesis enabled for the control of NC size, which allowed us to investigate the effect of size on the degree of charge transfer. We also investigated the role that surface chemistry plays in charge transfer by altering the synthetic methods to achieve different levels of surface passivation. We found that charge transfer between TCNQ and InP NCs is possible, and smaller sizes produce more reduced forms of TCNQ. We also found that surface chemistry plays a large role in the charge transfer process. These simple NC-molecule constructs help us to gain a better understanding of more complex systems, and allow us to tailor intermolecular processes.

COLL 141

Anchoring group affects triplet energy transfer from semiconductor nanocrystals to molecules

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Triplet excited states may find use across the fields of photoredox catalysis, electroluminescence and triplet-triplet annihilation (TTA) based photon upconversion etc. Semiconductor nanocrystals (NCs) and acene derivatives, have been found to upconvert photons across the visible to near infrared wavelengths. As triplet sensitizers, semiconductor NCs offer advantages over molecular sensitizers in terms of photostability, broad absorption and spectral tunability. Here, to understand and optimize the triplet energy transfer (TET) from NCs to molecules, the effect of binding

groups on TET is investigated. In this work, 9 functionalized anthracene derivatives with different binding groups are synthesized, and the TET from CdSe NCs to the anthracene derivatives are investigated by transient absorption spectroscopy and steady state upconversion. Diphenylanthracene was used as the annihilator during upconversion. Among all the derivatives, carboxylic acid and phosphonic acid functionalized anthracene show the highest upconversion quantum yields (QYs) of 13.5% and 13.3% respectively, followed by the anilinyl (3.56%) and amino anthracene (0.789%). Sulfur-containing derivatives such as thiol, dithiocarbamate, and dithioic acid anthracene lead to upconversion QY of ~0.1%. The TET rates extracted from transient absorption data match the results from upconversion QYs. The low TET rates and upconversion QYs with sulfur-containing anthracene derivatives and amino anthracene may be explained by hole transfer from NCs to anthracene ligands, or the n to π^* transitions that impede the TET from NCs to anthracene.

COLL 142

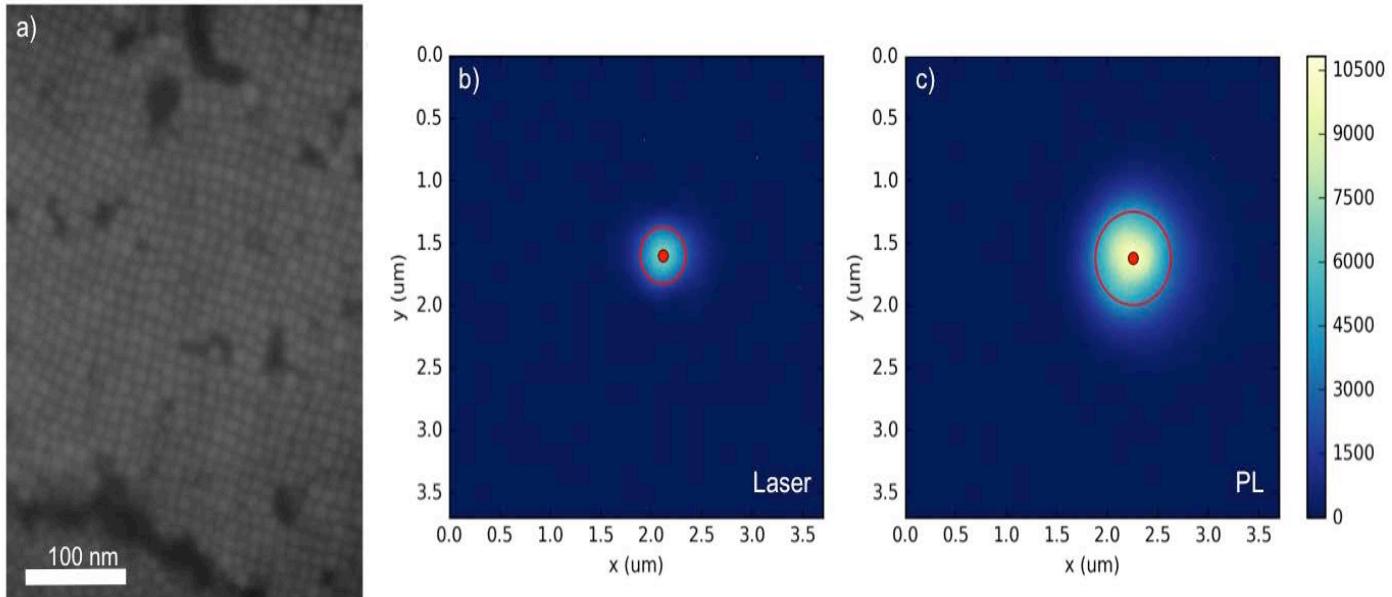
Long-range exciton transport in cesium lead halide perovskite nanocrystals organized in ordered nanoscale assemblies

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Fully inorganic cesium lead halide perovskite nanocrystals (NCs) are a novel colloidal material displaying remarkably bright photoluminescence (PL) characterized by high quantum yields of 50-90% and narrow emission linewidths of 12-42 nm. In addition, compositional control and quantum-size effects allow for the precise and continuous tuning of bandgap energies over the entire visible spectral region.

The cubic perovskite crystal structure yields NCs with a cubic shape, 4-15 nm in side length. Taking advantage of their affinity for hydrophobic surfaces, they can be assembled in highly ordered monolayers in which the cubic NCs are organized in arrays with parallel edges. The close proximity of this arrangement and the high polarizability of these NCs allow for efficient exciton migration between adjacent NCs through Förster Resonant Energy Transfer (FRET). The monolayer layout confines the available paths for exciton transport in two dimensions, enabling the accurate study of the transport effects, mechanisms and anisotropy using super-resolution based optical imaging techniques combined with steady-state and time-resolved spectroscopy. Evidence of FRET-like transport is found in accelerated relaxation times and spatial expansion of the excited state ensemble. FRET-mediated long-range exciton migration over distances exceeding 200 nm is observed, and the impact of the inter-NC energetic disorder on the observed optical signatures is discussed.

This system allows for the first demonstration of such long-range exciton transport in NCs solids opening up new possibilities for functional, exciton-based optoelectronic devices made of cesium lead halide perovskite NCs.



a) SEM image of an ordered monolayer of cesium lead bromide NCs. b) Optical image of the spatial profile of the laser used to excite the NC monolayer. The spot is approximately Gaussian with a ~ 460 nm FWHM (red circle). c) Optical image of the spatial profile of the photoluminescence produced by the NC monolayer when excited with the laser shown in b). The spot is approximately Gaussian with a ~ 770 nm FWHM (red circle). The ~ 210 nm difference in radius between the two spots is likely due to FRET-mediated exciton transport.

COLL 143

Stable n-type thermoelectric multilayer thin films with high power factor from carbonaceous nanofillers

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We present a new approach to fabricate n-type organic thermoelectric nanocomposites through a layer-by-layer (LbL) method. An alternate deposition of double walled carbon nanotube (DWNT)-dispersed in polyethyleneimine (PEI) and graphene-dispersed in polyvinylpyrrolidone (PVP) solutions generated a highly layered nanocomposite in which DWNT with diameter in the range of 15-20 nm and graphenes (1.5 μm in diameter) formed an interconnected network between upper and lower layers. This unique combination exhibits that the electrical conductivity and Seebeck coefficient of 80 DWNT-PEI/graphene-PVP bilayer films (~ 320 nm in thickness) are very high (300 S/cm and -80 μV/K, respectively). In this first ever investigation of the n-type TE behavior of

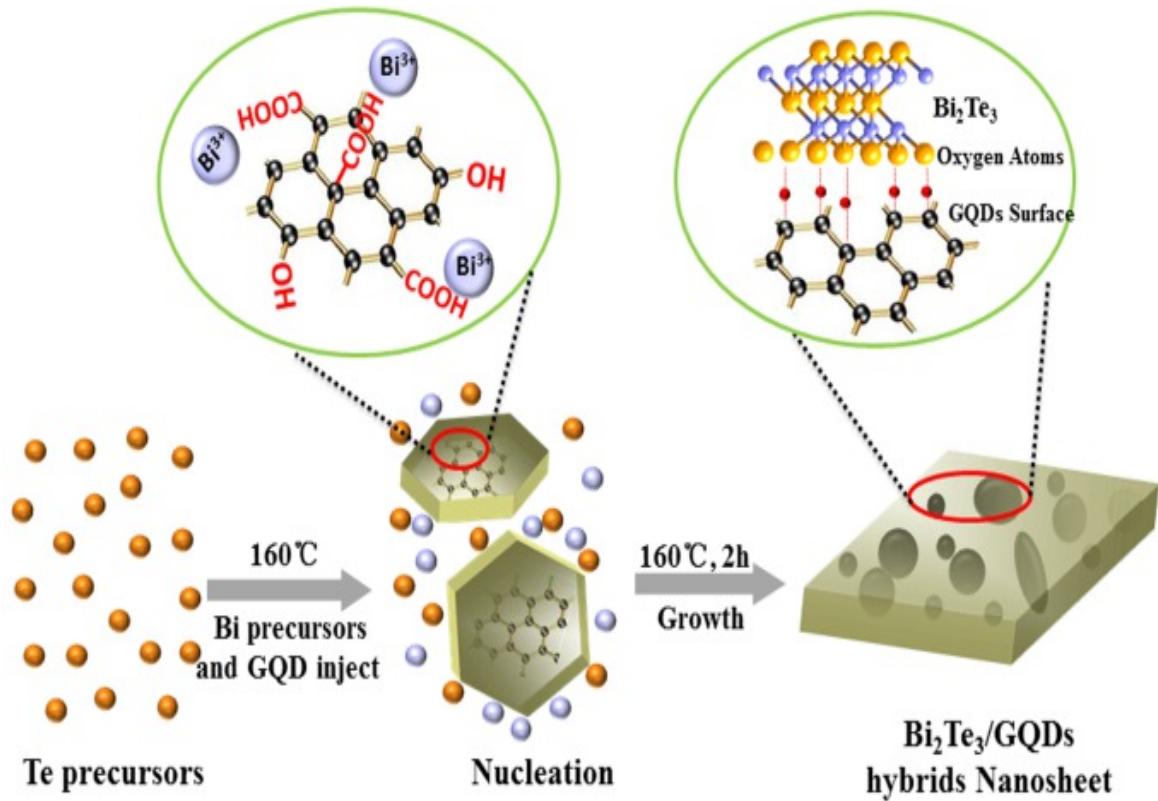
an LbL-assembled film, the resulting nanocomposites exhibit a remarkable PF of 190 W/mK² at room temperature, which is one of the highest values reported among organic n-type TE materials. A continuous 3-dimensional conjugated network, where DWNT bridges gaps between graphene sheets, provides more efficient electron transport and increases Seebeck coefficient due to improved carrier mobility. Furthermore, the graphene platelets aligned in the multilayers in the direction parallel to the substrate act as a barrier to permeating oxygen, imparting high stability in air over time. This novel n-type nanocomposite has the potential to open the way to low-cost and efficient thermoelectric materials, as well as to demonstrate the possibility of designing high performance p/n thermoelectric devices.

COLL 144

Rational design of Bi₂Te₃/graphene quantum dot hybrid nanosheet for enhanced thermoelectric performance

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Bi₂Te₃/GQDs hybrid nanosheet with a unique structure that GQDs homogeneously embedded in the Bi₂Te₃ nanosheet matrix were fabricated via a simple solution-based synthetic strategy. The oxygen-containing Bi₂Te₃/GQDs interface is crucial to optimize the thermoelectric transport properties of the Bi₂Te₃/GQDs hybrid, which could effectively scatter phonons across integrated length scales leading to very low lattice thermal conductivities, while should also effect the electron transport behavior by the modification of carrier mobility and concentration. Furthermore, by varying the size of GQDs, the thermoelectric performance of Bi₂Te₃/GQDs hybrid nanostructures could be further enhanced, which could be attributed to the optimization of the density and dispersion manner of GQDs in the Bi₂Te₃ matrix. Taking advantage of the maximum reduced κ_{tot} as well as a maintained power factor, the figure of merit ZT of the Bi₂Te₃/GQDs hybrid is greatly improved. A maximum ZT of 0.55 is obtained at 425 K for the Bi₂Te₃/GQDs-20nm, which is higher than that of the Bi₂Te₃ nanosheet without the hybrid nanostructure. This work provides the insights for the structural design and synthesis of Bi₂Te₃-based hybrid thermoelectric materials, which will be important for future development of broadly functional material system.



The solution synthesis process and formation mechanism of the Bi₂Te₃/GQDs hybrid nanosheet

COLL 145

Polarized optical spectroscopy of semiconducting polymers in an aligned mesoporous silica system for the study of polaron dynamics

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Semiconducting polymers have a wide variety of applications in organic electronics including solar cells, thermoelectric devices and LED displays, however the exciton and polaron dynamics that determine the efficiency of these devices are not well understood, particularly in terms of intra- versus inter-chain dynamics. So, we have developed a system of polymers in aligned mesoporous silica films, which allows for both isolation of small numbers of polymer chains and elongation of the polymer backbone. Because optical transitions in polymers occur along the backbone our system allows interchain and intrachain interactions to be probed separately using polarized optical spectroscopy. By using a wide variety of polymers, including push-pull polymers in this mesoporous silica system, we can use the optical studies to understand the effects of both chain conformation and aggregation across all types of semiconducting polymers. From our absorbance and fluorescence studies we have shown that polarization ratios of more than 20 can be achieved when the polymers are

in the pores. We can also study the peak shift of the emission peaks, and thus the exciton delocalization, in the aligned samples. We have seen that crystalline polymers are more likely to delocalize excitons between chains, even when confined to the pores while more amorphous polymers see a significant increase in intra-chain delocalization when aligned in pores. We have also seen that the structure of push-pull polymers and the nature of the electron withdrawing group affects both the ability to align in pores and the trends in excitons delocalization. Overall we have shown that this system can be used across all types of semiconducting polymers to understand the exciton and polaron dynamics in both inter and intrachain interactions.

COLL 146

Ultrasensitive probing of the local electronic structure of nitrogen doped carbon and its applications to 2D electronics, catalysis and bio-physics

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Chemical doping of carbon is an effective way to tailor their electronic and chemical properties such as band level alignment, charge carrier mobilities, and catalytic activity. Nitrogen doped carbon-based materials have received a lot of attention due to its premise in 2D electronics (e.g. as contact layer with tunable electronic properties), fuel cell applications (e.g. ORR) or metal-air batteries.

It has been shown that different bond types such as graphitic, pyrrolic, and pyridinic can exist in N-doped carbon, and they play a crucial role in determining the electronic properties both locally and for the whole matrix (doping effect). Core-level X-ray spectroscopy has been proven to be a powerful analytic method for characterizing different bond types in doped carbon. X-ray emission spectroscopy has the ability to map out the local electronic structure around elements in a site- and symmetry-specific

way, and direct comparison to DFT based theory is possible. However, XES has been inaccessible in the soft x-ray regime since the current technology lacks the sensitivity to measure the weak signal from low concentration dopants.

Superconducting transition edge sensor (TES) technology presents a unique opportunity to build novel detectors with greatly increased sensitivity in the soft x-ray regime while maintaining excellent energy resolution. We have commissioned a new generation soft x-ray superconducting TES spectrometer with a scientific motivation to probe the local electronic structure of ultra-low concentration sites in biology, chemistry, and materials, currently inaccessible in the soft x-ray regime due to the limited sensitivity of existing technology.

We will show the applicability of TES based spectrometers to provide detailed insight into the local electronic structure of nitrogen in graphene, carbon catalysts, carbon for chemical storage as well as nano-diamond. The applicability of this unprecedented photon in / photon out sensitivity in the soft x-ray regime to future in-operando studies of chemical transformations and the (potential) active role of nitrogen sites will also be discussed.

COLL 147

Probing the local electronic structure of a porphyrin-based single-layer covalent organic framework using STS

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Covalent organic frameworks (COFs) have attracted significant attention over the last decade due to useful characteristics such as robust covalent coupling, diverse geometries, and tunable functionality. Exploration of single-layer two-dimensional (2D) COFs is important for achieving a better understanding of their chemical and physical properties, as well as for paving the way toward integrating COFs into future electronic devices. Here we present the synthesis and electronic structure characterization of a porphyrin-based single-layer 2D COF having a square lattice with a core-linker configuration. Precursor molecules 2,5-dimethoxybenzene-1,4-dicarboxaldehyde (DMA) and 5,10,15,20-tetrakis (4-aminophenyl) porphyrin (TAPP) were deposited onto a Au(111) surface in ultra-high vacuum (UHV) and annealed to form a 2D COF through a Schiff-base condensation reaction. Scanning tunneling microscopy (STM) and spectroscopy (STS) were used to study the chemical and electronic structure of the resulting 2D COF. We find that this COF has a band gap of $1.98 \text{ eV} \pm 0.04 \text{ eV}$ and that both the conduction band minimum and valence band maximum states are primarily localized to the porphyrin core.

COLL 148

Structure formation, phase behavior, and dynamics of liquid crystals confined to nanopores

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Understanding the physical properties of liquid crystals (LCs) spatially confined to the mesoscopic scale is of fundamental and technological importance as a significant portion of LCs in device components is located near hard confining interfaces. Self-ordered nanoporous anodic alumina (AAO) membranes were used as an inorganic model matrix as it contains arrays of straight cylindrical nanopores, uniform in length and diameter, that can easily be infiltrated with LCs (5CB, E7 and HBC). The nematic-to-isotropic, crystal-to-nematic, and supercooled liquid-to-glass temperatures were studied in the LCs confined in self-ordered nanoporous AAO. The nematic-to-isotropic and the crystal-to-nematic transition temperatures are reduced linearly with the inverse pore diameter. The finding that the crystalline phase is completely suppressed in pores having diameters of 35 nm and below yields an estimate of the critical nucleus size. The liquid-to-glass temperature is reduced in confinement as anticipated by the model of rotational diffusion within a cavity. These results provide the pertinent phase diagram for a confined LCs and are of technological relevance for the design of LC-based devices with tunable optical, thermal, and dielectric properties. Similarly, another model LC system based on discotic mono-bromo hexa-peri-hexabenzocoronene (HBC-Br) were studied. Structure formation, phase behavior, and dynamics of mono-bromo hexa-peri-hexabenzocoronene (HBC-Br) are also strongly affected by the confinement of cylindrical nanopores with rigid walls. Using self-ordered nanoporous AAO-containing arrays of aligned nanopores with narrow size distribution as a confining matrix, pronounced alignment of the HBC-Br columns along the nanopore axes was found to be independent of the pore diameter. Hence, arrays of one-dimensional supramolecular HBC-Br wires with the columns uniformly oriented along the wire axes on a macroscopic scale were obtained, unlike with discotics bearing smaller cores. The formation of the crystalline herringbone structure is shifted to lower temperatures in nanopores with diameters of a few hundred nanometers, whereas the formation of this low-temperature phase is completely suppressed when the pore diameter is below 20 lattice parameters. Moreover, the cylindrical confinement affects the disc axial dynamics as well as the distribution of relaxation times.

COLL 149

NiS doped 3D MoS₂/graphene nanostructured hybrids as high performance hydrodesulfurization catalysts

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A facile and scalable preparation method for NiS doped nanostructured 3D assembly of 2D molybdenum sulfide and graphene porous aerogels was reported. These nanohybrids were *in-situ* synthesized from sulfur containing Mo (ammonium tetrathiomolybdate), graphite oxide and Ni oxalate under one step hydrothermal conditions. Further, thermal treatment at moderate conditions produces a highly interconnected macroporous network of thermally reduced GO having finely dispersed few-layered 2D MoS₂ nanosheets impregnated with NiS nanoparticles was observed. The resulting nanohybrids were deeply investigated by means of several techniques. XRPD, HRTEM, SEM, Raman and BET have been applied to obtain information on the morphology and the structure of the nanohybrid as well as on the vibrational and spectroscopic properties. These NiS doped 3D assemblies exhibits enhanced catalytic performance in the hydrodesulphurization (HDS) of dibenzothiphene (DBT) with sustained recyclability in compared to pristine 3D MoS₂/graphene and MoS₂. In addition to the NiS promotion, the highly exfoliated structure of MoS₂ nanosheets supported on porous graphene framework endowed these composites with abundant active sites for the electrocatalysis. The presented synthesis method can be applied into the large scale production of metal sulfide/oxide co-doped 2D MoS₂/graphene aerogels and opens new avenues for wide range of applications including electrocatalysis and advanced energy storage, as well as offer useful information to design newer functional hybrids composed of 2D materials.

COLL 150

Flexible impedance biosensor for folate receptor detection in cancer diagnostic

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The majority of deaths caused by common fatal diseases are because of the late detection of the disease. If the disease is detected early, it can be treated thus reducing the chances of death. Biosensors are a promising platform for quick and cost effective cancer detection with high sensitivity. Although biosensors utilizing biomolecules (e.g., DNA, RNA, proteins) are effective, they tend to suffer from the same disadvantage; they are sensitive to environmental conditions. Thus, reducing considerably their shelf life thereby diminishing their utility and reliability. In this work, a robust, inexpensive, flexible, and effective sensor was constructed and characterized by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), x-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM). The sensor was constructed using a Melinex^R polymer film with gold deposited on its surface. The first step of the sensor construction was the formation of a cysteamine self-assembled monolayer (SAM) used to covalently immobilize folic acid (FA) on the electrode's surface. AFM and XPS

experiments confirmed the SAM formation and the FA immobilization. A change in impedance was used to track the degree of binding between the folic acid molecules and the overexpressed folate receptor on the HeLa cell surface. A gradual increase of resistance on the electrode's surface was observed through time while exposed to the HeLa cells in solution. The electrochemical impedance of the sensor was linear from 100 cells mL⁻¹ to 5000 cells mL⁻¹. As a negative control, cells that do not overexpress folate receptor were used to monitor the change in impedance and little or no change was found over time. Eventually, this sensor can be used as a screening tool in potentially vulnerable patients for the early detection of multiple types of cancers that overexpress folate receptors as well.

COLL 151

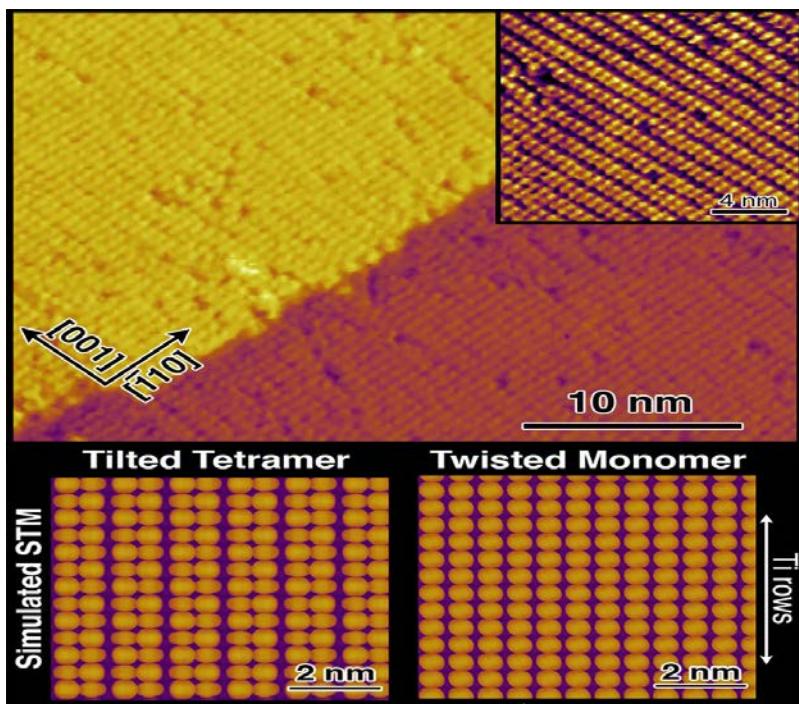
Deposition of self-assembled monolayers on TiO₂ in air and solution: Implications for photoreactivity and CO₂ photoreduction

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The reaction of organic molecules with TiO₂ nanocatalysts and surfaces is important for a wide range of applications, including the attachment of dyes in dye-sensitized solar cells, the control of reaction sites for shape-controlled nanocatalyst growth, and the functionalization of Ti surfaces for dental and biomedical implants. These applications require a chemical understanding of the structure, function, and stability of organic linkages to metal oxide surfaces.

We have prepared, imaged, and analyzed a wide variety of near atomically perfect, self-assembled monolayers from air or aqueous and organic solutions on the two major polymorphs of TiO₂: rutile and anatase. The structure and photoreactivity of these monolayers provides insight into their function. For example, we will show that strong π-π interactions between phenyl rings in a benzoate monolayer induce intramolecular rotations that destroy the extended π conjugation between the phenyl and carboxylate groups, presumably disrupting electron transport. This finding may have implications for the design of sensitizing dyes for photovoltaic applications. Interestingly, addition of an electron-withdrawing substituent, such as F, can disrupt these detrimental π-π interactions, restoring the extended conjugation.

The deposition of organic monolayers on well characterized surfaces of anatase (001) and rutile (110) allows direct comparisons of photoreactivity to be made. Anatase, the thermodynamically disfavored phase of TiO₂, is thought to be the more photocatalytically active phase; however, the poor availability of this polymorph has hindered understanding. We have developed methods to grow heteroepitaxial anatase (001) films with the size and chemical and morphological quality necessary for surface characterization by STM and polarized infrared spectroscopy. A comparative study of the photoreactivity of the two polymorphs will be presented.



COLL 152

Microplasma-based deposition of functional nanomaterials for energy storage applications

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A general method for plasma deposition of nanostructured transition metal oxides is presented. The technique uses a flow-through, micro-hollow cathode plasma discharge (supersonic microplasma jet) and volatile organometallic precursors to deliver a highly directed flux of growth species to a substrate (Fig. 1). This fabrication approach provides a general and tunable method to deposit a variety of functional and hierarchical materials (e.g., NiO, α -Fe₂O₃, CoO, and CuO) on virtually any substrate (conductors, insulators, polymers, fibers, and lithographic patterns) and may offer an alternative to traditional, multi-step chemical synthesis. The effects of deposition parameters, plasma operating conditions, and substrate type on film morphology, nanostructure, and surface coverage will be highlighted. Application examples to be discussed include NiO on carbon for pseudocapacitors and CuO for Li-ion batteries.

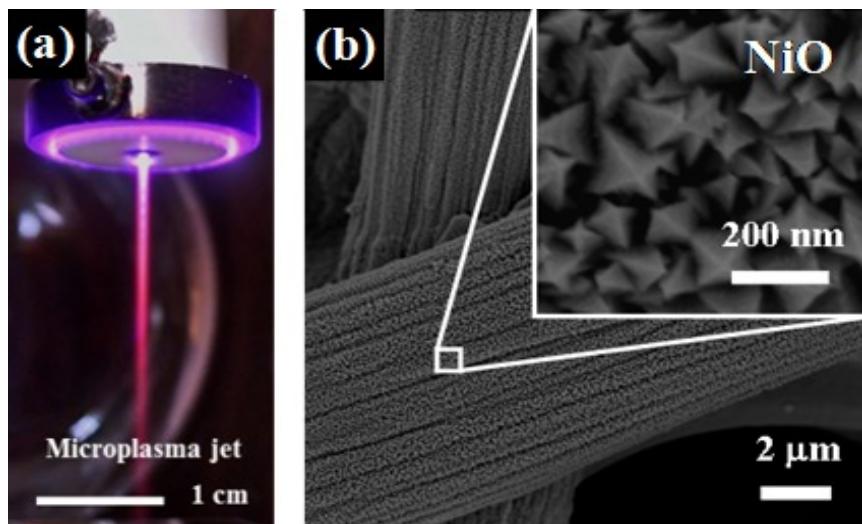


Fig. 1. (a) Photograph of an Ar microplasma jet operating at 15 Torr and 8.5 mA and (b) SEM images of NiO nanowires deposited on carbon fibers using a nickelocene-seeded microplasma jet.

COLL 153

Deposition of mixed metal nanostructures from bimetallic precursors using electrons: Insights from surface science

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Focused electron beam induced deposition (FEBID) is a nanofabrication technique, capable of creating a wide variety of size and shape selected metal-containing nanostructures using organometallic precursors. However, FEBID nanostructures often contain unacceptable amounts of contamination. This bottleneck in developing FEBID into a robust nanofabrication technology has provided the motivation to better understand the elementary reactions that occur during FEBID using a UHV surface science approach. An emerging aspect of FEBID involves the use of bimetallic organometallic complexes to create mixed metal nanostructures. In this presentation I will present findings on the electron stimulated reactions of two bimetallic complexes, $\text{CpFe}(\text{CO})_2\text{Mn}(\text{CO})_5$ and $\text{HFeCo}_3(\text{CO})_{12}$ studied using *in situ* X-ray Photoelectron Spectroscopy and Mass Spectrometry. Several important mechanistic details previously observed for organometallics that contain a single metal atom (e.g. $\text{W}(\text{CO})_6$ and $\text{Pt}(\text{PF}_3)_4$) are retained in bimetallic complexes, such as (i) the two-step sequential process of electron-stimulated reactions involving ligand desorption followed by ligand decomposition, (ii) the existence of ligands that are preferentially desorbed during the

first ligand desorption step (e.g. CO) and those that are retained and undergo decomposition (e.g. Cp). New findings include the observation that the fate of each metal atom appears to be determined from the nature of the surrounding ligands (i.e. electron stimulated reactions are localized). Moreover, the reason for the greater metal content often observed for bimetallic precursors appears to be a consequence of both the large fraction of volatile ligands ejected in the first step combined with the relatively inefficient electron-stimulated decomposition of the residual ligands.

COLL 154

Selectivity in liquid phase etching of III-V materials on the path to developing a gas phase self-limited etching method

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Bulk etching of III-V materials in liquid phase solutions is typically accomplished using an oxidizer such as H₂O₂ and an acid such as HCl. Both the oxidation step and the etching step are self-limiting. The etching rate in this chemistry follows a so-called volcano dependence as a function of a reactant concentration. For example, GaAs and InAs etch at about the same rate in 0.01 M HCl mixed with H₂O₂ over the range 0.01 to 1 M. A maximum etching rate of about 1 nm/s was measured at 0.1 M H₂O₂. Similar behavior was observed for GaSb and InSb. These materials etched at about the same rate over the range of H₂O₂ concentrations from 0.0001 to 0.01 M. Yet the maximum rate occurred at 0.001 M H₂O₂, which is a much lower concentration than where the maximum was measured for the arsenides. Bulk etching of III-V materials in aqueous oxidizing-acid chemistries is dominated by removal of the group V atom, which is the rate limiting step. In device fabrication, we would like to avoid processes that depend on the sacrificial growth of oxides from the group III and V atoms. If not removed completely, these oxides contain defects and create energy states in the band gap of the semiconductor that degrade electrical performance. Gas phase plasma chemistries based on oxidizers that do not contain oxygen are used to etch III-V materials. Although very low etching rates have been achieved, these processes are not truly self-limiting. A kind of self-limiting behavior has been achieved by resorting to timed etches. Atomic layer deposition (ALD) deposits conformal films on high aspect ratio structures because each half reaction is self-limiting. Increasing the temperature can cause another reaction to dominate and etch the surface instead of depositing a film. One example is the etching of GaAs oxides by TiCl₄. TiO₂ deposits below about 150°C. Above this temperature oxides are removed without depositing Ti leaving adsorbed Cl on the As-rich surface. The As-Cl termination blocks subsequent ALD of TiCl₄ and water vapor up to 50 cycles. If the As-Cl is desorbed by heating, TiO₂ deposits. Although oxide removal is very different from bulk etching of III-V semiconductors, common ALD precursors combined with an understanding of liquid phase etching reactions could identify candidate self-limited etching reactions for III-V materials.

COLL 155

Surface chemistry issues relevant to ALD processes

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A combination of modern surface-sensitive techniques has been used to study the mechanisms of the chemistry of several key metalorganic complexes proposed as possible precursors for the growth of metal thin films by atomic layer deposition (ALD) on a variety of substrates. In this presentation we will address a few recent examples from such studies. We will first discuss the reactivity of the precursor, providing examples for both highly reactive (amidinates) and more inert (cyclopentadienyl) ligands. The chemistry of the co-reactant will be discussed next, with examples for both reducing (hydrogen) and oxidizing (molecular oxygen) agents. Finally, the role of the substrate in activating the ALD precursors will be detailed. General conclusions extracted from these surface-science examples will be highlighted.

COLL 156

From fundamental electron-induced chemistry to novel unconventional FEBID precursor materials

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Focused Electron Beam Induced Deposition (FEBID) is a promising direct deposition technique for nanofabrication. FEBID is capable of producing free-standing 3D structures of sub-10 nm size. However, this technique faces challenges regarding purity and spatial resolution of the deposits as well as deposition speed. In Europe, the FEBID research landscape has thus joined forces within COST Action CM1301 – CELINA- to understand the fundamental chemistry behind FEBID and use this knowledge to develop superior precursor molecules and FEBID processes. The first part of this contribution will shortly introduce the work of CELINA.

In the second part we show that desorption experiments in ultrahigh vacuum are a valuable approach to gain insight into the fundamental chemical reactions underlying FEBID and discuss this on two examples. Desorption methods were used to study the electron-induced fragmentation behavior of typical FEBID precursor ligands. It has also enabled mechanistic insights into a previously discovered efficient deposit purification process based on water as a purification reagent.

The third part presents different FEBID experiments conducted with condensed precursor materials. Such thick precursor layers offer the advantage that deposition rates can be orders of magnitude higher than in the established gas-phase FEBID processes. The low-volatility platinum complex cisplatin has been selected as a

potential FEBID precursor because its ligand architecture bears the promise of being removed facilely by an electron beam. Additionally we emphasize the possibility to use ionic compounds for FEBID in condensed layers. This is achieved using ion soft landing of ionic species of known composition, charge state and kinetic energy. We demonstrate that soft-landing of mass-selected anions produces self assembling liquid films composed of ions and adventitious neutral molecules. A focused electron beam generates well-defined μm -sized structures in these films.

COLL 157

Influence of biomimetic brush nanostructures on the tribology of natural fiber bio-interfaces

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The tactile perception of hair by consumer and hair disentangling ability are key parameters that help the consumer's choice of shampoos and conditioners. Behind this sensorial perception, different tribological mechanisms are involved. In particular the geometry of the tribosystem (sliding object vs hair or hair vs hair) is important to determine which geometry is best to obtain the most relevant friction parameters to correlate either with tactile or disentangling capacity.

Polyethylene-glycol (PEG) grafted copolymers are known having the ability of self-assembling in aqueous environment to form polymer brushes on model surfaces that exhibit excellent lubrication characteristics. Thus, they are interesting models to explore their effect on the different tribological configurations previously mentioned.

We combined a technique for hair-hair friction, pin-on disk tribometry and Atomic Force Microscopy (AFM) to study the frictional behaviour of the homopolymer polylysine, poly(lysine-g-PEG) and poly(allylamine-g-PEG) in both aqueous and dry environments. Results in terms of friction force or friction coefficient and friction distribution show that a well structured polymer such as PLL-g-PEG exhibits by itself lubrication levels of a standard conditioner product. In addition these results correlate well with sensorial data irrespective of the different geometries used.

A critical discussion will be developed based upon the particular geometry and orientation of the fibres.

COLL 158

Coacervation and precipitation in polysaccharide–protein systems

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Precipitation poses a consistent problem for the growing applications of biopolymer coacervation, but the relationship between the two types of phase separation is not well understood. To clarify this relationship, we studied phase separation as a function of pH and ionic strength, in three systems of proteins with anionic polysaccharides: b-lactoglobulin (BLG)/hyaluronic acid (HA); BLG/tragacanthin (TG); and monoclonal antibody (mAb)/HA. We found that coacervation and precipitation are intrinsically different phenomena, responsive to different factors, but their simultaneity (for example with changing pH) may be confused with transitions from one state to another. We propose that coacervate does not literally turn into precipitate, but rather that both coacervate and precipitate are in equilibrium with free protein and polyanion, so that dissolution of one and formation of the other can overlap in time. While protein– polyanion complexes must achieve neutrality for coacervation, precipitation only requires tight binding which leads to the expulsion of counterions and water molecules. The pH-dependence of phase separation, considered in terms of protein and polyon charge, revealed that the electrostatic magnitude of the protein's polymer-binding site ("charge patch") plays a key role in the strength of interaction. These findings were supported by the inhibition of precipitation, seen when the bulky side chains of TG impede close protein–polymer interactions.

COLL 159

miRNA sensing plasma modified magnetic micromotor

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Nanotechnology provides a way to manipulate matter at the atomic and molecular scale. Mobility is desired in a wide range of applications, the use of self-propelled micro/nanomachines. Autonomous motion of micro motors have recently been used in many fields such as carry cargos, cancer cell screening, drug delivery, isolation of biological targets and nanosurgery. Among different kinds of self-propelled micro/nanomotors, attract the most attention due to the stable performance as well as ease of functionalization and control. In order to control micromotors with magnetic fields, biocompatible particle Fe₃O₄ was used in our study. The use of an external magnetic field is by far the most common approach reported in the motion control of self-propelling micro-motors and it is utilized to guide the micro motors to a desired direction or location. Fe₃O₄ magnetic nanoparticles (NPs) were waited in Ethanol for two hours and modified by RF rotating plasma method. First, magnetic nanoparticles were placed into the quartz vacuum chamber. After decreasing vacuum, NPs exposed to plasma for modification with –OH at 40Watt power. Fe₃O₄ and Fe₃O₄-OH NPs were dispersed in ethanol with helping ultrasonic bath. Dried NPs onto the glass were coated

Pt which was used for catalytic layer by RF magnetron Sputtering technique. Also, we described the use of magnetic micromotors for rapid and sensitive miRNA detection. miRNA sensing magnetic micromotors hybridization time and target concentration will study and for all parameters, speed and fluorescence intensity of micro motors will calculate by using NIKON Eclipse Optic LV100ND Microscopy.

COLL 160

Nanotransformation of vancomycin for overcoming Gram-negative bacteria intrinsic resistance

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Bacterial infections caused by drug resistant strains are one of the world's public health challenges and the development of alternative strategies is extensively being searched. Vancomycin is a glycopeptide antibiotic largely used for treatment of infections caused by Gram-positive bacteria. However, it has little effect against Gram-negative bacteria due to its inability to penetrate their outer membrane, impermeable to such large molecules.

The assemblies of molecules at nanometer dimensions confers unique properties, differing from those of the free molecules and the bulk materials with the same composition. The nanotransformation of the active agents themselves into nanosize has been applied in our group using the ultrasonic emulsification method to synthesize oil-filled nanospheres (NSs), in which the antimicrobial agent is located at the interface of the droplet. The nano-transformation does not alter the target of the drug or its chemical structure, while simply adding a support mechanism to its mode of action towards bacteria. This mode of action reduces the possibility of developing new resistant strains because bacterial membrane is highly evolutionarily conserved.

The observed penetration of the NSs within a Langmuir monolayer composed by bacterial membrane phospholipids has confirmed that the vancomycin nanospheres were able to interact with the membrane and affect the physical integrity of *Escherichia coli* cells, which was further visualized by scanning electron microscopy. The ability of Vancomycin NSs to kill biofilm was visualised using fluorescence microscopy and antibacterial assays and quantified using CBD-MBEC™ technique. The nanospherization of vancomycin boosted its capacity to inhibit the growth of Gram-negative *Escherichia coli* and *Pseudomonas aeruginosa*, making these bacteria up to 10 and 100 times, respectively, more sensitive to the antibiotic. Moreover, the antibiotic nanospheres eradicated biofilms of Gram-negative bacteria in the antibacterial-effective concentrations.

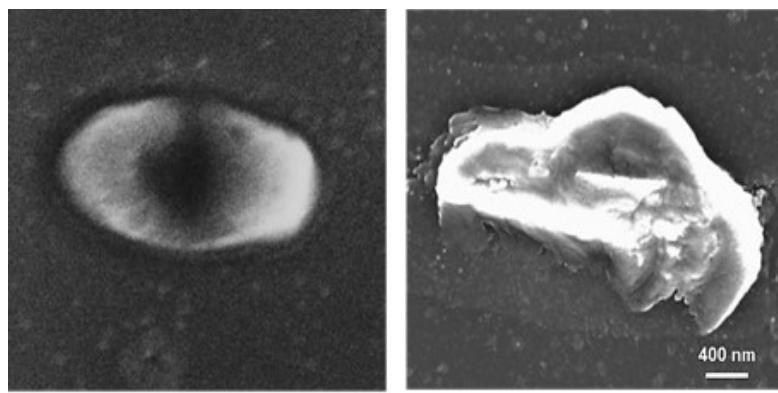


Figure 1. SEM micrographs of *E. coli* cells before and after treatment with $1.05 \pm 0.06 \times 10^{13}$ NSs/mL vancomycin NSs.

COLL 161

Fabrication of vanadium oxide thin films from colloidal vanadium oxide (VO_x) nanocrystals for smart window applications

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Vanadium oxide represents an important class of thermochromic materials employed in different technological applications such as intelligent window coating materials, catalyst, cathodes in Li-ion batteries, or in electrical, optical, temperature switching devices. Vanadium dioxide (VO_2) has attracted much attention because it is known to undergo a thermally induced, reversible metal-semiconductor phase transition. The outcome of this phase transition is temperature dependent non-linear optical and electrical characteristics. Particularly its optical properties change significantly in the visible and near-IR range at the phase transition temperature (T_c) around 68 °C. As the temperature exceeds T_c , it experiences a structural change and becomes less transparent and more reflective, which prevents a thermal radiation from excessively heating while remaining visually transparent. Therefore, this phenomenon can be applicable to energy saving smart window applications.

There are two important issues to be solved in order for this phenomenon to be a viable technology for smart window applications. First of all, T_c of thermochromic materials has to be lower and close to room temperature. There have been reported examples of lowering T_c by chemical doping of inorganic elements such as tungsten, molybdenum, niobium. Second, there should be a simple, scalable, reproducible, and cost-effective way to incorporate thermochromic materials on glass window materials.

We have developed solution-phase synthetic routes, including hydro- and solvothermal processes, to organically functionalized vanadium oxide (VO_x) nanocrystals in order to use them to fabricate nanostructured thin films. We have fabricated thin films on glass and indium tin oxide substrates either via drop casting or spin coating the solution of VO_x nanocrystals. As prepared VO_x nanocrystals and their thin films have been characterized by means of various analytical methods such as TEM, FE-SEM, XRD,

XPS, FT-IR and Raman spectroscopy. We find that the average VO_x nanocrystal size and its distribution depend strongly on the choice of solution compositions and reaction conditions and that thermal annealing of thin films resulted in a formation of crystalline VO_2 . Results of structural and spectroscopic characterizations on the formation of VO_x nanocrystals as well as their thin films before and after thermal annealing will be discussed in details.

COLL 162

Organic-inorganic microcapsules via immobilizing bicomponent colloidal particles at oil-water interface

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The design of efficient delivery systems to control the stability and release of active ingredients (such as volatile molecules) has become an important research area. Here, we report a type of unique Pickering emulsions stabilized by bicomponent colloidal particles, which contain two types of SiO_2 particles with different surface functionalities. These particles adsorbed at the oil–water interface were further immobilized to fabricate organic–inorganic microcapsules for the encapsulation of volatile molecules. The adsorption and embedment of colloidal particles at oil-water interface (microcapsule surface) were investigated. It is revealed that the particle adsorption/embedment at oil-water interface was significantly influenced by the SiO_2 particle components, owing to the different adsorption energy at oil-water interface and the synergistic interactions between these two different particles. The properties of the formed microcapsules (such as size, surface charges and particle loading) were also controlled by the SiO_2 stabilizer components. Moreover, these organic-inorganic microcapsules exhibited low permeability and unique mechanical behaviors upon compression compared with polymer-based microcapsules. These advantages of formed organic-inorganic microcapsules open up opportunities to fabricate ideal delivery systems for different applications, in particular in home care or personal care fields, where mechanical force is applied to trigger the release of encapsulated volatile ingredients.

COLL 163

Templated formation of fullerene stripes with tunable nanometer spacing onto physisorbed monolayers

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There is increasing interest in preparing materials with nanometer-scale control of composition. Physisorbed self-assembled monolayers (MLs) on graphite surfaces readily provide ordered 2D architectures, the composition and reactivity periodicity of which can be systematically tuned. Such 2D MLs can direct patterned capture of

"objects of interest" (e.g. fullerenes), as a first step to forming patterned 3D materials. We have developed a series of triphenyleneethynylene (TPEE) molecules that self-assemble on graphite surfaces to form stripes of reactive functional groups that are freely accessible above the MLs. Preliminary MALDI-MS (Matrix Assisted Laser Desorption/Ionization - Mass Spectrometry) experiments demonstrate that appropriately functionalized fullerenes can be captured by the reactive MLs. We are working to optimize capture protocols and to visualize captured fullerenes using various imaging spectroscopies.

COLL 164

Forming supported lipid multilayers by self-spreading

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Self-spreading solid-supported lipid bilayers enable directional and bio-functionalizable coatings of solids, with experimentally convenient kinetics. Here we demonstrate that integer multiples of stacked bilayers can also self-spread. The efficiency of forming multilayers correlates to lipid charge, substrate properties, and buffer conditions. We report on the multilayer forming efficiencies of dioleoyl-tailed lipids with a broad range of positive, negative, and polar headgroup mixtures. We characterize multilayers through fluorescence microscopy and imaging ellipsometry. We are currently examining the role of the substrate on multilayer formation, as well as the possibility of manipulating multilayers with electric fields.

COLL 165

Manganese-engineered iron oxide nanocomposites as T_1 - T_2 dual-modal contrast agents

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The T_1 - T_2 dual-modal magnetic resonance imaging (MRI) contrast agents can greatly improve the sensitivity and reliability by the beneficial contrast effects in both T_1 imaging with high tissue resolution and T_2 imaging with high feasibility on detection of a lesion. We report a facile one-pot synthesis of manganese-engineered iron oxide (MnIO) nanocomposites by thermal decomposition of iron-oleate and manganese chloride. The Mn/Fe molar ratios in the final nanocomposites can be well tuned by the Mn/Fe molar ratios in the reaction precursors. After PEG-phosphate coating, the manganese oxide-embedded iron oxide nanocomposites significantly increase the T_1 relaxivity with an enhanced positive contrast effect. Moreover, both r_1 and r_2 values of MnIO nanocomposites can be tuned by varying Mn/Fe ratios. Therefore, the facile synthetic

method and surface coating strategy, and the highly biocompatibility of MnIO nanocomposites promise the potential biomedical applications in MR imaging.

COLL 166

Water buffer action under nanoscale confinement studied by fluorescent pH indicator

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A black soap film is an ultrathin and self-supported molecular system constituted of two monolayers of amphiphilic molecules with their polar heads facing each other. Some researchers investigated the BSFs by UV-Vis absorption spectrum and resonance Raman spectroscopy to study the property of nanoscopically confined water. In this project, we have used a custom-built fluorospectrometer and a ratiometric fluorescent dye to determine the pH anomaly of BSFs consisted of different surfactants. The buffer action of nanometer scale water can thus be revealed by the fluorescence properties of the dye. With parallel experiments carried out in bulk and BSFs pulled from the same bulk, we managed to directly compare the pH difference of the two systems. Through global curve fitting, pH indicator's acid and base peak areas were differentiated, then the ratio of them plotted versus bulk pH values. We found that this ratio in BSFs were consistently higher than those of the corresponding bulk solution, suggesting lower pH value in BSFs. It may be due to some particularity of water only at nanometer scale. The difference between the CTAB bulk solution and the corresponding BSFs is bigger than that of SDS, because of the different charge of surfactants.

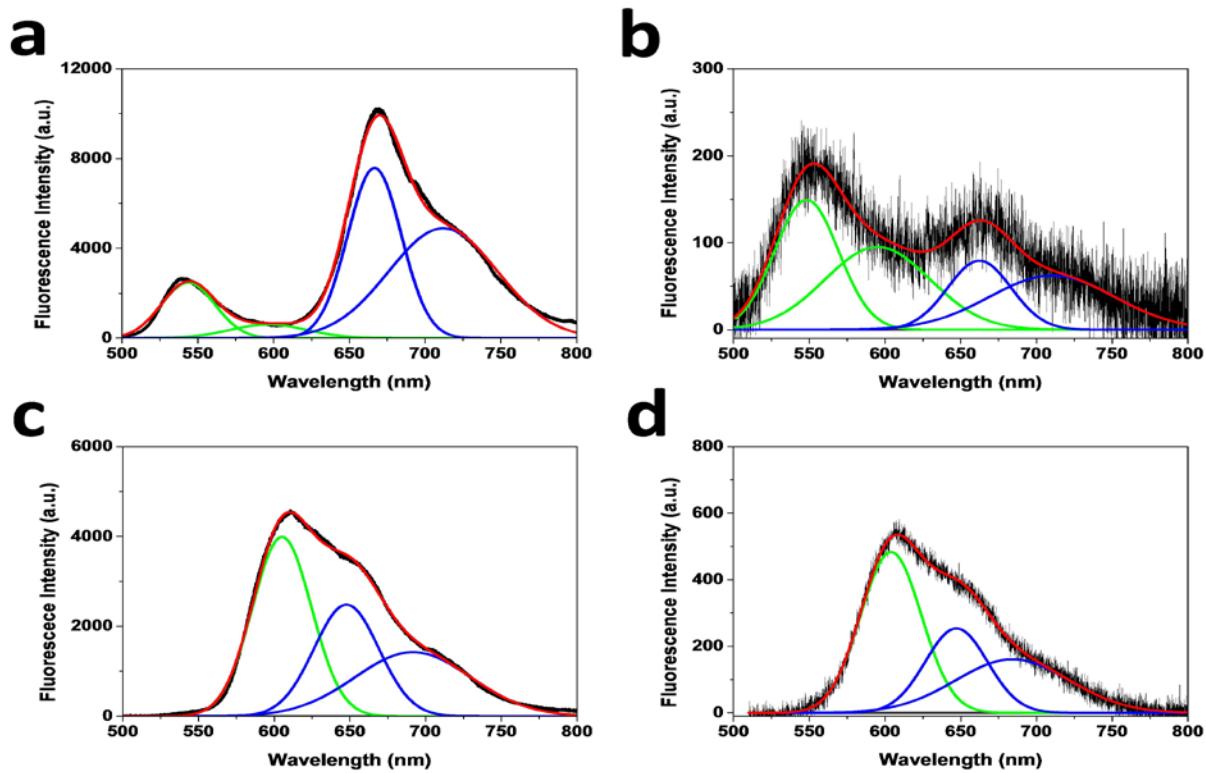


Figure 1. Fluorescent spectra and fitting results of the dye in (a) 0.01M CTAB solution (pH=6.70), (b) the BSFs from CTAB solution, (c) 0.01M SDS solution (pH=7.49) and (d) the BSFs from SDS solution.

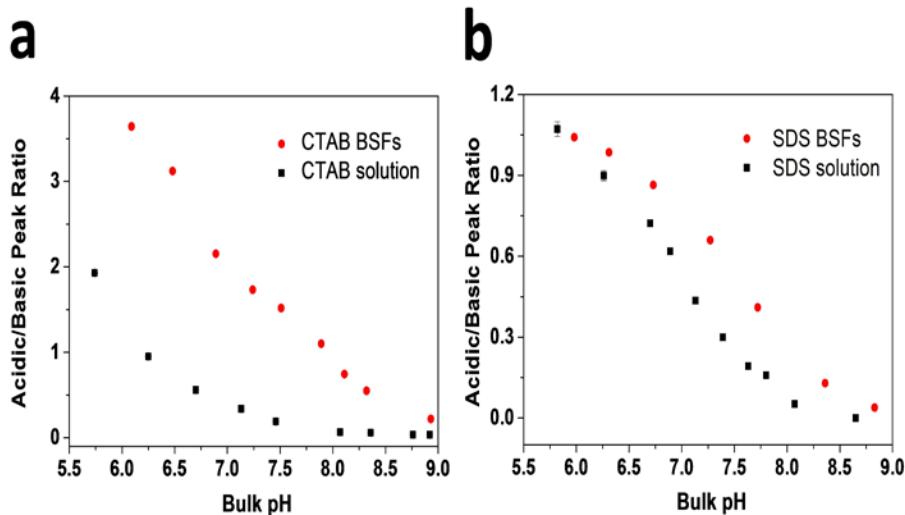


Figure 2. (a) The ratio of 0.01M CTAB solution and BSFs acid type peak area and alkali type peak area along with the change of pH value; (b) The ratio of 0.01M SDS solution and BSFs acid type peak area and alkali type peak area along with the change of pH value.

COLL 167

Quartz Crystal Microbalance with Dissipation (QCM-D) study of bacterial attachment process on surfaces of different hydrophilicity

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Bacteria can sense interfacial properties and secret bacterial extracellular matrix (ECM) as a biofilm to protect them from hostile environments. The formation of biofilm is also an important cue to understand the disease causing. Therefore, the ability to control biofilm formation and studying the effect of surface properties can reveal how bacteria interact with the surface and tailor its behaviors. Self-assembled monolayers (SAMs) are known for its versatility and convenience to modify surface. In previous work, serial surface property can be achieved by introducing two kinds of functional groups in different ratios. In this study, serial hydrophilicity surfaces were achieved by applying 1H,1H,2H,2H-Perfluoro-1-octanethiol and 8-mercaptop-1-octanol that provide hydrophobic $-CF_3$ and hydrophilic $-OH$ surface functionalization, respectively, in different ratios on gold surfaces. The composition on the surfaces was measured by x-ray photoelectron spectroscopy (XPS) and the water contact angle varied from 110° to 21° (surface energy 17 to 68 mJ/m^2). These SAM-Au coated quartz sensors were then used in a quartz crystal microbalance with dissipation monitor (QCM-D) to investigate near-surface viscoelastic changes between *Staphylococcus aureus* and serial hydrophilicity surfaces by recording shift in resonant frequency (Δf) and energy dissipation (ΔD) during 20h incubation. The specimens were fixed and observed by scanning electron microscope (SEM) to examine the distribution of bacteria and biofilm. While the Δf was expected to be positive for particle-like bacteria wobbling on the surfaces, all the QCM-D data showed negative Δf in this work. It suggested that the viscous ECM dominate the surface interaction. Furthermore, on more hydrophilic surfaces, resonant frequency steadily changed with time that indicated a single kinetic of biofilm formation. On the other hand, on hydrophobic surface, weak interaction and small Δf was observed initially. After ~ 4 h, as more ECM was secreted and deposited on the surface, bacteria started to interact with the surface and significant drop in resonance frequency was then observed.

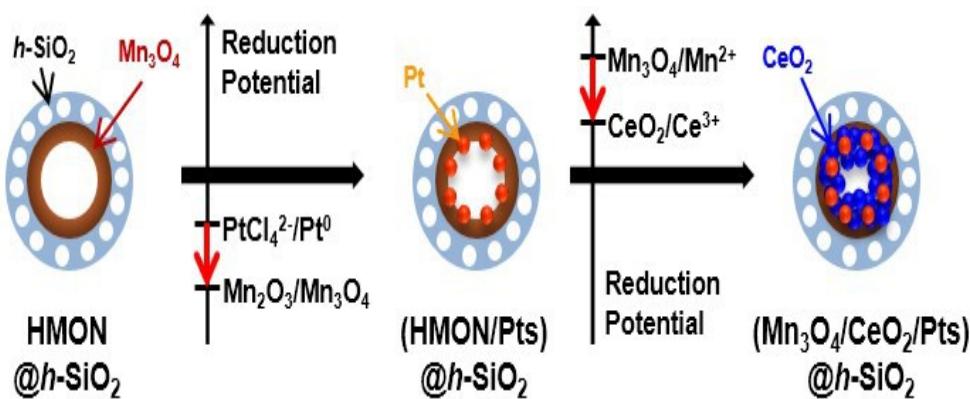
COLL 168

Synthesis of CeO_2 supported noble metal nanoparticles using mixed-valent Mn_3O_4 phase via galvanic replacement reaction

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This paper reports the result of our effort to enhance the variability of the post-synthetic protocol of functionalizing the preformed hollow nanoparticles which previously announced. The enhanced protocol produced hollow nano-reactor systems, in which

replace Mn_3O_4 layer –high density of ultrafine catalytic nanocrystals, such as Pt, Pd, Ir, and Rh, immobilized- with CeO_2 nanocrystals. The ultrafine nano-crystals maintained their size and were spread all over the replaced CeO_2 surfaces during the replacement reaction. The replacement reaction, called galvanic replacement reaction, can be occurred reducing metal precursor and oxidizing Ce^{3+} ion not only sequentially but also simultaneously on the Mn_3O_4 surfaces using Mn^{2+} and Mn^{3+} species each. As synthesized CeO_2 supported Pt nanoparticles in SiO_2 hollow shell performed synergetic catalytic activity for aerobic oxidation of carbon monoxide.



Protocol of functionalizing the hollow silica nano-particle with CeO_2 and noble metals

COLL 169

Control of dynamic wetting behaviors on smooth surface for liquid manipulator and slippery surface with multi functionality

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Learned by nature, dynamic wetting phenomenon on surfaces such as droplets' spreading, sliding, and asymmetric shaping have been intensely studied because of their potential fundamental applications (e.g. controlling droplet motion, forming liquid layer etc.). Such wetting behaviors have been controlled by surface nanotechnology and chemistry. For example, liquid layer is formed on *Nepenthes alata* bio-inspired solid structure *via* capillary-driven spread wetting, and a droplet motion is controlled by introducing anisotropic or gradient structure.

While various structures have been proposed for designing special wetting device, it is still difficult to obtain practical one since the existence of nanostructure limits the functions of transparency and mechanical robustness.

Here, we introduce a strategy to control dynamic wetting behavior of 'spread wetting' and 'droplet motion' on smooth coating ($R_{\text{rms}} < 1 \text{ nm}$). Instead of controlling surface nanostructure, we controlled the 'solid-liquid interaction' and 'flexibility' of hydrocarbon molecules tethered on surface using silane technology.

Figure A shows the wetting behavior of lubricant on C_{10} and Ph tethered area. The

spread-wetting behaviors differ with the solid-liquid interaction although both surfaces are smooth. Especially, Ph tethered surface performed superoleophilicity against hydrophobic liquid to form liquid layer due to the pi-interaction. The liquid surface performed excellent hydrophobicity, a high level of transparency and robustness thanks to the smooth structure.

Furthermore, we also introduce omniphobic liquid manipulation by patterning the two types of hydrocarbon molecules which have different wetting dynamics to achieve an unusual anisotropic droplet motion on smooth surface (**Figure B**).

We believe these technologies have potential not only for fluidic applications but also for the development of coating technology in the future.

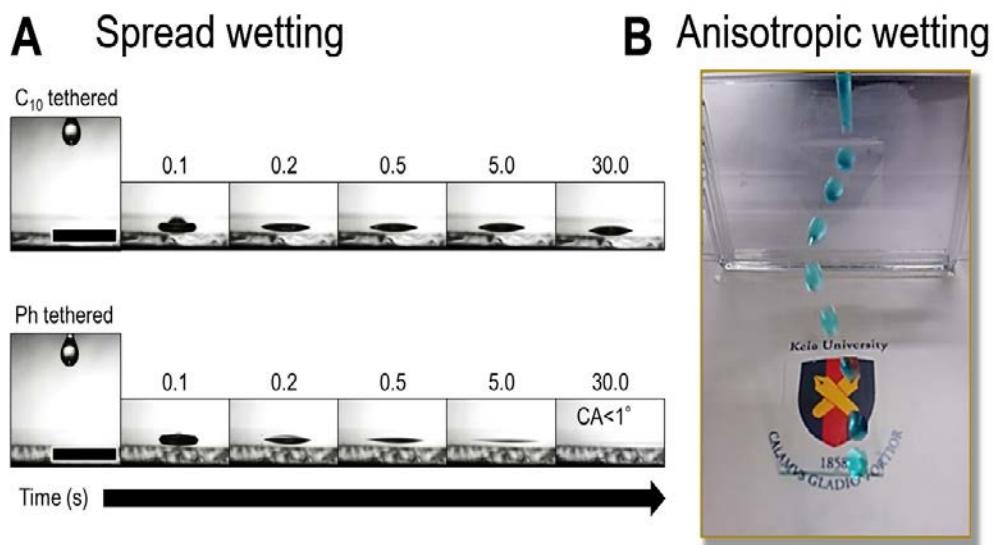


Figure (A) The spreading width W of hydrophobic liquid decyltrimethoxysilane droplet wetting on Ph and C_{10} tethered surface as a function of time τ . **(B)** Water droplet's S bending on Ph/ C_{10} patterned smooth surface.

COLL 170

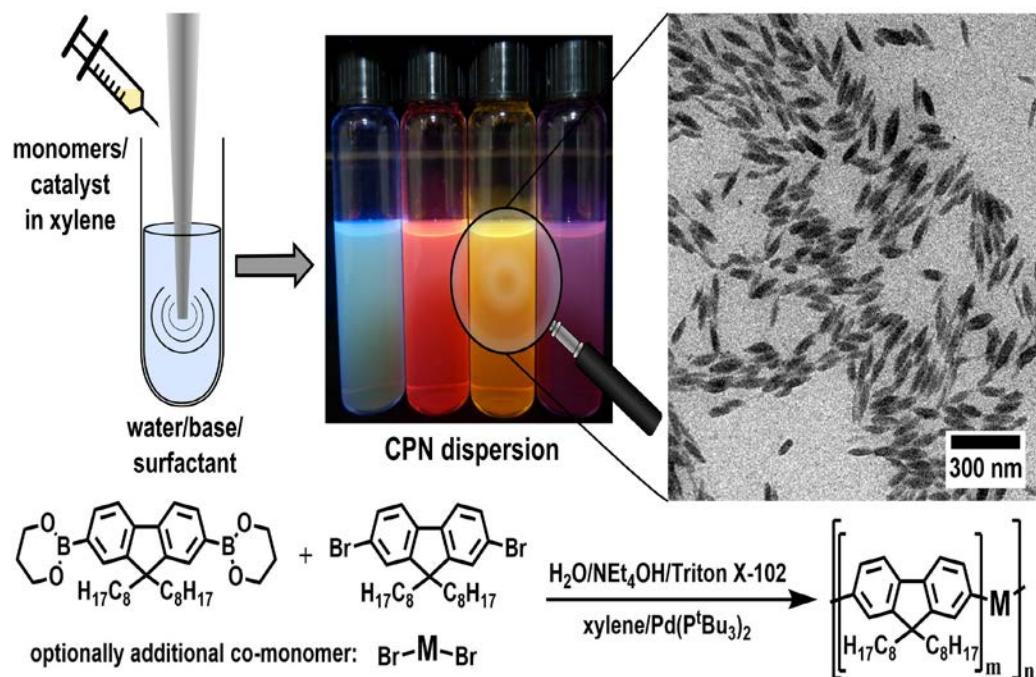
Anisotropic emission-tuned polymer nanoparticles through a scalable direct approach

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Beyond their composition, the shape of nanoparticles has a tremendous impact on their properties. Well known examples are shape dependent plasmon behavior or the internalization in cells. While this concerns individual particles, also inter-particle interactions are shape dependent. The self-assembly to organized structures is decisively determined by particle shape, particle packing and alignment as well as the directional interactions between the particles. Different from inorganic nanocrystals, the

accessibility of anisotropic polymer nanoparticles is underdeveloped. This applies in particular to conjugated polymer nanoparticles as an important class of materials.

Here, we report a reproducible preparation method to a range of stable dispersions of ellipsoidal shaped (aspect ratio of around 3.5) conjugated polymer nanoparticles, prepared via heterophase Suzuki-Miyaura coupling polymerization. The conjugated polymer nanoparticles exhibited a bright fluorescence emission with tunable emission wavelengths and quantum yields as high as $\phi = 78\%$. Structural investigation via UV-vis absorption and photoluminescence spectroscopy along with PXRD studies revealed that the nanoparticles are composed of the highly ordered β - and α' -phase within a nematic matrix. Preliminary studies on the origin of particle anisotropy suggest a concerted mechanism in which anisotropic shape evolves from segmental packing that occurs along with progressing chain formation by polymerization. Consequently, parameters that affect the colloidal state over the different stages of the particle generation as well as the polymerization rate are decisive for the ultimate shape (like choice of catalyst, total reaction volume, temperature and type of surfactant).

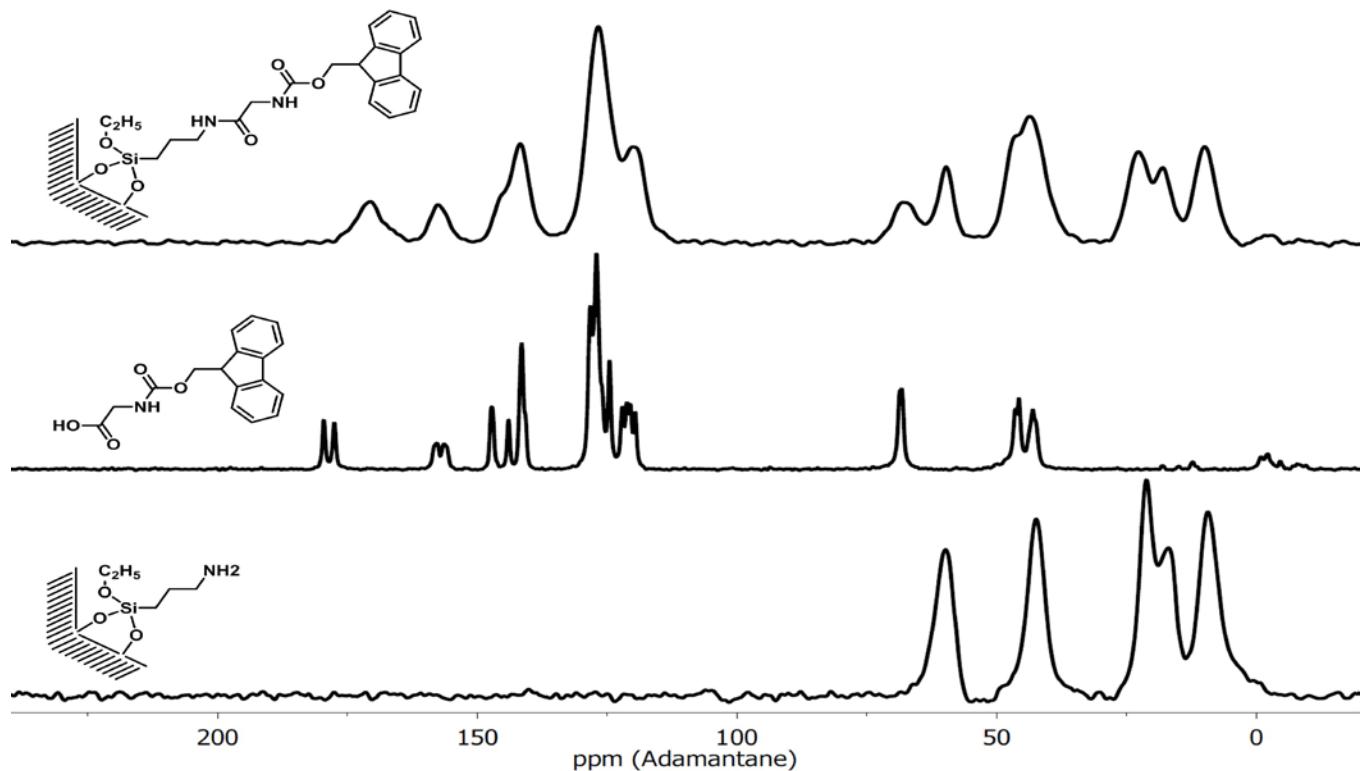


COLL 171

Biofunctionalized silica-nanopores: Synthesis and characterization by solid state CP-MAS-NMR

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Understanding biological materials is a major challenge for material scientists. Many of these natural occurring materials have useful properties for employing them as smart materials. Especially ion conducting materials such as biological membranes and ion channels may be used as sensors in a variety of technical applications. However, these complex materials have to be characterized in detail to understand their structure property relationship. A suitable way is the creation of model systems, which enable the selective optimization of their structure and thus their properties. Biologically modified silica-nanopores based on SBA-15 and MCM-41 materials employing different peptides may act as model systems for a better understanding of the structure of ion conducting materials. The combination of ^{29}Si and ^{13}C CP-MAS-NMR techniques provide information on the successful biological modification of the silica pore (figure 1). For a deeper structural understanding ^{15}N MAS-NMR seems to be the method of choice since ^{15}N shifts are strongly influenced by their chemical environment (especially hydrogen bonds). Nevertheless, ^{15}N -NMR suffers from its low intrinsic sensitivity, and thus requires sensitivity enhancement techniques such as Dynamic Nuclear Polarization (DNP) to perform these experiments on peptide functionalized material containing ^{15}N in natural abundance. The presentation will demonstrate the developing of proper synthesis strategies for defined peptide silica hybrid materials. This includes a high grafting density of peptides and the proof of covalent bindings. The surface structures are then characterized by a combination of solid state NMR and surface enhanced DNP.



Comparison of the ^{13}C CP-MAS-NMR spectra of NH_2 -functionalized support material (8 kHz), the Fmoc-Glycine (13 kHz) and Fmoc-Glycine immobilized on the silica material (13 kHz).

COLL 172

Investigation of a nanoscale surface area coverage by a self assembly of amyloidogenic peptides

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The characterization of adsorption of the amyloidogenic peptides, amyloid beta peptide 1-40 (Ab_{1-40}), alpha-synuclein (a syn), and beta-2-microglobulin (b2M) over nano-gold colloidal particle's surfaces were investigated by using pH dependent UV-Vis absorption spectroscopy. Amyloidogenic peptides generally support unfolded conformations around pH 4 and support folded conformations around pH 10. The peptide affinity of any sizes of gold colloid was confirmed to stably support a layer of peptide. When the peptides were placed over nano gold colloids they were observed to still cause unfolding at pH 4. This leads to a networking of surrounding peptides coated over the nano-gold resulting in a formation of 1 micro meter aggregates. However, there was no clear quantization of the percent of the nano-surface covered by peptide. We established a systematic scheme to extract the surface coverage ratio of peptide by using the pH dependent absorption peak shift. We discovered that critical pH (pH_o) and an inverse of the curvature at pH_o possessed a linear correlation. Since the larger pH_o shift corresponds to the more coverage of peptide, we were able to characterize the surface coverage ratio of peptides for each size of gold colloidal particle. We are currently attempting to rationalize the most appropriate oligomer unit which corresponds to each coverage ratio. This oligomer unit can be associated with the key structure of an intermediate of fibrillogenesis.

COLL 173

Investigation of reversible self-assembly of amyloidogenic peptides at nano-scale interface

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The folding process of the amyloidogenic peptide is regarded as the crucial conformational change leading to fibrillogenesis, which eventually triggers neurodegenerative diseases. Our recent studies indicate that a key oligomeric form associated with fibrillogenesis can be stably made provided by a metal surface potential. In recent studies, we successfully identified the layer of Beta-2-Microglobulin

(β 2M) to be approximately 0.9 nm in width over a 30 nm gold colloid surface. This layer is used to aggregate residual β 2M coated gold colloid particles under only acidic conditions, in which unfolded β 2M oligomers were formed. While we are not certain if this layer is a monolayer or multilayer, the oligomeric form can determine this thickness. Therefore, the layer's thickness showed signs of being dependent on the size of the gold colloid. We are investigating the stable form of the oligomer and associated layer's thickness over the gold colloidal size between 10 nm and 100 nm, as well as a pH ranging from 2-12.

COLL 174

Fabrication of antifreeze infused hydrophilic polymer/nanoparticle composite anti-icing coating for solar cells via spray layer by layer method

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Frost on solar cells causes the reduction of power efficiency. To overcome this problem, anti-icing coating is strongly required. The anti-icing coatings on the surfaces of solar cells require for high transparency besides anti-icing property. However, there are few reports of materials which satisfy both properties.

Here, we fabricated hydrophilic polymer/nanoparticle composite anti-icing coating with a total transmittance of 93% via spray Layer by Layer (LbL) method and antifreeze infusion as shown in Figure 1a. Polyethyleneimine (PEI) and Colloidal silica (SiO_2) were used as cation and anion respectively, and we selected Ethylene glycol (EG) as the antifreeze liquid.

We compared this antifreeze-infused coating with conventional hydrophobic coatings. Figure 1b shows the images of each sample in the condition at -15 °C and 50% RH. It indicates that our antifreeze-infused coating performed longer-stable anti-frosting property than those of superhydrophobic surface (SHS) and slippery liquid infused porous surface (SLIPS). In addition, the EG coated surface with polymer/nanoparticle composite layer delayed frost formation time compared to the surface without it. This suggests that the hydrophilicity and capillary force of the composite layer, along with hydrogen bonds between PEI and EG, prevent the aggregation of EG caused by its surface tension.

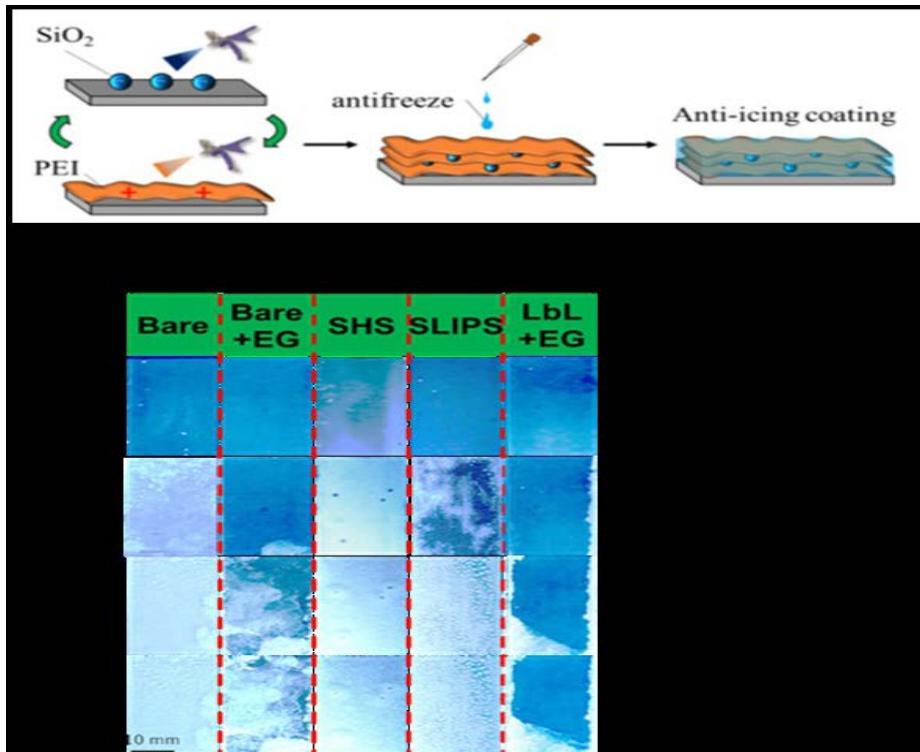


Figure 1. (a) Fabrication process of highly transparent anti-icing coating with antifreeze. (b) Time-lapsed images, at -15 °C and 50% RH, of bare glass without and with EG, hydrophobic surface (SHS, SLIPS), and our antifreeze infused coating (LbL+EG). White area shows the frosting parts, and blue area shows the non-frosting parts.

COLL 175

Shea butter infused with natural oils to generate a novel and natural antimicrobial moisturizer

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There are many challenges when discussing the topics of hair, nail, and skin care. Microbial infections, such as *Trichophyton rubrum*, are considered to be the most prevalent cause of skin and nail infections. Other bacteria known to cause skin issues include: *S. aureus*, β-hemolytic streptococci, and coryneform. Previous research has shown that certain types of raw butters and natural oils contain antimicrobial properties against these known dermatophytes. Our work focuses on the synthesis of antimicrobial surfaces with a formulation based on shea butter and other natural oils. Shea butter is a triglyceride derived from stearic acid and oleic acid. This type of butter has been tested and proven to demonstrate anti-microbial, anti-inflammatory, and hydrating properties. We incorporate into the shea butter various oils including Propolis, Neem Seed Oil,

Black Elderberry, Yarrow, Tamanu, Rosehip, Ginger, Sage, Argan, Guava Seed, Coconut Oil, and Dragon's Blood. Bacteriological results are described herein.

COLL 176

Effect of silica size on superhydrophobic property of filter media for water oil/separation

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This study investigated the effect of size of hydrophobic silica (SiO_2) on superhydrophobic property and separation efficiency of filter media for water oil/separation. The superhydrophobic filter was prepared by coating cotton textile with hydrophobic SiO_2 via sol-gel process. Tetraethylorthosilicate (TEOS), ammonia solution (NH_4OH), ethanol and de-ionized water were used as precursors for preparing SiO_2 particles. The volume ratio of ethanol to de-ionized water was varied to obtain different SiO_2 sizes ranging from 50 to 700 nm. Low surface energy silane coupling agents, including chlorotrimethylsilane (CTMS) and octadecyltrichlorosilane (OTS) were used for hydrophobizing SiO_2 surface. The optimum preparing condition to obtain the highest WCAs at $161.24^\circ \pm 0.61$ was to coat the cotton textile with hydrophobic SiO_2 having size of 568.10 ± 19.81 nm. Fourier transform infrared spectroscopy (FT-IR) study indicated silanizing between non-polar long chain alkyl silane with hydroxyl group on SiO_2 surface. The surface morphology of the superhydrophobic filter examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) showed that the surface was uniformly covered with spherical shaped hydrophobic SiO_2 . Scanning probe microscopy (SPM) analysis showed that the surface had high degree of hierarchical micro-nano scale roughness (RMS roughness = 151 nm). The superhydrophobic filters exhibited high water/oil separation efficiency and good reusability. They can be used for separating mixtures of water/oil including hexane, chloroform, diesel and soybean oil with the separation efficiency in range of 100 to 90%. The water/hexane separation efficiency was slightly reduced from 100 % to 94 % after 10 cycles of water/hexane separation.

COLL 177

Development of ion adsorbent from polybenzoxazine-based nanoporous materials

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Adsorption is a well-established technique to remove metal ions. The existence of Ca(II) and Mg(II) ions in water leads to problems in cooling and heating systems including clogging pipeline or the other industrial machines. In this work, an alkali-earth metals model solution, Ca(II) and Mg(II), was used to study the efficiency of using nanoporous polybenzoxazine as an alkali-earth metal ions adsorbent. Nanoporous polybenzoxazine was synthesized from bisphenol-A, formaldehyde and tetraethylenepentamine (TEPA) via a sol-gel process. The difference in solubility parameters between solvent and polymer affected the pore structure during phase separation. The benzoxazine particles dispersed in liquid (sol) agglomerate together to form a continuous three-dimensional network extending throughout the liquid (gel). The resulting nanoporous polybenzoxazine, it provided high porosity and high surface area. Especially, it can provide electron pairs of nitrogen atom in the main chain which can form a stable coordination covalent bond with divalent metals. Therefore, nanoporous polybenzoxazine was used as an anti-fouling adsorbent for water treatment. FT-IR was used to confirm the synthesis of polybenzoxazine. The thermal properties such as degradation temperature, % weight loss and curing temperature were investigated by using TG/DTA and DSC, respectively. The adsorption experiments were studied by atomic adsorption spectroscopy (AAS) to investigate the percent of metals removal. A batch equilibrium technique was carried out under the influence of pH, contact time, amounts of adsorbent, including the effect of pore characteristics. In addition, the metal adsorption efficiency of nanoporous polybenzoxazine, carbon xerogels and commercial activated carbon were compared.

COLL 178

Fabrication of nanoporous carbon as electrodes for supercapacitors

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Supercapacitors (SCs) are widely used in portable(digital) electronic devices, uninterruptible power supplies, and industrial power due to their attractive properties such as long life cycle, high power density, high energy density and fast charge/discharge rate. SCs can be classified into two categories based on their energy storage mechanism which are the electrical double layer capacitors (EDLCs) and pseudocapacitors. Electrode material is a key element in determining the ability of energy storage for SCs which should have high specific surface area (SSA) with an appropriate pore structure and also good conductivity. Polybenzoxazine (PBZ), as an additionally cured phenolic resin, was chosen as an organic precursor to prepare a nanoporous carbon as an electrode material. It was found that when using 4,4'-methylenediamine (MDA), the surface area of the resulting nanoporous carbon was 494 m²/g with the total pore volume of 0.81 cm³/g and the average pore size of 6.6 nm meaning that MDA-based nanoporous carbon showed the pore size in a range of small mesopore. For the electrochemical measurement of MDA-based nanoporous carbon

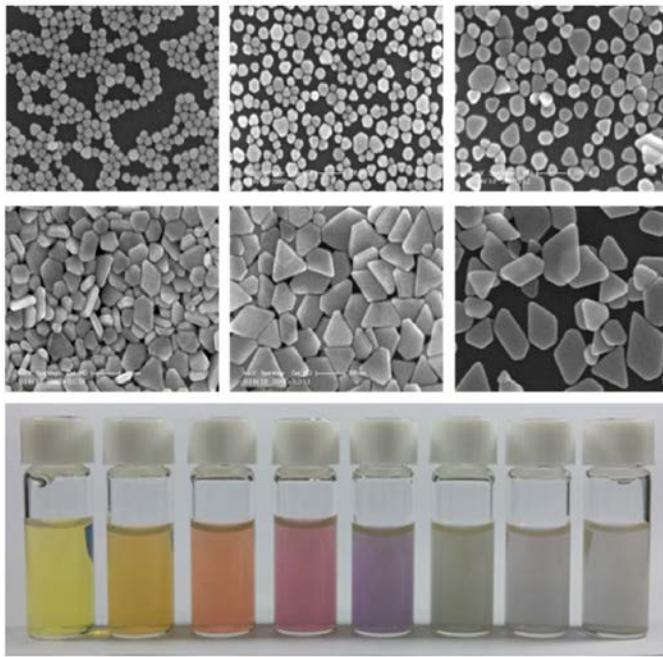
tested in 1.0 M of H₂SO₄ electrolyte showed the specific capacitance of 140.73 F/g at a scan rate of 1 mV/s. Moreover, the generation of meso-macroporosity and interconnected pore mainly depends on the phase separation mechanism of polymer and solvent in the sol-gel process. In this work, PBZ-based nanoporous carbon derived from ethylenediamine (EDA) was prepared via a sol-gel process using dimethylformamide (DMF) as a solvent. The effect of hexadecyltrimethylammonium bromide (CTAB) as a surfactant on its pore structure, aiming to increase the mesopore volume was studied. Then, the relationship between the specific capacitance and pore structure of the EDA-based nanoporous carbon was also investigated in 1.0 M of H₂SO₄ electrolyte to compare the results with MDA-based nanoporous carbon.

COLL 179

Silver nanoplate shape control: Use of halide ions to promote vertical growth

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The unique shape and crystalline structure of Ag nanoplates provide an interesting model system for investigating the roles of capping agents in controlling the evolution of the nanostructure shape during growth. This article describes a simple approach to the synthesis of Ag nanoplates with well-controlled shapes in which halide ions (including Cl⁻, Br⁻, and I⁻) guide the well-defined kinetically controlled synthetic route. The presence of the halide ions promoted vertical growth in the nanoplate structure, resulting in small thick nanoplates. The identity of the halide ion and the time, during the nanoplate growth process, at which the halide was added, could be adjusted to control the shapes of the Ag nanoplates by controlling the lateral and vertical dimensions of nanoplates. This shape control method permitted tuning of the localized surface plasmon resonance (LSPR) peaks of the Ag nanoplates over the visible and near-IR regions of the spectrum.



SEM images of the Ag nanoplate samples in the presence of halide ions, and a photograph of aqueous dispersions of the Ag nanoplates.

COLL 180

Luminescent solar concentrators using ZnTe/CdSe/CdS core/shell quantum dots

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A luminescent solar concentrator is a device that absorbs more light than a typical solar cell would, and then emits this light in a narrow range to a solar cell that is effective at this range. The goal is to allow this device to fluoresce in the infrared, where a more efficient solar cell can be used. Together the luminescent solar concentrator and solar cell could potentially lead to an overall better efficiency for the conversion of sunlight to electricity. Zinc telluride/ cadmium selenide/ cadmium sulfide core/shell quantum dots were synthesized in order to be embedded in the PMMA matrix to create a luminescent solar concentrator. The core/ shell quantum dots were synthesized via a method called hot injection. Absorbance and fluorescence were measured after the synthesis of each shell. Showing a final fluorescence peak at 900nm, the ZnTe/CdSe/CdS were successfully synthesized to fluoresce in the infrared. A luminescent solar concentrator prototype is currently being developed using these quantum dots.

COLL 181

Infusion of native oils to synthesize novel antimicrobial surfaces

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The challenge to maintain a sterile environment and protect patients in a clinical setting has grown in the recent years, due to the exposure of microorganisms. The discovery of the antimicrobial surfaces in previous research has shown a minimized growth in microorganisms such as bacteria, fungi, and viruses. Challenges still arise in creating surfaces because of the difficulty to industrialize, the non-uniformity throughout the surface, and the activity of the antimicrobial agent being washed off. Our work involves the utilization of agar to incorporate and fuse with plant essentials oils in varying concentrations. Agar is a polymer that is composed of subunits from the sugar, galactose. Agar surfaces are not degraded or eaten by bacteria and also serves as a firmer and stronger surface compared to other surfaces attempted in previous research such as Gelatin b. Agar as a gel is porous and can be used to measure microorganism motility and mobility. The gel's porosity is directly related to the concentration of agarose in the medium resulting in various levels of effective viscosity. The agar surfaces are infused with antimicrobial oils such as: Propolis, Neem Seed Oil, Black Elderberry, Yarrow, Tamanu, Rosehip, Ginger, Sage, Argan, Guava Seed, Myrrh, Frankincense, and Neroli. All surfaces have been tested against the gram positive bacteria strain *S. aureus*. Results have shown that majority of the essential oils utilized in research have efficient antimicrobial effects.

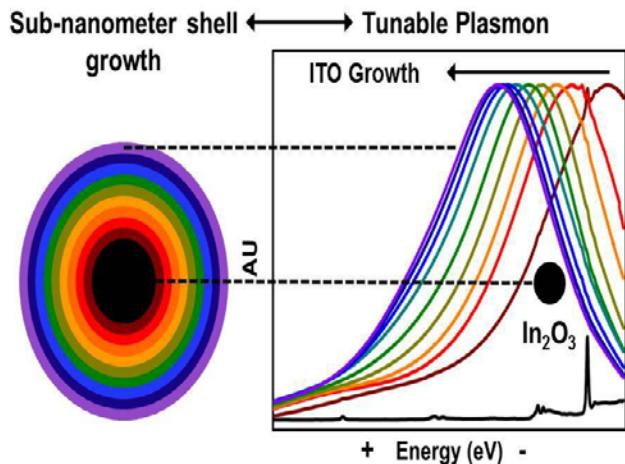
COLL 182

Tuning localized surface plasmon resonances in Sn-doped In₂O₃ through radial distribution of dopant atoms and core/shell architectures

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Doped metal oxide nanocrystals that exhibit tunable localized surface plasmon resonances (LSPRs) represent an intriguing class of nanomaterials that show promise for a variety of applications from spectroscopy to sensing. While previous synthetic methods for these materials have shown control over some nanocrystal plasmonic properties, fundamental questions remain regarding the effects of radial dopant position on the LSPR. Here, using tin-doped indium oxide (ITO) as a model system we show that a multi-stage, living growth synthesis allows angstrom-level control over nanocrystal growth and that we can use this approach to synthesize well-defined core/shell doped/undoped nanocrystals. From this level of synthetic control we illustrate that: 1) core/shell nanocrystal architectures can be tailored simply by adding precursor materials in the desired order, without core sample purification, 2) LSPR energies, dopant activations, as well as LSPR quality factors are highly dependent upon radial dopant distribution, 3) core/shell compositions beyond indium oxide can be used for the tuning of plasmonic properties. The experimental approach illustrated in this work highlights a new strategy in designing nanomaterials with tailored optical properties to

aid in new materials discovery, displays angstrom-level precision for the investigation of structure/property relationships on the nanoscale, and presents new opportunities for fundamental studies on LSPR excitations. This approach could be applied to a wide scope of inorganic nanomaterials, will enhance the understanding of dopant-induced properties of nanocrystals, and ultimately will open new avenues of nanocrystal design for the broader scientific community.



COLL 183

Pilot-plant study of using protein to reduce the lipophilic contaminants in paper mills

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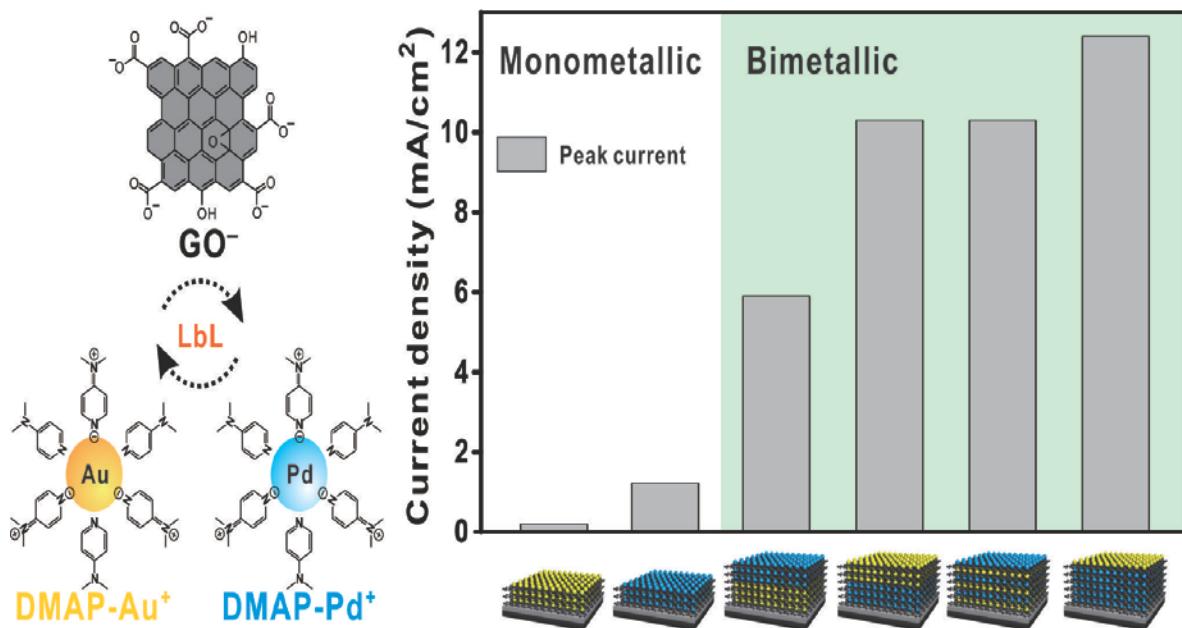
The presence of lipophilic contaminants such as waxes, binders, hot-melt and pressure sensitive adhesives (PSAs) in paper mills brings about many issues including weak internal strengths, poor quality as well as high production cost. Current study evaluates the application of soy protein that contains lipoxygenase enzymes as a cheap and environmentally-benign additive in the papermaking mill to tackle this problem. Thus, a series of trials were conducted on recycled pulps at pilot paper machine and the effect of soy protein on pulp contaminants was evaluated through fourier transform infrared spectroscopy (FTIR), optical analysis and deposit tendency test. The performance of the protein was mostly compared to talc as a common detackifier agent under the same experimental conditions such as temperature, pH, and chemical level. Obtained results confirmed the positive role of the protein in reducing the oil-loving contaminants in the produced sheets as well as enhancement of the corresponding mechanical strengths as a synergic effect. It was also revealed that such approach is quite cost-effective and can be considered as an alternative solution for the contaminants issue in the paper mills.

COLL 184

Unraveling the importance of controlled architecture in bimetallic multilayer electrode toward efficient electrocatalyst

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Even though traditional electrode fabrication methods such as simple mixing process have been used in various energy storage and conversion devices due to its handiness, these methods could not fully utilize and maximize the intrinsic properties of each active material. With the limited control over the internal structure of the electrode, it also often poses a significant challenge to elucidate the structure-property relationship between components within the electrode. Taking advantages of versatile layer-by-layer (LbL) assembly which can tailor nano-architecture of hybrid electrodes, here we report electrocatalytic thin films for methanol oxidation by adjusting the assembly sequence of LbL films composed of the Au and Pd nanoparticles (NPs) and graphene oxide (GO) nanosheets. In case of co-assembled bimetallic LbL structure of $(GO/Au/GO/Pd)_n$ where respective Au and Pd NPs are supported with GO nanosheets, the electrocatalytic activity is significantly higher than that of respective monometallic LbL electrode (i.e. $(GO/Au)_n$ and $(GO/Pd)_n$). To further investigate the architecture effect on the electrochemical behavior, Au and Pd NPs are assembled with GO in a different relative position of hybrid multilayer electrodes. It is proved that the electrocatalytic activity can be highly tunable by the position of metal NPs in the LbL structure, suggesting the structural dependence of charge and mass transfer between the electrolyte and the electrode, which is otherwise impossible to investigate in a simple conventional electrode fabrication method. Because of the highly tunable properties of LbL assembled electrodes coupled with electrocatalytic NPs, we anticipate that the general concept presented here will offer new insights in the nanoscale control over the architecture of the electrode toward development of novel electroactive catalysts.



Layer-by-layer (LbL) assembled multilayer electrodes and catalytic effect for methanol oxidation reaction

COLL 185

Rational design and fabrication of TiO_2 p-n homojunction for photoelectrochemical and photocatalytic water splitting

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Rational design and fabrication of junctions between semiconductors is an effective way to improve the photoelectrochemical and photocatalytic water splitting, and specifically, p-n homojunction is considered as a very promising structure. We fabricate TiO_2 p-n homojunction by decorating n-type oxygen-defected TiO_2 QDs on p-type titanium-defected TiO_2 surface. The composite structure and O/Ti-vacancies are testified by characterizations. The "V"-shaped Mott-Schottky plot and anodic shift of onset potential in I-V curves verify the characteristics of p-n homojunction. P-n homojunction is much more efficient in charge separation and transfer than p-type, n-type and n-n type-II homojunction, leading to the significantly high photoactivity. Compared with p- TiO_2 , p-n homojunction TiO_2 possesses 5-fold and 1.7-fold higher performances in photoelectrochemical and photocatalytic water splitting, respectively. This work provides new opportunities to design and fabricate highly efficient TiO_2 photocatalysts for water splitting.

COLL 186

Preparation of 2D porous Co₃O₄ nanofoils via graphene mimicking

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In this presentation, the efficacy of graphene mimicking for the preparation of a new type of 2D oxide nanofoils is introduced. 2D nanoscale oxides have attracted a large amount of research interest due to their unique properties. We report a straightforward synthetic approach to prepare 2D porous Co₃O₄ nanofoils using graphene oxide (GO) as a sacrificial template. By taking advantages of the catalytic ability of Co₃O₄ to degrade carbon backbones, as well as the thermal instability of graphene, porous 2D Co₃O₄ nanofoils consisting of Co₃O₄ nanocrystals (ranging about 10 to 20 nm in diameter) were successfully synthesized without the loss of the 2D nature of GO. Our 2D porous Co₃O₄ nanofoils as a lithium storage material exhibited a high reversible capacity of 1279.0 mAh g⁻¹ even after 50 cycles. This is vastly superior to the theoretical capacity of Co₃O₄ based on the conversion mechanism from Co₃O₄ to Li₂O and metallic Co. The extraordinary capacity of our 2D porous Co₃O₄ nanofoils may come from the peculiar 2D nanostructure and high pore volume, which promote a reversible electrochemical reaction. These reactions may include the conversion reaction between Co₃O₄ with lithium and the reversible formation of an organic SEI layer on the surface of the Co₃O₄ nanofoils.

COLL 187

Morphological control of colloidal aluminum nanocrystals

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Aluminum nanoparticles support plasmon resonances across the visible spectrum and into the UV regime, surpassing the traditional plasmonic metals which are intrinsically limited by interband transitions at short wavelengths. These high-energy plasmon resonances paired with the relative abundance and low cost make Al a superior replacement for the noble metals, such as Au and Ag, for plasmonic applications. To make use of these properties, the precise control of nanoparticle shape, size, and surface chemistry is necessary. However, unlike the synthesis of noble metal materials, Al nanoparticle synthesis is limited to completely inert reaction conditions. As a result, there is an increased challenge in the rational design of synthesis for size and shape control of Al nanoparticles compared to aqueous-phase nanoparticle growth systems. Here, we examine the effect of weakly coordinating solvents for the controlled growth of Al nanocrystals. We choose ethers, tertiary amines, and tertiary phosphines as three unique classes of solvents, each with a varying affinity for the growing nanocrystal surface. These solvents can play a dual role as either solvent or capping agent depending on their volumetric ratio during nanocrystal formation. We find that diamine

solvents alter the nucleation process, resulting in highly twinned nanostructures while ethereal solvents result in mainly single-crystal geometries. Conversely, phosphine solvents are weakly interacting with both the Al precursor and growing surfaces of Al nanocrystals, yielding quasi-spherical particles. Through the systematic combination of these three classes of growth directing solvents, we have observed new nanoparticle morphologies absent in the unmixed solvents. These results provide a foundation for the rational design of Al-based plasmonic applications.

COLL 188

Room-temperature formation of Cu-Ag bimetallic heterostructured nanocrystals via galvanic exchange

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Copper and silver are known to phase separate in bulk materials. Hence, bimetallic nanoparticles made of these metals offer a unique opportunity to synthetically control the stoichiometric composition and chemical ordering. There have been reports in the literature of the formation of either core-shell nanoparticles or bifacial heterodimers. However, due to the difficulties in performing elemental analysis on sub-10nm particles, no study presents a systematic treatment of how different morphologies can be accessed in a controlled manner. Here, we report a new room-temperature galvanic-exchange-based synthesis that allows access to the formation of several types of heterostructured Cu-Ag bimetallic nanoparticles, including both heterodimers and core-shell particles. Using STEM-EDS with highly-sensitive X-ray detectors, we are able to unambiguously identify the location of both metals with sub-nm precision. The role of post-synthetic oxidation has also been investigated with oxygen-free electron microscopy imaging.

COLL 189

Effect of ZnS on structural and optical properties of CulnS₂ quantum dots

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The CulnS₂-based quantum dots (QDs) have been showed to have various potential applications including photovoltaic devices, light emitting devices and biomedical imaging. Comparing to Cd-based QDs, which contain carcinogenic cadmium, CulnS₂ QDs could have a greater potential in biomedical applications. Another advantage of these QDs is that they show longer fluorescence lifetimes than both molecular probes and Cd-based QDs, which opens up their potential for fluorescence lifetime imaging

(FLIM) and time-gated imaging (TGI). However, since CuInS₂ QDs are not as well-studied as Cd-based QDs, it is not yet understood which factors are important to optimize these properties.

In this work, we show that upon adding ZnS to CuInS₂ QDs, the quantum yield increase up to 60% after 12 hours, the emission wavelength is blue-shifted and the particle sizes do not change. These results suggest that there is cation exchange reaction rather than forming a ZnS shell on top of CuInS₂ QDs.

High resolution TEM (HR-TEM) will be taken to calculate the lattice parameters of the nanocrystals. The energy dispersive X-ray (EDX) and inductively coupled plasma mass spectrometry (ICP-MS) will be used to determine the atomic composition of the QDs. These data can help us to understand the shelling mechanism, such as whether there is a cation exchange process or not. Also, X-ray photoelectron spectroscopy (XPS) will be used to investigate the composition on the surface of the QDs.

COLL 190

Combined ionic and hydrogen bonding in polymer multilayer thin film for high gas barrier and stretchiness

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A unique polyelectrolyte multilayer thin film, with a high gas barrier even after significant strain, was produced using a combination of ionic and hydrogen bonding. Layer-by-Layer (LbL) assembly was used to deposit branched polyethyleneimine (PEI), polyacrylic acid (PAA), polyethylene oxide (PEO), and PAA quadlayers. Altering the deposition pH of the various layers resulted in different physical and mechanical properties. PEI/PAA/PEO/PAA quadlayers assembled at pH 10/4/2.5/2.5 grow much thicker than the same film with all components at pH 3, which mainly results from in-and-out diffusion of the partially charged polyelectrolytes (PEI at pH 10 and PAA at pH 4). The change in pH during the film assembly induces a porous structure in the 10/4/2.5/2.5 film that results in poor gas barrier. Films deposited on 1 mm thick polyurethane rubber at pH 3 exhibit a densely packed structure with no pores. A 20 QL film (~ 1 μm thick) achieves an oxygen transmission rate 15 times lower than uncoated rubber due to the synergistic effect of the interdigitated layers of ionic and hydrogen bonding. When stretched 10 %, the barrier improves by a factor of 28 relative to uncoated polyurethane. This combination of stretchability and high gas barrier is unprecedented and offers the opportunity to produce much higher barrier elastomers.

COLL 191

Direct amination of HPHT ND surfaces for biodetection

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In the field of oncology, there is a need for enhanced cancer detection methods that can verify cancer at the single-cell level. High pressure, high temperature (HPHT) nanodiamonds with nitrogen vacancy centers (NVC) are an emerging fluorophore that can detect both electric and magnetic fields. NDs are attractive for biolabelling due to their electron spin properties, all-carbon matrix, and long-term photostability, but have not been fully utilized as an active sensor in biological systems. The surface chemistry of HPHT NDs, a current bottleneck in the fields' progress, plays a vital role in colloidal stability, bioconjugation and NVC photophysics. This project focuses on the modification of HPHT ND surfaces with amine chemistry through gas phase chemistry. Past investigations showed that oxidized HPHT NDs have an alcohol-rich surface similar to bulk diamond. Amination chemistry was carried out in a high temperature tube furnace with reactive gases and were characterized with NEXAFS, XPS, Raman spectroscopy, and FTIR. NEXAFS nitrogen K-edge spectra are suggestive of multiple kinds of C-N bond orders including amines, imines and nitriles. Our goal is to form a homogenous amine (-NH₂) terminated surface. Overall, the reactive amine groups provide a strong foundation for further chemistry, such as antibody/antigen conjugation, small molecular library screening and neuron membrane staining. We use small molecule conjugation for use in cancer cell screening assays as a demonstration of the efficacy of amine based chemistry on nanoscale diamond surfaces.

COLL 192

Assessment of color strength and pigment stabilization using microencapsulation of anthraquinone dyestuffs with epoxy resin

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Microencapsulation is popular technique which solid, liquid and gaseous ingredients are wrapped within another material for the purpose of shielding the active ingredient from the surrounding environment. The main purpose of this study is to obtain thermally stable dyestuff microcapsules for melt spinning applications. The thermosetting resin used in this experiment as the shell material, the main characteristics of the thermosetting irreversible reaction with epoxy resin. The post-curing will not be changed patterns by high temperature environmental impact. Avoid the core material affected by the ambient temperature to produce cracking or discoloration.

The properties of dyestuff microcapsules have been analyzed by scanning electron microscopy (SEM), Fourier transform infrared (FTIR), thermal gravimetric analyzer (TGA), differential scanning calorimeter (DSC), particle size, and microscope to determine the change in the structure of the dyestuff microcapsules, type, size and size

distribution of the microcapsules and the environment temperature. The microDYEs had high protection of the microcapsules surface smooth and stable, heat-resistant material.

COLL 193

Control of cesium lead halide perovskite nanocrystal morphology and photonic properties

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Inorganic CsPbX₃ perovskite nanocrystals have a range of photonic properties that make them appealing for applications in photovoltaics, light emitting diodes, lasers and quantum optics. Through ligand engineering and post synthetic treatments we have developed synthetic methodologies to control the nanocrystal form factor, size and resulting light emission properties including color, emissive quantum yield, and orientation of emitted photons.

COLL 194

Use of a simple and general approach to modify the surfaces of monodisperse metal oxide nanocrystals with a wide variety of silane coupling agents

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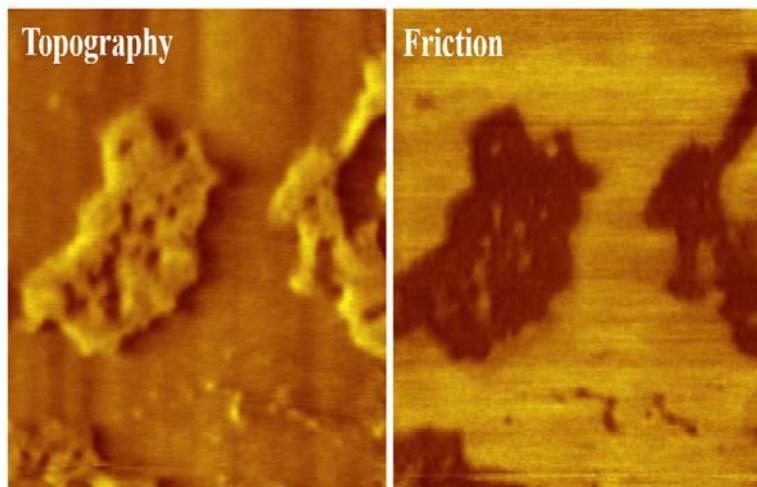
Precise control of nanocrystal (NC) surface chemistry is critical in developing NC-based applications. Traditional non-aqueous colloidal routes to synthesize semiconducting NCs often produces particles stabilized by long-chain hydrocarbons, which limits their functionality and solubility. One solution to this dilemma is the use of silane coupling reagents to modify the surface of the NCs post-synthesis. Here, using a widely-applicable “living” synthetic method to first synthesize oleate-stabilized oxide NCs, we demonstrate the use of a simple method to graft a wide variety of silane reagents onto the surface of the nanocrystal, replacing oleate ligands. For each reaction, we characterized the particles using transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS), thermogravimetric analysis (TGA), and X-ray photoelectron spectroscopy (XPS) to deduce the composition of the surface. Using this general approach, we are able to alter the solubility of the NCs, add specific functionality, and incorporate the particles into a polymer matrix, all without a change in the core size of the NCs.

COLL 195

Nano-tribological properties of single monolayers and mixed monolayers of octadecylcarboxylic acid and octacosanoic acid

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Single monolayers of octadecylcarboxylic acids (C18) and octacosanoic acids (C28) and mixed monolayers with ratios of 75%-25%, 50%-50%, and 25%-75% were formed spontaneously on the [0001] basal surface of α -aluminum oxide (single crystalline sapphire) using solution deposition methods. The binding nature and hydrophobicity of the monolayers were analyzed via diffuse reflectance infrared Fourier transform spectroscopy (DRIFT), and water contact angle measurements, respectively. Atomic force microscopy (AFM) was employed to investigate frictional properties of the monolayers in addition to acquisition of surface topography. DRIFT spectra confirmed the formation of highly ordered monolayers with mono/bidentate binding. Water contact angles indicated hydrophobic nature of single monolayers and mixed monolayers. The degree of hydrophobicity increased as the composition of C28 increased. Topographic and friction images demonstrated that the mixed monolayers form less frictional islands of C28 surrounded by the physically lower and highly frictional C18 layer.



A representative topographic image and a friction image of a mixed monolayer with ratio of C18:C28=25:75.

COLL 196

Synthesis and characterization of novel hydrogel beads for selective interactions with carbonaceous nanomaterials

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Recent innovations in the purification of single-walled carbon nanotubes (SWNTs) using commercially available hydrogel beads (Sephacryl S200) intended for size-selective protein purification has spurred interest in the quantitative description and optimization of this process. Areas of focus have primarily been on the nature of SWNT separation surfactant, system pH, and system temperature. Interestingly, an alternative route to process optimization lies in studying the nature of the separation medium (hydrogel bead) itself. This project aims to synthesize high-quality separation media tailored specifically for the isolation of preparative scale single-chirality aliquots of SWNT. Potential applications for achievement of this goal lie in the areas of nanoscale electronics, biological imaging schemes, and near-infrared active photovoltaics. Novel hydrogels produced demonstrate selective interaction with semiconducting SWNT.

COLL 197

Exploration of the growth mechanism of AgGaS₂ semiconductor nanoparticles

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In this work, we focus on characterizing the formation and growth of colloidal silver gallium sulfide (AGS) nanocrystals. AGS has the potential to be used as a replacement for cadmium sulfide due to its comparable band-gap of 2.65eV. Additionally, understanding its growth can help in clarifying the properties of other I-III-VI systems such as CIS, which exhibits similar optical properties. Using a high temperature, air-free synthesis, we have controllably grown monodisperse nanocrystals in a range of sizes. The reaction has been monitored at various stages throughout the growth in order to understand how the synthetic parameters affect the quality of the growing nanoparticles. In investigating the reaction, it was found that silver sulfide initially forms, and subsequently incorporates gallium and additional sulfur into the lattice, converting to AGS over time. Improved uniformity of both shape and size has been achieved through optimizing the surfactant system, allowing the nanocrystals to anneal at higher temperatures, and optimizing precursor concentrations. Particles have been characterized by transmission electron microscopy for shape, size, and distribution analysis, as well as optical absorption and emission spectroscopy for band gap behavior, and EDS for compositional analysis.

COLL 198

Tuning the optical properties of AgGaS₂ nanocrystals

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In this work, we demonstrate the ability of silver gallium sulfide (AGS) nanocrystals to emit over a wide range of wavelengths from blue-green to orange. Using a high temperature, air-free synthesis, we can controllably grow AGS nanocrystals with varying degrees of crystallinity. By growing the crystals with an intentionally poor crystal structure, internal defects are introduced into the lattice which lead to broad trap-state emission similar in width and wavelength to the characteristic emission observed in copper indium sulfide nanocrystals. By annealing at higher temperatures the expected chalcopyrite structure is improved, and the much shorter wavelength, band-gap emission is observed. Incorporation of zinc into the crystal structure has also been used to further tune the emission through both alloying and shelling. Particles have been characterized by TEM and XRD for shape and structural analysis, optical absorption and emission for band-gap and trap-state behavior, as well as ICP and EDS for compositional analysis.

COLL 199

Tunable whiteness coloration behavior on rutile TiO₂ ceramic pigment

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Titanium dioxide (TiO₂) is used as a white pigment for architecture, cosmetic, and paint because it efficiently scatters visible light, thereby imparting whiteness, brightness and opacity. This work describes a means of improving the whiteness and reflectivity of ceramic coated TiO₂ pigment. A great deal of effort has been devoted to improving efficiency of white pigments such as using chlorine method, modifying rutile TiO₂ and post-treatment with a TiCl₄ precursor. To retain and enhance the physical properties of white pigment, we adopted core-shell system with the silica (SiO₂), aluminum oxide (Al₂O₃) and zirconium dioxide (ZrO₂) as shell materials. Especially, various shell approaches have been developed for light harvesting in white pigments with introducing light-scattering materials and chalk resistance. Control of the shell thickness and whiteness of the TiO₂ pigment was important factor for high quality outdoor white pigments and their shell thickness was achieved by regulating the reaction time, concentration and shell materials.

COLL 200

Describing the mechanisms involved in Amot associated membrane binding and fusion

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Amot proteins have been shown to control cell proliferation and differentiation and can selectively bind with high affinity to phosphoinositol containing membranes. This binding event is linked to endocytosis, changes in cellular polarity, and apical membrane sequestration of nuclear transcription factors associated with development of cancer phenotypes. The Amot coiled-coil homology (ACCH) domain has the unique property to selectively bind monophosphorylated phosphatidylinositols (PI) in a similar manner as FYVE, PX and PH domains. Although the lipid selectivity and membrane binding of the protein has been well characterized, the mechanisms involved in the Amot coiled-coil homology domain (ACCH) binding and fusing these membranes are not yet known. The work presented will give insight into the stepwise process of membrane association followed by membrane fusion events by defining the residues that drive these events using fluorescence resonance energy transfer, lipid spots blotting, and protein spot blots. The results will then be extrapolated into a model to the mechanisms that drive the specific activities.

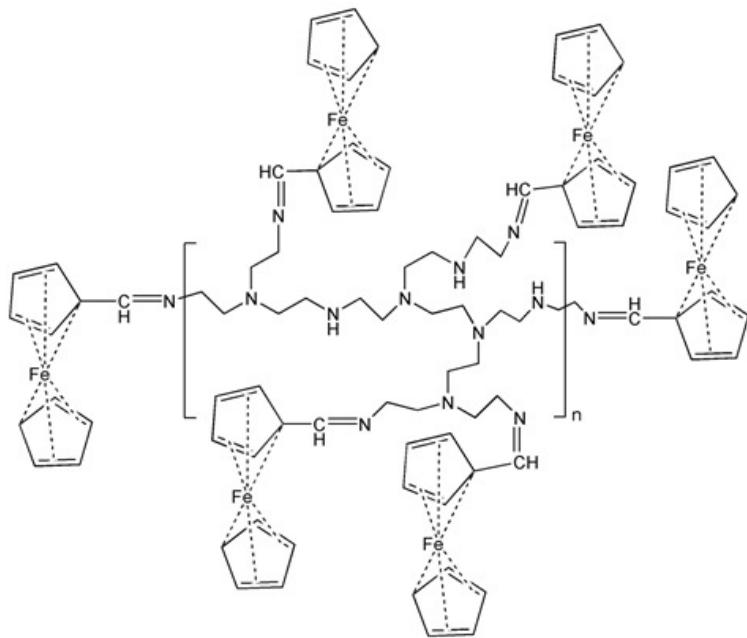
COLL 201

Ferrocene-modified PEI microgels

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Polyethyleneimine (PEI) microgels were synthesized and characterization according to the literature. Here, we report the Ferrocene modification of PEI microgels (Ferrocene-PEI) from the reaction of Ferrocenecarboxaldehyde with PEI microgels, and the scheme of the modification reaction is given in (Scheme 1).

The Ferrocene-PEI microgels were characterized via FT-IR, SEM, TG analysis, and the degree of modification of PEI microgels with Ferrocene was determined from the amounts of Fe ions via Atomic Absorption Spectroscopy (AAS). The Ferrocene-PEI microgels show diamagnetic moment predicted by magnetic susceptibility measurements with the Gouy method, and confirmed by FT-IR of modified microgel.



Scheme 1. The schematic presentation of Ferrocene modified PEI microgels.

COLL 202

Decrystallization of crystals using gold nano-bullets and the metal-assisted and microwave-accelerated decrystallization technique

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Gout is caused by the overproduction of uric acid and the inefficient metabolism of dietary purines in humans. Current treatments of gout, which include anti-inflammatory drugs, cyclooxygenase-2 inhibitors, and systemic glucocorticoids, have proven to produce harmful side-effects. Our research laboratory has recently introduced an innovative approach for the decrystallization of biological and chemical crystals using the Metal-Assisted and Microwave-Accelerated Evaporative Decrystallization (MAMAD) technique. The MAMAD technique utilizes microwave energy and gold nanoparticles. The microwaves is used to heat and activate the gold nanoparticles that reacts as “nano-bullets” and rapidly disrupt the crystal structure of biological crystals placed on planar surfaces. In this study, crystals of various sizes and compositions were studied as models for tophaceous gout at different stages (i.e., uric acid as small crystals (~10–100 µm) and L-alanine as medium (~300 µm) and large crystals (~4400 µm). Our results showed that the use of the MAMAD technique resulted in the reduction of the size and number of uric acid and L-alanine crystals up to >40% when exposed to intermittent microwave heating (up to 20 W power at 8 GHz) in the presence of 20 nm gold nanoparticles with exposure up to 120 seconds. This study demonstrates that the

MAMAD technique can be potentially used as an alternative therapeutic method for the treatment of gout by effective decrystallization of large crystals, similar in size to those that often occur in gout.

COLL 203

Tailoring the surface architecture of gold nanoparticles to engage nanoparticle-cell interactions

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With the immense growth of nanotechnologies for biomedical applications there is a significant interest in the scalable production of smart nanomaterials with intelligent surface design. While a variety of nanomaterials exists, and have been studied *in vivo* and *in vitro*, their physical parameters are not constrained in these studies making data interpretation about their biological transformations and interactions difficult to study at the chemistry-biology interface. Consequently, there is a gap in knowledge in our understanding how nanoparticle architectural design affects their biological transformations, motility, nanoparticle-biological interactions, endocytosis, exocytosis, and clearance mechanisms. Given the critical need to successfully transform nanomaterials into efficient drug delivery and imaging agents, well-defined nanomaterials with tightly-controlled size and shape whose NBIs are well understood are of significant interest. Here we will describe the design of hybrid lipid-membrane coated AuNPs of varying size and shape that are anchored with a long-chained hydrophobic thiol to control membrane rearrangement and instability. Changes in the localized surface plasmon resonance (LSPR), TEM, and DLS analysis will be employed to evaluate the dispersion characteristics and surface coverage of the suite of AuNPs. Since the ultimate goal is to relate how the nanoparticle design features and their physiochemical properties relate to nanoparticle-cell interactions, we will also discuss the features of lipid-coated AuNPs that lead to particle instability and that enable enhanced cellular uptake and localization within various cell lines. Collectively, we expect that the use of well-characterized AuNPs of constrained shape, size, and surface architecture should allow us to tease apart specific nanoparticle features that drive NBI and mechanisms of endocytosis and exocytosis so that we can harness this knowledge to redirect their behavior to overcome their translational barriers.

COLL 204

One step and one pot fabrication of gold nanoparticles with ethambutol

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Ethambutol, an antituberculosis drug, was fabricated with gold nanoparticles *via* a one-step and one-pot process. The precursor salt, hydrochloroauric acid trihydrate, was

reduced to gold nanoparticles by ethambutol. The resulting pink-colored colloidal solution showed a distinct surface plasmon resonance band at 529 nm, which indicated the successful formation of gold nanoparticles. Thermogravimetric analysis showed that the prepared product composed of 30.5% organic components and 69.5% gold nanoparticles. The face-centered cubic structure of gold nanoparticles was verified by high-resolution X-ray diffraction analysis. Mostly spherical-shaped gold nanoparticles with a mean diameter of 45.95 ± 7.21 nm were observed in high-resolution transmission electron microscopy images. Hydroxyl and amine functional groups of ethambutol were major contributors to the reduction of gold salt to gold nanoparticles confirmed by Fourier transform infrared spectroscopy. The colloidal solution of gold nanoparticles was stable up to 28 days in cell culture medium with retaining the λ_{\max} of the surface plasmon resonance band and their hydrodynamic size. Therefore, this simple and straightforward synthetic strategy has the potential to be an efficient fabrication method for ethambutol delivery using gold nanoparticles.

COLL 205

Gold nanocatalysts synthesized using *Bupleurum falcatum* extract and their catalytic performance in 4-nitrophenol reduction reaction

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Gold nanoparticles were synthesized using *Bupleurum falcatum* extract and their catalytic performance was assessed in 4-nitrophenol reduction reaction. The extract played a role as a reducing agent to reduce gold salt to gold nanoparticles which is an entirely green (or eco-friendly) strategy. Five different concentrations of the extract (0.01% ~ 0.05%) were utilized to produce spherical gold nanoparticles. The colloidal solution had a purple color with the average size ranging in 10.4 ± 2.3 nm ~ 17.7 ± 4.5 nm. The size of the gold nanoparticles increased with the decrease of extract concentration. The surface plasmon resonance band was observed at 542 nm. High resolution X-ray diffraction patterns verified the face-centered cubic structure of crystalline gold nanoparticles. The maximum catalytic activity in 4-nitrophenol reduction reaction was observed when the lowest concentration of the extract (0.01%) was used for the synthesis. These results demonstrated that plant extract is a valuable natural source for the production of gold nanocatalysts.

COLL 206

Green synthesis and catalytic activity of gold and silver nanoparticles prepared using gallic acid

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Two types of metallic nanoparticles, gold and silver nanoparticles, were synthesized using gallic acid as a reducing agent for the comparison of catalytic activity in 4-nitrophenol reduction reaction. During synthesis, no other chemicals were utilized except gallic acid. Gallic acid is abundant in plants, such as red wine, white wine, spinach, oak bark, grape and green tea. Its biological activities include antibacterial, anti-inflammatory, antioxidant, antiviral, anticancer and anti-obesity activities. The synthetic progress was monitored by UV-visible spectrophotometry. The surface plasmon resonance bands of gold and silver nanoparticles were observed at 536 and 392 nm, respectively. FT-IR spectra demonstrated that the carboxylic acid groups of gallic acid contributed to the reduction of metal salts to metallic nanoparticles. High-resolution transmission electron microscopy (HR-TEM) and atomic force microscopy images revealed that both nanoparticles were spherical-shaped. The average particle size of gold nanoparticles was determined to be 44.4 nm in HR-TEM images and 54.4 nm by dynamic light scattering in aqueous medium. The average size of silver nanoparticles was smaller than that of gold nanoparticles: 14.1 nm in HR-TEM images and 33.7 nm by dynamic light scattering in aqueous medium. High resolution X-ray diffraction analyses verified a face-centered cubic structure of the synthesized metallic nanoparticles. Silver nanoparticles showed a higher rate constant than gold nanoparticles in the 4-nitrophenol reduction reaction. Reverse-phase high-performance liquid chromatography was employed to obtain the conversion yield of 4-nitrophenol to 4-aminophenol. Silver nanoparticles exhibited an excellent conversion yield in the range of 96.7-99.9 %.

COLL 207

Laponite bioactive nanocomposites for orthopedic applications

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Successful treatment of segmental bone defects depends on the ability of a surgical implant to integrate with bone tissue through osseointegration. Osseointegration is facilitated by osteoblasts, which are the cells responsible for bone growth and fracture healing. Osteoblasts secrete hydroxyapatite (HAP), the inorganic component of bone, which provides bone with high compressive strength crucial for skeletal support. Traditionally, hydroxyapatite coatings have been applied to implants to promote osseocompatibility about the bone-implant interface. We are currently exploring alternatives to these coatings including clay/bionanocomposite materials that can bridge the metallic implant and bone surfaces to promote osteoblast proliferation, bone matrix development, and osseointegration. Laponite based clay nanoparticles offer advantages over HAP owing to their hierarchical structures and inclusion chemistry which afford lamellar ordering, drug inclusion, and localized drug delivery. Bionanocomposite films were fabricated on 3D printed titanium alloy substrates using facile colloidal dispersion and deposition techniques including drop casting from aqueous solution and electrodeposition. Clay/polymer heterointerfaces, surface nanomorphology, and composition were studied using atomic force microscopy and scanning electron

microscopy coupled with energy dispersive spectroscopy. These studies shed light on the use of Laponite as an inexpensive alternative to HAP for the development of tunable bioactive bone-implant interfaces for orthopedic implants.

COLL 208

Viscoelastic behavior of alkyl ether sulfate systems containing nano-sized colloidal silica

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Surfactant systems incorporating rod-like or wormlike micelles are widely utilized in both industrial and consumer products. While the viscoelastic behavior of such systems provides desired aesthetic and end-use properties, there is often a need to further modify the rheological properties of such systems for certain applications. These wormlike micelle (WLM) systems behave much like polymer systems. Furthermore, incorporation of nano-sized particles can interact with the large polymer-like WLM structures to alter rheological behavior. While there are number of studies that have focused on the effect of particles on rheological behavior in cationic surfactant systems, fewer studies have been done on systems containing anionic surfactants. In this study, relaxation behaviors in systems containing sodium alkyl ether sulfate and sodium carbonate were studied. The anionic surfactant was commercial grade material with an average chain length of twelve carbons and one ethoxy (EO) group. WLM behavior was achieved through the addition of sodium carbonate. Ludox® TMA, a nano-sized colloidal silica, was employed at different concentrations in the WLM systems.

Temperature was varied between 5 and 45°C. Relation was characterized in terms of the Maxwell model, but was only found to adequately describe data below the threshold of $\omega t \sim 1$. The Maxwell model failed to describe behavior at higher frequencies. A modified expression with an additional relaxation mode adequately described relaxation throughout the frequency range studied. It was also found that zero-shear viscosities generally increased with an increase in silica concentration, and relaxation times decreased. The decrease in relaxation time is in contrast to results from some studies, but is in agreement with others. Preliminary results of measurements of relaxation due to a compressive stress via ultrasonic attenuation measurements in the surfactant/particle systems are also discussed.

COLL 209

Probing the catalytic properties of Ni-based bimetallic phosphides for deep hydrodesulfurization

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Global demand for transportation fuels continues to rise while environmental standards for sulfur impurities in fuels have become more stringent. Upgrading crude oil feed stocks via deep hydrodesulfurization (HDS) is necessary to meet the ultra-low sulfur standards for transportation fuels. Transition metal phosphides (e.g. Ni₂P, Ru₂P) represent a new class of hydrotreating catalysts that show promise for improved HDS properties relative to conventional molybdenum sulfide based catalysts. Incorporating a second metal into Ni₂P can be used to tailor the catalytic properties (activity, selectivity) for improved hydrotreating performance. Bimetallic phosphide catalysts having the formulas Ni_xRu_{2-x}P/SiO₂ (M = Ru, Rh) were synthesized over a range of compositions. Metal hypophosphite precursors prepared via incipient wetness were reduced via temperature programmed reduction (TPR). The resulting catalysts were characterized using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and CO chemisorption. The XRD patterns showed single phase materials having average crystallite sizes of 5-10 nm. CO chemisorption measurements showed an increase in active site density for the higher nickel content catalysts (e.g. Ni_{1.75}Ru_{0.25}P/SiO₂). HDS measurements were carried out using a model feed of 1000 ppm 4,6-dimethyldibenzothiophene (4,6-DMDBT) in decalin over a range of temperatures (533-653 K). A substantial increase in HDS activity was observed for the bimetallic phosphides having high nickel contents. For the Ni_xRh_{2-x}P/SiO₂ series, the product selectivity was observed to change with metal composition; for Rh-rich phases ($x < 0.25$), the hydrogenation product (3,3'-dimethylbicyclohexane) was favored while for Ni-rich compositions ($x > 0.25$) the partially hydrogenated product (3,3'-dimethylcyclohexylbenzene) dominated. The HDS results for the TPR-prepared Ni_xRu_{2-x}P/SiO₂ catalysts will be compared with those for mesoporous silica encapsulated nanoparticles Ni_xRu_{2-x}P(@mSiO₂) of similar composition and size.

COLL 210

Dabrafenib drug release system based on gold nanoparticle carriers for treatment of melanoma cancer

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The BRAF gene in humans encodes the protein B-Raf, or serine/threonine-protein kinase B-Raf, an important signaling protein in cellular growth. Mutations in this gene are associated with human cancers including melanoma. Melanoma claims approximately 9000 lives per year in the US alone and the current treatment options include surgery, chemotherapy, and radiation. Dabrafenib is a drug used to inhibit B-Raf proteins and has shown promising inhibition of cancer cell growth with a specific B-RafV600 mutation. The goal of our study is to develop a controlled release delivery system for dabrafenib avoiding its devastating side effects and damage to healthy tissues. In this work, we have utilized gold nanoparticles as the carriers for dabrafenib delivery. The gold nanoparticles were functionalized with mercaptobenzoic acid (MBA) and bound dabrafenib via an amide bond formation. This bond is stable at physiological pH but cleaves at low pH. The surface-enhanced Raman spectra indicate that at a pH of

5.5, the MBA signals increase in intensity over time while no change in MBA signal was observed at physiological pH of 7.4. This increase of MBA signal is due to the amide bond breaking and drug release, resulting in the MBA exposure. The proposed new dabrafenib drug release system based on gold nanoparticle carriers can be used as a controlled release delivery system for dabrafenib for targeted use on melanoma and other cancers with the B-RafV600 mutation.

COLL 211

Controlled release of lenvatinib from multi-functional nanoparticles monitored by surface-enhanced Raman scattering

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Thyroid cancer occurrence frequency has been on the rise in recent years. Throughout the past decade diagnoses have been increasing at a rate of approximately 5% per year with the number of related deaths increasing at 0.9 % per year. Typically, this form of cancer yields optimistic prognoses with 20 year survival rates of 90 %. However, there are instances in which the cancer is particularly aggressive resulting in 10 year survival of as low as 15%. The conventional approach for treatment is surgical removal of the tumor. Lenvatinib, 4-[3-Chloro-4-(cyclopropylcarbamoylamino)phenoxy]-7-methoxy-quinoline-6-carboxamide, offers a chemotherapeutic treatment for thyroid cancer. Lenvatinib acts as an inhibitor to tyrosine kinase, which is crucial to proper metabolism functionality. Though it does provide an alternate mode of treatment, it is in no way limited to only damaging cancer tissue. This damage to healthy tissue coupled with the plethora of other adverse effects ranging from nausea to hyper tension, yields hefty consequence to treatment. Through the use of gold nanoparticles, a targeted drug delivery system has been developed. The drug has been immobilized via amide bond formation to the gold through a linker molecule. Targeting ligands, folic acid and transferrin, have been attached to gold nanocarriers as well. The amide bond is stable under normal physiological conditions of pH 7.4 but breaks, releasing the drug, under the low pH conditions of cancer tissue, which is typically around pH 5.5. The multifunctionalized nanoparticles recognize the cancer tissue by attaching to overexpressed transferrin and folate receptors, which can then mediate endocytosis of the loaded nanoparticle.

COLL 212

Growth of SiO₂ shells on fluorescent nanodiamond cores for biodetection

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Early detection and improved cancer sensing tools are crucial for increasing cancer patient survival rates. High-pressure high-temperature (HPHT) fluorescent nanodiamonds (FNDs) are an emerging probe for biolabeling and cancer detection due to the unique photophysics of the nitrogen vacancy center (NVCs). FNDs are ideal biolabelling probes because they are non-cytotoxic, contain no heavy metals, are an IR emitter (575-800 nm) and have long term photostability. Current surface chemistry protocols of HPHT FNDs are not mature and robust modification of FNDs poses a challenge due to their chemical inertness. Here we accomplish the synthetic growth of SiO₂ shells (3-25 nm) onto FNDs using wet chemistry. Silica growth is controlled by fixed reaction times and particle size is measured using DLS, SEM and TEM. Silica priming of the diamond surface is thought to proceed by nucleophilic attack of tetrahydroxysilane forming a silyl ether bond (C-O-Si-OH₃) to the diamond surface. Surface functionalization is probed via FTIR and synchrotron based X-ray techniques (NEXAFS and XPS). Grafting of PEG moieties onto the silica shell stabilizes the FNDs colloidally in biological environments while amine and sulfhydryl moieties act as anchors for bioconjugation. Bioconjugation to a small molecule library was performed and confirmed via DLS, gel electrophoresis and optical microscopy. Biolabelling of HeLa cells with functionalized FNDs was performed to confirm biospecificity and long term imaging.

COLL 213

Room temperature monolayer ZnS growth on CdS and CdSe cores

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Quantum dot Light Emitting Diodes (LEDs) utilize semiconducting nanocrystals that possess properties that vary from their bulk materials making for a more cost effective and tunable fluorescence color emission. Due to these characteristics the goal was to maximize the fluorescence efficiency of quantum dots that could be incorporated in LED devices. Using an insulating layer to minimize surface imperfections should increase the fluorescence of the resulting crystals. Previous methods to achieve insulating shells including Zinc Sulfide (ZnS) always required use of the hot injection method. A shell of ZnS was grown on Cadmium Sulfide (CdS) and Cadmium Selenide (CdSe) quantum dot cores utilizing the room temperature colloidal atomic layer deposition (c-ALD) method. This ZnS layer possessed a wider band gap for insulation. The resulting core shell quantum dots showed significantly increased fluoresce in comparison with the cores and thus made for a better material to be incorporated into quantum dot LED prototype devices.

COLL 214

Ligand influence on the branching of gold nanocages

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Plasmonic gold nanoparticles (AuNPs) have been extensively studied in the past decades due to their unique properties and possible applications. AuNPs exhibit localized surface plasmon resonance (LSPR) and show strong optical resonances for visible and near-infrared wavelengths. The intensity and position of the plasmon resonance heavily depends on the size and shape of the plasmonic structure and the surrounding medium. Non-spherical AuNPs, such as gold nanocages and multibranched nanoparticles exhibit unique and precisely tunable plasmonic properties. In this context, anisotropic AuNPs generally show plasmon resonance in the near-infrared (NIR) region in which soft biological tissues are highly transparent which enables deep penetration of NIR-irradiation for biomedical applications. Also, anisotropic particles exhibit efficient heating when they are irradiated at their maximum wavelength, which is already extensively used for cancer-related photothermal therapy. In this work, we used monodisperse gold nanocages, with polyvinylpyrrolidone (PVP) as surface ligand (AuNC@PVP), synthesized by galvanic replacement using silver nanocubes as scaffolds. In a second step, we exchanged the surface ligand with thiolated PEG of different chain lengths (0.2, 0.6, 1, and 5 kDa), to obtain PEGylated AuNC. These already NIR absorbing structures were used as seeds for Au/Ag branch growth. The formation of multiple branches and anisotropy enhancement showed to increase the NIR plasmon related properties. In these study, we determined the role of the ligand in the growth of the AuNCs branches to afford control in the size, number, and position of the branches, as well as the plasmonic absorption. Also, we screened the photothermal conversion upon laser irradiation in the NIR regime in comparison with AuNC and to compare the photothermal properties between the structures achieved with different ligands.

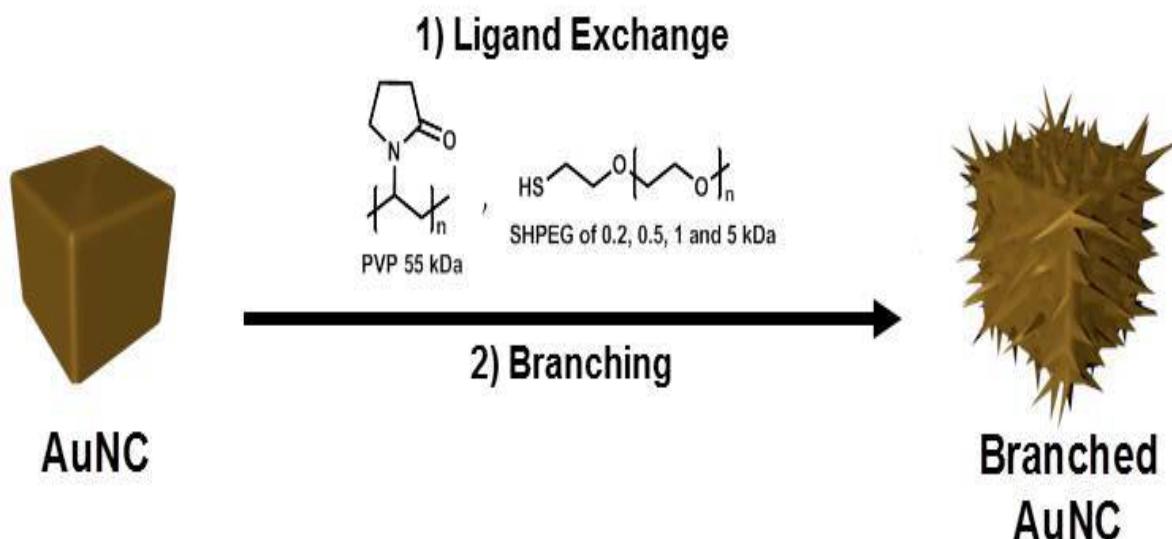


Figure. Schematic representation of branched gold nanocages synthesis

COLL 215

Proposing a two-molecule multiplexed neuromorphic system: The first step towards a chemically based artificial brain

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Information acquisition, processing, and storage involving brain neurons consists of electrical *and* chemical components. While functionally organized micro- and nanostructures have been developed to model electrical aspects of brain neurotransmission, the complexities of chemical transmission cannot be investigated using these structures as yet. Examples of the fabrication of artificial synapses in neuromorphic systems based purely on electronic synapses exploit mechanisms such as fingering *via* oxide or sulfide reduction. Despite some promising results, these approaches completely overlook the highly multiplexed and heterogeneous chemical networks of neurotransmitter molecules that are fundamental to complex brain function.

We propose a synthetic multi-molecule neuromorphic system, initially employing two native neurotransmitters and related molecules. Our approach is based on state-of-the-art aptamer-based field-effect transistor sensors that have been optimized for responding to specific neurotransmitters. These sensors are placed on the same substrate and are able to work simultaneously and in an interconnected manner with one another, *i.e.*, the concentration of one analyte influences the concentration of the other, consequently altering the responses of the corresponding sensor. This biomolecular analog-to-digital transducer represents a basic working principle behind chemical transmission and information processing in synapses, opening new avenues for the study of brain chemistry, molecular networks, and for introducing native biological strategies to enrich the potential capabilities of neuromorphic computing.

COLL 216

Synthesis of MoS₂/Fe₃O₄ nanocomposites with peroxidase-like activity for applications in H₂O₂ and glucose detection

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We demonstrate synthesis of Fe₃O₄ nanoparticles exfoliated MoS₂ nanosheets that show peroxidase-like activity via catalyzing oxidation of the peroxidase substrate 3,3,5,5-tetramethylbenzidine (TMB) in the presence of H₂O₂. Kinetic analysis shows that the catalytic behavior follows typical Michaelis–Menten kinetics and the reaction rate in MoS₂/Fe₃O₄ nanocomposite sheets is significantly higher than either MoS₂ nanosheets or Fe₃O₄ nanoparticles. Based on the peroxidase-like activity, a highly sensitive colorimetric method for H₂O₂ and glucose detection is developed. Due to their simple preparation and robust nature and low limit of detections, MoS₂/Fe₃O₄ nanocomposites show great potential towards the development of affordable, portable, and point-of-care diagnostics.

COLL 217

Hydrothermal formation of various metal oxides using oxalic acid as a capping agent

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Unique geometries and methods of synthesizing metal oxides can provide added benefits to the areas of catalysis and electro-optical devices. In this study, a single-pot hydrothermal method of producing various metal oxides were explored using oxalic acid as a capping agent along with metal oxide precursors. The impact of reaction temperature, duration, pH, oxalic acid concentration, and precursor concentration were explored. Using SEM, XRD, and BET, data illustrates the impact variables have on metal oxide geometry (rod, sheet, sphere, etc.) and crystalline morphology (XRD results) both pre- and post- high temperature annealing.

COLL 218

Production and characterization of activated carbon containing polyvinyl alcohol microcapsules

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Microcapsules containing super activated carbon (SAC) were prepared using the spray drying method. JMP statistical analyses and design of experiment software was used to reduce the number of formulations needed for this research's experimental design, where sixteen formulations were created. These formulations contain different amounts of polyvinyl alcohol, SAC, and water. The resulting microcapsules were characterized using the spray-dried microcapsules' yields, Scanning Electron Microscopy (SEM), Infrared (IR) spectroscopy, Transmission Electron Microscopy (TEM), Brunauer–Emmett–Teller (BET) instrument, and a Cahn balance. SEM was used to examine the morphologies (shapes), sizes, and clustering patterns of the microcapsules. It was found that the uniformity on the basis of size and shape varied among the different formulations using the same spray drying conditions. The microcapsules varied in size between approximately 1 to 50 µm in diameter. Their shapes were found to be either perfectly spherical, or non-spherical solids having one or more indented and/or jagged edges. The degree of clustering also varied among the formulations. Infrared (IR) spectroscopy was used to verify the presence of functional groups –CH (~3000 cm⁻¹) and –OH (~3300 cm⁻¹) in the polyvinyl alcohol microcapsule wall. Transmission Electron Microscopy (TEM) was used to measure the microcapsules' wall thicknesses. BET was used to measure the SAC's specific surface area before and after they were encapsulated for all formulations, and the Cahn balance was used to measure the adsorptive capacity of SAC both before and after they are encapsulated. Eventual application of these SAC microcapsules will be in development of hazardous chemical barrier materials, where they will be loaded into a microporous membrane, and their polyvinyl alcohol shell wall will be dissolved and extracted, leaving behind the resulting activated carbon containing membrane.

COLL 219

Single step dipping method of fabricating $\text{Fe}_3\text{O}_4/\text{PVDF-HFP}$ composite porous material for magnetically controllable oil-water separation

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Recently, oil-spilling in the sea is a worldwide environmental problem and thus effective oil collection technique is highly required. One of the major strategies is using hydrophobic and oleophilic porous materials to absorb oil while it repels water. Here, techniques to remote-control the materials contacting with oil/water mixture are required so to apply for collecting oil even in hazardous area. One approach is embedding magnetic particles into oil absorbents, which enables the absorbents remotely contact with oil driven by magnetic force. There are few reports of magnetic oil absorbents and most of them achieved by multi-step processes or using hazardous materials, which inhibits their practical use.

In this study, we introduce a single step dipping method to give magnetic and hydrophobic/oleophilic properties to melamine foam sponge structure. The absorbent was fabricated by dipping into the mixture of Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) as a hydrophobic polymer and synthesized Fe_3O_4 nanoparticles as magnetic particles dissolved in tetrahydrofuran(THF). The coated material showed hydrophobicity and oleophilicity whereas it maintained intrinsic softness and light weight (Figure 1). Thanks to the presence of Fe_3O_4 , the material performed magnetic controllability on water guided by a magnet as shown in Figure 2. Such simple method of designing smart wetting system can be helpful for development of material engineering.

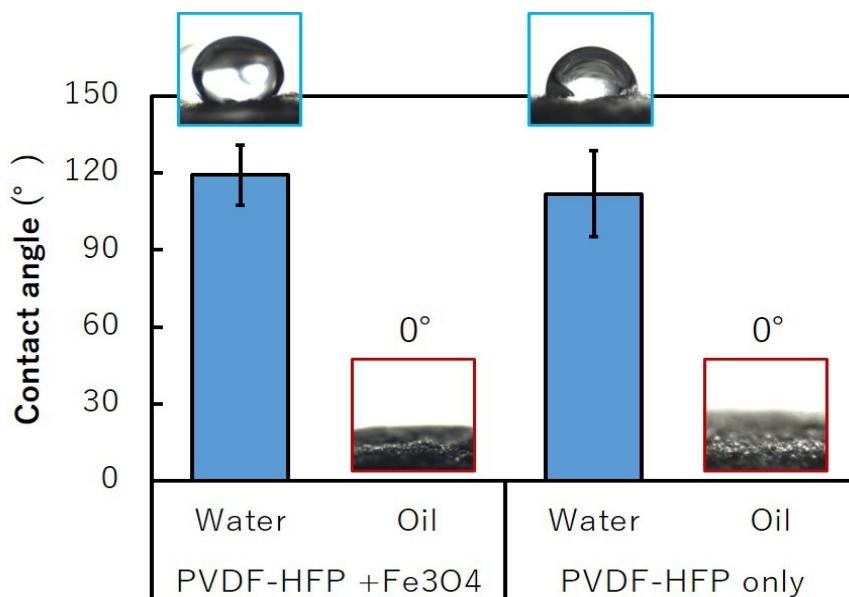


Figure 1. Water and oleic acid contact angles on $\text{Fe}_3\text{O}_4/\text{PVDF-HFP}$ composite or PVDF-HFP coating. Inserted images show appearances of each droplets on the surface.

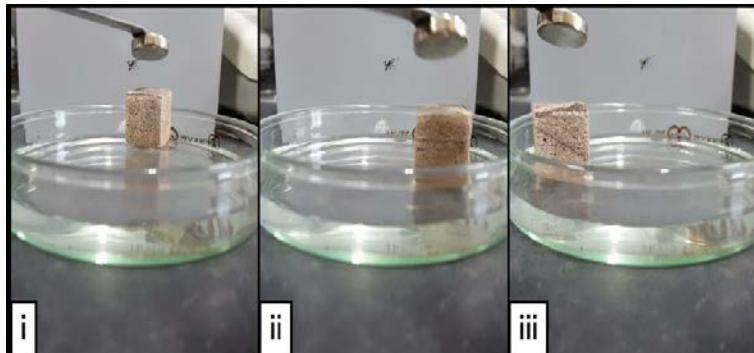


Figure 2. Time-elapsed photo images of magnet navigation of the oil absorbent floating on water.

COLL 220

Synthesis and characterization of metallic nanoparticles using dendrimer-templating technology

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The objective of this research project is to synthesize multi-metal nanoparticles using the dendrimer-template method to fight against microbes. We will focus on synthesizing multi-metal nanoparticles with an appropriate matrix that can help increase the efficacy against microbes.

Researchers discovered the development of such nanoparticles require the knowledge of the physiochemical properties of the nanoparticle and biological aspect of the microbe. The physiochemical and biological capabilities will be modified to ensure the aim of efficacy against microbes is achieved. With this in mind, we hope to attack microbes that other nanoparticles cannot annihilate by increasing the efficiency using multi-metal nanoparticles. Previous research from Curry et al. shows that when “increasing the concentration of the dendrimer-encapsulated Ni(0) nanoparticles in the presence of *Escherichia coli* (*E.Coli*) lead to an increase in the amount of antimicrobial activity observed”. Furthermore, this study was observed on *Bacillus Subtilis* (*B. Subtilis*) resulting in the inactivity of nickel nanoparticles due to the different outer structure composition of the bacterial walls; *B. Subtilis*, a gram negative bacteria has one extra lipopolysaccharide layer when compared to gram positive bacteria such as *E. Coli*. However, upon reducing the size of Ni particles formed compared to the bacteria, the antimicrobial activity increased. Moreover, their research was unable to indicate whether the antimicrobial activity exhibiting the inhibition of bacteria growth occurred

within cell membrane or outer layer disrupting cell walls. Thus is in this study, we aim to determine whether the inhibition of cell growth is occurring within the cell membrane, out layer disrupting, or unidentified location in the bacteria, and address whether the size of the nanoparticles play a role in its inhibition.

COLL 221

Synthesis and surface properties of poly(methyl methacrylate-butyl acrylate)/polythiourethane core-shell nanoparticles by new click reaction with soap-free emulsion polymerization

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Poly(Methyl methacrylate-Butyl acrylate) (MMA-BA)/Polythiourethane [PMBA-PTU] core-shell nanoparticles were synthesized by "New Click Reaction" based on a prepared poly(MMA-BA) copolymer nanoparticle using soap-free emulsion polymerization. "New Click Reaction" is defined as reaction between 1,1,2,2-perfluorodecanethiol (PFDT) and trimethylsilyl isocyanate (TMI), in which PFDT and TMI are subsequently catalyzed by triethylamine (TEA) to produce a polythiourethane network, forming core-shell nanoparticles. To demonstrate that trimethylsilyl groups of TMI can be used as surface coating agents, several were reacted with cellulose. From field-emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM), the resulting core-shell nanoparticles are in good spherical shape and their shell is consisted of a compact PTU layer with water-oil repellent property. Finally, the roughness of PMBA-PTU films were analyzed by atomic force microscopy (AFM). In accordance to the thickness of PMBA-PTU films, the roughness of this films was found to vary.

COLL 222

High density immobilization of oligonucleotides on semiconductor and gold nanoparticles within seconds

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DNA-coated nanoparticles (NPs) have been used in numerous applications such as for biosensing and drug delivery. A number of challenges are confronted in the preparation of NP conjugates. One such challenge derives from surface charge, as nanoparticles are often stabilized with a coating of negatively charged ligands. Therefore, an electrostatic repulsion is present when attempting to conjugate oligonucleotides. The

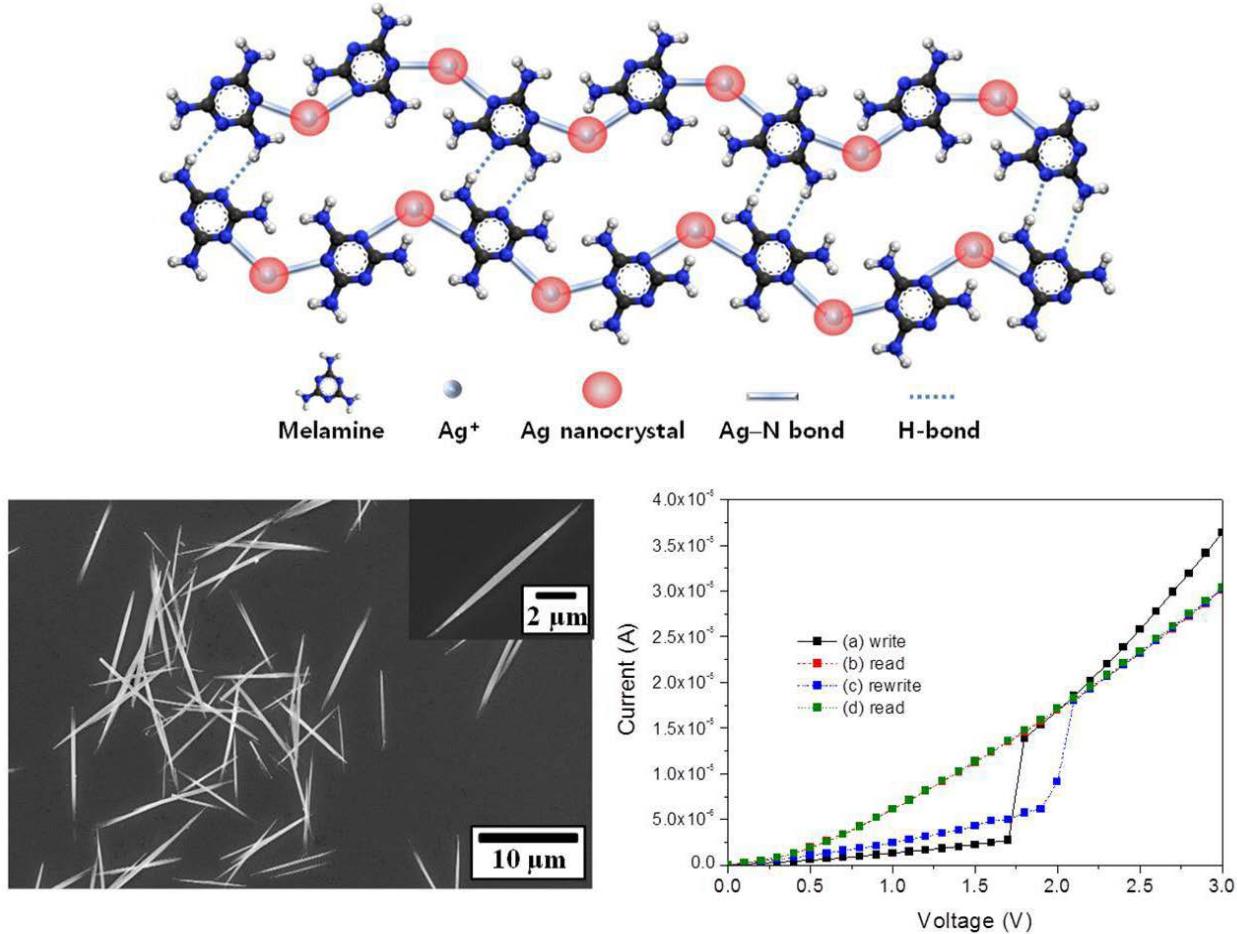
result is that the conjugation process can be a slow process, sometimes taking 1-2 days to achieve the highest surface density. The effect is compounded by electrostatic repulsion between neighboring oligonucleotide strands on the NP surfaces, which tends to lower the surface density. Herein, we report a novel method that enables conjugation of oligonucleotides with surface densities up to the theoretical limit in less than 1 min. Negatively charged NPs are first loaded onto the surface of positively charged magnetic beads (MBs) to create MB-NP conjugates. When added to a suspension of MB-NP conjugates, oligonucleotides are electrostatically adsorbed onto the MB surfaces. This creates a high oligonucleotide concentration in the vicinity of the nanoparticles, and pushes the conjugation reaction forward. A combination of fast electrostatic attraction and oligonucleotide preconcentration at the MB interface enables oligonucleotide conjugation with the highest surface density that is physically possible to be achieved within seconds.

COLL 223

In situ synthesis of Ag nanocrystal-embedded metal-organic framework microneedles showing electrical bistability properties

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Ag nanocrystal-embedded metal-organic frameworks (MOF) microneedles were synthesized *in situ* by introducing melamine into a polyol process, and were shown to display electrical bistability. The one-dimensional morphology of the structures could be explained by the formation of bonds between AgNO₃ and melamine, leading to the formation of N-Ag(I)-N chains, and the formation of melamine-melamine hydrogen bonds between these chains. The polyol 1-5 pentanediol, which was adopted as the reaction medium, enabled the continuous formation of Ag nanocrystals in the reaction mixtures, and the formed Ag nanocrystals were embedded inside of the MOF microneedles. When we checked the electrical properties of these Ag nanocrystal-embedded MOF microneedles, they showed electrical bistability reproducibly, so that it was possible to demonstrate the write state, read state, and rewrite state. Although these microneedles did not display sufficiently high level of performance to readily apply them to memory devices, they should, after further intensive studies, find use in memory devices, sensors, photocatalysts and so on.



Schematic illustration of the formation of the MOF microneedles, SEM image of the Ag nanocrystal-embedded Ag(I)-melamine product, and current–voltage (I–V) curves for revealing the electrical bistability properties

COLL 224

One-step synthesis of silver nanoplates with high aspect ratios: Using coordination of silver ions to enhance lateral growth

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The single-step production of Ag nanoplates with high aspect ratios is of great significance for their applications to the bendable or stretchable electrodes, but the development of a facile synthetic method remains a great challenge. In this paper, a coordination-based strategy was successfully employed to produce, in a single step, Ag nanoplates with high aspect ratios. Optimal Ag nanoplates were synthesized in the presence of acetonitrile, which served both as the co-solvent and as the ligand to form complexes with the Ag^+ ions. Coordination effect of the Ag^+ ions by acetonitrile apparently decreased the rate of the reduction of these ions, leading to a decrease in

the number of seeds formed in the nucleation step. Decreasing the number of seeds in this way, while keeping the concentration of the Ag precursor constant, resulted in the formation of larger Ag nanoplates. This new synthetic method specifically enabled the formation of Ag nanoplates with lateral dimensions exceeding 1 μm and with thickness values of approximately 30 nm. These Ag nanoplates were found to show electrical percolation in a short sintering time and high electrical conductivity when they were directly used as metal inks to produce conductive patterns for printed electronics.



A schematic illustration of the reaction pathways that led to the formation of Ag nanoplates with high aspect ratios.

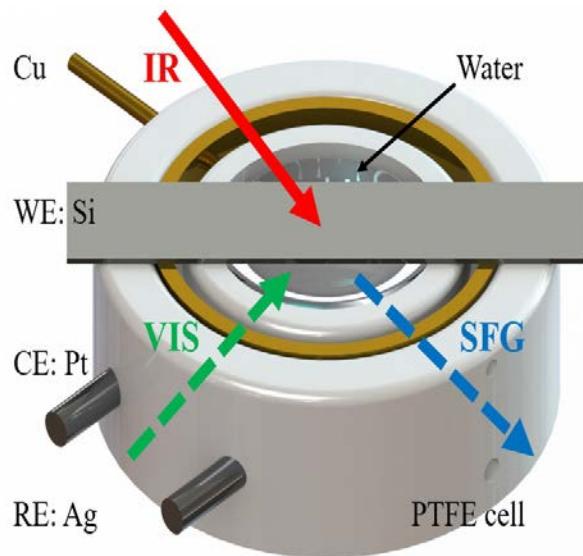
COLL 225

Sum-frequency vibrational spectroscopy of electrified water interfaces

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The behavior of water molecules under a DC electric field plays a key role in many important phenomena of fundamental science and applications, such as electrolysis, water dissociation, catalysis, and protein folding, etc. However, the molecular-level information of such systems is yet to be elucidated due to the lack of appropriate *in situ* probing. Here we use sum-frequency vibrational spectroscopy (SFVS) to investigate the interfacial water spectra under the DC electric field supplied by a silicon electrode. In previous studies, the electric field was often generated at the interface via surface charging, and tuned by modifying the pH value and/or ion concentration of the solution. In our case, the DC field is tuned independently from the composition of the bulk

solution and terminal groups of the surface, which facilitates the extraction of the DC electric field effect on interfacial water molecules. Meanwhile, the native SiO₂ layer prevents the electrolysis or other reactions at the interface. By tuning the bias voltage on Si electrode, we find the net orientation of interfacial water molecules to change, as well as the overall hydrogen bonding strength through the interaction with the SiO₂ substrate.



PTFE cell configuration. The silicon wafer is placed on the top as the work electrode (WE). An Ag wire and a Pt wire are used as the reference electrode (RE) and the counter electrode (CE), respectively. The Sum frequency (SF) beam is generated from the silicon/water interface, excited by an infrared (IR) beam and a visible (VIS) beam.

COLL 226

Microplotted semiconductor channels for organic thin film transistors

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Directional solidification of a film can improve crystallinity and carrier mobility in semiconducting films. Solution processes for the use of the organic semiconductor, 2,7-diethylbenzo[b]benzo [4,5-thieno[2,3-d] thiophene (C8-BTBT), in organic thin film transistors were examined. Notably, a Sonoplot GIX Microplotter was employed for direct-write printing of C8-BTBT semiconducting films. Although the microplotting procedure is not fully optimized it proves to be a superior fabrication method to spin-coating. Hole mobilities in microplotted films around an order of magnitude higher than spin-coated films were recorded.

COLL 227

Systematic examination of bimetallic architecture in Pt-Pd nanocatalysts

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Bimetallic nanoparticles of Pt and Pd often show higher activity for formic acid electrooxidation (FAEO) when compared to their monometallic counterparts. The mechanism behind this improvement is still debated as many factors can influence the surface-adsorbate interactions at a metal surface and include particle size, shape, composition, and architecture (e.g., hollow or core@shell). Here, size- and shape-controlled core@shell nanoparticles are studied as catalysts for FAEO in order to systematically examine the contribution of lattice strain on catalyst performance. Specifically, {100}-terminated Pd@Pt, Pt@Pd, Pd, and Pt nanocubes were synthesized and their electronic and catalytic properties were compared. The nanocube shape was selected as both Pd(100) and Pt(100) show the highest activity for FAEO when compared to other low index Pd and Pt surfaces, respectively. The Pd@Pt and Pt@Pd architectures were prepared by seeded methods and selected to compare systems where the shell metal is compressed *versus* in tension. This difference arises due to the lattice mismatch between the core and shell metals. The monometallic counterparts, Pd and Pt, serve as references to these strained systems, with all samples being characterized by advanced electron microscopy, electrochemical methods, and X-ray photoelectron spectroscopy. Through this research, nanoparticle architecture is shown to be an effective lever to systematically control surface strain in bimetallic systems. As FAEO is a model for other organic fuel systems, this study should more broadly accelerate catalyst design.

COLL 228

Reporting rotational dynamics of intracellular cargos with Janus particles

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Intracellular cargo transport underlies a multitude of essential cellular functions. Various human diseases such as amyotrophic lateral sclerosis (ALS) and Alzheimer's disease are characterized by dysfunctional cargo transport. This highlights the significance of understanding regulatory mechanism of cargo transport. The translational movement of cargos has been the focus in the past effort to interpret the cargo transport and the functions of motor proteins. In contrast, the rotation of cargos has been poorly understood, even though the tug-of-war between motor proteins is predicted theoretically to cause rotation of cargos. Our limited knowledge about the cargo rotation

is due to the lack of method to directly measure cargo rotation in living cells. In this presentation I will demonstrate our recent progress to address this critical need. We designed novel optically anisotropic particles as rotational probes. With them, we are able to track the translation and rotation of cargos in living cells with high spatial and temporal resolutions. Our results demonstrate that the cargo rotation is not only a simple act from the tug-of-war of motor proteins, but is also influenced by the intracellular environment.

COLL 229

Smart colorimetric patches based on plasmonic nanoparticle-decorated thermoresponsive microgels

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The colorimetric sensors with high optical response are of great interests in various industrial and medical applications owing to unique advantages such as direct detection of stimuli without external power source and real-time visualization of stimuli. Here, we present a thermo-responsive smart colorimetric patch based on the plasmonic gold nanoparticles (AuNPs)-decorated poly(isopropylacrylamide) (PNIPAM) microgels. For the practical application to flexible colorimetric patch, the AuNPs-decorated PNIPAM microgels were deposited on the polydimethylsiloxane (PDMS) substrate. The structural color of our colorimetric patch changes according to the temperature condition due to the temperature-controlled dimensional change of PNIPAM microgels, leading to the change in distances between plasmonic AuNPs. Compared to bulk gel structure, the microgel structure has a much larger change of surface area due to the thermo-responsive three-dimensional volume change, which enables a significantly increased colorimetric response. The colorimetric patch with optimized size of AuNPs and crosslinker density of PNIPAM microgels showed a large shift in plasmonic absorption peak from ~530 nm to ~650 nm wavelength due to the thermo-responsive plasmon resonance change from individual to coupled AuNPs. As a proof-of-demonstration, we applied AuNPs-decorated PNIPAM microgels as a pressure-induced erasable pad, which can be utilized as an erasable security marker.

COLL 230

Antibacterial layer-by-layer coating of nanoparticles

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Bacteria-mediated diseases are global healthcare concern due to the accelerated emergence and spread of drug resistant bacterial strains. Cationic compounds are

considered membrane active biocidal agents having a great potential to control bacterial infections while limiting the emergence of drug resistance. Herein, the versatility and simplicity of the Layer-by-Layer (LbL) technique was used to functionalize poly (methyl vinyl ether-co-maleic anhydride) nanoparticles with a highly antibacterial aminocellulose conjugate in a multilayer fashion. The assembly of cationic bearing aminocellulose with negatively charged hyaluronic acid on the particles surface was confirmed by the alternations of their surface charge and size after each deposition step. Stable polyelectrolyte-decorated particles with an average size of 600 nm and zeta potential of ± 40 mV were developed after five LbL assembly cycles. The antibacterial properties of these particles against *S. aureus* were significantly improved when the polycationic aminocellulose was applied as a top layer. The large number of amino groups available on the particles surface allows for the interaction with intrinsically anionic bacterial cell wall leading to irreparable membrane damage and complete eradication of *S. aureus* after 24 h treatment, while the hyaluronic acid improve their biocompatibility. This specific mechanism of action is believed to diminish the possibility for selection of new resistant strains and is a great promise in controlling bacterial contamination.

COLL 231

Optical properties and controllable chiro-optical handedness of symmetric and asymmetric dimer nanocrescents

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Asymmetric dimer nanocrescents fabricated using copper mask nanosphere template lithography elicit giant circular dichroism (CD) responses. Chiro-optical activity, commonly used to distinguish between molecular chiral enantiomers, illustrates light-matter interactions that depend dramatically on plasmonic structural characteristics. Dimer nanocrescents exhibit enhanced chiro-optical activity and switches in CD handedness relative to tilt. Detailed analysis also shows these structures exhibit orientation dependent handedness and additional control in handedness is observed relative to sample rotation. In aluminum nanocrescents, the structural features of dimers are evaluated to understand gap dependency in the connecting crescent tip region and the role of this gap in CD activity. Optical activity is compared using symmetric and asymmetric plasmonic dimer nanocrescents (i.e., nominally achiral and chiral nanostructures) and their potential application in probing chemical systems is discussed.

Asymmetric dimer nanocrescent



COLL 232

Peelable temporary coatings by waterborne self-crosslinkable urethane dispersions

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We synthesized waterborne self-crosslinkable urethane dispersions for non-toxic peelable temporary coatings. Poly(caprolactone diol) and isophorone diisocyanate(IPDI) were used for polyurethane(PU) prepolymer and sulfonic acid-containing diol was also added as a water-soluble diol. Amine terminated silane coupling agent was used to produce silane-terminated PU prepolymers that can be self-crosslinked after drying. We characterized particle sizes of self-crosslinkable urethane dispersions as a function of sulfonated diol content and measured film formation rate by changing the ratio of silanol groups to PU prepolymer. Coating films were prepared by drying at room temperature and their peel strengths were measured and modified with additives such as glycerol and poly(ethylene glycol) for simple removal by peeling or stripping. Film strengths were also controlled by the hard segment concentration in PU polymer, which depends on the relative amount of IPDI to poly(caprolactone diol).

COLL 233

Identification of Gram-positive bacterial cell wall components responsible for interactions with cationic nanoparticles

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As nanoparticle use in industrial applications and consumer goods continues to increase, the need grows to understand the potential impacts of these particles on

organisms in the environment. To understand the interaction between nanoparticles and bacterial cell surfaces at a molecular level, we used cell-wall mutants of the model Gram-positive bacterium *Bacillus subtilis* to test the hypothesis that particular cell surface components govern these interactions. The three strains employed differed in the composition of their wall teichoic acid chains (WTA), prominent negatively charged surface structures. Minimal differences were measured between the toxicities experienced by these mutants upon exposure to cationic-functionalized gold nanoparticles (MPNH₂-AuNPs). However, fluorescence assisted cell sorting showed that the mutant with only d-alanine moieties on the WTAs experienced interaction with MPNH₂-AuNPs to the largest extent, demonstrating the crucial role WTA construction plays in dictating interactions with cationic nanoparticles. Analysis of the surface potentials of the three strains demonstrated that the mutant with only d-alanine moieties on the WTAs had the most anionic character, suggesting that the effect of WTA structures on the bacterial-nanoparticle interaction is primarily mediated through electrostatics.

COLL 234

Impact of natural organic matter on the interaction of functionalized diamond nanoparticles with model bacterium *S. oneidensis* MR-1

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Natural Organic Matter (NOM) has shown to influence nanoparticle interactions with organisms. Studies with model supported lipid bilayer with lipopolysaccharides has demonstrated that at higher NOM concentrations, the interactions of lipid bilayers with poly(allylamine hydrochloride) functionalized nanodiamond (PAH-ND) decreased. The purpose of this work is to examine the modified interactions by NOM at a whole cell level, using a model gram-negative bacterium, *Shewanella oneidensis* MR-1. To test this hypothesis, bacterial viability was first assessed by colony counting and growth-based viability assays. *BacLight* Live-Dead assay was also utilized to investigate bacterial membrane damage. Together with ND Zeta potential results at varying NOM concentrations, we observed that a decrease in both toxicity and membrane damage by PAH-ND to *S. oneidensis* occurred at a similar NOM level where a charge reversal of the ND was observed.

COLL 235

Adsorption and decomposition of a chemical warfare agent simulant on copper and molybdenum oxides

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Filtration systems for absorption and decomposition of chemical warfare agents (CWAs) are the first line of defense against exposure to these toxic compounds. Composite materials (such as ASZM-TEDA) commonly used in filtration systems consist of high-surface-area carbon supports impregnated with various metal oxides, including CuO_x and MoO_x. Despite decades of work to develop highly effective and versatile filtration materials, little is known about the mechanisms of CWA degradation by material surfaces and filter deactivation/poisoning, in part due to the challenges involved with spectroscopic characterization of filtration material surfaces under operating conditions. Enabling the rational design of more advanced filtration and decomposition materials for broad-spectrum protection against CWAs and other toxic industrial compounds requires a sophisticated understanding of the chemical mechanisms behind CWA sorption and degradation on the molecular scale.

We will present the APXPS study of adsorption and decomposition of dimethyl methylphosphonate (DMMP), a CWA simulant, on polycrystalline oxide surfaces of copper and molybdenum. APXPS enables examination of these surfaces and adsorbed species upon exposure to DMMP and other common atmospheric gases, such as water vapor. We find that DMMP adsorbs mostly intact on MoO_x surfaces, and our results suggest that undercoordinated metal atoms and/or surface hydroxyl groups are the adsorption sites. Multiple decomposition products are observed on CuO_x surfaces, and the oxidation state of the metal appears to influence the decomposition pathway. Complementary density functional theory (DFT) studies corroborate our experimental findings and are used to propose likely decomposition pathways.

COLL 236

Degrafting of poly(poly(ethylene glycol) methacrylate) brushes from planar and spherical silicon substrates

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Densely grafted, hydrophilic polymer brushes produced via surface-initiated controlled radical polymerization have been shown to undergo degrafting upon exposure to aqueous media. This degrafting process has been proposed to involve swelling-induced, mechanochemically facilitated hydrolysis of bonds located at the brush-

substrate interface. While a number of studies have described degrafting of hydrophilic polymer brushes, only little is known about the key structural parameters of these thin films that dictate this process. Using a series of PPEGMA and PPEGMEMA brushes produced by surface-initiated atom transfer radical polymerization (SI-ATRP) we investigate the influence of three parameters; (i) the chemical structure of the ATRP initiator; (ii) the molecular weight of the surface grafted polymer chains and (iii) surface curvature. Studies performed with PPEGMA and PPEGMEMA brushes grown from substrates modified with different ATRP initiators indicated that hydrolysis of both siloxane as well as ester/amide bonds contributes to degrafting. For the PPEGMA and PPEGMEMA brushes investigated in this study, degrafting was observed to be less pronounced with increasing molecular weight of the polymer tethers, which was attributed to the inverse molecular weight dependence of the swelling properties of these brushes. Finally, experiments with PPEGMEMA modified silica nanoparticles revealed the influence of surface curvature and suggested that degrafting is more pronounced as surface curvature decreases.

COLL 237

Encapsulation of responsive liquids in coaxial nanofibers via electrospinning

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The behavior of responsive fluids, such as liquid crystals and shear thickening fluids, has been predicted to be significantly enhanced by confinement. Coaxial electrospinning is a facile and relatively simple method to create polymeric nanofibers with core-shell morphology, in which the core can be composed of responsive liquids. The polymeric sheath provides confinement to the responsive liquid in nano-sized cavities, the diameters of which were controlled through tuning electrospinning parameters. Furthermore, the effect of polymer-liquid interface was explored by systematic modulation of the polymer composition across a range of polar, non-polar, and functionalized surfaces. Initial progress towards uniform and aligned fibers characterized by optical microscopy, SEM, TEM, XRD, and initial dynamic testing is presented. The properties of coaxial fibers were compared to bulk properties to identify the roles of confinement and polymer interactions in efforts to develop a theoretical model.

COLL 238

Efficient photocatalytic activity of SnO₂-deposited ZnS nanobelts

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SnO_2/ZnS nanocomposites of SnO_2 quantum dots (QDs)-deposited ZnS nanobelts having highly enhanced photocatalytic activity and photostability have been fabricated via a facile two-step hydrazine-assisted hydrothermal process without involving any surface treatments. The photocatalytic activity of SnO_2/ZnS nanocomposites with a Sn-to-Zn molar ratio ($R_{\text{Sn/Zn}}$) of 0.1 is 3 times higher than that of pristine ZnS nanobelts and 17 times higher than that of commercial ZnS . The incorporation of SnO_2 QDs increases the photocatalytic efficiency of ZnS nanobelts due to the following reasons: photogenerated charge carriers are readily separated owing to type II band configuration and direct contact at interfaces without having any linker molecules; active surface sites are increased to adsorb more dye molecules; the light absorption range is extended to the visible region, generating more charge carriers on the surfaces of heterojunction structures. The decay time, as well as the intensity, of the band-edge emission of SnO_2/ZnS nanocomposites at 325 nm decreases progressively and rapidly with the increase of $R_{\text{Sn/Zn}}$, indicating that fast electron transfer takes place from photoexcited ZnS nanobelts to SnO_2 QDs. Thus, the higher photocatalytic degradation efficiencies of SnO_2/ZnS nanocomposites are considered to result mainly from the increased separation rates of photogenerated charges. The photostability of SnO_2/ZnS nanocomposites is also improved due to the protection and charge-separation effects of decorating SnO_2 QDs.

COLL 239

Carbon nanomaterials for biomedical applications as antioxidants and drug delivery vehicles

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Carbon nanomaterials are a useful platform for applications in medical research, and have been applied as drug delivery vehicles, biosensors, imaging agents, tissue scaffolds, and therapeutics. This work covers the use of highly oxidized carbon nanomaterials called PEG-HCCs (PEGylated hydrophilic carbon clusters) and PEG-GQDs (PEGylated graphene quantum dots) as drug delivery vehicles and as antioxidants. PEG-HCCs and PEG-GQDs catalytically convert superoxide to oxygen and hydrogen peroxide at a rate faster than most single-active-site enzymes, and they also quench hydroxyl radicals, making them very potent antioxidants. PEG-HCCs have been shown to carry out therapeutic functions that have been unattainable from enzymes or traditional small molecule antioxidant treatments; they have been studied *in vitro* and *in vivo* and were successfully applied to treat models of traumatic brain injury, stroke, cancer, rheumatoid arthritis, and multiple sclerosis. This work covers the synthesis, characterization, and antioxidant mechanisms of PEG-HCCs and PEG-GQDs as well as their recent use to treat autoimmune diseases in rats, to treat traumatic brain

injury and stroke in rats, and to act as drug delivery vehicles to image cancer cells and treat a glioblastoma model in mice. In addition to the applications of these nanomaterials, this work also explores the antioxidant mechanism of PEG-HCCs and PEG-GQDs using small molecule analogs that mimic their activity. Through extensive electrochemical and physical characterization and preliminary *in vitro* and *in vivo* work, we are working to elucidate the exact interactions of these materials with superoxide and other reactive oxygen species. This work will cover the synthesis, characterization, and testing of novel small molecule antioxidants and implications to the antioxidant activity and biomedical applications of our nanomaterials.

COLL 240

Magnetically induced heat generation in magnetic nanoparticles for environmental remediation

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Organic dyes are often released into the wastewater as byproducts of manufacturing of various products including textiles, paper and pharmaceuticals. These dyes have long half lives and breakdown into products that are toxic, mutagenic or carcinogenic. As a result, a viable technology is needed to selectively scavenge these species and remove them from water sources. Magnetic nanoparticles, e.g. Fe₂O₃, are efficient sorbent materials for environmental remediation processes. In this research, organic dyes were adsorbed onto magnetic nanoparticles and then remotely desorbed using an alternating magnetic field. When exposed to an alternating magnetic field, magnetic nanoparticles absorb the energy and release it as heat in a highly localized, controlled and non-contact manner. The magnetic functionality and ability to remotely control and activate desorption allows for the easy recovery and recyclability of the sorbent. The effect of nanoparticle functionality, composition and shape on magnetic induced heating was also investigated and will be described in detail.

COLL 241

Fabrication of Si nanopillar array for ultralow reflectivity

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The reduction of surface reflectivity is an important approach to improve the performance of optical and optoelectronic devices. Herein, we greatly suppressed the reflectivity of silicon surface by silicon nanopillar arrays, which were fabricated by metal-assisted chemical etching. In the fabrication process, polystyrene spheres were self-assembled into a monolayer on a Si substrate, and subjected to reactive ion

etching(RIE) process to reduce their size. The size of the spheres was controlled by tuning the RIE duration. Then the treated monolayer of polystyrene spheres was used as shadow mask for creating a metal nanohole template, which was used for the fabrication of silicon nanopillar array based on metal-assisted chemical etching. The average reflectivity of silicon surface was suppressed to lower than 0.1% from 45% at the wavelength range of 250-1050 nm, and it remained below 1.2% when the incident angle changed from 0° to 70°. We investigated the effect of the height and diameter of the nanopillars on the reflectivity, which revealed that the reflectivity decreased with increasing the height of nanopillars, and the reflectivity peaks blue shifted along with reducing the nanopillar diameter. The results indicate that the antireflection performance can be tuned by adjusting the height and diameter of nanopillars. Therefore, this method may be applied for reducing and tuning the reflection of Si surface.

COLL 242

Nucleobase and nucleotide coordinated Au(I/III) nanoparticles for anticancer therapeutics

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Stable Au (III) and Au (I) complexes, including cyclometallated gold complex, are promising candidates for anticancer drugs that exhibit potent in vitro and in vivo antitumor activities against human carcinoma xenografts tumors. Herein, a supramolecular synthesis route was presented for hierarchical self-assembly of coordinated adenine-Au (III) complexes into colloidal nanoparticles. During the polymerization process, the addition of adenosine triphosphate (ATP) and thiolated poly(ethylene glycol) was found to greatly improve the particle size control as well as the colloidal stability to against demetallation in physiological conditions. The coordinated Au-nanoparticles comprise 8% of ATP and most of molecules were deposited on the surface. However, the as-prepared colloidal Au-nanoparticles could be easily decomposed in high glutathione (GSH) levels, leading to a fast release inside living tumor cells. When incubated with cancer cells, the coordinated Au-nanoparticles displayed a significant in vitro antitumor effect with low IC₅₀ value (~42 uM). Apoptosis analysis also confirmed that the nanoparticulate formulation promoted a higher cell dead rate of cancer cells than Au ions with the same dose. The relation of intracellular GSH concentration to Au-nanoparticles was found by pretreatment of GSH inhibitor. Photosensitizer were furthermore incorporated into the supramolecular assemblies and an increased Au-based therapeutic efficacy for prostate cancers treatment was successfully achieved. Overall, these nanoparticulate Au-bearing complexes represent an attractive alternative to overcome the failure of cisplatin resistance in traditional chemotherapy.

COLL 243

Identification of promising electrografting precursors for the modification of electrode surfaces

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Modification of an electrode through the application of a film or coating to its surface can be effected using electrografting. This electrochemical technique can be used to imbue the surface with certain properties or to immobilize moieties, such as catalysts or biomolecules. Precursor molecules are electrochemically oxidized or reduced to produce radicals that can then form bonds to the electrode surface. Our research aims to identify promising electrografting precursors and study the surfaces that are derived from them. The precursor molecules and electrografting methods used to prepare modified electrode surfaces will be presented, as well as characterization of the surfaces using electrochemistry, vibrational spectroscopy, and microscopy.

COLL 244

Synthesis and characterization of ceramic-coated α -FeOOH yellow pigments

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We studied on the synthesis and characterization of the yellow color ceramic pigment. Iron based pigment can be controlled the coloration through the oxidation or cation exchange method in the red, yellow, black pigments. The colors of pigments can be controlled by adjusting certain experimental parameters. Especially, color of nano size pigments were tuned by controlling of their size and morphology. For example, the particle size can affect colors such as a vivid red color of nano-sized hematite particles. We design and synthesize α -FeOOH nanorods was controlled by the reaction conditions. Also, high quality yellow coloration was obtained after silica coating. Details of the coloration and phase structure of α -FeOOH were characterized by UV-vis, CIE Lab color parameter measurements, SEM (scanning electron microscopy) and XRD (powder X-ray diffraction).

COLL 245

Zwitterionic polymers for chronic wound management

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Zwitterionic polymers (ZP) recently emerged as biomaterials with excellent bio- and haemo-compatibility. The protein adsorption on their surfaces is lower even compared to the golden standard in the field – poly(ethylene glycol). Moreover, ZP are known to swell more in salt solutions than in pure water, which is known as the antipolyelectrolyte effect. Thus, the ZP combine antifouling properties with high ability to absorb wound exudate and at the same time maintain the moisture environment of chronic wound. Nevertheless, their potential for chronic wound management is still unrevealed. In this work, two types of ZP networks were synthesized comprising in their structure zwitterionic moieties. Both ZP types are salt-sensitive. In addition, polysulfolobetain (PSB) is thermoresponsive, while polycarboxybetain (PCB) is pH sensitive, allowing for modulation of their structure and functional properties by external stimuli. The PSB and PCB hydrogels were characterized in terms of their physicomechanical properties, biocompatibility and inhibitory activities towards bacterial biofilms and major enzymes causing chronicity of the wounds, such as myeloperoxidase and matrix metalloproteinases. The potential of the hydrogels for chronic wound treatment was confirmed by *ex-vivo* experiments with clinical exudates.

COLL 246

Solvent free synthesis of nanostructured MoS₂/S-TiO₂ photocatalysts for visible light driven water splitting and dye removal

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Ecofriendly and eminently efficient visible-light driven catalysts for water splitting and dye removal are of great interest due to its exceptional properties. Designing a visible light active catalysts will be a notable and green research as significant amount of solar radiation constitute of visible light. In this work, we demonstrated a quick and facile solvent free synthesis approach to develop nanostructured MoS₂/S doped TiO₂ hybrids as a potential catalyst for water splitting and dye removal applications. The method employed in this study contributes to a cost- effective large scale production of visible light driven photocatalyst .The dye removal and hydrogen production for these nanohybrids exhibited an enhanced performance compared to MoS₂ and TiO₂ individually

COLL 247

Second harmonic generation studies of indomethacin adsorption to phospholipid membranes

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We monitored adsorption of a non-steroidal anti-inflammatory drug (NSAID), indomethacin, to a supported lipid bilayer composed of phospholipids of varying lipid

phase and head group charge. These experiments were conducted under physiologically-relevant drug concentrations and at a range of pH conditions. We monitored second harmonic generation (SHG) signal at the aqueous-bilayer interface to quantify the number of adsorbed drug molecules and determine the impact of lipid fluidity, alkyl chain length and head group charge. Twice as much indomethacin adsorbed to liquid crystalline-phase lipids compared to gel-phase lipids. At neutral pH, indomethacin is negatively-charged and adsorbs with a lower binding affinity to lipids containing negatively-charged lipid head groups compared to zwitterionic lipids or lipids containing positively-charged head groups. We varied temperature in our experiments to determine the enthalpic and entropic contributions to the free energies of adsorption. These studies provide a molecular-level picture of how variations in cell membrane composition impact the adsorption of a representative NSAID. Studies of indomethacin release from supported lipid bilayers were also conducted in aqueous conditions and indicate that a phospholipid-coated drug delivery device containing indomethacin may be remotely triggered by changes in temperature.

COLL 248

Targeted detection of mRNA biomarkers using graphene oxide and upconversion nanoparticles

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Graphene oxide (GO) has emerged in the last decade as one of the most promising materials for biosensing, due to its functional versatility and quenching properties. Additionally, the property of GO to physisorb single stranded DNA via π-stacking interactions but not double stranded DNA, allows for the creation of several types of Graphene-oxide DNA sensors. These sensors can be applied to multitude of different targets, from the detection of metal ions to biomolecules such as proteins and RNA. In this poster, we demonstrate a sensor that can detect mRNA biomarkers, which can be critical in the diagnosis of diseases. Most of the current methods for detection of mRNA are time consuming and fail on achieving high levels of specificity and sensitivity in the presence of complex biological environments. Here we present a sensor based on graphene oxide and DNA-coated upconversion nanoparticles, which detects mRNAs relevant to Alzheimer disease and prostate cancer. Our sensor can detect mRNAs at the fM range and within complex biological environments

COLL 249

Synthesis of large spherical and anisotropic gold nanoparticle dimers using a seeded-growth method

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The capability of bringing together nanoparticles into programmed 2D or 3D structures has enabled the assembly of novel nanomaterials with unique physical and chemical properties. Conceptually, nanoparticle dimers are the simplest type of assembly and many strategies are already available for their synthesis. In the case of gold nanoparticles (AuNPs), the most elegant and precise way to form gold nanoparticle dimers, trimers and tetramers is by using DNA scaffolds. However, there are currently limitations for using this approach for the formation of dimers of large spherical ($>30\text{nm}$) and anisotropic gold nanoparticles. These include the difficulty of separating large spherical AuNPs with a discrete number of short DNA strands using gel electrophoresis and the difficulty of functionalising anisotropic AuNPs with a discrete number of oligonucleotides. In this poster we present a seeded-growth method for the synthesis of dimers of either large spherical or anisotropic gold nanoparticles. The first step of the synthesis involves the formation of small gold nanoparticles. Dimers of these particles are obtained through hybridisation of double stranded DNA and covalently linked by click chemistry. These dimer seeds then react with gold precursor, reducing agent, and in the case of anisotropic particles, a surfactant. After purification, ligated dimers of larger particles or anisotropic nanoparticles are obtained and their optical properties are being studied. The use of the seeded method allows straightforward synthesis of complex types of gold nanoparticle dimers.

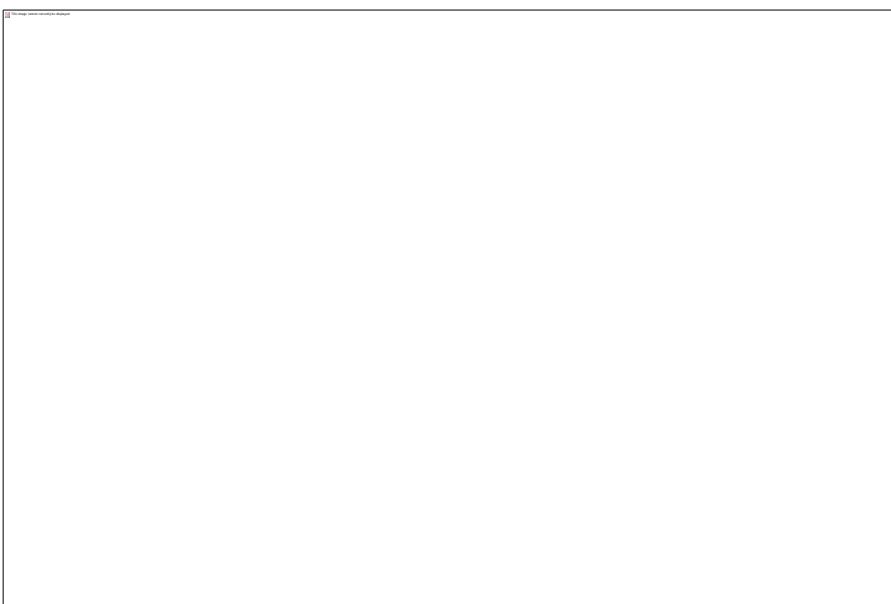
COLL 250

Aptamer-gold nanoparticle colorimetric assay evaluation of the role of DNA, small molecule targets, and gold nanoparticle interactions via NMR

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Colorimetric aptamer-based assays for the detection of small molecules, proteins, and cells are of great interest. The unique properties of gold nanoparticles (AuNPs) and aptamers are utilized for the detection of targets with the unaided eye. The intricate interactions of DNA-aptamers and AuNPs, especially in the presence of target molecules, are not well understood. For these assays, aptamers are absorbed onto the surface of AuNPs. In turn, the aptamers stabilize the AuNP solution by increasing the surface charge, which keeps the nanoparticles from aggregating. Aptamer-target binding alters the stability of the AuNPs resulting in a color change. We have investigated the riboflavin binding aptamer (RBA) used in the design of a colorimetric assay involving AuNPs and the DNA-aptamer. RBA consists of a total of 29 DNA bases—15 bases in the loop and a 7 base pair stem in the absence of riboflavin (target). It is believed that the RBA forms a G-quartet structure in the presence of the target. For these investigations, the RBA was chosen for its simple structure—a stem

and loop (or hairpin)—and known activity as a recognition element in the design of colorimetric assays. Initial nuclear magnetic resonance (NMR) investigations indicated that the stem and loop structure was too stable and prevented the formation of the G-quartet with the aptamer's native 29 base structure. The G-quartet was able to form only when the buffer used was altered to include potassium ions, essential for G-quartet formation, and the temperature was raised 15 °C above room temperature. We then altered the native RBA structure by weakening the stem strength—either shortening the stem length or mismatching the stem pairs. The aptamer variants were then investigated for their activity in colorimetric assays. Further NMR investigations provided essential DNA structural details of the aptamer variants. These investigations provide crucial information into the mechanism and function that governs AuNP-aptamer based colorimetric assays.



Effects of aptamer stem length on sodium chloride induced aggregation of AuNPs

COLL 251

Modification of zinc oxide nanoparticles with perfluorophosphonic acids

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Zinc oxide (ZnO) nanoparticles have semiconductive properties that can be modified to increase the performance and efficiency of solar cells. ZnO nanoparticles are inexpensive and abundant, making them ideal for use as an electron transfer layer in the structure of inverted solar cells. A relatively simple and cost efficient method of surface modification is forming self-assembled monolayers (SAMs) onto the surface of ZnO via adsorption. SAMs can greatly alter the physical and chemical properties of ZnO

to make it more suitable for a wide variety of applications. The formation of perfluorinated phosphonic acids are being utilized for this project due to the highly electronegative nature of fluorine. Specifically, 12-pentafluorophenoxydodecyl phosphonic acid, 2,3,4,5,6-pentafluorobenzyl phosphonic acid, and (1H,1H,2H,2H-Heptadecafluorodec-1-yl)phosphonic acid have been used to form thin films on the ZnO nanoparticle surfaces. Fourier transform infrared spectroscopy, scanning electron microscopy with energy dispersive spectroscopy, cyclic voltammetry, electrochemical impedance spectroscopy, X-ray photoelectron spectroscopy, and ultraviolet photoelectron spectroscopy have been used to analyze and characterize the modified nanoparticles and determine the effects that each of the different phosphonic acids have on the ZnO. The perfluorinated phosphonic acid SAMs have formed strong chemically bonded films on the ZnO, and the work functions of the modified ZnO nanoparticles have been tuned due to the dipoles in the C-F bonds. The work function was found to be higher than that of unmodified ZnO which is crucial for its inclusion in inverted solar cells.

COLL 252

Modification of nitinol nanoparticles with self-assembled alkylphosphonate films

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Nitinol (NiTi) nanoparticles, which are a fifty-fifty metal alloy of nickel and titanium, are valued because of their corrosion resistance and superelasticity. NiTi is best known for its shape memory, as the bulk metal can physically change shape when transitioned by heat or pressure between the austenite and martensite forms. NiTi has potential in biomedical tools, nanofluids, and nickel alkaline batteries. To be able to utilize the NiTi nanoparticles, the surface requires modification, specifically by phosphonic acids. The metal oxide surface readily adheres to these acids, forming self-assembled alkylphosphonate films. In this study, phosphonic acids, including 16-phosphonohexadecanoic acid, octadecylphosphonic acid, and 12-aminododecylphosphonic acid were used to form an ordered self-assembled monolayers on the NiTi nanopowder. These surface modifications could be used in the preparation of nanofluids in order to improve their suspension. NiTi nanofluids have the ability to change electrical and thermal conductivity at the transition temperature, producing a smart nanofluid. The modified NiTi nanoparticles were then characterized using attenuated total reflectance infrared spectroscopy, powder X-ray diffraction, X-ray photoelectron spectroscopy, scanning electron microscopy-energy dispersive X-ray spectroscopy, cyclic voltammetry, electrical impedance spectroscopy, and ^{31}P solid-state nuclear magnetic resonance. Stability testing were performed on the NiTi nanoparticles to examine the effects of solvent rinse, humidity, and temperature over time. Isoelectric point of NiTi was also determined by analyzing zeta potential of NiTi at varying pH values. Based on spectroscopic data, the phosphonic head group is expected to adsorb in a mixed bidentate/monodentate binding motif at the surface of the

NiTi nanoparticles. This allows the NiTi nanoparticles to be modified in order to provide the ideal physical and chemical properties for a variety of applications.

COLL 253

Tannic acid-mediated green synthesis of gold nanoparticles and their catalytic reduction of 4-nitrophenol

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Tannic acid is a plant-derived polyphenolic compound which is abundant in coffee, red wine, green tea and immature fruits. In the present report, tannic acid was used as a reducing agent to synthesize gold nanoparticles (AuNPs). No other chemicals were introduced during the synthetic step except tannic acid. Five different concentrations of tannic acid were utilized to prepare the following three kinds of AuNPs. (i) Preparation of an AuNP colloidal solution using tannic acid as a reducing agent (TA-AuNPs), (ii) Centrifugation of TA-AuNPs and re-dispersion with de-ionized water (*cf*-TA-AuNPs), and (iii) Preparation of AuNPs via *in situ* crystallization on a solid matrix using graphene oxide (TA-AuNPs-GO). Characteristic surface plasmon resonance (SPR) bands at 500~600 nm were observed for both TA-AuNPs and TA-AuNPs-GO. The SPR band of *cf*-TA-AuNPs was broadened and red-shifted when compared with that of TA-AuNPs. Mostly spherical-shaped TA-AuNPs and TA-AuNPs-GO were observed in high-resolution transmission electron microscopy images. The average sizes of TA-AuNPs and TA-AuNPs-GO were measured as 18~35 nm and 4~33 nm, respectively. The catalytic activity of these three AuNPs was evaluated in 4-nitrophenol reduction reaction. The rate constants decreased in the order of TA-AuNPs-GO, *cf*-TA-AuNPs, and TA-AuNPs. Furthermore, the rate constant increased with the decrease of the tannic acid concentration. When compared with TA-AuNPs, the rate constants of *cf*-TA-AuNPs and TA-AuNPs-GO increased 1.45~2.25 and 2.25~4.49 fold, respectively. Although only one-tenth of the catalytic amount was utilized, the rate constant of TA-AuNPs-GO was the highest among the three kinds of AuNPs. Consequently, there was a great enhancement of the catalytic activity in 4-nitrophenol reduction reaction when the solid matrix such as graphene oxide was employed during *in situ* crystallization.

COLL 254

Green gold nanoparticles synthesized using *Artemisia capillaris* extract and their catalytic performance

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Green gold nanoparticles were synthesized by *Artemisia capillaris* water extract as a reducing agent (AC-AuNPs). *A. capillaris* has been used in Chinese traditional medicine and possesses antibacterial and anticancer activities. Five different concentrations of the extract (0.015 ~ 0.055%) were used to synthesize AC-AuNPs with hydrochloroauric acid trihydrate as precursor salts. Moreover, the extract present in AC-AuNPs was removed by centrifugation resulting in *cf*-AC-AuNPs. The catalytic activity of both CA-

AuNPs and cf-AC-AuNPs were evaluated using the 4-nitrophenol reduction reaction in the presence of excess sodium borohydride. The characteristic surface plasmon resonance (SPR) bands of AC-AuNPs were observed at 534 ~ 543 nm. Mostly spherical-shaped AC-AuNPs were observed in high resolution transmission electron microscopy and their average size was measured as $16.88 \pm 5.47 \sim 29.93 \pm 9.80$ nm. By increasing the extract concentration during the synthetic process, the SPR bands had a tendency to blue-shift. High-resolution X-ray diffraction analysis of AC-AuNPs revealed a face-centered cubic structure. Phytochemical screening and FT-IR spectra confirmed that amino acids, flavonoids and phenolic compounds in the extract were major contributors to the reduction of Au salts to AC-AuNPs. With the decrease in average size, the rate constants of both AC-AuNPs and cf-AC-AuNPs increased in the 4-nitrophenol reduction reaction. The catalytic activity of cf-AC-AuNPs increased up to 50.4% when compared with AC-AuNPs. Thus the removal of the extract by simple centrifugation greatly enhanced catalytic activity of AC-AuNPs.

COLL 255

Designing a model cell membrane to investigate the absorption of nanoparticles in our skin

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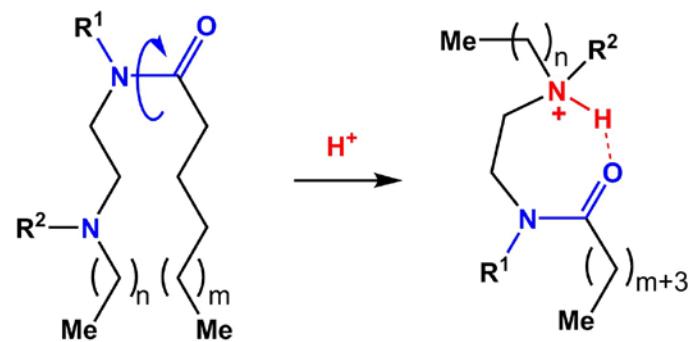
The Langmuir Monolayer Technique is used to study surface chemistry and can be used to model the cell membrane of a eukaryotic cell. Liposomes can also be used as a model due to the lipid bilayer that is produced allowing for the interpretation of how particles interact with the hydrophilic and hydrophobic regions of the membrane through analysis by fluorescence. Nanoparticles of titanium dioxide and zinc oxide will be introduced to monolayers of lipids containing cholesterol and lignoceric acid and also to liposomes to investigate how metals interact within the cell membrane in order to ultimately determine if the particles in over the counter beauty products embed our skin. The compression isotherms of four lipids, cholesterol, cholesterol sulfate, lignoceric acid, and N-oleoyl-d-sphingosine, that are major components of the epithelial cell membrane have already been established at body temperature conditions in order to interpret how the lipid behaves in the skin. Liposomes are being used as a technique to study the bilayer due to the ability to analyze them via fluorescence spectroscopy. A fluorescent lipid is introduced to the lipid or lipids that are being studied and the liposomes are then tested using a fluorimeter that allows for a graphical display of the excitation and emission in order to determine if the incorporation of the titanium oxide or zinc oxide causes fluidity in the membrane. Preliminary results show that the addition of cholesterol to lignoceric acid fluidizes the membrane. We hope to show that the addition of the titanium dioxide and zinc oxide will increase the fluidity of our membrane system utilized for modeling epithelial cells.

COLL 256

pH-induced conformational switch in novel amide-based amphiphiles and their potential application in liposomes for targeted drug delivery

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A series of amide-based amphiphiles able to perform a conformational switch upon protonation has been synthesized and studied using ^1H -NMR titration techniques. Incorporating these amphiphiles as acid-sensitive components into a lipid bilayer, we prepared and tested pH-responsive liposomes for targeted drug delivery. The acid-induced conformational flip disrupts the liposomal membrane and triggers a cargo release in acidic environment.



COLL 257

Two-dimensional nanoparticle array and cluster formation by supercritical fluid deposition

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Nanoparticles (NPs) can be deposited as two-dimensional (2D) clusters into nanostructures of silicon substrate using supercritical fluid CO_2 (sc- CO_2) as the medium. Due to its unique properties including gas-like penetration, liquid-like solvation and near zero surface tension, sc- CO_2 is capable of depositing NPs into nanometer-sized shallow wells which cannot be achieved by traditional solvent deposition methods.

Nanoparticles tend to fill nano-structured shallow wells first, and then, if sufficient nanoparticles are available, they will continue to cover the flat areas nearby, unless defects or other surface imperfect areas are available. SEM images of two-dimensional gold (Au) nanoparticle arrays formed on silicon surface from 2 to a dozen or more of the Au nanoparticles are given to illustrate the patterns of nanoparticle array formation in

sc-CO₂. Formation of 2D NP arrays in large areas on silicon substrate surface is also described.

COLL 258

Epoxide chemistry on the Si(100)-(2x1) surface

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The reactions of simple epoxides on the Si(100)-(2x1) surface were studied experimentally and computationally. A single dimer cluster model was used to mimic the surface reactive sites and the adsorption of the epoxides was treated using density functional theory. The computational results indicate that the initial interaction of the silicon surface dimer with the oxygen atom of the epoxide ring is facile and is then followed by C-O bond cleavage resulting in the ring opening of the epoxide. This leads to the formation of a five membered ring after carbon attachment across the silicon dimer. The ring formation reaction appears to be readily accessible at room temperature. Thermal desorption mass spectrometry of epoxide dosed Si(100)-(2x1) provides evidence in support of the computational results describing the Si-O bond formation and epoxide ring opening reactions. These findings indicate that epoxide surface chemistry may be a promising route to thermally controllable silicon surface functionalization.

COLL 259

Targeted delivery of chemotherapeutic drugs and adjuvants using gold nanoparticle carriers

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A variety of nanoparticle carriers have recently been investigated as vehicles for the targeted delivery of anticancer drugs to reduce the drugs side effects and improve their efficacy. In this work, the nanocarriers with immobilized chemotherapeutic drug Methotrexate (MTX) and adjuvant Leucovorin (LEU), used in treatment of several types of cancers, including the lung, breast, head and neck, blood, and bone cancers, have been designed and tested in simulated media. The toxicity of MTX can drastically affect the bone growth. The adjuvant, LEU, is a chemotherapy toxicity reducer that when administered after MTX treatment, reduces toxicity and side effects of MTX without affecting overall efficacy. However, since these drugs are administered intravenously or orally, this still causes severe side effects because the drugs interact with both healthy and cancerous sites. Combating this involves targeted drug delivery. The targeted nanocarriers developed in this work were based on spherical gold nanoparticles and nanorods which were functionalized first with mercaptobenzoic acid (MBA) and p-

aminothiophenol (pATP) by forming a mixed thiolate self-assembled monolayer film. MTX was immobilized on the nanocarriers through amide bond formation with MBA, while the targeting agent, folic acid (FA), was amide-bonded to pATP. The MTX and FA loaded nanoparticles were placed in two buffers of different pH: a PBS buffer of pH 7.4 and an acetate buffer of pH 5.5. The Raman measurements confirm the release of drugs at lower pH and a negligible leakage of drugs at physiological pH of 7.4. Hence, the proposed targeted cancer therapy may lead to lower toxicity of the treatment to healthy tissues as compared to the non-targeted intravenous or oral drug distribution.

COLL 260

Static light scattering studies of the aggregation process in the isotropic phase of chromonic surfactants in water

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Chromonic surfactants are amphiphilic molecules consisting of a polyaromatic central core with hydrophilic groups on the periphery or aromatic rings linked by hydrophilic functional groups. In contrast to conventional amphiphiles where the onset of aggregation occurs at a specific concentration (known as the critical micelle concentration), chromonic dye molecules typically show an isodesmic aggregation pattern where stepwise growth at all concentrations yields a distribution in aggregate size. Fluorescence spectroscopic studies in our laboratory suggest that the structure of a chromonic dye influences the concentration- and temperature-dependence of the aggregation process. As a complementary technique to confirm the aggregation behavior observed spectroscopically, in this study we have used static light scattering to monitor the aggregation of four chromonic surfactants in water: sunset yellow FCF, acid red, benzopurpurin 4B, and methyl orange. Measurement of static light scattering intensities is one of the most common techniques for monitoring self-assembly, and, when combined with our spectroscopic analyses, is a powerful approach to reveal the relationship of chromonic structure and aggregation behavior. We confirm the isodesmic nature of the aggregation process for these chromonic surfactants and determine further that the aggregation process is both enthalpy- and entropy-driven

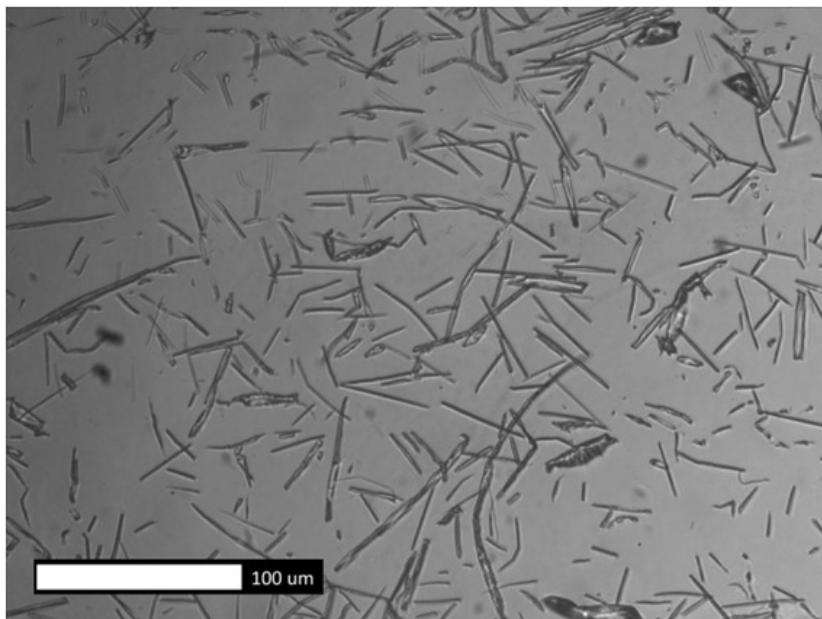
COLL 261

Standardization and characterization of nonspherical micro and nano bubbles by cerato-ulmin hydrophobin

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Micro and nano bubbles have garnered much of their interest from the pharmaceutical and food industry for drug delivery and fat replacement. Even at their much smaller size,

the shape of these bubbles still mimic their macro sized brethren as a sphere which is the most energetically favorable with the lowest surface area possible. Hydrophobins are a class of amphipathic proteins with a high surface activity derived from various fungi. Cerato-ulmin (CU) is a small, hydrophobic protein from the Class II hydrophobin family and forms micro and nano bubbles when agitated in solution. We have found that the hydrophobin CU does not form spherical bubbles and forms a variety of nonspherical shapes that are stable up to 30 days. Our study addresses the lack of reproducibility in bubble formation, examines the effect of processing conditions on bubble morphology, and probes the protein film with small angle x-ray and neutron scattering (SAXS/SANS).



COLL 262

Highly active cuprous oxide photocathode for the selective photoelectrochemical reduction of carbon dioxide

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The catalytic activity and specificity of gold nanoparticle (Au NPs) seeded cuprous (I) oxide (Cu_2O) thin films reduction of carbon dioxide (CO_2) is investigated using linear sweep voltammetry (LSV) or cyclic voltammetry (CV). The photocatalytic electrode is fabricated by first loading Au NPs using a block copolymer template of polystyrene-*block*-4-vinylpyridine (PS-**b**-4VP) on to indium tin oxide (ITO). Then highly active Cu_2O is electrodeposited by bulk electrolysis at constant potential. The Au NPs are used as nucleation sites to control the size and form of the Cu_2O . The addition of the Au NPs not only increases the surface area to volume ratio of the Cu_2O but also harnesses the localized surface plasmon resonance (LSPR) effect of the NPs for increased photon

absorbance. A thin titanium oxide (TiO_2) coating is then applied via sol-gel method to protect against photocathodic degradation of the Cu_2O typical in aqueous electrolyte solution.

COLL 263

Stabilization and reaction of small molecules on $\text{TiO}_2/\text{Au}(111)$ inverse model catalysts

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The adsorption of CO_2 , CO , and H_2O , components of important industrial reactions including the water gas shift (WSG) reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) and CO_2 hydrogenation to methanol, were utilized to investigate the catalytic activity of TiO_2 nanoparticles supported on $\text{Au}(111)$. Systematic studies of TiO_2 nanoparticle coverage were conducted using temperature programmed desorption to understand the adsorption and reaction of these molecules over the inverse model catalyst. Increasing the coverage of TiO_2 nanoparticles led to an increased desorption temperature of CO_2 . The stabilization of CO_2 by the presence of TiO_2 nanoparticles indicates the potential of the material to act as a low temperature hydrogenation catalyst. It was expected that adsorption of CO and H_2O on TiO_2 nanoparticles supported on $\text{Au}(111)$ would exhibit WGS chemistry, however interestingly, the formation of formaldehyde was observed. The production of formaldehyde is likely a result of the reduced state of the surface which promoted the hydrogenation of CO .

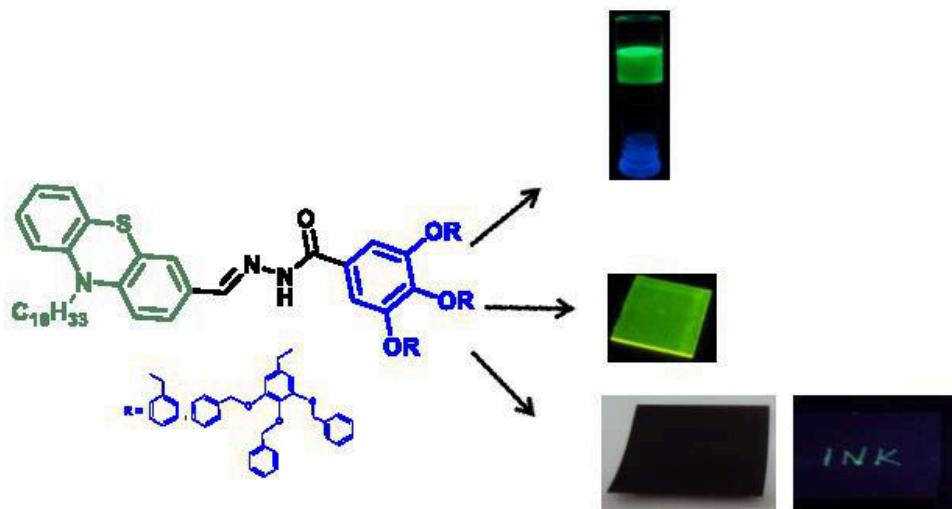
COLL 264

Phenothiazine cored poly (aryl ether) dendrons: Phase selective gelation, hydrophobization, oil spill recovery, antiwetting property and formation of fluorescent ink

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Low molecular weight gelators (LMWGs) readily self-assemble into rods, ribbons, fibers, or other nano-sized aggregates of different morphologies in specific solvents, through hydrogen bonding, $\pi-\pi$ stacking, London dispersion forces, solvophobic forces and other types of essential van der Waals interactions to form three-dimensional molecular networks. LMWGs have sparked great interest since they can be utilized to prepare sensors and actuators, tune drug delivery and devise functional materials in shape memories and display systems. Poly(aryl ether) dendrons are attractive candidates for preparing robust gel systems. Poly (aryl ether) dendron-linker-phenothiazine based LMWGs formed fluorescent gels in various oils selectively in a biphasic mixture of sea water/oil (1/1, v/v). They are used for oil spill recovery. These gels were characterized

by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) experiments. These gelators also formed fluorescent thin film in a glass substrate which is good enough hydrophobic to repel water. Anti-wetting and self-cleaning properties are the highlights of these thin films. By carefully adjusting the visco-elastic properties of these gels, they can be used as fluorescent (secure) inks. This property reveals that the supramolecular gels are mouldable and applicable.



COLL 265

Synthesis of perfluoro-acrylate-silane co-polymer nanocapsules using emulsifier-free emulsion polymerization: Water-oil repellent and surface properties

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Perfluorooctyltriethoxysilane(PFOES) was used as a shells for strong bonding on the core and water-oil repellent, also used Butyl acrylate(BA) and Hydroxyethylene methacrylate(HEMA) as shells to improve the characteristics of water-oil using hydrophilic and hydrophobic. Poly(MMA)/Poly(PFOES-BA-HEMA) core-shell particles were polymerization with 4-styrenesulfonic acid sodium salt hydrate (NaSS), which served as a reactive surfactant via seed emulsion polymerization using two stage show growth method. The demonstrate that triethoxysilane groups of PFOES can be used as surface coating agents, several were reacted with cellulose. The structure morphology and water-oil repellent property of the core-shell nanoparticle were confirmed by Field-emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM), Contact Angle. The analytical results indicate that the core-shell were polymerization with good spherical shape and water-oil repellent.

COLL 266

Synthesis of lanthanum doped titanate nanotube through a facile hydrothermal route

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TiO₂ photocatalysts have been studied extensively since the past decades due to its ability to capture energy from sunlight and utilize the energy for various applications including photodegradation and clean energy production. It has been shown in many literatures that the nanostructured TiO₂ has an improved photocatalytic activity due to higher surface area, better light scattering, and improved electron transportation. In our works, we are developing a facile hydrothermal synthetic route of titanate nanotube and doped-titanate nanotube. The preliminary results indicate the presence of doped element, La, in the inter-wall layer of titanate nanotube. The synthesized nanotube is further studied for the application in CO₂ reduction. We expected that the doped titanate will have an improved photocatalytic activities and the developed synthetic method is applicable for other elemental doping of titanate nanotube.

COLL 267

Performance enhancement of fluorescent dyes using nanoparticle encapsulation strategies for LED applications

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The incorporation of fluorescent dye molecules into nanoparticles (NPs) has been widely used in bioapplications. By contrast, few researchers have focused on applying such systems for light emitting diode (LED) and luminaire design despite the commercial availability of LEDs that use dyes as down-convertors. Here we examine the potential for dye doped nanoparticles to enhance LED brightness and power efficiency by improving the reliability of dye molecules. Towards this end, we encapsulate commercially available dyes, suitably modified with a reactive silica precursor, into silica NPs via a modified Stöber method. Transparent dye doped silica NP/silicone nanocomposites and free dye liquid solution are prepared. The morphology and optical properties of solid and liquid samples are investigated by scanning electron microscopy, confocal microscopy, UV-Vis absorption, fluorometer and integrating sphere. The results demonstrate a strong dependence of relative quantum yield on dye doping concentration in NPs. Long time aging tests are conducted under blue LED with

a wavelength of 455 nm for 24 hours. Dye doped silica NP/silicone nanocomposites present a higher photostability than the free dye liquid samples. Novel dye doped silica NPs and their nanocomposites are a potential route to achieving high photostability, high transparency and high efficiency downconverters in next-generation LED and luminaire design.

COLL 268

Synthesis of carboplatin like Pt²⁺ complexes with azide and alkyne functionalities for nanomedical applications

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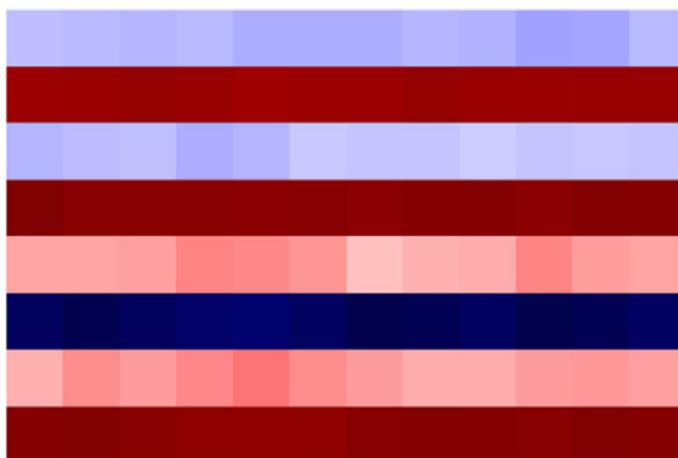
Click reaction is quick, versatile and biocompatible, thus making it an important step in modern organic synthesis of biologically active molecules. Platinum (II) complexes, are one of the most potent anticancer agents available in the clinic, but their high aquation rate leads to high systemic toxicity and limits the dosage. We describe the synthesis of carboplatin like Pt²⁺ complexes that have the free azide or alkyne group available for click coupling reactions, making it possible to attach the Pt²⁺ complexes to other supports. The complexes are synthesized from diethyl methylmalonate precursor via malonic ester synthesis followed by the reaction with a Pt²⁺ precursor activated with silver nitrate. Preliminary biological testing in the isogenic ovarian cancer cell lines A2780 (chemo naïve) and A2780-CP70 (chemo resistant) demonstrates high biological activity of the complexes. The IC₅₀ [A2780] concentrations calculated for our platinum complexes is 0.510 mM. This value is significantly lower than IC₅₀ value for model drug carboplatin 6.461 mM, and reach the level observed for highly potent cisplatin 0.799 mM. The solubility of both complexes in water is ~ 1 mg/ml. Our Pt²⁺ complexes were successfully immobilized onto gold nanocrystal (AuNC) surface, conjugated to small peptides, and currently are being implemented into larger nanoparticle (NP) scaffolds based on poly-lactic-co-glycolic acid (PLGA) polymer and PAMAM dendrimers. The Pt²⁺ loading into the different carriers proceeds via simple copper catalyzed click reaction. Preliminary in vitro testing shows that the biological activity of the complexes was retained after the click reaction and Pt²⁺ was detected inside the cell's nucleus. This methodology can be extended further to conjugate active Pt²⁺ species onto other supports.

COLL 269

Field theory for ligand alignment on nanoparticles: Prospects for self–assembly driven by phase transitions

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Nanoparticles can be assembled into large arrays, but currently we do not possess control over forces governing self-assembly at the nanoscale. It has been observed that alkyl chain molecules passivating nanocrystal surfaces have an important role in dictating particle interactions. These ligands go through an order-disorder phase transition on a CdS surface as temperature is increased. Simulations show that the alkyl chains arrange in an alternating gauche-eclipsed pattern, but this alternation gets destroyed closer to the phase transition. It is unclear if the defects in the ligand pattern are essential for the disorder transition to occur. Hence, we are investigating their role by performing biased simulations. Umbrella sampling on the ligands is used to determine the free energy surface as a function of their average alignment. As a result, the equilibrium behavior at a given temperature has been obtained with the Weighted Histogram Analysis Method (WHAM). Using this information, we are also working to describe the order-disorder phase transition by postulating a coarse-grained model with an effective Hamiltonian inspired by Landau-Ginzburg theory.



Top-down view of the CdS surface, showing chains with a gauche C-C bond (blue) and chains with only eclipsed bonds (red). Presence of two adjacent rows of the same color indicates a defect.

COLL 270

Delivery of biomolecules into solid-supported lipid bilayers using nanolipoprotein particles

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Determination of the native three-dimensional structure of a protein is key to elucidation of its innate functionality. Although advances in NMR spectroscopy, X-ray crystallography, and cryo-electron microscopy have enabled accurate structural characterization of numerous types of proteins, analysis of integral membrane proteins (IMPs) remains challenging due to onerous obstacles associated with obtaining purified IMPs in sufficient yield; conventional methods for extraction and crystallization typically rely on the use of harsh detergents which disturb native IMP structure. In distinction from established protocols in the literature, this project aims to render IMPs amenable to high-resolution structural characterization by delivering them into a polymer-cushioned supported lipid bilayer (SLB) system using nanolipoprotein particles (NLPs). For preliminary experiments, we selected the polyacrylic acid (PAA)-cushioned SLB because of its robust construction, ease of preparation, and defined pH responsiveness. By micropatterning the PAA cushion with UV-ozone photolithography prior to lipid bilayer deposition, we were able to produce unique structural features where the biomembrane bridged across adjacent regions of PAA in some instances. To evaluate whether biomolecules transferred to SLBs from NLPs in solution, we used epifluorescence microscopy. Results indicated that lipids and the receptor tyrosine-protein kinase, ErbB2/HER2, transported spontaneously from NLPs to PAA-cushioned SLBs. Interestingly, ErbB2/HER2 only exhibited lateral mobility in SLB regions where biomembrane bridging had occurred. In ongoing work, we are investigating NLP-mediated delivery of IMPs to surface-functionalized SLBs.

COLL 271

Polyelectrolyte multilayers for controlled FGF-2 release and improved cell attachment on cell culture surfaces

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Self-assembled polyelectrolyte multilayers (PEMs) are materials capable of increasing cellular attachment rate and controlling the release of signaling molecules such as growth factors on cell culture surfaces. While many current substrates such as tissue-culture treated polystyrene and glass are cost effective, their surface properties are not tuned to specific cell lines. This, in addition to the fact that current processes require the manual addition of growth factors on a regular basis, results in inconsistent cell production and a large labor investment. For this reason, much research in the field has been focused upon improving cellular scaffolds. PEMs are a possible solution and have been shown capable of modifying surface energy, roughness and stiffness of a substrate, along with maintaining the bioactivity of growth factors over the course of several days. These improvements allow for the creation of new cell culture surfaces capable of more consistent and rapid manufacturing of cells for research and therapeutic applications, such as implant and repair of bone and muscle in traumatically injured patients.

In this work, basic fibroblast growth factor (FGF-2) was adsorbed onto polystyrene and glass substrates. A PEM was formed through dip coating poly(methacrylic acid) and

poly-L-histidine. We found that this combination was capable of releasing bioactive FGF-2 over a one-week period. It was also found that the addition of the PEM increased the surface energy and roughness of the substrate. These properties were shown to be tunable through modification of assembly conditions, such as pH and combination of polyelectrolytes. Cell staining results confirmed that the PEM-modified surfaces were capable of improving cell replication over a several day period. The results show that layer-by-layer formation of PEMs is an efficient method of creating not only effective but tunable cell culture surfaces.

COLL 272

Removal kinetics of 2-Chloroethylsulphide (CEES) by iron oxide nanoparticles

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Considering ever increasing treats of chemical attacks not only during regular wars, but also by terrorist organizations, decontamination and disposal of chemical agents gain increasing importance. Sulphur mustard (SM) is a chemical warfare agent that can form blisters on skin and in the lungs once exposed. Because of their high toxicity, direct handling of chemical agents is not feasible for regular laboratory investigations. Instead, simulant compounds that have similar chemical structures to those of real chemical warfare agents are often investigated. 2-chloroethylsulphide (CEES) is one of the simulant compounds of sulphur mustard. For the removal of CEES, various metal oxide were studied as reactive sorbents, most notably oxides of Ca, Mg, Ti, and Zn. Recently, decomposition of CEES by zero valent iron (ZVI) and iron oxides were reported. In this study, we report on the synthesis of Iron Oxide Nanoparticles (IONPs), which are in the form of magnetite (Fe_3O_4), and the removal efficiency of CEES by the synthesized iron oxides. Cyclohexane was used as a solvent to dilute CEES. After dilution, the synthesized iron oxide powder was mixed and stirred in the solution to remove CEES. Concentration of CEES in the solution was measured by HPLC. Removal kinetics of CEES by IONPs will be discussed and compared with that of other metal oxides such as titania and MgO.

COLL 273

Assembly and disassembly of fluorescent graphene oxide for optical detection of enzymatic activity

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Fluorescent graphene oxide (fGO) was randomly assembled upon addition of various metal ions, which led to the significant quenching of its fluorescence. It was found that the kinetics of fGO aggregation and fluorescence quenching depended significantly on the types of metal ions such as Ni^{2+} , Cu^{2+} , Zn^{2+} , Co^{2+} , and Fe^{3+} and their concentrations. The randomly assembled fGO was then disassembled in the presence of phosphatase enzymes, which resulted in restoration of the quenched fluorescence of fGO. The fluorescence responses of fGO to the phosphate enzymes provided kinetic parameters such as a maximum velocity and a Michaelis constant for the enzymatic reactions. In addition, this sensing principle based on the assembly-disassembly of fGO allowed for the detection of inhibitors.

COLL 274

Modification of the surface of zinc oxide nanoparticles in order to increase efficiency of solar cells

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Self-assembled monolayers (SAMs) are molecules that bind to solids through adsorption. SAMs can be used as sensors for lethal bacterial enzymes, pH and conductivity indicators, and can inhibit corrosion. SAMs are incredibly useful due to the ability for chemical binding of molecules to the surface of a metal, like zinc oxide (ZnO), and can greatly change chemical and physical properties. ZnO specifically has a large variety of properties that are useful for surface modification. These properties include a wide band gap (3.37 eV), high exciton binding energy (~60 meV), and stable wurtzite structure. Through the process of SAMs, the surfaces of ZnO nanoparticles are modified with 16 phosphonohexadecanoic acid, 11 phosphonoundecanoic acid and 11 undecynylphosphonic acid. After binding an organic compound to a ZnO surface, a fluorescein, specifically 5 aminofluorescein, is attached to the organic molecule in order to serve as a fluorescent marker that can be used as a photosensor to facilitate charge transportation. By changing the properties of the ZnO surface layer, solar cell efficiency can be altered by increasing energy efficiency. The sample concentration and use of "linker" molecules will be altered in order to determine the optimum conditions for the modifications to the ZnO surface and the success of modification will be determined using infrared spectroscopy, dynamic light scattering, zeta potential, ultraviolet-visible spectroscopy, scanning electron microscopy, and electrochemistry. UV-Vis spectroscopy was used to determine the band gap of the surface modified nanoparticles. Band gap is the minimum energy required to excite an electron that is in its bound state into a free state in order to participate in conduction. By lowering the band gap, conductivity can occur more easily making ZnO ideal for solar cells. Initial testing has indicated that the band gap of our surface modified molecules is lower than that of the ZnO bulk material.

COLL 275

Alkyl desorption from Si(100)-2x1 by nonadiabatic hydrogen elimination

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While the hydrogen elimination reaction is frequently invoked when describing the dissociative desorption mechanisms of molecules from surfaces, its kinetics are less understood. This desorption mechanism occurs on Si(100)-2x1, an environment with highly directional, singly-occupied surface bonds in rows of dimers. The antiparallel nature of the dangling surface bonds gives rise to a low-lying electronic excited state following a spin flip. Using a combination of experimental and theoretical techniques, we demonstrate that the production of alkenes from halogenated alkanes on the Si(100) surface is driven by nonadiabatic β -hydrogen elimination, during which the electronic spin multiplicity of the system changes from singlet to triplet. Rate constants calculated with nonadiabatic transition state theory with the Landau-Zener probability of transition indicate that nonadiabatic reaction channels are kinetically favored, despite the reaction being nominally spin-forbidden. Experimental desorption rates obtained using temperature programmed desorption yielded activation energies in strong agreement with the theoretical energy barrier to the minimum energy crossing point between the two spin states. The relatively low values for the probability of transition and rate constants through the crossing point are consistent with the spin-forbidden, nonadiabatic step being the kinetic bottleneck.

COLL 276

Aqueous multiphase emulsion droplets as cellular mimics: Production and utilization

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Non-membrane bound compartments within the cell have been shown to be vital to cellular function. Such intercellular organization is governed by physical influences of the crowded and phase-separated environment within cells. In order to study the effects of compartmentalization, cellular mimics demonstrating these aspects of cells are desired. Aqueous multiphase system water-in-oil emulsion droplets provide such a platform. These droplets are typically composed of multiple distinct phase-separated regions, each rich in a specific neutral polymer (such as poly(ethylene glycol), dextran, or Ficoll). These regions provide unique partitioning effects as well as crowded environments within which cellular reactions may be studied. Microfluidic techniques

have been developed to exert control over droplet composition and morphology. The effect of these physical characteristics upon the extent of reaction and reaction rates is currently being explored. Previous work utilizing such a system has demonstrated successful observation of transcription and translation of fluorescent proteins within droplets. Expanding on these results, modifying the droplets' attributes (such as phase composition, relative phase volume, and droplet size) changes the availability of reaction components due to phenomena such as diffusion effects and effective concentration. This work provides a foundation of a physical understanding of emulsion-based cellular mimics upon which many biological reactions may be studied.

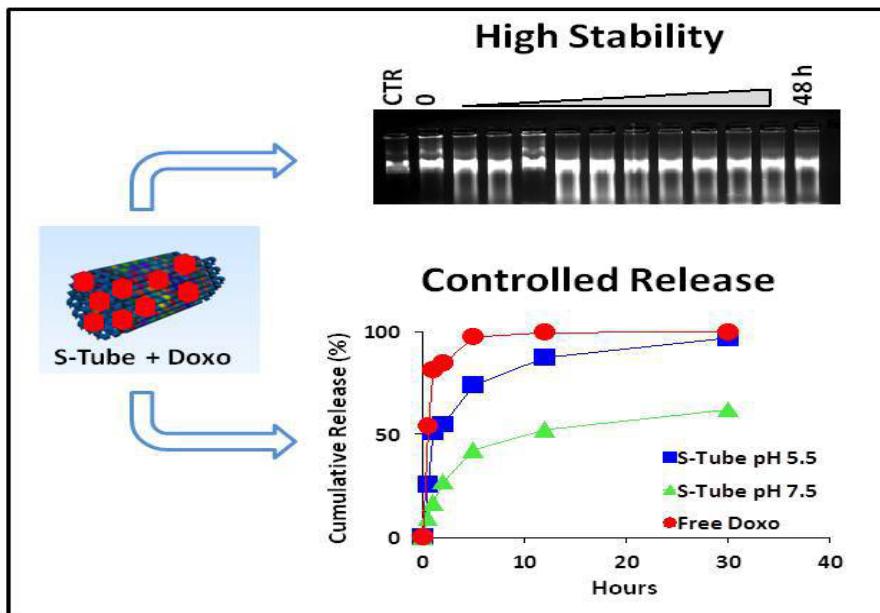
COLL 277

Novel DNA origami structure for Doxorubicin delivery

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DNA origami represents an excellent evolution of nanostructured intelligent systems for drug delivery. Recently, the ability of DNA origami to increase drug efficacy has been demonstrated in cancer therapy. Different shape, dimension and logically assembled DNA origami could be utilized to precisely increase antitumor efficacy and decrease toxicity of commonly utilized chemotherapeutic drugs based on tumor properties.

In our approach, we have synthetized and characterized a DNA nanotube with the size of 30 nm (s-tube). Our structure has excellent stability in serum (>48 hours), high loading capability (>35% w/w of doxorubicin) and slow release at physiological pH. Importantly, these properties are superior when compared with others DNA origami previously published. The cytotoxic effect of different DNA origami was tested *in vitro* on five cell lines: MDA-MB 231 (breast cancer), DLD1 and LOVO (colon cancer) sensitive and multi-drugs resistant. The experiments showed no significant difference among the nanostructures. The *in vitro* data are similar to the results obtained with liposomal doxorubicin (Doxil), which has been shown to be effective only *in vivo* by improving the pharmacokinetics profile of the drug. For this reason, we analysed the biodistribution of s-tube in a mouse model. It was demonstrated an accumulation of s-tube primarily in the liver and in the spleen. A preliminary pharmacokinetics analysis showed a better profile of s-tube/doxorubicin over the free drug. These data strong support the advantages of DNA origami in the drug delivery field and encourage us for further *in vivo* studies to develop a tailored approach for cancer patients.



COLL 278

Label-free detection and quantification of specific proteins in complex biological fluids through clogging in cellulose paper

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Electricity-free methods for conducting biomedical diagnostics can be profoundly impactful. Current diagnostic technologies can be divided into two general categories: lab-based tests, such as enzyme-linked immunosorbent assays (ELISAs), and Western Blots, which can involve multiple incubation and washing steps and require the use of sophisticated instruments for quantification (but are extremely sensitive), or point of care tests that employ capillary wicking of reagent containing liquids to perform qualitative colorimetric tests of simple analytes. While clogging is often treated as a nuisance to be avoided, in this poster we present work from our group that demonstrates clogging-induced changes in the properties of the flow of a colloidal suspension imbibing through a porous matrix (paper) can be used to quantify colloid concentrations. We find that within a certain range, the rate of wicking of the liquid is correlated with the concentration of colloids. This technique can, in certain situations, replace light-scattering based techniques for quantifying the concentration of colloids in a suspension. Applications wise, we have applied this phenomenon to devise a diagnostic test that measures the amount of antibodies in a liquid sample in less than 10 minutes by monitoring the clogging of insoluble precipitates that form when an antibody-containing sample is mixed with complementary antigens (a precipitin reaction). This is the first demonstration, as far as we know, of the quantification of specific protein

concentrations in paper-based devices through a non-colorimetric, label-free, homogenous immunoassay format.

COLL 279

Paper-based growth of liposomes and proteoliposomes using PAPYRUS in ionic buffers

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Formation of liposomes of complex lipid compositions in high ionic strength buffers is challenging with the techniques that are used currently. This poster reports on our studies of the effects of varying ionic strengths of the buffer solution and the lipid composition in the newly developed PAPYRUS technique (Paper-Abetted liPid hYdRation in aqUeos Solutions). We find that a two-step procedure, where a concentrated ionic stock solution is added after an initial growth period resulted in greatly improved yield and size of liposomes through PAPYRUS. We discuss our results based on the importance of electrostatic repulsion on the mechanism of growth of liposomes on paper-based substrates, and demonstrate the incorporation of membrane-associated proteins in the liposomal membranes and soluble proteins within the lumen of the liposomes.

COLL 280

Photochemical study of silver nanoparticles formed from the reduction of silver ions by humic acid

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This study focuses on the ability of silver ions and humic acid to form silver nanoparticles (AgNPs) in the presence of UV and visible light. Silver nanoparticles have a number of industrial applications due primarily to their antimicrobial properties, but these properties pose an environmental threat. AgNP's can directly disrupt sensitive ecosystems by harming bacteria. Consumption of AgNPs results in silver ions entering waterways; the presence of silver ions raises the question of whether nanoparticles can reform in environmental waters.

As our data show, AgNPs can form from the reaction of silver nitrate and humic acid in the presence of UV and visible light. In order to better understand the role of different species in the AgNP growth mechanism, the effects of additives on the growth rate of AgNPs was monitored by UV visible spectroscopy. The evolution in time of nanoparticle size was monitored by dynamic light scattering (DLS) and transmission electron microscopy.

COLL 281

Nanoparticle system based on tripeptide oil in water emulsion to deliver Au nanocrystals and taxol for cancer therapy

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Taxol-based therapy is used for the treatment of many types of cancers, including breast, ovarian, or lung tumors. Although the effectiveness of taxol, the antimicrotubule agent, is high, its low aqueous solubility limits the dosage. The goal of this study is to develop a nanoparticle (NP)-based system for delivery of taxol at high dosages to address this limitation. Our work explores oil in water nanoemulsions stabilized with self-assembling tripeptide DFF as a platform to encapsulate taxol. The size of NPs was confirmed with transmission electron microscope and ranges from 250 to 600 nm, depending on the oil to DFF ratio, with low polydispersity of 0.11. The efficiency of taxol encapsulation was determined to be 1.5 mg per 787 mg of oil. Stable NPs can be synthesized in different temperatures ranging from 37 to 70°C in phosphate buffer. In addition, the NP platform can be modified to include gold nanocrystals (AuNCs), which offer dual modality applications. In vitro studies are underway to determine the NP's biological activity. In parallel studies we explore the DFF stabilized AuNCs for mRNA delivery. To that end, we synthesize water soluble AuNCs with positive surface charge using variety of polymers. The mRNA is immobilized on the AuNCs's surface via electrostatic interactions between positively charged amine groups on the polymer and negatively charged phosphate groups of mRNA. Most importantly, the synthesis of DFF stabilized AuNC-mRNA proceeds at 4°C, which prevents mRNA degradation. The in vitro studies are underway to determine the transfection efficiency of the DFF-AuNC-mRNA NPs. This system could potentially find applications in NP-mediated delivery of mRNA for therapeutic genome editing using CRISPR technology.

COLL 282

Decoupling mechanisms of palladium nanoparticle synthesis on a biotemplate

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Monitoring the adsorption of chloro-palladate species and reduction of the palladium ions on biotemplates (TMV and BSMV) is crucial to elucidating the mechanism by which

palladium nanoparticle form and coat the virus surface. UV-Vis spectroscopy, X-ray absorption spectroscopy, transmission electron spectroscopy and Ultra- and Small-Angle X-ray Scattering are used to study the adsorption, reduction processes and coating of palladium on the virus surface. The rates of adsorption and reduction are also determined. Furthermore, adsorption equilibria of the chloro-palladate ions and the rate of reduction of the palladium ions is affected by the concentration of “free” chloride ions. The reduction of the Pd ions was mediated by the presence of the viruses and the rate of reduction increased with an increase in temperature.

COLL 283

Direct correlation of atomic structure and emission dynamics in single colloidal core/shell nanostructures

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Colloidal preparations of nanostructures give rise to variations in the structure and photo-physics of individual particles, even for the best syntheses. Engineering ideal structures requires examining these variations at the single particle level. To this end, we have developed a methodology to unambiguously correlate the structure, composition and optical properties of the same nanostructure. Here, we explore the correlation of single dot-in-thick-shell and dot-in-rod core/shell morphologies. Such core/shell hetero-structures are of interest as LED down converters, luminescent concentrators and single-photon emitters. The correlation of shape, lattice defects, core locations and emission dynamics is presented for these nanostructures.

COLL 284

Effect of fluctuations on excited state rates in core/shell quantum dots

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Colloidal semiconductor quantum dots have received significant interest and attention due to their increased photostability, tunable, sharp, and bright emission profiles and their solution processability. For these reasons, they have been used as phosphors in displays and as probes for bioimaging. These applications require tuning the radiative and nonradiative rates such that radiative recombination dominates. This is often achieved by addition of an epitaxial shell to reduce the nonradiative rate. Addition of a

shell also directly impacts the radiative rate. For this reason, understanding the radiative rate upon shell growth is of interest. Previous studies have primarily treated the core and shell material statically in determining the excited state properties. By combining temperature-dependent transient photoluminescence measurements with atomistic simulations we demonstrate that nuclear fluctuations within the quantum dot can significantly alter the radiative rate in CdSe/CdS quantum dots. We show that nuclear fluctuations can result in local and transient trapping of primarily the electron close to the interface between the core and the shell materials. This results in a decrease of the radiative rate, which we show to be dependent on both the core and shell dimensions of the quantum dot. These findings are significant because it suggests that fluctuations can play a significant role in determining excited state properties of quantum dots and suggests that a statistical treatment is necessary to fully capture excited state dynamics in colloidal quantum dots.

COLL 285

Adsorption and decontamination of alpha-synuclein from medically and environmentally-relevant surfaces

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Alpha-synuclein is an amyloid protein which has been implicated in the development of Parkinson's disease. Recently, concerns over medical instrument decontamination have motivated an interest in α -synuclein attachment to surfaces. In this study, we evaluated adsorption and desorption of α -synuclein to two surfaces: stainless steel and a gold surface coated with a 11-Amino-1-undecanethiol hydrochloride self-assembled-monolayer (SAM). Attachment of α -synuclein was investigated using *in-situ* combinatorial quartz crystal microbalance with dissipation and spectroscopic ellipsometry. Increased α -synuclein adsorption was observed onto the charged SAM surface (maximum areal mass 394.91 ng/cm²) when compared with the stainless steel surface (maximum areal mass 131.38 ng/cm²). We determined that after attachment, introduction of a 1N NaOH solution could completely remove α -synuclein adsorbed on the stainless steel surface while a small amount α -synuclein still remained on the SAM surface. When the concentration of α -synuclein in the influent solution was increased from 10 μ g/mL to 100 μ g/mL, the areal mass adsorbed to the stainless steel increased from 85.91 ± 3.23 ng/cm² (95% CI [79.45, 92.37]) to 134.91 ± 0.21 ng/cm² (95% CI [134.5, 135.3]). Dynamic Light Scattering data showed that larger α -synuclein fibrils were likely preferentially attached to the stainless steel surface. Our results suggest that 1N NaOH is an effective decontaminant for medical surfaces and that larger α -synuclein fibrils are preferentially attached to stainless steel surfaces. Increased α -synuclein attachment was observed on the charged SAM surface, and residual α -synuclein was

observed after treatment with 1N NaOH, indicating incomplete decontamination of this surface.

COLL 286

Effects of ice-binding proteins from cold-adapted insect *Tenebrio molitor* on calcite crystallization

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The formation of sparingly soluble and insoluble inorganic salts (i.e., scale deposits) is a major problem for industrial and domestic water transportation. To control scale deposits, chemical scale inhibitors are commonly used. Commercial antiscaling agents include polyelectrolytes that dissociate phosphonates, carboxylates, and sulfonates anionic groups. However, it is imperative to identify highly efficient polymeric inhibitors and environmentally friendly antiscalants, in particular, to replace phosphonate inhibitors due to their environmental risks. Certain polypeptides with charged groups have been extracted from organisms and found to efficiently control the nucleation and crystallization of minerals. Their structures are attractive models for better understanding the inhibitor-mineral interactions and designing next generation antiscalants. Ice-binding proteins or antifreeze proteins (AFPs) from cold-adapted organisms (e.g., fish, insects, and plants) can bind to specific ice surfaces, thereby inhibiting the nucleation and crystallization of ice. AFPs can also control the crystallization of some non-ice like compounds by interacting with the crystalline surfaces of these compounds. We correlate the charge and molecular properties of the polyelectrolytes with their efficiencies in inhibiting the scale crystal formation. A beetle AFP from *Tenebrio molitor* (TmAFP) having regular spaced charged residues on its surfaces is prepared and studied here. Calcium carbonate (CaCO_3), a common scale deposit, is a scalar of interest in this study. We investigate the effects of TmAFP on the formation of CaCO_3 . Our results show that the presence of TmAFP inhibits the formation of CaCO_3 resulting much fewer and smaller CaCO_3 crystals. The achieved CaCO_3 crystals in the absence and presence of TmAFP are both characterized to be calcite using Fourier transform infrared (FTIR) spectroscopy and mass spectrometry (MS), which suggests that the presence of TmAFP does not change the polymorph of CaCO_3 . By analyzing the charged residues on the surfaces of TmAFP and calcite surfaces, we propose that TmAFP may affect the formation of calcite via adsorption to the crystalline surfaces of CaCO_3 . This study provides better understanding for scale control as well as new designs for green antiscalants.

COLL 287

Characterization of ordered naphthalene diimide films deposited in soils substrates from floating films at the air-water interface

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Naphthalene diimides (NDIs) have shown promise as n-type semiconductors in numerous organic-electronic applications where controlled molecular packing is critical for effective function. The controlled development of highly-organized, 2-D assemblies of NDI thin films at the air-water interface and subsequent film deposition onto solid substrates have been investigated. A Langmuir-Blodgett trough was successfully employed to control the film morphologies at the air-water interface, as established by analysis of deposited NDI thin films. Film morphologies and molecular alignment were studied via optical transmission microscopy, atomic force microscopy and x-ray crystallography.

COLL 288

Investigations of cationic gemini surfactants by NMR relaxation and diffusion

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Ionic gemini surfactants adopt various aggregation morphologies that depend on the structure of the surfactant, surfactant concentration, and both the identity and concentration of counter ions in solution. Variation of these properties can yield dramatic changes in micellar aggregate behavior, which are not readily predictable. The Critical Micelle Concentration (CMC) and sphere-to-rod transition of several cationic gemini surfactants, alkanediyl-alpha-omega-bis(dodecyldimethylammonium) bromide, 12-n-12 2Br, with n = 2, 3, and 4, were studied using the NMR parameters of chemical shift, relaxation, and pulsed-field-gradient diffusion. The calculated CMC values from chemical shift, relaxation and diffusion were lower than published literature values using other techniques like tensiometry, fluorescence, etc. The relaxation measurements yielded the lowest CMC values and were especially sensitive to the sphere-to-rod transition. A variety of probe molecules were explored to report micellar surfactant self-diffusion in these ionic gemini surfactants, and studies were extended to the single chain analog and other common surfactants. These non-polar probe molecules are necessary to distinguish between diffusion of the micellar aggregate and the measured surfactant diffusion value because the micelles are in dynamic equilibrium with the free surfactant in solution. The ability of probe molecules to accurately report diffusion of the micelle is dependent on the octanol/water partition coefficient. Partition coefficients of 5.5 or greater provided the most accurate value for diffusion of the micelle, although the probe may not be necessary if the concentration of surfactant is 15-30x the CMC. Overall, NMR measurements are a suitable method for characterizing the CMC and sphere-to-rod transitions, and the performance of various probe molecules depends on the partition coefficient of the probe.

COLL 289

Modular approach for the attachment of protein domains to the exterior of the P22 virus-like particle scaffold

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Virus like particles (VLPs) have come under intense interest in the past decade for use in constructing advanced nanomaterials for a range of applications. Interest stems from their unique size, typically in the 10-100 nm range, and often homogeneous structures formed via biologically encoded assembly of proteins into regular, well defined structures. The size of VLPs make them particularly attractive for biomedical applications, where they can easily travel through circulatory systems and readily enter cells. The P22 VLP derived from the *Salmonella typhimurium* bacteriophage P22 has been shown to be a very robust and versatile VLP platform among VLP systems reported to date. To expand the capabilities of utilizing the P22 VLP as a platform for constructing nanomaterials, developing modular methodology for the modification of the exterior of the P22 VLP is desirable. Decoration of the exterior with protein domains could be used to attach protein domains which can direct assembly of higher order VLP materials in a specified manner, incorporate new catalytic or functional activities, and integrate immune stimulating antigens for constructing immunotherapeutic materials. The research presented here examines a modular approach for the covalent attachment of large proteins/protein domains to the exterior of the P22 VLP. The strategy is to exploit the C-terminus of P22 CP as an attachment site for large proteins by utilizing sortase mediated ligation to form a covalent peptide bond between the exposed P22 CP C-terminus and proteins of interest engineered with N-terminal poly-glycine tags. For the studies presented here, the attachment of two different proteins to the P22 VLP were examined, green fluorescent protein (GFP) and the head domain from the influenza hemagglutinin protein (HA_{head}). GFP provides a useful protein for visualizing attachment to the P22 VLP surface for verifying proof of concept and attachment of HA_{head} shows a modular approach that is able to incorporate immunostimulating antigen. Results show effective cross-linking of N-terminal poly-glycine containing proteins for external display of proteins from the P22 VLP platform.

COLL 290

Zinc chalcogenide nanostructures as flame retardant coatings

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Fires cause approximately 1.3 million accidents annually that result in 3,257 deaths, 15,775 injuries and an estimated \$11.6 billion in direct property losses. Flame-retardant materials play an increasingly important role in reducing or preventing damage caused by fires. Organo-halogen, phosphorus, and nitrogen-containing compounds are among the different types of fire retardants developed in the past several decades. In this

study, we report that ZnO and ZnO/ZnS core/shell microparticles and nanorods show promising behavior as flame-retardant materials when coated onto cotton fabrics. Properties such as heat release rate, total smoke release and mass loss rate of the materials were tested using a cone calorimeter. ZnO and ZnO/ZnS nanorods were able to reduce the heat release rate and total smoke release from 117.77 kW/m² and 18.3 m²/m² to about 70 kW/m² and 6 m²/m², respectively. ZnO and ZnO/ZnS microparticles reduced heat release rate and total smoke release to 100 kW/m² and 13 m²/m², respectively. Zinc chalcogen coatings show promising flame retardant properties while being cost-effective, environmentally friendly and reproducible.

COLL 291

Preparation of nitrogen enriched hierarchically nanoporous carbon from polybenzoxazine precursor for CO₂ capture and storage

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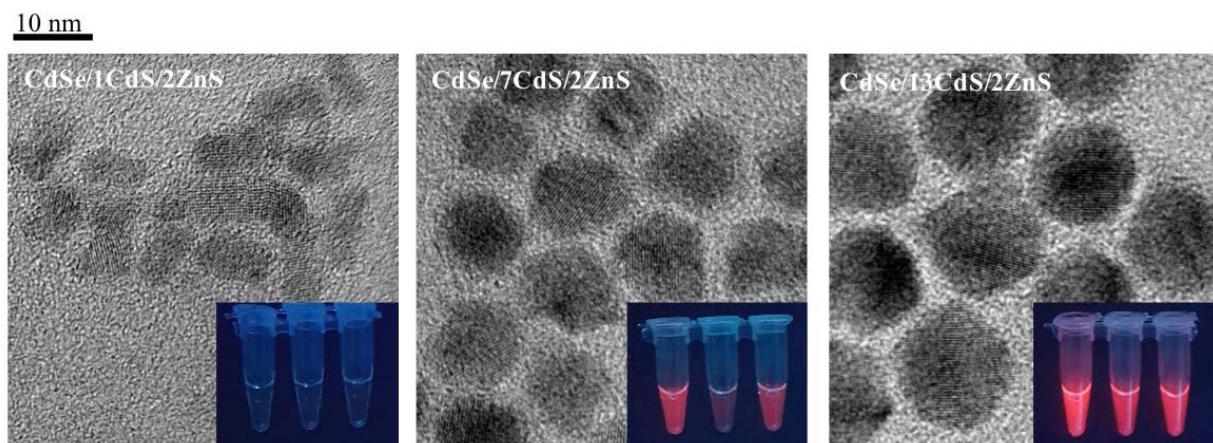
Recently, developing efficient methods for carbon dioxide capture and sequestration has attracted much attention because of a series of environmental problems, such as global warming issues and the rising of sea levels. Adsorption by porous carbons, especially by nitrogen-enriched porous carbons shows great potential to reduce the cost, save energy, and avoid additional environmental problems. It was found that nanoporous polybenzoxazine which was synthesized from Bisphenol-A, formaldehyde and tetraethylenepentamine (TEPA) showed CO₂ adsorption at 30 °C around 3.5 mmol/g with a high BET surface area of 943 m² g⁻¹. In this study, bisphenol-A, formaldehyde and melamine were used as a polymer precursor. Nanoporous polybenzoxazine was prepared via a sol-gel process. The resulting cryogel showed many advantageous properties, such as interconnected pore structure, molecular design flexibility, excellent thermal stability, high char yield, no need of catalysts or additives, no generation of byproducts, high surface area, high pore volume, high porosity, and near-zero shrinkage upon polymerization. The CO₂ adsorption capacity of this nanoporous melamine based polybenzoxazine would be compared with that of TEPA based nanoporous polybenzoxazine.

COLL 292

Giant Nanocrystal Quantum Dots (gNQDs) as Förster Resonance Energy Transfer (FRET) donors

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Semiconductor core/shell quantum dots (QDs) are effective Förster resonance energy transfer (FRET) donors due to their bright and photostable fluorescence. QDs with thick semiconductor shells, also known as ‘giant’ nanocrystal quantum dots (gNQDs) have previously been shown to exhibit reduced blinking and enhanced chemical stability compared to traditional QDs. We further quantify their benefits, including increased brightness and reduced loss of quantum yield (QY) after ligand transfer, and weigh these advantages against the disadvantage of increased donor size in a FRET system. Our findings show that the molar extinction coefficient is augmented by an order of magnitude when increasing shell thickness. While FRET efficiency decreases as QD size increases, the dramatically increased brightness of gNQDs allows for detection of lower sensor concentrations. Furthermore, we establish an optimal shell thickness that is bright and efficient enough to monitor changes by eye, demonstrating potential utility in digital (YES/NO) point-of-care diagnostic devices.



TEM images of thin (left), medium (middle), and thick shelled (right) QD donors. Insets show each donor used as an enzymatic cleavage test sensor. Tubes show QDs only (left), QDs+peptide: FRET sensitized QD quenching (middle), QD+peptide+enzyme: QD emission recovery (right). Sensor concentration for all tubes was 25nM and acceptor to donor ratios were 24. The amount of enzyme added was 1nmol.

COLL 293

Advances in correlating the optical and structural behavior of single quantum dots

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A new technique which uses an ultrathin silicon dioxide imaging platform allows for detailed determination of the structure, chemical composition, and optical properties of a single nanostructure. This technique has permitted direct identification of both optimal

and sub-optimal quantum dot structures within the ensemble – providing information that can be used in conjunction with decades of synthetic knowledge to accelerate development of viable quantum dot technologies. By using this advanced characterization method, a variety of structural and chemical properties (such as crystal structure, spatially precise chemical composition, and shape) can be correlated with a chosen optical performance metric (fluorescence quantum yield, fluorescence lifetime, biexciton quantum yield, etc.). Exploration of this parameter-function space is providing insight into quantum dot development that would otherwise be unattainable.

In this presentation, we will discuss recent developments in structure-function analysis for single quantum dots, with an emphasis on “giant” thick shell colloidal quantum dots. We have performed extensive analysis of correlated optical and structural data for green-emitting nonblinking “giant” quantum dot syntheses. Through this comprehensive investigation, we have expanded the current library of “dark” quantum dot structures, enhancing the scope of understanding of material defects that make a single quantum dot non-emissive. Finally, we have studied behavior of quantum dots in extreme environments and correlated this behavior with quantum dot structure.

COLL 294

Potential of indium tin oxide nanoparticles to produce reactive oxygen species in environmental systems as a result of Sn level and location

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Indium tin oxide (ITO) is a semiconductor that is highly transparent to the visible light wavelengths, resistant to high temperatures, and easily deposited as a thin film. These properties of ITO have led to its wide use in applications requiring a transparent, conductive coating, including LCD and touch screens, window de-icing coatings, and smart windows. This study attempted to elucidate the potential for production of reactive oxygen species (ROS) and their associated cytotoxicity by indium tin oxide nanoparticles (nITO) in environmentally relevant conditions. Spherical nITO of size <10 nm were synthesized with Sn-dopant levels of 5, 8, and 10 % by mass with two different conformations: uniformly-distributed Sn and surface-segregated Sn. The synthesized nITO were characterized in the following ways: size and shape were confirmed by HR-TEM, Sn-distribution and optical bandgap by UV-vis-NIR spectroscopy, aqueous stability and aggregation kinetics by SLS and DLS, and electronic bandgap and flat-band potential by cyclic voltammetry and electrochemical photocurrent measurements of deposited nITO. Electrochemical results suggest that nITO can produce (ROS) upon illumination by UV light in aqueous systems, which could contribute to cytotoxicity through oxidative stress and/or lysing of cell membranes. Generally, a uniform distribution of Sn in the nITO lattice is expected to lower electronic bandgap energies, which should result in higher ROS-production potential than nITO particles with the

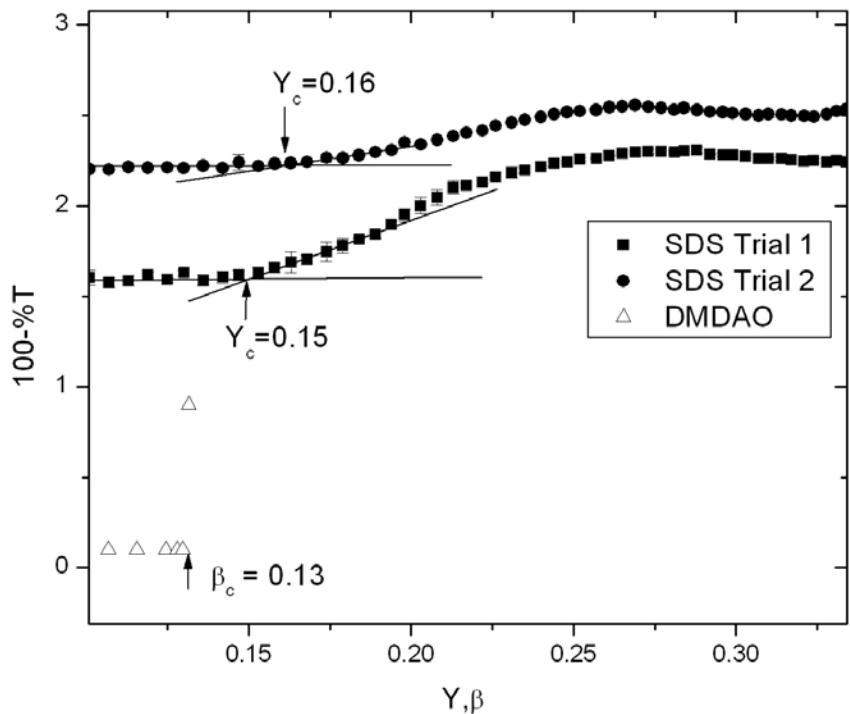
same dopant level of surface-segregated Sn. Expanded bandgap energies determined for both uniform- and surface-segregated Sn dopant are dependent on St content; a maximum band gap energy was observed for each case. The results provide guidance for optimizing St dopant amount and conformation to reduce toxicity of nITO.

COLL 295

Effect of micelle polydispersity on first order phase transitions in polyelectrolyte-colloid systems

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Charged micelles interact strongly with oppositely charged polymers to form soluable complexes. The surface charge density of micelles are able to be varied to a great extent which makes them a great model for the interactions of polyelectrolytes and oppositely charged colloids. Two systems were considered in this study, firstly, the cationic micelle composed of dimethyldodecylamine oxide (DMDAO) associated with the oppositely charged polyelectrolyte poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS). The other system consists of mixed micelles containing the anionic surfactant sodium dodecyl sulfate (SDS) and non-ionic surfactant Triton X-100 (TX-100). Type-1 titrations were conducted for these two systems to observe the abruptness in scattering when the surface charge density is near the critical point. The formation of soluable complexes is thought to be a first order phase transition represented by a discontinuity in the derivative of transmission with respect to surface charge density. This condition is true for micelles constituting of DMDAO, for which the degree of micelle protonation of incipient binding (β_c) is indicated by a sharp increase in scattering. However, in cases with mixed micelles such as SDS/TX-100 the abruptness of the phase transition is spread over a wide range of Y, or mole fraction of SDS. It appears that this phenomenon is due to micelle polydispersity with respect to surface charge density.



COLL 296

Modification of magnetite nanoparticle surface through Sn₂ substitution of the hydroxide functional group with a chloride group

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In areas like medicine, environmental remediation and catalytic reactions, nanoparticles with magnetic characteristics are frequently used. Ferric magnetites (Fe_3O_4) covered with sodium oleate result in nanoparticles with a range of 83nm-95nm. These reactants form a carbon-carbon double bond which is oxidized with potassium permanganate (KMnO_4) and transformed into carboxylic acid. The diameter of the nanoparticles decreased in size after being oxidized which presented the range of 68nm-77nm. Two methods were utilized to modify the oxidized surface. The first method employed thionyl chloride while the second method used hypochloric acid. In both methods, the chloride ion was used in excess to substitute the carboxyl functional group for a chloride group in the modified surface magnetite. Analytic techniques like infrared spectroscopy and x-ray diffraction were used to determine functional groups in the surface and its crystalline composition. The magnetic properties of the nanoparticles were determined by magnetic saturation. Using thionyl chloride, the infrared displayed the presence of the

chloride ion in the surface with a frequency of 673.23cm^{-1} while the Hypochloric acid was 570.39cm^{-1} .

COLL 297

Asymmetric silica encapsulation toward colloidal Janus nanoparticles: Concave nanoreactor for template-synthesis of electocatalytic hollow Pt nanodendrite

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A novel reverse microemulsion strategy was developed to asymmetrically encapsulate metal-oxide nanoparticles in silica by exploiting the self-catalytic growth of aminosilane-containing silica at a single surface site. This strategy produced various colloidal Janus nanoparticles, including Au/Fe₃O₄@asy-SiO₂, which was converted to an Au-containing silica nanosphere, Au@con-SiO₂, by reductive Fe₃O₄ dissolution. Use of Au@con-SiO₂ as a metal-growing nanoreactor allowed templated synthesis of various noble-metal nanocrystals, including a hollow dendritic Pt nanoshell which exhibits significantly better electrocatalytic activities for the oxygen reduction reaction than do commercial Pt/C catalysts

COLL 298

Functional interphases based on peptidomimetic-coated gold surfaces

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Functionalization of interphases with antifouling polymers is essential in the development of materials for biomedical applications. Peptoids, a class of biomimetic peptides, have shown great antifouling properties and high resistance to degradation. Here we propose to design peptoids of various architecture and carbohydrate composition to investigate the application of peptoids as non-fouling polymers on gold surfaces.

Quartz crystal microbalance with dissipation (QCM-D) was used to investigate the binding kinetics of terminal thiolated peptoids and glycopeptoid onto gold sensors. The peptoids saturated the gold surface within a few minutes forming a stable monolayer. The grafting density increased with the concentration of peptoids in solution (density of $0.39/\text{nm}^2$). The monolayer provided a non-fouling coating similar to PEG when exposed to a solution of bovine fibrinogen in PBS. Furthermore, the presence of carbohydrate residues on the peptoids affected the hydration percentage and non-fouling properties of the monolayer.

Taken together, our results showed that peptoids could rapidly form an efficient non-fouling monolayer onto gold surfaces. Our findings are essential to reach optimal peptoid compositions on gold nanorods (AuNRs) for therapeutics applications.

COLL 299

pH-responsive Fenton reaction performing polymeric micelles: Applications in anticancer and antibacterial therapy

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Reactive oxygen species (ROS) are a collective term of small, highly reactive oxygen-derived species and radicals, including superoxide anion, hydrogen peroxide and hydroxyl radical and play essential roles in living organisms. However, its overproduction induces oxidative damages to biological molecules in cells, leading to cell death. Cancer cells, compared to normal cells, are under oxidative stress associated with an elevated level of ROS and are more vulnerable to oxidative stress induced by ROS generating agents. Thus, manipulation of the ROS level provides a logical approach to kill cancer cells preferentially, without significant toxicity to normal cells and great efforts have been dedicated to the development of strategies to induce cytotoxic oxidative stress for cancer treatment. Fenton reaction is an important biological reaction in which irons convert hydrogen peroxide to highly toxic hydroxyl radicals that escalate ROS stress. We developed Fenton reaction-performing polymer (PolyCAFe) micelles as a new class of ROS-manipulating anticancer therapeutic agents. Amphiphilic PolyCAFe was designed to incorporate H₂O₂-generating benzoyloxycinnamaldehyde and ferrocene in its backbone and self-assembles to form micelles that serve as Nano-Fenton reactors to generate highly cytotoxic hydroxyl radicals, killing cancer cells preferentially. PolyCAFe micelles could accumulate in tumors preferentially to remarkably suppress tumor growth, without toxicity to normal tissues. The Nano Fenton reactors could also kill bacteria in *P. aeruginosa*-infected mice and significantly increased the survival rate. This study demonstrates tremendous translatable potential of Nano-Fenton reactors as a new class of anticancer and antibacterial agent.

COLL 300

Potential of nontoxic materials to treat dentinal hypersensitivity and promote tooth remineralization

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Dental hypersensitivity is the result of movement of fluid inside dental tubules, small canals inside the dentine layer. Our research aims at the development of new tooth pastes and other dentifrices that will help tubule occlusion. Approaches explored are layer by layer (LBL) deposition, cross-linking, and functionalized nanoparticles. In LBL, positively and negatively charged materials are applied in alternating sequences to tooth samples. Currently, we focus on alginic acid, chondroitin, and chitosan - biocompatible molecules that are known to cross-link with calcium ions and polyanions respectively, or electrostatically interact with one another. Partial occlusion is observed under both mild washing conditions as well as a sonication challenge. Diffusion of calcium ions through the gels formed by the abovementioned materials leads to remineralization of a tooth surface *in vitro*. Observing depth of tubule occlusion via focused ion beam (FIB) and conducting clinical trials are our goals for the future work.

COLL 301

Substitution effects in aniline on electrochromic properties of hybrid flexible device

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Tungsten oxide (WO_3) is one of the most frequently used cathodically colored inorganic electrochromic material because of good stability and long working life. In comparison with inorganic electrochromic materials, conjugated polymers such as polyaniline (PANI) generally display multicolor, faster response speed, higher coloration efficiency as well as easy to optimize their electrochromic features through molecular tailoring. Hybrid devices are a progressive systems with integration of advantage of inorganic material and conjugated polymers. They generally display improved electrochromic performances.

In this study, WO_3/PANI derivatives-based hybrid powders were prepared via an rf rotating plasma modification method. Both WO_3 and hybrid films were deposited onto indium tin oxide (ITO) coated PET films via the electron beam evaporation technique. the morphology and elemental analysis of the hybrid films were investigated using scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX). The optical and electrochromic performance (such as the contrast, coloration efficiency, etc.) of ECDs including WO_3 -PANI derivatives were investigated in comparison with ECD including pure WO_3 films.

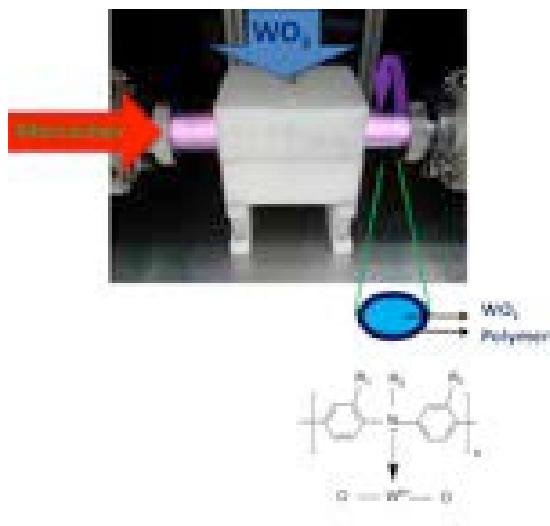


Figure 1. RF rotating plasma process and possible coordination bonds formed between PANI or its substitue derivatives and WO_3 in hybrid powders or WO_3/PANI or its substitute derivatives

COLL 302

Removal of car batteries heavy metals contaminants from aqueous solutions with composite chitosan/alginate coated magnetite beads

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The use of nanoparticles is finding new applications in practically every field of science; nanoscale materials seems to have many possibilities to be integrated for diverse applications related the environment. Magnetic nanomaterials are of great interest due to its interactions with magnetic fields. Using the co-precipitation method in an oxygen free medium, magnetite nanoparticles (Fe_3O_4) were synthesized ranging in diameter from 75nm to 120 nm. Chitosan and alginate are environmentally friendly biopolymers which were incorporated into the synthesized magnetite matrix. These magnetic composite beads were used to remove heavy metals contaminants, specifically those related to the disposal of car batteries such as lead (Pb) and cadmium (Cd). In order to improve the percent of removal efficiency of composite modified surfaces of magnetite nanoparticles selected surfactants such as, caprylyl sulfobetaine and quinine sulfate, were integrated to the synthesis. Sorption test for each modified-surface composite beads were subjected to initial concentration of ~3ppm Pb, and ~2ppm of Cd in water samples. Determination of removal sorption capabilities were measured by inductive couple plasma mass spectrometer (ICP-MS). In addition point of zero charge and attenuated transmittance reflectance-Fourier transform infrared (ATR-FTIR) were used

to define physical properties of the composite. Preliminary results of the removal percent will be available.

COLL 303

Antitumoral activity of (-)-epicatechin loaded chitosan nanoparticles *in vitro* and *in vivo*

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Breast cancer is the neoplasia increased morbidity and mortality in women around the world. The search of new therapeutic strategies against this cancer has focused on natural products, such as polyphenols, specifically flavonoids. In this context, our group has shown that (-)-epicatechin (a flavonoid) has an antiproliferative effect on cell lines of breast cancer. However, flavonoids are molecules prone to degrade when exposed to physical, chemical and biological factors, which limits its activity *in vivo*. Aim: Therefore, we focus on developing (-)-epicatechin loaded chitosan nanoparticles to improve the stability of (-)-epicatechin and to evaluate *in vitro* and *in vivo* antitumoral activity.

Methods: the chitosan and (-)-epicatechin loaded chitosan nanoparticles were obtained by supramolecular self organizing and both were characterized by particle size, zeta potential, polydispersity index (PI) and morphology. The entrapment efficiency and drug loading of (-)-epicatechin were determined by spectrophotometric method. The antitumoral activity *in vitro* was determined in breast cancer cell by MTT assays and the antitumoral activity *in vivo* was determined in syngeneic transplant model cancer in BALB/c mice. Results: We obtained nanoparticles with size of 200 nm, zeta potential negative and IP smaller than 0.2 and morphology was spherical shape. We observed a major antitumoral effect *in vitro* and *in vivo* of nanoparticles with (-)-epicatechin compared with the flavonoid in its free form. Conclusion: The data obtained in this work, suggesting that the (-)-epicatechin loaded chitosan nanoparticles have potential therapeutic values in the treatment of breast cancer.

COLL 304

Morphology-controlled self-assembly and synthesis of photocatalytic nanocrystals

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Abilities to control the size and shape of nanocrystals in order to tune functional properties are an important grand challenge. Here we report a surfactant selfassembly induced micelle encapsulation method to fabricate porphyrin nanocrystals using the optically active precursor zinc porphyrin (ZnTPP). Through confined noncovalent interactions of ZnTPP within surfactant micelles, nanocrystals with a series of morphologies including nanodisk, tetragonal rod, and hexagonal rod, as well as amorphous spherical particle are synthesized with controlled size and dimension. A phase diagram that describes morphology control is achieved via kinetically controlled nucleation and growth. Because of the spatial ordering of ZnTPP, the hierarchical nanocrystals exhibit both collective optical properties resulted from coupling of molecular ZnTPP and shape dependent photocatalytic activities in photo degradation of methyl orange pollutants. This simple ability to exert rational control over dimension and morphology provides new opportunities for practical applications in photocatalysis, sensing, and nanoelectronics.

COLL 305

Morphology-controlled synthesis and metalation of porphyrin nanoparticles with enhanced photocatalytic performance

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The design and engineering of the size, shape, and chemistry of photoactive building blocks enables the fabrication of functional nanoparticles for application in light harvesting, photocatalytic synthesis, water splitting, phototherapy, and photodegradation. Here, we report the synthesis of such nanoparticles through a surfactant-assisted interfacial self-assembly process using optically active porphyrin as a functional building block. The self-assembly process relies on specific interactions such as $\pi-\pi$ stacking and metalation (metal atoms and ligand coordination) between individual porphyrin building blocks. Depending on the kinetic conditions and type of surfactants, resulting structures exhibit well-defined one- to three-dimensional morphologies such as nanowires, nanoctahedra, and hierarchically ordered internal architectures. Specifically, electron microcopy and X-ray diffraction results indicate that these nanoparticles exhibit stable single-crystalline and nanoporous frameworks. Due to the hierarchical ordering of the porphyrins, the nanoparticles exhibit collective optical properties resulted from coupling of molecular porphyrins and photocatalytic activities such as photodegradation of methyl orange (MO) pollutants and hydrogen production.

COLL 306

Investigation into the synthesis and oxidative toxicity associated with colloidal C₆₀ nanoparticles

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Buckminsterfullerene, C60, is a nanoparticle of current interest due to its unique properties and wide range of applications from biomedical uses to the conversion of energy. It is estimated, that roughly 10 tons of buckminsterfullerene is being produced each year. The current disposal method and MSDS follows that of carbon black, due to the lack of environmental and biological impact data for C60. Despite being hydrophobic, when pristine C60 comes into contact with water, aggregation begins to take place to yield hydrophilic colloids, termed *n*C60. Several synthesis methods have been developed, including simply stirring pristine C60 in water open to ambient atmosphere, ultrasonication treatments, as well as several solvent exchange methods. When forming colloidal C60, it has also been found that the oxide adduct, C60O, is necessary in forming the colloids. To evaluate the environmental impacts of *n*C60, several oxidation studies will be conducted. First, using dihydrorhodamine 123 as a fluorescent tag, where we will be measuring oxidation via fluorescence. Second, we will evaluate the product of reactive oxygen species (ROS) using various enzymes. Lastly, in an effort to use *n*C60 as a reagent, we will conduct experiments where we subject the aggregate to a long lipid like chain, and evaluate the modifications via ¹H-NMR. Some of the earlier literature shows that *n*C60 causes oxidative damage, however it has been proven that these results stems from the use of solvents such as tetrahydrofuran in the synthesis method. This present study aims to synthesize colloidal C60 using the various methods above, with and without the use of THF, and conduct the three oxidation studies described. All information and data will be presented herein.

COLL 307

Study on protein conformation and bio-activity of antibodies immobilized on varied nanofibrous membranes

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Biological activity of chemically immobilized enzymes on nanostructured solid supports is determined by chemical structures of functional groups on the solid surfaces, which may affect the conformation of the proteins at varied levels. Thus, control of the protein conformation on the surfaces and interaction between proteins and the solid surfaces play a crucial role in fabrication of biosensors by using immobilized enzymes. Here, we fabricated varied nanofibrous membranes from these polymers, including silica, poly(vinyl alcohol-co-ethylene) (PVA-co-PE), and polystyrene (PS), which have different hydrophilicity and protein compatibility. Then, selected antibodies (Abs) were

immobilized onto these nanostructured polymers via varied polyethylene glycol (PEG) chain lengths and functional groups. Disuccinimidyl carbonate (DSC) demonstrated high interference to conformation of antibodies because of its high reactivity to amine groups on N-terminal of proteins. Cyanuric acid (CC) was found to provide the most stable covalent bonds with the protein and light influence on protein conformation.

Fluorescence spectroscopy, circular dichroism (CD) spectroscopy, attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy and bio-activity to specific antigens were used in determination of bioactivities of the proteins immobilized on the nanofibrous membranes.

COLL 308

Microfluidic multifunctional capacitive sensors using ionic liquid electrodes and CNT/PDMS composites for simultaneous sensing of pressure and temperature

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There are many studies of demonstrating capacitive sensors for various purposes such as detecting pressure, body motions, and temperature variation. However, its performing principle is mainly dependent on physical and geometrical changes of dielectric layers. In this study, we developed a new class of microfluidic capacitive sensors with utilizing ionic liquid serving as electrodes and CNT/PDMS composites (CPCs) as a dielectric layer. The working principle of our microfluidic sensors was investigated with geometrical changes of microfluidic channel and variations of electric double layer (EDL) capacitance. Our microfluidic capacitive sensors showed detection of localized pressure, lateral pressure movement, and even temperature variations with high sensitivity. By using multimodal capability, the microfluidic capacitive sensor was successfully performed as a keypad and applied to a bottle and human skin. This microfluidic capacitive sensors could offer great opportunity of development for future stretchable and flexible electronic devices such as wearable electronics, soft robotics, electronic skin, and human healthcare systems.

COLL 309

Surface modification of conductive polymer thin films by femtosecond laser direct writing

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Conductive polymers have taken very high attention due to the great potential for organic electronics such as organic light emitting diode (OLED), organic photovoltaic (OPV), organic field-effect transistor (OFET) and so on. However, they have some

limitations for the commercial industry because of their inadequate device performances compared to conventional electronics based on inorganic materials. A great deal of methods have been investigated to improve poor conjugated polymer based electronics. Here, We propose tunable and selective areal conductive polymer surface modification method for spin-cast films of poly(3-hexylthiophene)(P3HT):[6,6]-phenyl-C61-butyric methyl ester (PCBM) system by the laser direct writing. Surface embossed structures were induced at a laser fluence below the ablation threshold fluence of the thin film. The electrical properties were measured using conductive AFM and vertical diode devices. Grazing incidence x-ray scattering results revealed that the concentration of face-on P3HT crystals increased dramatically in the laser irradiated region compared to the pristine region of the thin film. The alkyl chains of P3HT polymer in the photo-expanded region were highly aligned along the polarization direction of the laser. The micro-RAMAN spectra confirmed that neither the chemical composition nor the planarity of the conjugated back bone varied after femtosecond laser irradiation. This laser direct writing technique opens a new route to fabricating efficient organic semiconductor devices using a non-contacting non-toxic approach.



COLL 310

Photothermal heating of nanoparticles for activation of initiators for radical polymerization

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The photothermal heating of nanoparticles has been shown to enhance the reactivity for certain thermally initiated reactions. This effect allows for the reaction to occur at much lower bulk temperature and efficiently utilize the energy from the light. This study has undertaken experimentation to test carbon black nanoparticles' ability to photothermally activate a thermal initiator for radical vinyl polymerization. The initiator used was dibenzoyl peroxide and the vinyl monomer was styrene. These were combined with THF and nanoparticles and illuminated while stirring. The resulting mixture is filtered and then analyzed afterwards via gas phase chromatography and NMR. Because the radical resulting from thermal decomposition goes on to initiate vinyl polymer chains, we can use the degree of monomer conversion and length of polymer chains to extrapolate the rate of thermal decomposition. Through this extrapolation significant enhancement in reactivity over bulk heating has been shown. Additionally, the molecular weight distribution of polymers resulting from this process show distinct deviation from the polymers formed through bulk heating. The results indicate that nanoscale heating performed by the nanoparticles uniquely interacts with the bulk system, and elucidates how they may be used to manipulate the resulting distribution of polymers. These findings pave the way for future research for unique applications of photothermal heating.

COLL 311

Ambient STM study of sequentially adsorbed octanethiol and biphenylthiol monolayers on Au(111)

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The mixed monolayer of biphenyl-4-thiol (BPT) and octanethiol are studied at the molecular level using a scanning tunneling microscope (STM) on Au(111) in ambient conditions. The creation of clearly coexisting domains occurs when octanethiol monolayers are immersed in BPT solutions, and is dependent on the concentration of BPT to which the sample is exposed. When coexisting on the surface, BPT and octanethiol form highly segregated domains.

COLL 312

Rotating disk electrode characterization of soluble redox active polymers for use in nonaqueous redox flow batteries

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Nonaqueous Redox Flow Batteries (NRFBs) have potential for greater energy storage than their aqueous counterparts. NRFBs are attractive devices for grid energy storage,

leveling the input from renewable sources such as solar and wind. One of the main problems with NRBs so far has been simultaneously overcoming the low electrolyte conductivity, worsened by low ionic conductivity through ion-exchange membranes, and the large crossover of redox active materials. Our approach to solving these issues is to use a size-exclusion approach, as opposed to charge selectivity, by means of macromolecular charge storage coupled to porous separators. In this manner, the transport of charge-balancing supporting electrolyte species is possible while still maintaining the separation of the redox active species, thus enabling high Coulombic efficiency.

Redox active polymers (RAPs) are poly-electrolytes that can be used as charge storage materials in size-selective NRBs. RAPs have physico-chemical properties that depend on the ionic strength of the RAPs in solution. Therefore, elucidating the mechanisms and kinetics of charge transfer of these soluble macromolecules is imperative in order to produce efficient NRBs. Because of this, RAPs were electrochemically characterized in various solvents at various electrolyte concentrations and analyzed for respective effects on reactivity, polymer structure and film formation. Rotating disk electrode voltammetry is a method of electrochemical characterization of conductive species in solution. Electrolyte concentrations were tested at 10, 100, and 500 mM TBAPF₆ with ferrocene and viologen RAPs used as analytes. Nonaqueous solvents such as acetonitrile, dimethylformamide and propylene carbonate were tested at these varying concentrations. Polymers showed promise in functioning at higher electrolyte concentrations. Higher concentrations of electrolyte could also overcome problems imposed by film creation from adsorption. However, more viscous solvents caused deviation from expected reactivity kinetics.

COLL 313

Synthesis of WS₂ by low-pressure chemical vapor deposition

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Two-dimensional layered transition metal dichalcogenides (TMDs) show great potential in optoelectronics for their characteristic electronic and optical properties. But the synthesis of large-area and uniform film is a prerequisite for device application.

Generally, the isolation of few-layered transition metal dichalcogenides has mainly been performed by mechanical, chemical exfoliation and chemical vapor deposition. Here, tungsten disulfide films were deposited on the surface of silica substrate with low-pressure chemical vapor deposition method. Raman spectroscopy and AFM measurement confirmed that these tungsten disulfide films were uniform and few-layered. This method is more efficient and repeatable than mechanical and chemical exfoliation which is difficult to prepare large-area and uniform film. The influence of temperature, gas flow, pressure and anneal time on tungsten disulfide film growth was studied and the best synthesis condition was determined. This work also provide some

general guidelines for other two dimensional (2D) syntheses of transition metal dichalcogenides(TMDs) .

COLL 314

Effect of substituents on anthracene transmitters on triplet transfer from CdSe nanocrystals

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The mechanism of energy transfer from donor to acceptor is important for various energy applications. Here, a hybrid organic-inorganic upconversion system is investigated, in which energy is transferred from CdSe nanocrystals (NCs) (sensitizer) to the triplet state of a transmitter down an energy cascade to a 9, 10-diphenylanthracene (DPA) annihilator. Then two DPA molecules in their triplet excited states collide with each other during triplet-triplet annihilation (TTA) to emit a photon higher in energy than the incident light.

In order to explore the effect of isomeric substitutions on the transmitter for triplet energy transfer (TET) between NC donor and molecular acceptor, two groups of anthracene isomers have been applied as transmitter. The transmitters are anthracene carboxylic acid (ACA) and anthracene dithiocarbamate (ADTC), with substitutions on the 1-, 2- or 9- positions of the anthracene ring. Each isomeric acceptor is expected to bind in a unique orientation with respect to the NC donor. The upconversion quantum yield (QY) of different isomers and TET rate from CdSe NC to different isomers have been investigated separately using steady photon upconversion QY measurements and ultrafast transient absorption spectroscopy. The photon upconversion QYs show a trend where 9-ACA (12%) > 1-isomers (3%)> 2-isomers (1%)> 9-ADTC (0.1%), which is reflected in the rates of TET where a maximum of $3.8 \times 10^7 \text{ s}^{-1}$ for 9-ACA was obtained. The molecular excited state energy levels were measured both in solution and polymer hosts to relate structure to TET. This work confirms that molecular substitutions on anthracene dramatically affect excited states levels, which in combination with orbital overlap, critically affect Dexter-based TET.

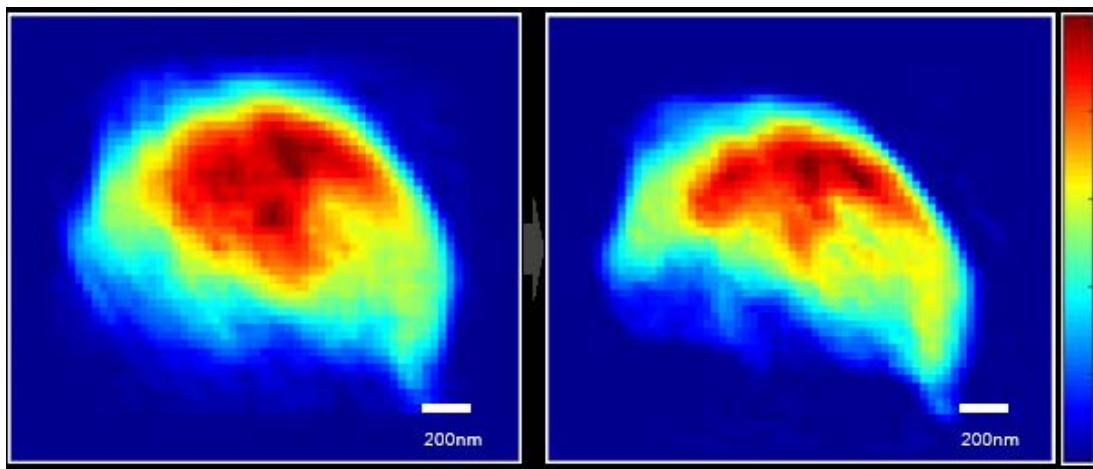
COLL 315

X-ray imaging observation of interfacial changes between epoxy and metal particles during thermal curing

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Epoxy resin is a thermosetting material. A curing process are achieved by reaction of epoxy itself or by reaction with the hardener. many of epoxy require heat about 180°C. During the curing process, chemical reactions occur and the structure of the material changed from a liquid type to a cross-linked solid type. The structure that formed by curing determine the chemical, mechanical properties associated with the degree of curing. The formation of these chemical cross-links induce the volumetric shrinkage. This shrinkage affects to the matrix and eventually the residual stresses are remained in composite structure. The residual stresses could affect to submicron metal particles that exist in the epoxy matrix.

Cu/Ag particles that has a core/shell structure were used to investigate the interface between epoxy and Ag metal, and also between Ag and Cu metal. The metal particles were mixed with epoxy resins, hardener. the sample were measured after 120°C 20 min, and 180°C 40 min. A coherent x-ray diffraction imaging and scanning transmission x-ray microscopy, transmission x-ray microscope (TXM) was used to measure the interfacial changes.



COLL 316

Effects of OH and Cl adsorption on the surface structure of $\alpha\text{-Fe}_2\text{O}_3$: A density functional theory study

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The passive film formed on the surface of iron can protect iron from further corrosion. The dominant structure for the outer layer of the iron passive film formed in alkaline environment is hematite ($\alpha\text{-Fe}_2\text{O}_3$). Chloride has been suggested to play a major role in the depassivation of this passive film under the same conditions but the mechanism of

depassivation is still under debate. The interactions of α -Fe₂O₃ (0001) surface with OH and Cl were studied using density functional theory (DFT) to examine the mechanism of the Cl-induced depassivation. OH is slightly more stable on the surface with strong preference for atop site while Cl is stable on multiple adsorption sites but most stable on atop site. The effects of OH adsorption and Cl adsorption on the surface structure of α -Fe₂O₃ are similar and they are mostly on the first two layers causing an increasing distance between the two layers. Calculations of Cl adsorption at different coverages show that the surface structural effects are localized. The co-adsorption of OH and Cl causes the greatest structural change on the surface and a larger change than the OH and Cl only adsorption at the same overall coverages. The structural changes caused by the adsorption are relatively small suggesting that the adsorption on its own is unlikely to initiate the depassivation process on pristine Fe terminated α -Fe₂O₃ (0001) surface.

COLL 317

Solid-liquid equilibrium of binary mixtures with curved interface

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It is well-known that curved interfaces have an effect on solid-liquid equilibrium (SLE) especially in nanoscale systems. The Gibbs-Thomson equation describes the curvature induced freezing point depression and the Ostwald-Freudlich equation describes the effect of curvature as solute precipitation. In this research, we use Gibbsian composite system approach to rigorously derive the thermal, mechanical and chemical conditions for SLE in a binary system with a curved interface due to confinement in a capillary. We develop equations to calculate the freezing temperature, the precipitation temperature and, for the first time, the eutectic point as a function of solute concentration and radius of curvature. We use the glycerol-water system to investigate the effect of curvature on SLE. The binary system is important in not only for its practical applications, but also is the simplest for theoretical treatment because it renders pure ice and pure glycerol for the solid phase upon freezing and precipitating process, respectively. Here, we develop the composition-temperature phase diagram with the effect of curved solid-liquid interfaces compared with the traditional phase diagram where the interface is assumed to be flat. When the radius of the curvature decreases to nanometers, the freezing point and the eutectic point will shift compared with the flat interface values. Given that understanding binary system is important in chemical engineering, this research on the effect of curvature on SLE phase diagrams will be valuable in food industry, soil science, cryobiology, nanoporous materials and nanoscience applications.

COLL 318

Peptide loaded microgels as antimicrobial surface coatings

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Microgels are weakly cross-linked polymer colloids, which can be made responsive to various stimuli. In the context of drug delivery, microgels are of particular interest as carriers for biomacromolecular drugs, such as peptides and proteins, offering both protection against enzymatic degradation and triggered release. While microgel suspensions are becoming increasingly understood, much less is known about surface-bound microgels. Addressing this, we here report properties of electrostatically triggered surface-bound microgels, as well as their use as delivery systems for antimicrobial peptides (AMPs). In doing so, we investigate effects of microgel charge density, pH, and ionic strength on microgel volume transitions at surfaces, surface-induced microgel deformation and nanomechanical properties, as well as consequences thereof for peptide loading and release, using a battery of experimental techniques, including AFM PeakForce QNM, QCM-D, ellipsometry, and confocal and cryoTEM microscopy.

COLL 319

Coexisting coacervate systems to model aqueous phase separated compartments in biology

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The importance of liquid-liquid phase separation in biological systems has become a major topic of current research, however the underlying forces that govern the behavior of non-membranous liquid organelles (such as the nucleolus, stress granules, PML bodies, etc.) are not completely understood. Complex coacervate systems are an appealing model system for liquid organelles, as they can be composed of similar classes of molecules (e.g. peptides and nucleic acids) and behave similarly to the liquid organelles observed in biology. Through the use of synthetic polymers, model RNAs and peptides we are able to investigate the physicochemical properties of coacervate systems and develop an understanding of the potential mechanisms of liquid phase separation in biological systems. Complex coacervate systems composed of both synthetic and biologically inspired polyelectrolytes yield systems capable of coexisting coacervate phases with unique properties. I will discuss how kinetic trapping can be used to maintain multiple coacervate systems in the same solution simultaneously, outline and identify necessary conditions to assemble and manipulate multiple unique coacervate systems in the same environment.

COLL 320

Responsive nanogels as carriers for antimicrobial peptides

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Due to increasing antibiotic resistance, antimicrobial peptides (AMPs) are receiving considerable attention as potential therapeutics. AMPs are often sensitive to proteolytic activity and therefore require a carrier system for protection and drug delivery. Nanogels are lightly cross-linked polymer colloids, frequently displaying dramatic swelling/deswelling transitions in response to different stimuli. They are of particular interest as carriers for biomacromolecular drugs, such as peptides, since they offer a water-rich environment, thus reducing detrimental conformational changes and aggregation, at the same time providing protection against enzymatic degradation and allowing controlled or triggered release.

We here investigate effects of nanogel charge on AMP loading and release, using a library of poly(ethyl acrylate-co-methacrylic acid) nanogels, investigated with ellipsometry, confocal microscopy, particle size- and z-potential measurements. In addition, membrane interactions of AMP-loaded nanogels are addressed, translating from biophysical studies to investigations of functional consequences, including antimicrobial activity, cell toxicity, inflammation, and proteolytic stability.

COLL 321

Membrane interactions and antimicrobial effects of layered double hydroxide nanoparticles

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Layered double hydroxide (LDH) nanoparticles have the potential to be used as antimicrobial agents and carriers of antimicrobial peptides (AMPs). As with many inorganic nanoparticles, membrane interaction and destabilization is important for the mode of action and critical for the successful use of LDH nanoparticles as therapeutics. By combining AMPs with inorganic nanoparticles, it may be possible to protect the AMPs from proteolytic inactivation something which limits their widespread use.

The use of LDH nanoparticles, as therapeutics, requires a straightforward understanding of membrane interactions and the factors that determine them. We have

investigated the effect of particle size on LDH interactions with both bacteria and mammalian mimicking lipid membranes as well interaction and antimicrobial effect of an AMP/LDH nanoparticle system. Taken together, these findings demonstrate a set of previously unknown nanoparticle behaviors, including dual mode killing/clearance of bacteria and cooperative LDH/AMP membrane activity, of potential therapeutic interest.

COLL 322

Three dimensional (3D) plasmonic hot spot for label-free sensing and effective photothermal killing of multiple drug resistant superbugs

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Drug resistant superbug infection is one of topmost threats to human health for our society. Plasmonic nanoparticles can be used for ultrasensitive bio-imaging and photothermal killing through the amplification of electromagnetic fields at nanoscale “hot spots”. One of the main challenges in plasmonic imaging and photothermal killing is the designing of plasmonic substrate with large number of “hot spots”. Driven by the need, this article reports the design of three dimensional (3D) plasmonic “hot spots” based substrate using gold nanoparticle attached hybrid graphene oxide (GO) which breaks the traditional 2D limitation. Experimental result shows that the 3D substrate has the capability for highly sensitive label-free sensing and it generates high photothermal heat. Reported data using p-aminothiophenol conjugated 3D substrate shows that the surface enhanced Raman spectroscopy (SERS) enhancement factor for 3D “hot spots” based substrate is more than two orders of magnitude higher than the two dimensional (2D) substrate and five orders of magnitude higher than zero dimensional (0D) p-aminothiophenol conjugated gold nanoparticle. 3D- Finite-Difference Time-Domain (3D-FDTD) simulation calculations indicate that the SERS enhancement factor can be greater than 10⁴ due to the bent assembly structure in 3D substrate. Reported experimental results demonstrated that 3D-substrate based SERS can be used for finger-print identification for several multi-drug resistant superbugs with detection limits of 5 colony forming unit /mL. Experimental data show that 785 nm near infrared (NIR) light generate around 2 times more photothermal heat for 3D substrate with respect to 2D substrate and it allows the rapid and effective killing of 100% of the multi-drug resistant superbugs within 5 minutes of 785 nm NIR light exposure.

COLL 323

Asymmetric and multi-compartment polymersomes as structural analogues of eukaryotic cells

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Polymersomes are robust self-assembled vesicular structures that are widely employed in a variety of domains from nanomedicine to artificial cell design. Control over their membrane diffusion properties and structural integrity is crucial for their future development, especially as artificial cell models. Compartmentalization in eukaryotic cells is a crucial feature that allows separation and protection of species as well as simultaneous different enzymatic reactions to take place independently in a confined space with high spatio-temporal control. A number of techniques have been developed to afford structural analogues of eukaryotic cells, namely multi-compartment systems, such as double-emulsion, layer-by-layer assembly, micro-fluidics or phase transfer of emulsion droplets over an interface. Liposomes in liposomes are the first compartmentalized systems that appeared in the literature. More recently, polymeric vesosomes (polymersomes in polymersomes) were developed and used as scaffolds for cascade enzymatic reactions. These complex systems both mimic the structural and functional characteristics of the eukaryotic cell and thus provide a simplified biomimetic model that can serve as a tool for the understanding and the study of the cell properties. The mixing of different biomaterials (i.e. lipids and polymers) is a new attractive orientation that widens the use of vesicular carrier platforms for cell mimicry. We focused our research on designing structural analogues of eukaryotic cells. We developed multi-compartment cell-like systems composed of nano-sized liposomes entrapped in the lumen of giant poly(butadiene)-*b*-poly(ethylene oxide) vesicles. We herein present the first reported liposomes in polymersomes system for temperature-triggered independent release of two encapsulated model drugs. In addition, we present vesicles formed with an asymmetric lipid (inner leaflet) / polymer (outer leaflet) membrane as biomimetic models of biological membranes.

COLL 324

Assessing the influence of oxidizing agents when preparing colloidal spinel-type MgMn_2O_4 nanocrystals

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Spinel-type MgMn_2O_4 nanocrystals represent a promising semiconductor with applications in energy storage as cathode materials for magnesium rechargeable batteries. Presently, thermolysis of complex organic precursors in high boiling point solvents represent the most direct route towards highly crystalline and monodisperse semiconductor metal oxide nanocrystals.

Reports of MnO and Mn_3O_4 nanocrystals exist where researchers start from Mn(II) salts of formates, acetates, or acetylacetones. Above 200 C, Mn(II) is shown to be stabilized by the organic ligand used and MnO nanocrystals are formed. However, at lower temperatures, the decomposition of Mn salts appears to thermodynamically favor the formation of spinel-type Mn_3O_4 , which contains both Mn(II) and Mn(III) states. Synthetic conditions are usually inert and only the oxygen from the salt's anion is expected to contribute to the anion lattice of the product. Atmospheric O_2 has been

used as an oxidizing agent to assist in the formation of spinel Mn_3O_4 nanocrystals at 210 C. Furthermore, while organic salts of Mn(III) exists, no reports exist of its use as a precursor in the production of manganese oxide nanocrystals.

Herein, we report the formation of colloidal nanocrystals of manganese oxide compounds using Mn(II) acetate and Mn(III) acetylacetone precursors in high boiling point solvents of oleylamine and octadecylamine. Following, the influence of molecular and atmospheric oxidizing agents on product composition was investigated as well. Furthermore, post-treatment with magnesium precursors has been accomplished to form nanometric spinel-type $MgMn_2O_4$ cathode for magnesium batteries. Product purity and structural properties was characterized with powder x-ray diffraction and thermogravimetric analysis. Crystal size and morphology was characterized using electron microscopy imaging methods.

COLL 325

Hollow silica particles: Measurement of mechanical stability through mercury porosimetry, and development of a low cost, scalable process for hollow silica

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Hollow silica particles (HSPs) are versatile materials that could find use in many applications, from drug delivery, light-scattering, thermal and sound insulation, etc. Most often, hollow particles are made through silica deposition onto a template, which is often destructively removed through calcination. Designing mechanical stability of hollow particles is important for both the applications where they need to remain intact as well as those where they need to break down. We have made a series of HSPs with increasing wall thickness through a template approach. Mercury porosimetry (MIP) was then used to determine their mechanical stability, which represents the novel use of the technique. The study showcases the ability to design the mechanical stability of hollow particles for a variety of uses.

One of the problems preventing wide use of HSPs lies in their cost as well as extremely dilute tetraethoxysilane (TEOS) conditions under which they are most often made. We have developed a cost-effective method for hollow silica, which rests on using sodium silicate. This atom-economical, inexpensive silica precursor allows for much higher concentration during the template-coating step (10wt% vs. <1wt% for TEOS-based routes). In addition to that, we have used a methyl methacrylate (MMA)-based template that can be thermally depolymerized, thereby opening a possibility of template recycle, without the need for organic solvents. In the present study, 78% of MMA used for template synthesis was recycled from core/shell particles, demonstrating the possibility of making hollow particles under conditions suitable for industrial scale-up without compromising the strict control of their parameters.

COLL 326

Polyampholyte microgels: From molecular design to ionic traps and switches

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Aqueous polymer microgels bearing ionisable groups are functional macromolecular colloidal structures with a strong application potential in drug delivery, biomaterials, adsorbents and coatings. In a large family of polyelectrolyte microgels polyampholyte microgels exhibit extraordinary properties due to the co-existence of oppositely charged groups in crosslinked polymer networks. Such colloids can invert their surface charge or exhibit reversible ionic crosslinks at different pH leading to the strong change in the size, shape and swelling degree.

Present paper will present an overview about synthesis, characterization, functionalization and application of polyampholyte microgels as building blocks for design of functional materials. In particular, different synthesis methods (precipitation polymerization, polymerization in W/O emulsion) were developed that allow application of different molecular reactive building blocks (monomers, macromonomers, crosslinkers) and control the amount and distribution of ionisable groups and charges in microgels. Using controlled synthesis methods microgels with controlled size, narrow size distribution and statistical, core-shell and Janus-like distribution of ionisable groups were synthesized.

The behavior of polyampholyte microgels in aqueous solutions was investigated to understand their properties like swelling/deswelling, charge modulation and colloidal stability. The experimental data combined with theoretical calculations and simulations indicate that amount, distribution and balance between ionisable groups in microgels govern their properties in aqueous solutions.

Ampholyte microgels were used as cargo for the uptake/release of polyelectrolytes and proteins, colloidal templates for the biomineralisation and controlled growth of the CaCO₃ nanocrystals as well as building blocks for design of functional coatings.

COLL 327

Tannin-mediated layer-by-layer assembly of titania nanocrystals for efficient UV-protective colloidal materials

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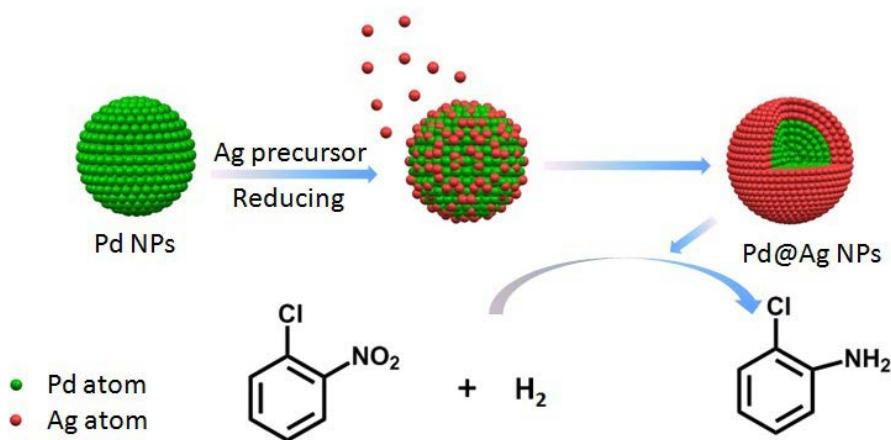
Wide bandgap semiconductors such as titanium dioxide nanocrystals (TiO_2 NCs) have been widely used for a broad range of applications including photocatalysts, cosmetic products, paints, and UV screening materials because of their excellent photostability. However, the structural instability (e.g., aggregation) followed by changes in intrinsic properties and reactive oxygen species (ROS) generated by oxidative chemical reactions when exposed to UV light often limit the utilization of TiO_2 NCs for the practical applications. Here we introduce multi-layered TiO_2 -tannin hybrid colloidal porous materials that can suppress the photochemical generation of ROS. Highly open porous poly(methyl methacrylate) (PMMA) microspheres (*p*-MS) are prepared by a single oil-in-water emulsification and utilized as a support to immobilize TiO_2 NCs. Colloidal TiO_2 NCs are synthesized by a sol-gel method in the presence of a base that accelerates the condensation of hydrolyzed titanium precursors. Tannic acid, one of the polyphenols, is coated onto the surfaces of the *p*-MS in an aqueous milieu, which mediates a spontaneous deposition of colloidal TiO_2 NCs on the surfaces of the *p*-MS by the formation of ligand-to-metal charge transfer complex between tannic acid and TiO_2 . Multi-layered TiO_2 NCs are assembled within the *p*-MS through layer-by-layer (LbL) coatings of tannic acid and TiO_2 NCs, which exhibit excellent UV protection due to the unique porous structures and good dispersity of the hybrid MS without the aggregation of TiO_2 NCs. Furthermore, in a murine model, the hybrid MS exhibit excellent anti-UV skin protection in terms of epidermal hypertrophy, inflammatory infiltrates, and keratinocyte apoptosis without significant long-term toxicity presumably due to efficient scavenging of ROS by tannin. This study suggests that the tannin-mediated LbL assembly can be easily used to develop inorganic-polymer hybrid colloidal materials in an aqueous milieu particularly for a promising UV light screening application against UV-induced ROS.

COLL 328

Size and shell thickness-controlled synthesis of Pd@Ag core-shell nanoparticles for enhanced catalytic hydrogenation performance

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A series of Pd@Ag NPs with well-controlled sizes and structures were successfully prepared by a sequential reduction method. In this synthetic process, we obtained 6 nm Pd NP initially, followed with Ag deposition to form Ag layer. The thickness of Ag layer can be precisely controlled, which led to an adjustable Pd exposure on the surface of the NP as well as tunable catalytic property. The alumina-supported Pd@Ag NPs illustrated a superior selectivity in catalyzing hydrogenation of o-chloronitrobenzene. The enhanced catalytic performance of Pd@Ag NPs possibly originates from the core-shell interaction, which adjusts the electronic state of surface Ag atoms to be suitable for selective o-chloronitrobenzene hydrogenation.



COLL 329

Development of supramolecular particles made from guanosine derivatives to study and modulate the immune system

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Colloidal particles are attractive to study biological systems and to deliver therapeutic agents more effectively. The focus of the work is to continue the development of colloidal supramolecular particles made from guanosine derivatives with the longer-term goal of determining structure-activity relationships aimed at modulating the immune system. We have demonstrated that an imidazole containing 8-aryl-2-deoxyguanosine derivative (8ArG) self-assemble into hierarchical colloidal particles termed supramolecular hacky sacks (SHS). These SHS particles can encapsulate and deliver biomedically relevant cargo like small molecule drugs, fluorescent probes, proteins, and plasmid DNA. Preliminary data demonstrate that the structure of the constituent 8ArG is critical for the biological activity of the SHS. Thus, we have set out to determine what structural features are essential for the latter and how it can be manipulated. This presentation will focus on the synthesis and characterization of a series of isomeric and isosteric 8ArG derivatives, as well as preliminary studies of their self-assembly into their SHS. The characterization of such particles relies on a combination of various techniques like NMR, IR, UV/Vis, fluorescence studies, DSC, and DLS. Furthermore, we will also study how such variations in the structure impact the biological activity (e.g., cellular uptake and trafficking) as well as the immunological activity. We expect these new particles to provide further insight into the potential for developing new delivery agents for DNA vaccines.

COLL 330

Fabrication and characterization of platinum coated with solution processed graphene

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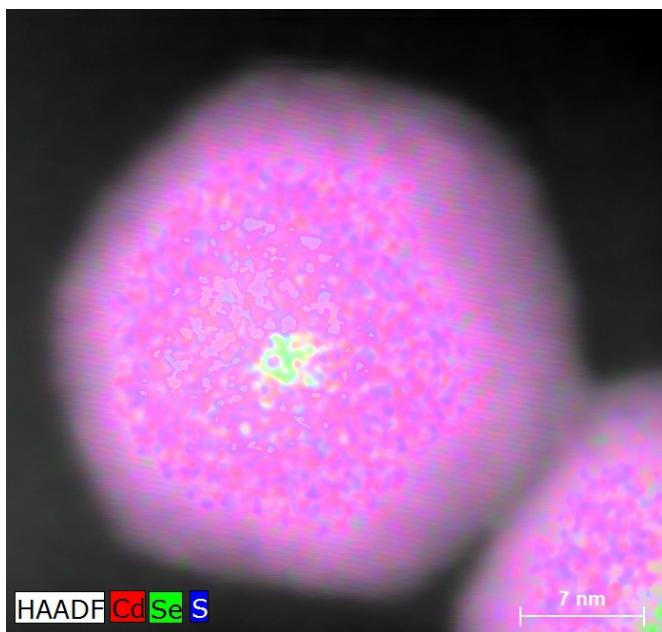
Dye-sensitized solar cells (DSSCs) are an attractive alternative to conventional silicon-based solar cells, largely due to its simple fabrication process and low-cost materials. However, the cost of platinum counter electrode and its dissolution in the I^{3-}/I^- electrolyte are drawbacks of the well-established platinum counter electrode based DSSCs. Graphene is a promising candidate for platinum substitution or coating due to the high surface area, low charge transfer resistance and corrosion resistance. In this work, graphene ink is produced by liquid phase exfoliation of pristine graphite. The Pt counter electrode and graphene ink coated on Pt counter electrode are made by various coating methods. N719 is used as the dye in our devices. The coatings are characterized by scanning electron microscopy and Raman spectroscopy. Performance of the devices is compared under a solar simulator. We find that graphene coated Pt counter electrode based DSSCs show efficiency as high as $1.25 \pm 0.10\%$, with 0.71 V open circuit voltage, 0.358 fill factor and $210.36 \pm 14.38 \Omega$ series resistance. The device efficiency is 6 times ($0.19 \pm 0.05\%$) higher than that of pure Pt electrode using the same device structure. Our results indicate graphene ink have the potential to be a viable, low cost counter electrode material for DSSCs.

COLL 331

Electron microscopy in color: Revealing chemical complexity in emergent nanocrystal systems utilizing advanced STEM-EDS

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Transmission and Scanning Transmission Electron Microscopy have played a critical role in the development of cadmium-based colloidal quantum dots. However, grey-scale images and lattice measurements are insufficient to accurately characterize the complex heterostructures of emergent nanocrystal emitters. The advent of modern energy dispersive spectroscopy (EDS) systems coupled with bright electron sources has greatly enhanced the ability to visualize the chemical composition of nanomaterials with sub-nm resolution. Specifically, the quad-EDS detector design of the Tecnai Osiris enables rapid elemental mapping of colloidal nanocrystals prior to the onset of obvious beam damage. In conjunction with our optical correlation method, we have utilized HRSTEM and STEM-EDS to directly investigate the affect specific chemical and structural motifs have on the individual particles optical properties. Recent results on giant shelled CdSe/CdS, graded alloy CdSSe/CdS and Zn_3N_2 nanocrystals will be presented. Zinc Nitride nanocrystals, a promising earth-abundant fluorophore, pose a significant challenge due to their air and beam sensitivity. Additionally, sample preparation considerations and progress towards STEM-EDS tomography of individual core/shell nanocrystals will be discussed.



COLL 332

Hybrid lipid-coated silver nanoparticles differentially shielded from Ag⁺ release

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The growth in nanotechnology applications comprised of silver nanoparticles (AgNPs) has led to a significant interest in understanding their possible environmental and human health impacts. The diversity of commercially available AgNP products are often proprietary, not well-defined, and undergo rapid surface oxidation and dissolution of Ag⁺, making their assessment difficult to study. Most studies, thus far, have focused on the environmental and biological effect of Ag⁺, which provides a baseline for the potential effects and impacts of AgNPs to organisms and ecosystems. Studies designed to evaluate the effects of AgNPs directly have been limited as they undergo dissolution to Ag⁺. Consequently, there is a gap in our current understanding of the relative contribution of the physiochemical parameters, such as shape, size, and surface coating, on nanoparticle stability, nanoparticle-biological interactions (NBI), biouptake, and ecotoxicity. Given the critical need to identify features of AgNPs over Ag⁺ that induce toxicity and disrupt ecosystems, well-defined AgNPs with tightly-controlled size and shape that can be modified to tune Ag⁺ release is of significant interest. Here we will discuss the design of hybrid lipid-coated AgNPs that are differentially shielded to Ag⁺ release and surface oxidation. We will show that shielded AgNPs can be simulated through the use of long-chained hydrophobic thiols that anchor lipid membranes in a tight packing arrangement to prevent surface oxidation, Ag⁺ release, aggregation, and instability. UV-Vis and transmission electron microscopy studies will show that the thiol-chain length plays a very important role in simulating shielded and unshielded AgNPs. Furthermore, this design strategy can be applied to AgNPs of varying size and shape.

The ability to control Ag⁺ dissolution is important as it has practical commercial implications and allows us to determine the relative influence of Ag⁺ to AgNP on human health and the environment directly to inform risk management decisions.

COLL 333

Gadolinium oxide nanocrystals as T₁ MRI contrast agents: Balancing colloidal stability with surface accessibility

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Gadolinium oxide nanocrystals with a sulfonated polymer coating can be applied as MRI contrast agents. One significant challenge faced in designing a nanocrystal as a T₁ MRI agent, as opposed to a T₂ contrast agent, is the requirement that water must be able to come within several angstroms of surface gadolinium atoms. Successful materials must then possess a surface which both prevents aggregation in biological media and ensures surface accessibility. Here we exploit the plate-like geometry of gadolinium oxide nanocrystals to achieve these two aims. These nanocrystals are formed at high temperature in organic solvents and subsequently phase transferred into biological media using a sulfonic acid co-polymer. The crystals' anisotropic shape provides gadolinium atoms on the thin plate edges which remain uncoated and thus available to water. The relaxivities of these materials are one order of magnitude (15 times) larger than commercial T₁ contrast agents and other gadolinium-containing nanoparticles. The magnetic field dependence of their relaxation rates and the relatively weak size dependence of their relaxivity suggest that inner-sphere water relaxation at the edges of the nanocrystal are responsible for the high relaxation rates. . The nanocrystals show no appreciable in-vitro cellular toxicity even though they are readily taken up by cells and retain their functionality in the intracellular environment. In vivo the nanocrystals have comparable blood circulation life time compared to molecular gadolinium agents and are cleared by the hepatobiliary system. Their cellular uptake enables MRI imaging to be applied to cellular detection as illustrated in the differentiation of non-alcoholic fatty liver disease in mice.

COLL 334

Engineering a thermoresponsive nanogel with a photothermal core for cancer cell specific binding

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Superparamagnetic Fe_3O_4 is a nontoxic near infrared photothermal material that has captured considerable attention. Recently efforts have been made to improve its targeting property for magnetic resonance imaging and thermal therapy. In some cases, targeting is realized by specific binding to certain marker proteins on cancer cell membranes. PNIPAM is one of the most studied thermo responsive polymer. PNIPAM based hydrogels undergo reversible physical changes in response to external temperature stimuli. This feature makes it an ideal candidate for many applications. Among the more promising application is to mimic the function of natural proteins. The interaction between synthetic polymers and proteins mainly depends on a combination of hydrophobic, electrostatic and hydrogen bonding interactions which can be adjusted by changes in the content of hydrophobic and/or charged monomers. In this work we describe superparamagnetic Fe_3O_4 nanoparticles that are coated with SiO_2 then further modified with a NIPAm-based copolymer. The copolymer was designed with intrinsic affinity for Hela cells. The optimization of the nanogel formulation suitable for Hela cell binding and its photothermal behavior will be described.

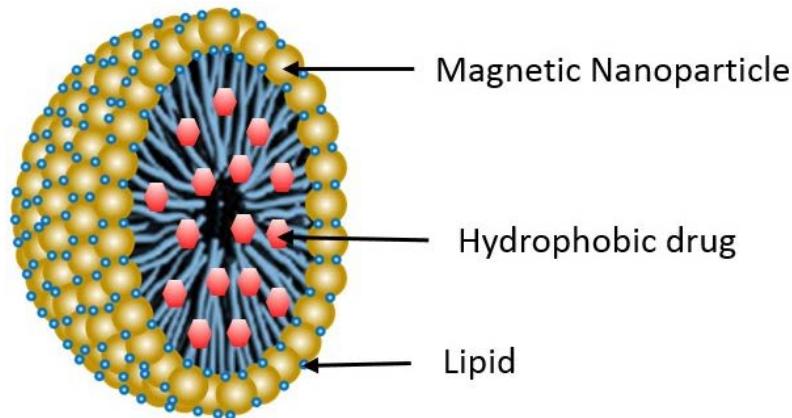
COLL 335

Magnetic nanocapsule: A novel theranostic agent in biomedicine

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Magnetic nanostructures (MNS) have emerged as promising functional probes for simultaneous diagnostic imaging and therapy of cancer, Alzheimer's and cardiovascular diseases. The diagnostic potential of MNS arises from their role in enhancing localized contrast in magnetic resonance imaging (MRI). The therapeutic prospects of MNS stem from thermal activation under external applied radio frequency (RF) field for thermal therapy and/or actuated release of therapeutic cargo at the target site. We report a novel magnetic nanostructure called magnetic nanocapsule (MNC) made of magnetic nanoparticles and phospholipids that provides better contrast enhancement than isolated magnetic nanoparticles and a large hydrophobic core for drug loading. The surface of the MNC is composed of magnetic nanoparticle and lipid heads assembly due to the complementary functional groups while their core is formed of non-polar lipid tails. The hollow core of MNC allowed as high as 50% loading of hydrophobic drug (paclitaxel) and their release was actuated via thermal activation of MNS. Drug loaded MNC were successfully internalized into liver hepatocellular carcinoma (HepG2) cells and resulted in more than 60 % cell death under external RF field. Due to the assembly of magnetic nanoparticles, these nanoconstruct exhibited r_2 relaxivity of $560 \text{ mM}^{-1}\text{s}^{-1}$, 1.5 times higher than r_2 of isolated magnetic nanoparticles and approximately 6 times higher than commercially available T_2 contrast agent Feridex®. The ability to deliver

hydrophobic drugs in addition to enhance MR contrast demonstrates the potential of the MNC as a promising theranostic agent for biomedical applications.



COLL 336

Using molecular dynamics to investigate the effect of intra- and inter-strand hydrogen bonding on sequence-chirality specific adsorption of single-stranded DNA (ssDNA) onto Single-Walled Carbon Nanotubes (SWCNTs)

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The unique structural, optical, and electronic properties of single-walled carbon nanotubes (SWCNTs) lend themselves to a breadth of potential applications. However, a difficulty in realizing widespread use of these materials is the polydispersity of samples in terms of size, chirality, and handedness due to the uncontrolled nature of current synthesis techniques. Numerous separation techniques with related protocols have been developed for use on SWCNTs. Most protocols involve adding surfactants to suspend the tubes in an aqueous media before using techniques such as ion-exchange chromatography (IEX) or aqueous two phase extraction (ATPE) to separate the SWCNTs based on their physiochemical properties. Single-stranded DNA (ssDNA) has proven to be an effective dispersant that exhibits sequence-chirality specific binding behavior. Experimental work has displayed the ability to exploit this specificity to tune the separation for particular nanotube chiralities. However, the mechanism that leads to optimal ssDNA-sequence/ SWCNT-chirality pairs is not understood and the search for further successful pairs requires lengthy trial and error studies. In this study, we are using replica exchange molecular dynamics (REMD) simulations to compare the adsorption of experimentally determined optimal and unfavorable sequence-chirality pairings as a means to determine the factors that lead to optimal binding. Our studies show that all ssDNA sequences adsorb on the SWCNT surface and form a network of intra- and inter-strand hydrogen bonds. However, the nature of the binding network that forms is unique for different pairings and can be roughly cast into the categories of stabilizing, non-stabilizing, and destabilizing. Current work is focused on developing quantitative measures that describe the binding process to clearly identify these

categories. These investigations work towards our ultimate goal of providing better insight into the sequence-chirality specific binding mechanism, and eventually developing a model that allows for the prediction of other pairs leading to the efficient sorting of a desired nanotube chirality.

COLL 337

Chiroptical responses of helical arrays of plasmonic nanoparticles around anisotropic nanopillars

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Chiral plasmonic nanomaterials present preferential interactions with circularly polarized lights originated from their geometries in mirror. Recently substantial efforts have been made in the area of synthesis of such materials, however understanding of chiroptical responses from these complicated structures were not fully understood yet. In this work, we examined the model structures with helical arrays of plasmonic nanoparticles with presence of anisotropic nanopillars at center. In previous studies, the anisotropy of nanopillars was typically ignored due to complexity. We investigated the chiroptical responses of such models with variance of anisotropy in nanopillars based on the calculation via finite elements method (FEM). The results show that the anisotropy of center nanopillar can have significant effects on the chiroptical response of overall chiral nanostructure. Calculated circular dichroism (CD) spectra can be changed into opposite sign in the specific conditions of negative birefringence. In addition, we could observe that, when refractive index of anisotropic pillars are large enough > 2.5 , the chiroptical responses can be significantly enhanced by 17 times in maximum. At last, the optical properties of surrounding media can effectively shift the peak positions and the magnitudes in the CD spectra. Our calculations show the significance of anisotropy, which has not been conceived as important parameters. We believe that this work will deepen the understanding of chiroptical responses in the area of chiral nanomaterials and further will help to pave the way toward various applications such as optical devices, biosensors, and chiral catalysis.

COLL 338

Solution-processed photovoltaic devices utilizing Semiconductor Excitonic Nanoshells (SENS)

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Excitonic solar cells represent a promising technology for low-cost production of renewable energy. Fabricated from “soft” materials, such as organic molecules or colloidal quantum dots, these devices offer unique advantages that are not found in first or second generation photovoltaics. Of a particular benefit are the tunable band gap of excitonic absorbers and the solution-phase deposition of the device active layer. The appeal of this technology, however, is compromised by the poor electrical conductivity of solution-cast films. Limited by the small size of excitonic colloids, the electrical transport in nanostructured solids occurs via tunneling or “hopping” of photoinduced charges, which strongly impedes the electrical flow to electrodes. To mitigate this issue, we have explored a novel class of solution-processed solar cells which enable a high electrical conductivity in the excitonic absorber layer. The core of the innovation lies in the unique geometry of colloidal nanocrystals which channels the motion of electrons and holes into the shell domain of a composite nanostructure. As a result, the quantum behavior of electrical charges can be achieved even in large-diameter semiconductor nanoparticles. A larger “grain” size promotes a faster and more extended diffusion of charge carriers, which should ultimately lead to an improved charge extraction from the photovoltaic film.

COLL 339

Hybrid nano-antibacterials to control biofilm-associated infections

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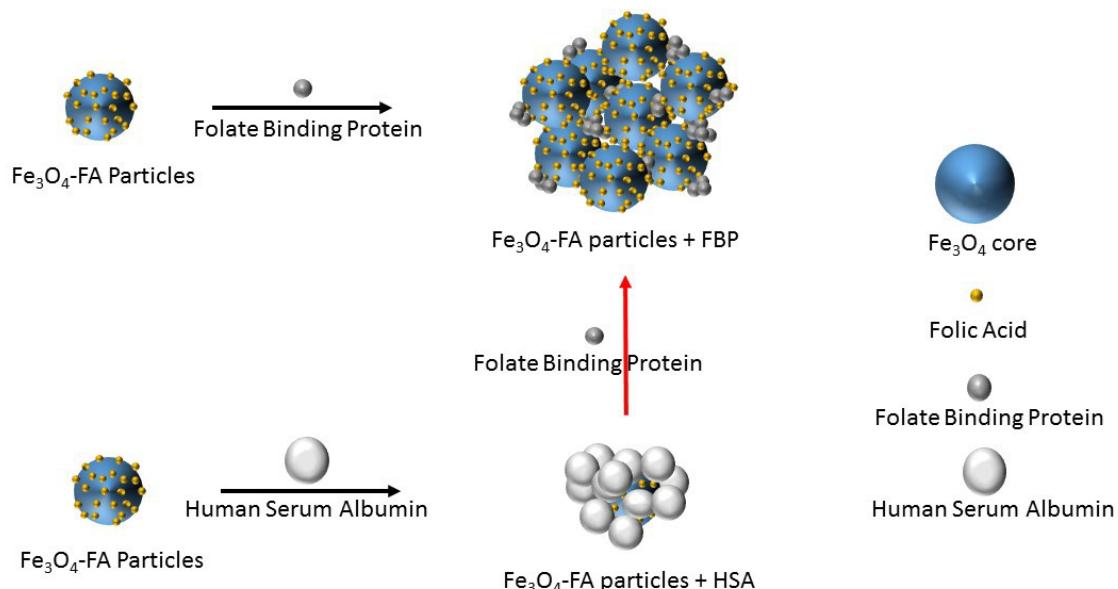
The emergence of drug resistant bacterial strains is one of the most serious problems in modern medicine and the difficulties in finding new antibiotics make it even more challenging. The increasing resistance of bacteria in the form of both planktonic cells and biofilms established on medical devices calls for novel antibacterial strategies for the prevention and treatment of bacterial diseases. In this study, the efficiency of the commercially available antibiotic gentamicin was synergistically enhanced via the combination of two innovative strategies: i) attenuation of bacterial virulence by enzymes interfering with bacterial quorum sensing (QS), and ii) ultrasound-assisted nanotransformation of the antibacterial agent. Nanospheres of gentamicin alone were able to inhibit the growth of Gram-negative *Pseudomonas aeruginosa* by 2 logs, but did not show a potential to affect the bacterium drug resistant biofilm phenotype. On the other hand, the sonochemically generated hybrid nano-antibacterials comprising gentamicin and QS inhibiting acylase enzyme completely eradicated *P. aeruginosa* in both free floating and sessile forms. These nanospheres were also shown to penetrate within a Langmuir monolayer, composed of bacterial membrane phospholipids, confirming their capacity to interact and consequently disrupt bacterial cell membrane. The obtained hybrid nano-antibacterials with complimentary modes of action were not found innocuous towards human fibroblasts (BJ-5ta cells) in their antibacterial-effective concentrations, and therefore represent valuable alternatives to control drug-resistant biofilm associated infections at reduced antibiotic dosage.

COLL 340

Folate binding protein self-aggregation drives agglomeration of folic acid targeted iron oxide nanoparticles

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Folate conjugated nanomaterials have been widely investigated for drug and imaging agent delivery. In this work, two folic acid (FA) conjugated iron oxide particles (IOP), a ~40 nm diameter FA-IOP and a ~450 nm diameter FA-IOP (FA-SeraMag), were synthesized. Both particles aggregated in the presence of serum folate binding protein (FBP) at physiological concentration and buffer conditions including the presence of human serum albumin (HSA). Mixing 0.01% w/w FA conjugated iron oxide particles with FBP induced agglomeration generating an average hydrodynamic particle diameter of 3800 ± 1100 nm for ~40 nm FA-IOP and 4030 ± 1100 nm for FA-SeraMag as measured by dynamic light scattering (DLS). The presence of excess HSA (600 mM) did not prevent agglomeration. Atomic force microscopy measurement provided additional insight into particle morphology with the detection of individual particles in the agglomerate. This behavior is an example of a triggered cascade. A protein structural change is induced by FA-binding, the structural change favors aggregation of the FBPs on the particle surface, and this further triggers the agglomeration of both the ~40 and ~450 nm diameter IOPs.



COLL 341

Oxidation state dependence of capping agent for site-selective silica coating of gold nanorods

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In addition to their size-dependent properties, anisotropic nanoparticles often exhibit shape-dependent properties such as the dependence of the localized surface plasmon resonance of gold nanorods on the aspect ratio of the nanorod. Nanoparticle surface chemistry can also be affected by shape, which has important implications for nanoparticle synthesis and assembly. Much of the research into the shape-dependent surface chemistry of nanoparticles has focused on the anisotropic functionalization of gold nanorods. Over the past decade there have been many publications demonstrating the selective functionalization of the ends of gold nanorods leading to end-to-end assembly. Recently, it has been shown that the anisotropic surface chemistry of gold nanorods can be applied to selectively coat the ends with silica, or by first functionalizing the ends with poly(ethylene glycol) methyl ether thiol (PEG-SH) to coat the sides. It has been suggested that by selectively reacting with the surfaces at the ends of the nanorods the PEG-SH blocks the ends while cetyltrimethylammonium bromide at the sides templates silica shell growth; however, side-silica shells are difficult to reproduce. After studying the reaction conditions leading to side-silica shell formation it was found, surprisingly, that the oxidation state of PEG-SH is an important factor for the synthesis of side silica shells. We have demonstrated that when the added PEG-SH is in the form of a thiol no silica shells form but when the disulfide is used side silica shells form.

COLL 342

Precisely tuning size, dopant incorporation, and radial distribution of dopants in metal oxide nanocrystals via a continuous, living growth synthesis

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Control of nanocrystal (NC) size, dispersity, and composition is critical for the exploitation of their unique properties. Traditional synthetic methods to produce well-defined metal oxide NCs often rely on the high-temperature decomposition of metal precursors, or the rapid injection of reactive metal species. These methods often possess drawbacks that limits NC size control, composition control, and hinders scalability. Recently, there is a new method to synthesize a wide variety of doped, core/shell, and binary oxide NCs (including In_2O_3 , $\gamma\text{-Fe}_2\text{O}_3$, Mn_3O_4 , CoO , and ZnO) in high-yield through a metal catalyzed esterification synthesis. Unlike traditional nonaqueous synthetic methods to produce oxide NCs, this method relies on the slow addition of metal carboxylate into a long-chain alcohol at elevated temperatures (> 200 C). We have found through small-angle x-ray scattering (SAXS) and transmission electron microscopy (TEM) analysis that the synthesis shows remarkable similarities to a living polymerization reaction, in that NC size can be precisely controlled through the amount of metal precursor added. Additionally, we have found that a wide variety of

transition and post-transition metals can be easily incorporated into the host lattice in a controlled manner. Our work focuses on the size and composition control of monodisperse In₂O₃ and transition metal (TM)-doped In₂O₃ NCs in high-yield over a large size range (2-30+ nm).

COLL 343

Biopolymer hydrogels embedded with lignin-silver nanocomposites with broad activity against antibiotic-resistant clinical isolates

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The increasing incidence and severity of hospital-acquired infections, especially those caused by drug-resistant bacteria, call for the development of novel strategies to face this concerning reality. In this study, a one-step enzymatic approach was used to synthesize multifunctional hydrogels of thiolated gelatin and lignin capped silver nanoparticle (AgNPs) as therapeutic platforms for treatment of chronic wound infections. Solvent-free green synthesis of AgNPs was performed in presence of lignin biopolymer serving as both reducing and doping agent to improve the stability of the colloidal dispersion. The resulting AgNPs were about 20 nm in diameter and did not agglomerate even after one month storage. The lignin-doped AgNPs were highly efficient against a panel of nine Gram-positive and Gram-negative bacteria, including multi-drug resistant phenotypes. The particles were further incorporated enzymatically into biopolymer hydrogels with antioxidant capacity and potential to inhibit major enzymes governing the chronicity in wounds, such as the myeloperoxidase and collagenase. Moreover, these nanocomposite hydrogels eradicated *S. aureus* bacterial biofilms by up to 80 %. The demonstrated bioactivities of the hydrogels together with their good biocompatibility and high swelling capacity make them suitable for chronic wound care.

COLL 344

Microwave-assisted synthesis and characterization of nanomaterials

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Nanomaterials possess novel properties as the size of particles decreases to nanoscale. To understand and exploit these unique properties, we need to develop effective strategies to synthesize nanoparticles with controllable size, shape, and

composition. In this presentation, we focus on synthesis of gold and silver nanoparticles due to their unique optical properties and ease of fabrication. This presentation describes results of microwave-assisted irradiation aimed at developing the ability to control the size and composition of gold and silver nanoparticles. We used laboratory microwaves which are becoming common tools in research and teaching laboratory. Compared to conventional means of heating, microwaves provide shorter reaction times and better reproducibility. The key component of microwave-assisted irradiation is that nanoparticles synthesis can be completed within minutes thereby saving time and energy. The reduction in reaction time makes it possible to complete the synthesis and acquire spectroscopic data for characterization of the products within the same laboratory period. An array of characterization techniques such as transmission electron microscopy and UV-Vis spectrophotometry were used. Most of the synthesis work was performed by High School students during the Hampton University's NanoHU summer research program.

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Nitrogen enriched hierarchically nanoporous carbon derived from one-pot sol-gel synthesis of polybenzoxazine precursor for CO₂ capture and storage

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Lately, nanoporous carbons which have micro-mesopores structure, high surface area and nitrogen functionalities can enhance the CO₂ adsorption efficiency because the basic nitrogen groups can interact with CO₂ gas. In this study, polybenzoxazine, an additional cure phenolic resin, was used as a carbon precursor since the molecules can be easily designed to incorporate nitrogen functional groups without complicated synthesis procedures. The micro-meso porous carbons with high nitrogen content were prepared through a facile one-pot sol-gel synthesis, using silica nanoparticles as a hard template to generate mesoporous structure. The morphology of nanoporous carbons was investigated by FE-SEM. The Autosorp 1-MP was carried out to determine the surface area, particle size and pore volume. The effect of pyrolysis temperature to obtain nitrogen enriched nanoporous carbon was confirmed by using XPS and elemental analyzers. As a result, activated nanoporous carbon using 40%wt. silica colloidal template and pyrolyzed at 800°C exhibited high CO₂ uptake (1.233 mmol/g at 30°C, 1 bar). The adsorption of CO₂ was increased because the pyridine and pyridone types of nitrogen on the surface of the nanoporous carbon reacted with CO₂ gas, as well as the physical adsorption on the micro-meso porous structure.

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Occlusion of sulfate-based diblock copolymer nanoparticles within calcite: Effect of varying the surface density of anionic stabilizer chains

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Polymerization-induced self-assembly (PISA) offers a highly versatile and efficient route to a wide range of organic nanoparticles. In this paper, we demonstrate that poly(ammonium 2-sulfatoethyl methacrylate)-poly(benzyl methacrylate) [PSEM-PBzMA] diblock copolymer nanoparticles can be prepared with a relatively high or a relatively low PSEM stabilizer surface density using either RAFT dispersion polymerization in a 2:1 v/v ethanol/water mixture or RAFT aqueous emulsion polymerization, respectively. We then use these model nanoparticles to gain new insight into an emerging topic in materials chemistry – the occlusion of organic nanoparticles within inorganic crystals. Substantial differences are observed for the extent of occlusion of these two types of anionic nanoparticles into calcite (CaCO_3), which serves as a suitable host crystal. A low PSEM stabilizer surface density leads to uniform nanoparticle occlusion within calcite at up to 7.5 % w/w (16 % v/v), while minimal occlusion occurs when using nanoparticles with a high PSEM stabilizer surface density. This counter-intuitive observation suggests an *optimum* anionic surface density is required for efficient occlusion, which provides a hitherto unexpected design rule for the incorporation of organic nanoparticles within inorganic crystals.

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Core@Shell architecture: Enhancing catalytic performance

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The catalytic performance of nanoparticles has an important impact both from a fundamental understanding of materials chemistry and practical applications such as proton exchange membrane fuel cells (PEMFC). Noble metal nanoparticles in particular have received significant attention in recent years owing to their excellent catalytic properties; however, they are often susceptible to poisoning by intermediate species which hinders their performance. Bimetallic nanoparticles can show improved poisoning resistance and activity when compared to their monometallic counterparts. We chose Rh@M nanocrystals as a model system, where M = Ir, Pd and Pt. A series of Rh@M nanocubes were synthesized with different shell thicknesses and have been characterized by TEM, XRD and STEM-EDS. We demonstrate through XPS and cyclic voltammetry studies that the electronic and strain effects of a model Rh@M system can be manipulated to enhance the performance of the catalysts for formic acid electrooxidation (FAO).

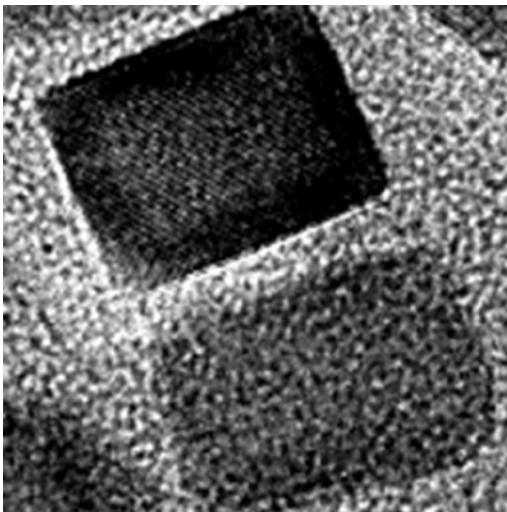


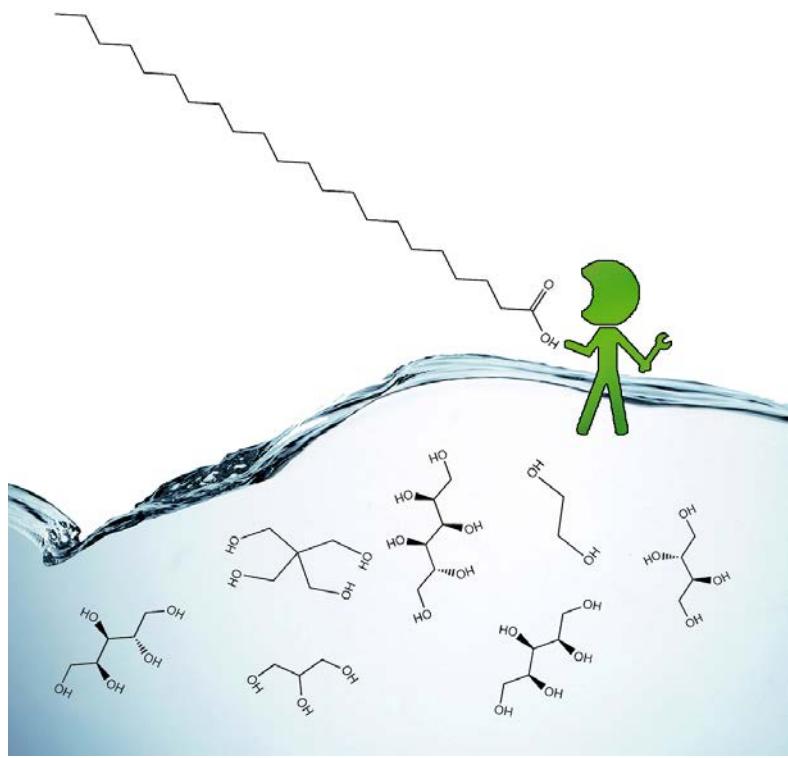
Figure 1. TEM image of Rh@Pt nanocubes used in the oxidation of formic acid.

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Biocatalytic synthesis and characterization of ultra-long-chain fatty acid sugar alcohol monoesters

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An array of ultra-long-chain fatty acid sugar alcohol monoesters, with behenic acid as an acyl representative and sugar alcohols altered from ethylene glycol to glycerol, erythritol, pentaerythritol, arabitol, xylitol and sorbitol, were enzymatically synthesized in high purity and selectivity. The molecular structures of the synthetic compounds were confirmed by ^1H NMR, FT-IR and MS analysis, and the thermal properties were primarily characterized by DSC analysis. The molecular packing and thermal properties of synthetic sugar alcohol monobehenates (SAMBs) were investigated by Temp-Ramp-FT-IR. For in vivo application purposes, the enzymatic lipolysis of synthesized SAMBs was examined by a PPL (porcine pancreatic lipase)-mediated in vitro digestion test, and improved resistance of most SAMBs to enzymatic lipolysis, in comparison to glycerol monopalmitate, was observed. FT-IR spectroscopic analysis of the thermotropic phase transitions of the synthetic SAMBs indicated that the thermal collapse temperatures do not vary significantly as the polar head alters, suggesting their thermostabilities are largely governed by hydrophobic interactions among the alkanyl chains, while the size, properties and volume of the polar heads may determine the packing patterns. Systemic mapping of the structure–property–function relationship of SAMBs revealed the potential of these compounds for multipurpose applications. Ethylene glycol and glycerol monobehenates enable orthorhombic packing, and could find applications in cosmetic formulation, whereas sorbitol monobehenate is capable of forming stable surfactant-free nanoparticles, which could be excellent excipients for solid lipid nanoparticles for use as delivery cargo for drugs and food ingredients.



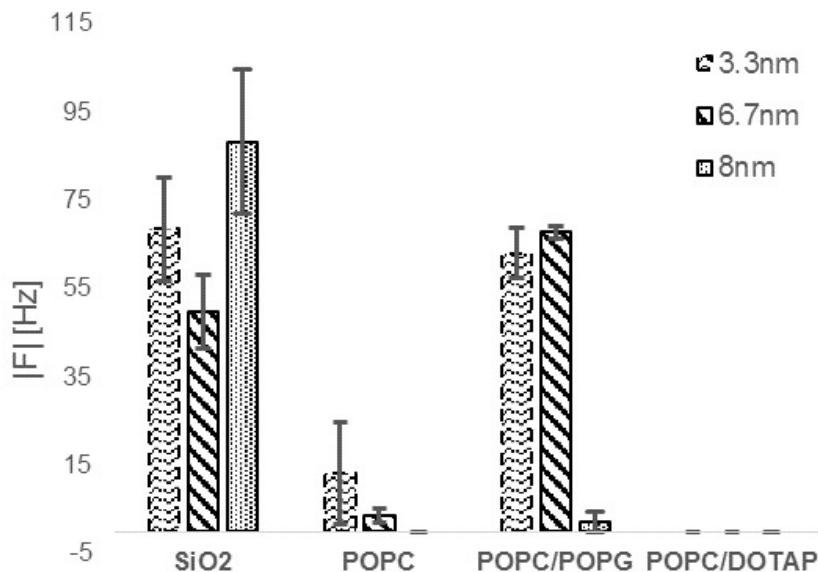
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Interaction of size-tailored PEGylated iron oxide nanoparticles with lipid membranes and cells

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Iron oxide core-shell nanoparticles are gaining ever increasing interest for separation and imaging in biotechnology and biomedicine, due to supposed low cytotoxicity and their superparamagnetic properties. Hydrophilic polymer-coated nanoparticles are believed to have low nonspecific interactions in biological systems, but much additional work in-vitro and in-vivo is needed to understand their detailed interactions with proteins, membranes and cells. We investigated monodisperse ($SD < 5\%$), single-crystalline and superparamagnetic magnetite nanoparticles of different core size and densely grafted with poly(ethylene glycol) ($Mw=5kDa$), with particular emphasis on their interaction with biological membranes. Membrane interactions will determine nonspecific recognition and uptake by cells. These nanoparticles demonstrated no cytotoxicity and low cell uptake in in-vitro culture of HeLa and HEK cell lines. However, using Quartz Crystal Microbalance (QCM) a strong DLVO-type interaction could be demonstrated with anionic membranes that simulate eukaryote membranes. This interaction was only present in nonphysiological buffer with low ionic strength. Only

low, weak and transient binding was observed to zwitterionic phosphocholine membranes. Core size seems to have an effect, with the smallest core size (3.3nm) yielding the strongest interactions while 8nm cores displayed almost no interaction. These results imply that dense polymer grafting and nanoparticle curvature are crucial parameters to control interactions between biomedical core-shell nanoparticles and their biomolecular environment, in particular cell membranes. The interaction between nanoparticle and membrane was furthermore shown to not perturb membrane structure by Differential Scanning Calorimetry (DSC).



Nanoparticle binding to model membranes measured by QCM for different core size in MQ water

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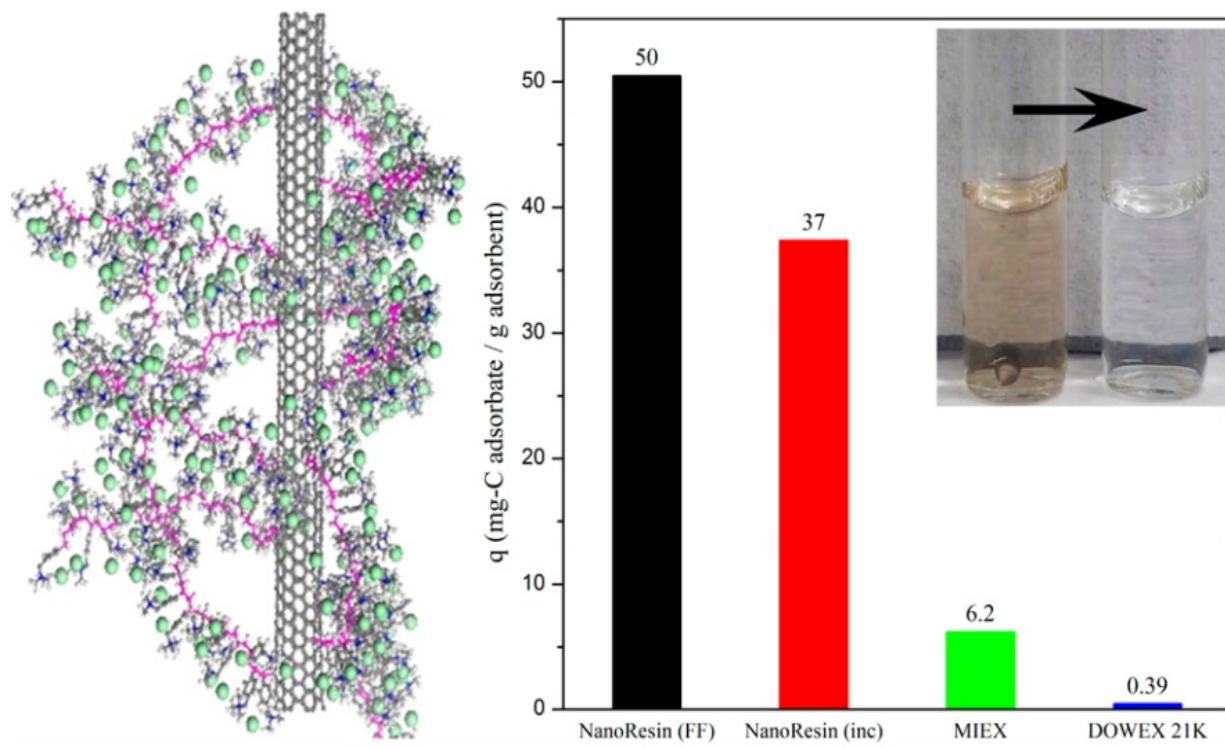
Aqueous synthesis, characterization and optimization of novel nanostructures for water purification

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As demand for clean drinking water increases, the need to utilize less ideal water sources also increases. To compensate, new and more efficient purification methods must be developed. Natural organic matter (NOM) contamination is an emerging human health issue, as NOM can be converted to harmful disinfection byproducts during the disinfection process of water purification. Anion-exchange resins have been demonstrated as an emerging method for removal of NOM from water. Our NanoResin is a novel nanoparticle utilizing short chain (8-30 unit), quaternary-ammonium based anion-exchange polymers covalently attached to carbon nanotubes. This allows us to couple the high specific surface area of the carbon nanotube to the binding efficiency of

the polymer. The narrow diameter of the resin allows the binding sites to be easily accessible to the targeted contaminants, resulting in a fast equilibrium time. This allows the NanoResin to function as a contact resin, with a 10 s equilibrium time compared to 30 min for commercial AER.

We have explored alternative substrates including multi-walled nanotubes and nanofibers, and compared performance based off mass efficiency and equilibrium time. We have also explored the kinetics of the aqueous polymerization reaction in order to optimize polymer growth and minimize poly-dispersity in a greener synthetic pathway. Characterization of the NanoResin and polymer growth will be presented through Raman spectroscopy, surrogate molecule and real water testing, and H-NMR spectroscopy. These characterization methods show the NanoResin to be a mass efficient fast filtration method. The conformation of the resin has been characterized using SEM and TEM.



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MRI reporter contrast agents for ultrasound ablative therapy

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High intensity focused ultrasound (HIFU) is an effective ultrasonic ablative technique that is minimally invasive and suitable for solid tumor surgical operations at anatomically challenging areas. As a result, HIFU can often be coupled with magnetic resonance imaging (MRI) for image guided ultrasound therapy. Our group has previously developed hollow silica nanoparticles of 500 nm and 2 um filled with perfluoropentane (PFP) liquid or gas as ultrasound contrast agents. The PFP encapsulated silica nanoshells can also enhance the cavitation induced mechanical ablation of HIFU therapy and generate larger tissue lesion with less ultrasound power and duty cycle. Due to PFP droplet cavitation, the silica nanoshells become fragmented after HIFU insonation. By depositing gadolinium onto the surface of the silica nanoshells via template ion exchange, the silica nanoshells can additionally act as MRI contrast agents. Alternatively, 6 nm gadolinium oxide nanoparticles have been further synthesized via the polyol route and encapsulated within the silica nanoshell hollow space. Due to limited water contact, the encapsulated gadolinium oxide nanoparticles exhibit weak T1 signal attenuation under MRI imaging. However, after HIFU insonation resulting in fragmented particles and releasing the encapsulated gadolinium oxide nanoparticles, MRI signal is recovered. We have demonstrated a new class of materials that can act as a reporting contrast agents for biomedical imaging. The reporting contrast agents reflect ultrasonic therapeutic efficacy directly via MRI imaging.

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***Sapindus mukorossi* fruit extract mediated synthesis of silver nanoparticle and study of its catalytic and antibacterial activity**

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Plant extract mediated synthesis of metal nanoparticle from metal ions has created tremendous opportunity to improve the synthesis related issues like process simplicity, cost effectiveness, product quality, environment-compatibility etc. The power of reducing and stabilizing agents such as phenolic compounds, flavonoids, terpinoids, polysaccharides, enzymes and other proteins, etc. present in extract have determined the efficiency of extract for synthesis of metal nanoparticle. In this study we have chosen *Sapindus Mukorossi* fruit (soapnut or soapberry) as a part of continuous effort of our laboratory to find out the potential plant extract towards the applications related to metal nanoparticle synthesis. We have demonstrated the aqueous extract of the pericarp of *Sapindus mukorossi* fruit can act as reducing as well as stabilizer to produce highly monodisperse silver nanoparticles. Cyclic voltammetry was studied to know the redox potential of the extract under experimental condition. The UV-vis spectra and selected area electron diffraction pattern (SAED) confirmed the existence of metallic

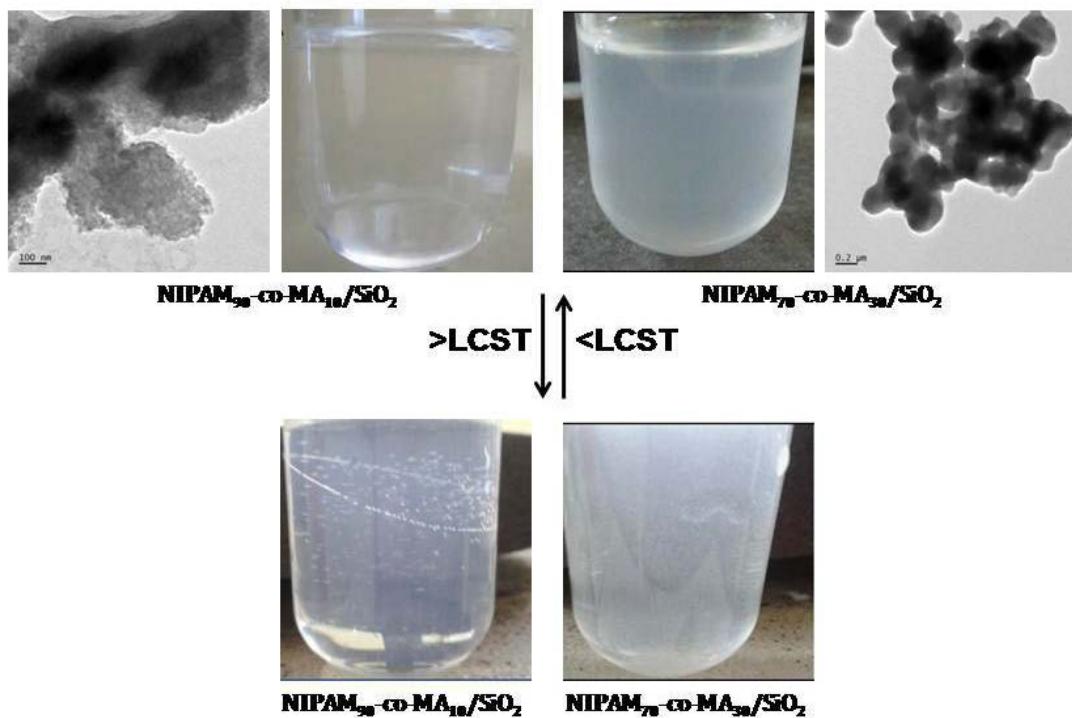
silver nanoparticle. The UV-Vis spectra of one year aged sample reflect the high stability of as-synthesized nanocolloidal dispersion. Transmission electron micrograph shows particles are almost spherical with average diameter 3.5 ± 0.3 nm. The as-synthesized silver nanocolloid (AgNC) showed moderate antibacterial activity against *Bacillus subtilis*, *Staphylococcus aureus*, *Escherichia coli* and *Pseudomonas aeruginosa*. Catalytic efficiency of the AgNC has been also evaluated against degradation of common environmental pollutants p-nitro phenol and Eosine blue.

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Autocatalytic sol-gel synthesis of organic-inorganic hybrid material

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Thermoresponsive organic-inorganic hybrid material was successfully prepared from N-isopropyl acrylamide and maleic anhydride by an auto catalytic sol-gel method. The synthesized hybrid material was characterized by diverse methods such as infra-red spectroscopy, scanning electron microscopy, transmission electron microscopy, etc. The obtained hybrid materials showed porous network structure and nano distribution of inorganic domains surrounded by the polymer medium. By tuning the size of inorganic nano domains clear solutions to colloidal suspensions can be made. These materials found immediate application as fillers in epoxy resins.



TEM image and volume phase transition of thermoresponsive hybrid material

COLL 354

Synthesis and adsorption studies of quaternized magnetic cellulose nanocomposite as adsorbent for hexavalent chromium removal

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Nowadays, various industries have introduced toxic heavy metals such as copper, nickel, zinc, cobalt, cadmium, lead, and chromium into surrounding environment. These heavy metals pose adverse effects to human health and other living organisms when they accidentally exposed at high concentration, especially for chromium. This study quaternized magnetic cellulose nanocomposite was obtained from precipitation of quaternized cellulose and magnetic nanoparticles in the presence of ammonia solution under nitrogen atmosphere. Results of the nanocomposite obtained from Fourier transform infrared spectroscopy (FT-IR), CHN analyzer, Zetasizer, Scanning electron microscope (SEM), X-ray diffraction (XRD), and Vibrating sample magnetometer (VSM) provided evidence of quaternization. The nanocomposite showed high adsorption efficiency in the pH range of 2-3. The adsorption kinetics was fast and independent of initial hexavalent chromium concentration.

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Hybrid microemulsion (uE)/sol-gel chemistry to synthesize and harvest CaTiO₃:Cr³⁺ NIR nanophosphors

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Rare-earth-doped CaTiO₃ phosphors are traditionally prepared by sol-gel or solid state grinding followed by a two-step high-temperature calcination. Here for the first time alkoxides and thermodynamically stable W/O Winsor type IV microemulsions (uEs) with small (<10nm) discrete methanol-aqueous reactors stabilized by CTAB surfactants/butanol cosurfactants have been combined to produce and harvest NIR-emitting nanophosphors. In combination these generate designer dispersed nanoparticles (NPs) of NIR phosphors. Specifically, methanol solutions of Ca²⁺(0.2M) and Cr³⁺(0.02M) hydrated nitrates (where ~4moles H₂O is present for every mole of Ti(i-OPr)₄) were induced to form nanoreactors in a colourless octane microemulsion. To this was added Ti(i-OPr)₄ (pure; 3.36M) that diffused to react within the methanol-water nanoreactors (see Figure 1). This radical route is an alternative to classic bulk sol-gel and simple solid-state methods. Here we describe the use of this approach to produce novel persistent NIR emitting perovskite CaTi_{1-x}O₃:Cr³⁺_x (non-gallate) nanophosphors. Their characterisation by emission decay time constants, TEM, SEM-EDX, XPS, SIMS,

and XRD is described before and after calcination. The nanophosphors appear useful for signage, emission signature modification, medical tagging and bio imaging applications.

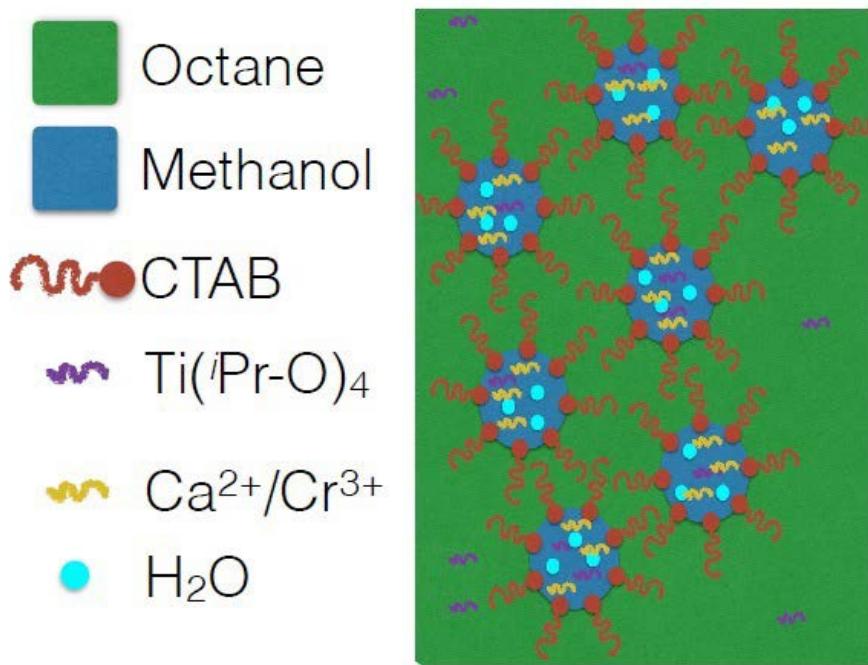


Figure 1

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Effects of the template removal methods and pH on formation of hierarchical porous silica using natural rubber as template

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Hierarchical porous silica (HPS) was synthesized via green sol-gel process by using sodium silicate solution and skimmed natural rubber (NR) latex as silica precursor and template, respectively. Both raw materials are cheap and environmentally friendly. The influences of the template-to-silica ratio, the template removal method (either calcination or solvent extraction), and the pH on the pore properties were investigated. During the silica formation, the presence of NR particles generated macropores in the HPS and slightly increased the interspacing of silica agglomerates. The NR existence did not disturb the spacing within the agglomerates. The morphology and thermogravimetric analysis results confirmed the suitability of calcination in template removal, compared with solvent extraction. Furthermore, the calcination process was three times as faster

than the solvent extraction. The morphology of HPS could be regulated by changing pH as pH not only influenced the size of primary silica particles, but also the strength of the interactions between the NR template and the primary silica particles.

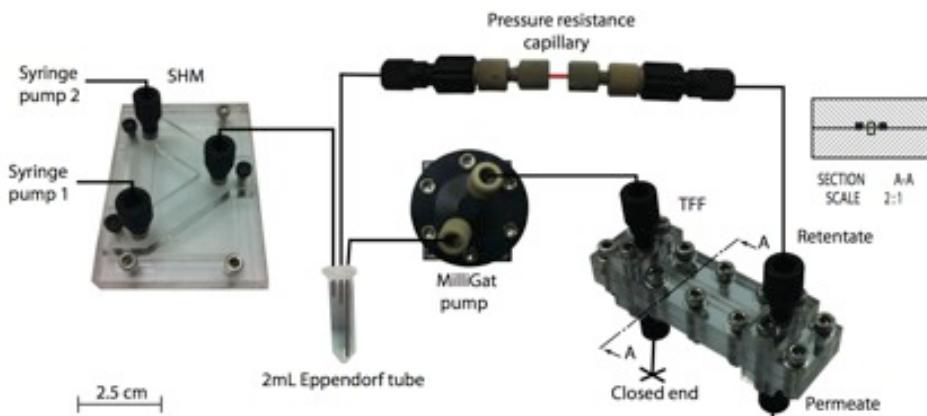
COLL 357

Miniaturised continuous processing units for rapid synthesis and purification of liposomes

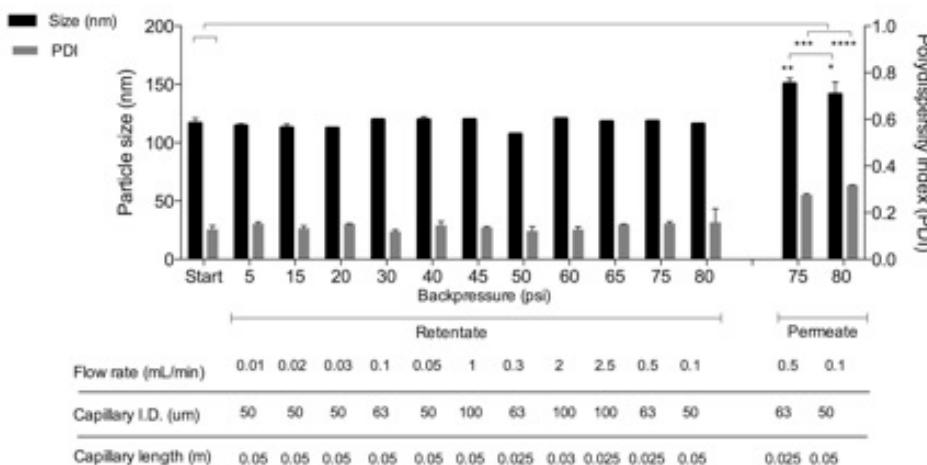
Nikolay Dimov¹, n.dimov@ucl.ac.uk, Elisabeth Kastner², Yvonne Perrie³, Nicolas Szita¹. (1) Advanced Centre for Biochemical Engineering, University College London, London, United Kingdom (2) Aston Pharmacy School, School of Life and Health Sciences, Aston University, Birmingham, United Kingdom (3) Strathclyde Institute of Pharmacy and Biomedical Sciences, University of Strathclyde, Glasgow, Scotland, United Kingdom

Liposomes are a well-established formulation strategy to improve drug delivery and enhance therapeutic outcomes for a range of drugs, such as pharmaceuticals, biopharmaceuticals, and vaccines. Currently, manufacturing methods include the use of solvent injection, reverse-phase evaporation and emulsification methods. Such methods have the disadvantage of involving multi-step processes, often adopt large amounts of organic solvents and are limited to batch-release processes. Upon administration, the pharmacokinetic profile and fate of liposomes is dictated by their size and therefore controlling particle size and polydispersity (PDI) is one of the key issues in the manufacturing process of liposomes and is a key parameter in the product specifications. To produce liposomes in a controlled size range, downsizing through extrusion or homogenisation is often adopted. This adds further steps to the manufacturing process and exposes the liposomes and drug constituents to harsh and potentially detrimental processing conditions.

In our current research, we describe a microfluidic liposome purification process based on a tangential flow filtration (TFF) microfluidic device. The purification is combined with liposome manufacture unit, a staggered herringbone micromixer (SHM), through an intermediate vial to sustain independent control over the fluidic flows in each unit. The miniaturized system presented here facilitates the complete removal of the free drug without loss of lipids, previously only achieved by time intensive dialysis. This robust process train facilitates the identification of prospective formulations, optimal operating conditions, scale-up parameters, whilst significantly reducing the time required for developing versatile adjuvant and drug delivering systems.



Miniaturised units for continuous liposome production.



Transmembrane pressure regulation and PDI.

COLL 358

Nanoparticle synthesis and harvesting from W/O microemulsions (uE)

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uEs were first defined just over 50 years ago providing low-energy routes to nanomaterials via the bottom-up nanotechnology of colloid chemistry. Such routes have their origins in the preparation of NiB, Pt, Pd and Rh nanoparticles (NPs). Effectively the dispersed water droplets are nanoreactors. Often one uE contains a reductant (e.g. NaBH₄) and another uE contains reducible cations (e.g. Ni²⁺). Reaction occurs as a result of nanoreactor droplet exchange defining the size of the inorganic NPs produced. The size of the droplets rises with the volume % water in the microemulsion and varies

with the type and concentration of surfactant, cosurfactant, hydrocarbon and aqueous solution.

Here we describe the advantages of using water-in-oil microemulsions to nanoengineer a range of NP pigments, BaSO₄ scale controllers, doped BaSO₄ chemical-looping combustion catalysts, BaFe₁₂O₁₉ ferrites, hollow TiO₂ photocatalysts and IR nanophosphors.

For example, NIR 720nm-emitting zinc gallostannate/germanate with Cr doping nanophosphors have been prepared by urea coprecipitation within the dispersed water nanoreactors in stable water/n-octane/sodium dodecyl sulfate (SDS)/1-butanol microemulsions at 373K. So have SWIR 1500nm-emitting NaYF₄:Yb-Er single-photon down conversion and ErGdVO₄ three-photon quantum cutting nanophosphors. NIR-emitting nanophosphors had persisting emissions at 700 and 720nm showing decay constants of 41s (lower than for phosphors produced by a solid-state reaction (480s)).

We show that there are major advantages to nanomaterials.

Figure 1. (a) Mg²⁺- and (b) Sr²⁺-doped BaSO₄ nanoparticles (NPs) for pigment and catalytic use produced in C₁₂EO₄ W/O uEs on cooling and harvesting the organic phase that separated out at 268K. Scale bar = 50nm. (c) SEM, (d) emission spectra and (e) emission decays for solid-state and uE zinc gallostannate/germinate (ZGG) phosphors with Cr doping

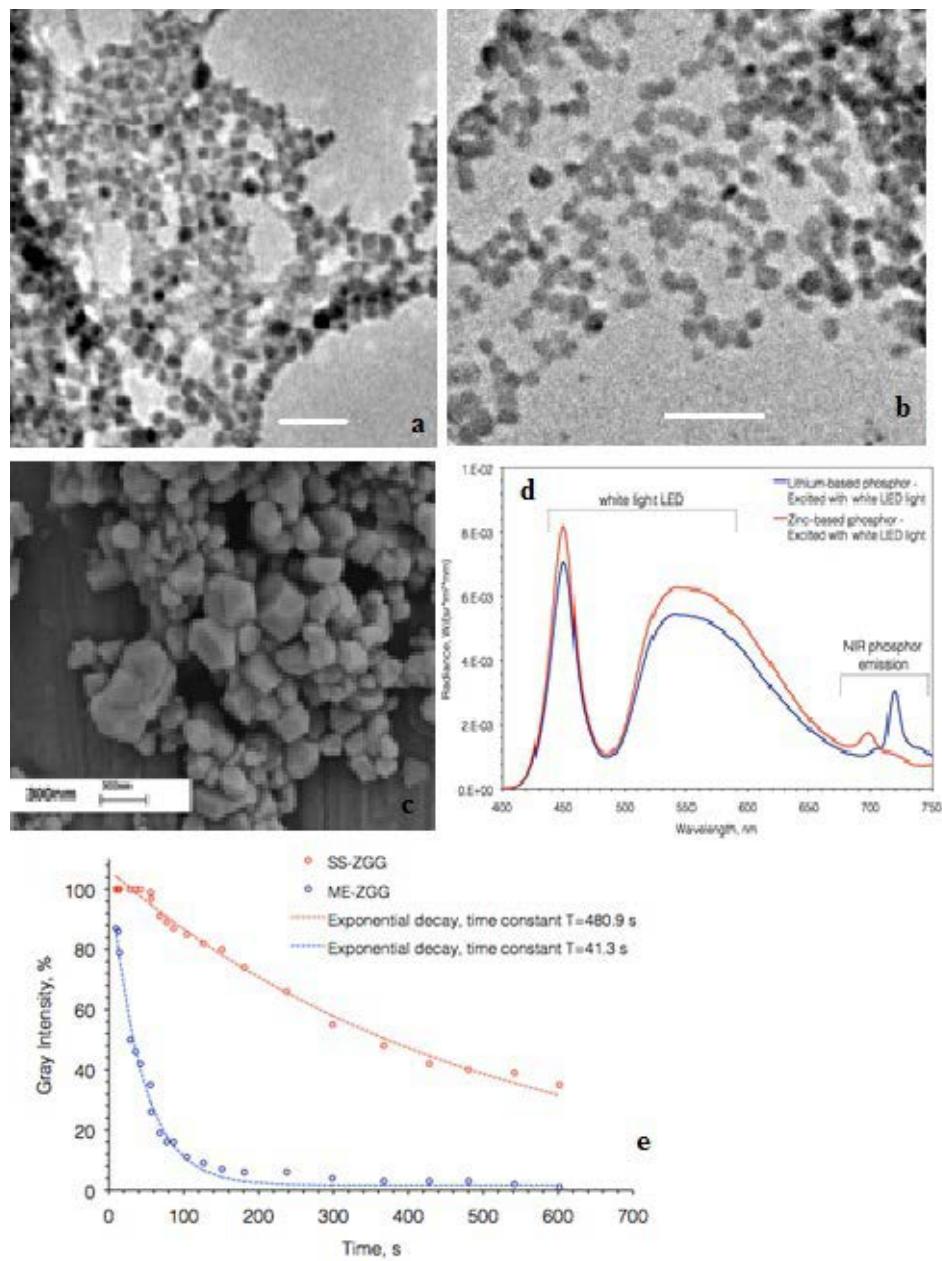


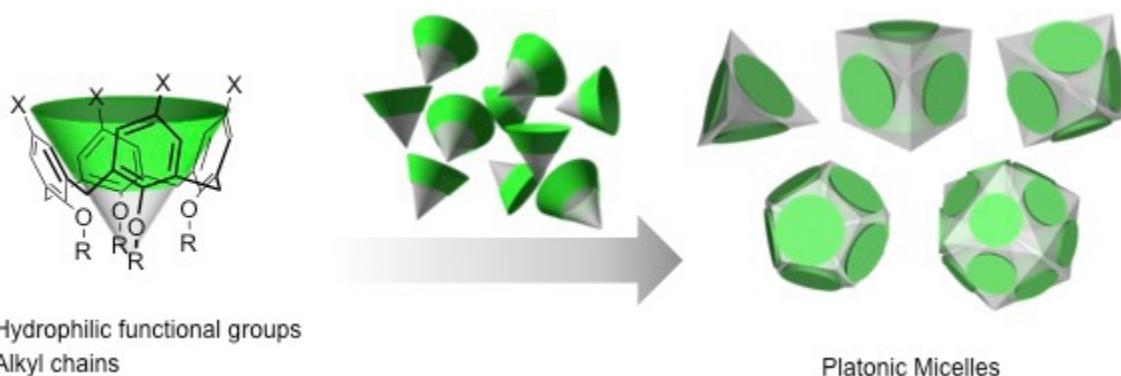
Figure 1

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Platonic micelles: A novel aggregation behavior of sulfonatocalix[4]arene-based micelles

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We have recently discovered that some calix[4]arene-based lipids self-assemble into completely monodisperse micelles in terms of the aggregation number (N_{agg}). Interestingly, the N_{agg} s are always consistent with the face number of Platonic solids, indicating the formation of polyhedral structures. We believe that this is a common feature of the micelles with small aggregation number less than 20. Sulfonatocalix[4]arene-based lipids are the most familiar lipid in calix[4]arene-based lipid systems, and have been used in many researches in academia. In this study, we have investigated the structure of sulfonatocalix[4]arene-based micelles using small angle scattering techniques and analytical ultracentrifugation measurements. We will discuss the effects of the salt concentration as well as the alkyl chain length on the micellar structures in the meeting.



COLL 360

Visible light photoactivity of 1-D TiO₂ by targeted decoration of transition metal nanodots

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The application of one-dimensional TiO₂ nanotubes is largely dependent on the photo-generation of electron-hole pairs (excitons) and the longevity of the excitons to conduct through the material. In this current research, the TiO₂ nanotubes are functionalized with different transition metals to extend the activity in visible range of the solar spectra. Two different approaches are followed to successfully decorate the nanotubes with the metal clusters: one pot alkaline hydrothermal approach is used to locate the metal clusters on the surface of the nanotube and metal complex solution is used to deposit within the lumen of the nanotubes. The specific location of the metals triggered specific optical and chemical properties as seen in UV-Vis, Raman and FTIR spectroscopy. The new material shows excellent performance for visible light photocatalytic oxidation of refractory 2, 4 dichlorophenol (DCP) pollutant.

COLL 361

Effects of osmolytes on caffeine partitioning thermodynamics

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This project illustrates the effects of nine osmolytes on the partitioning thermodynamics of caffeine between aqueous and cyclohexane phases. The stabilizers such as betaine and sarcosine decrease the Gibbs free energy for caffeine transfer and enhance caffeine transfer from the aqueous to cyclohexane phase. On the other hand, the denaturants such as urea and guanidinium salts behave the opposite to hinder the caffeine transfer. Gibbs free energy for caffeine transfer was measured at different temperatures to obtain the enthalpy and entropy for caffeine transfer. Caffeine transfer from the aqueous to cyclohexane is entropically driven, though the differences between osmolytes arise primarily from the enthalpy of caffeine transfer. ^{13}C and ^1H NMR spectroscopy were employed to determine the specific interactions of each osmolyte with caffeine molecule.

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Elucidating distinct Au(111) and TiO₂/Au(111) surface sites for the selective oxidation of ethanol to acetaldehyde

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Obtaining a molecular-level understanding of the reaction of alcohols with heterogeneous model catalysts is critical for improving industrial catalytic processes; such as the production of H₂ from alcohols. Studies with simple alcohols methanol and 2-propanol showed redox reactivity on nanoparticle TiO₂/Au(111) inverse model catalysts, but the role of distinct surface sites on the overall reactivity has not been investigated. In this work, ethanol operates as a probe molecule to investigate the role of Au, TiO₂, and TiO₂/Au interfacial surface sites on the catalytic properties of TiO₂/Au(111). Ultrahigh vacuum temperature programmed desorption (TPD) studies with ethanol/Au(111) elucidate previously unreported adsorption sites for ethanol on the surface. Ethanol molecularly adsorbs to Au terrace sites, step edges, and under coordinated kink sites with adsorption energies of -51.7 kJ/mol, -55.8 kJ/mol, and -65.1 kJ/mol, respectively. A TPD coverage study of ethanol/TiO₂/Au(111) indicates ethanol undergoes dissociative adsorption into H*(a) and CH₃CH₂O*(a) on the inverse model catalyst surface. The initial desorption temperature of ethanol from TiO₂/Au(111) ($T_{des} = \sim 235$ K) is at an intermediate temperature between the desorption temperatures from bulk Au(111) ($T_{des} = \sim 170$ K) and TiO₂(110) ($T_{des} = \sim 300$ K), indicating both Au and TiO₂ play a role in the adsorption of ethanol. Interestingly, temperature programmed reaction

spectroscopy (TPRS) experiments shows that nanoparticle TiO₂/Au(111) selectively oxidizes ethanol to acetaldehyde at ~500 K.

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Tuning dynamic two-dimensional supramolecular self-assemblies at surfaces by molecular design

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Self-assembly of highly-ordered 2D organic materials at surfaces is being explored as a route to develop next-generation functional materials, such as semiconductors, photovoltaics, sensors, and catalysts. Subtle changes in molecular structure can have a significant impact on supramolecular ordering and functional properties. Here, we report progress in understanding how to program supramolecular systems by comparing four families of planar, polyaromatic molecules, each of which can be tuned through rational design and synthesis across multiple supramolecular packing structures.

Characterization is conducted by scanning tunneling microscopy at the solution-graphite interface and grazing incidence X-ray scattering. Aryl-triazole oligomers, properly programmed with specific peripheral alkyl groups, can exhibit responsive behavior to chemical and electronic stimuli in switching between two supramolecular architectures; this response can be modeled in terms of competing van der Waals interactions and dipole alignment. Heteroaryleneethynylene-based macrocycles form two phases and can incorporate aromatic guests. Alkoxybenzonitrile molecules can be tuned by alkyl chain length between several close-packed structures, including one that incorporates the solvent in a 2D co-crystal. Tricarbazolo triazolophane macrocycles is designed with peripheral functional moieties to steer supramolecular architecture which is assembled through non-tradition hydrogen bonding. The ability to program and tune each of these supramolecular systems is contributing to a growing understanding of the rational design of molecular layers, which we are also working to translate into highly ordered thin films. Coupling these experimental results with theoretical calculations has provided important insight and feedback into the design process for these systems.

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Controllable self-assembly of peptoid material

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In Nature, protein self-assembly into one dimensional (1D), 2D and 3D structures creates materials exhibiting complex functions due to the high information content of the protein sub-units. Developing synthetic systems for which self-assembly can be similarly programmed through interactions between sequence-specific domains, but for which stability and predictability of assembly are enhanced, is critical to realizing bioinspired materials with similarly complex functions. Peptoids are a class of biomimetic sequence-defined polymers that assemble into 1D, 2D and 3D structures depending on the choice of sequence. In this research, we investigate the impact of introducing cyclodextrin headgroups into amphiphilic sequences that otherwise self-assemble into 2D materials by using *in situ* AFM to observe the pathway and dynamics of assembly in real time. We find that, on mica surfaces at low pH, these peptoids still assemble into 2D membrane-like structures, but rather than growing through the birth and spread of flat 2D islands as observed for small hydrophilic headgroups, the addition of the bulky cyclodextrin headgroup leads to formation of highly convoluted wormlike micelles that grow in length and coalesce to form a continuous 2D material with a uniform thickness of about 4 nm. At high pH and upon addition of Ca ions, assembly of this 2D material is followed by formation of cylindrical micelles many microns in length with uniform diameters that pack into bundles and cover the surface to form a complex 3D spaghetti-like architecture. In addition to altering the final peptoid architecture, increasing the pH leads to a decrease in the kinetics of assembly. When the mica substrate is replaced by SiO₂, cylindrical micelles form in two steps, starting with deposition of spheroidal precursors that are presumably spherical micelles and transforming into cylindrical micelles on the surface. To understand the evolution of architecture and kinetics with these changes in substrate and solution chemistry, we consider the role of pH and Ca ion concentration in modifying interfacial energy through their impact on both the mica and peptoid surface charge. Because the addition of cyclodextrin provides a large cavity for host-guest chemistry, mastering assembly of the various hierarchical structures reported here offers the potential for a range of applications.

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Towards the design, synthesis, and characterization of the self-assemblies of shape-persistent tricarb macrocycles

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Shape-persistent macrocycles are distinctly advantaged as building blocks for molecular materials. Resistance to changes in shape allow these macrocycles to predictably display encoded surfaces under a wide range of external stimuli; e.g., guests, heat, light, solvent, or pH. Tricarbazolo triazolophane (tricarb) macrocycles are representative of this class of molecule. Tricarb macrocycles have been shown to self-associate in solution and self-assemble into thin-films on surfaces. These prior findings have

inspired the design and synthesis of C_3 -symmetric and sequence specific macrocycles to begin to elucidate the rules that govern hierarchical self-assembly. Work towards elucidating the nature of these macrocyclic assemblies present in solution, investigated with small-angle X-ray scattering (SAXS), and on graphite, probed using scanning tunneling microscopy (STM), are presented here.

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Self-assembly of designed helical-repeat protein on mica characterized using atomic force microscopy

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Bio-Molecular self-assembly is one kind of crucial processes to the growth, survival and evolution of nature life. It underlies the construction of functional quaternary structures, like proteins in living organisms; and that is the requirement to the appropriate functions of proteins and cells. Interface cannot be neglected in the research of protein self-assembly; as in a number of cases, interface involves into the molecular self-assembly of proteins. Exploring the interaction between proteins and interfaces, not only does contribute to people's knowledge of nature life, but also benefits to a number of bio-engineer applications.

In this presentation, I explore the self-assembly behaviors of the designed helical repeat protein (DHR10-mica18) via atomic force microscopy (AFM). It is one kind of artificial protein with tandem repeating a simple helix-loop-helix-loop structural motif. It has been modified to attach to mica surface with certain orientation by attaching to negative charged mica surface. AFM records the self-assembly process and proves the concept of the design. The results further prove it is the combination of classical and two-step nucleation. And the effect of hydration layer during the adsorption is also been discussed. Such formed protein self-assembly layer may be used as template for further crystal nucleation and growth.

COLL 367

Rapid electro-formation of robust and transparent biopolymer gels in prescribed shapes

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Gels of biopolymers such as alginate are routinely used to encapsulate biological cells and proteins for applications in drug delivery and tissue engineering. These gels are

created by combining sodium alginate with a source of divalent ions like Ca²⁺. Recently, researchers have demonstrated the ability to deposit alginate gels using electric fields. For example, these gels can be deposited at the anode of an electrochemical cell where the local pH is considerably more acidic than in the bulk solution. However, these processes are limited to generating 2-D films of alginate, and the need for strong pH gradients hampers the inclusion of pH-sensitive species within the films. Here, we present an alternative approach for rapidly forming 3-D alginate gels upon application of an electric field. In this approach, a molded 3-D gel of agarose with dissolved CaCl₂ is placed in a beaker containing a sodium alginate solution. These are connected to a DC power source, and when a voltage is applied, an alginate/Ca²⁺ gel is formed around the agarose in a shape that is the inverse replica of the original mold. The alginate gels are transparent and robust, and the process is mild and compatible with pH-sensitive materials. Gels in several 3-D architectures can be formed by this method that cannot be achieved through conventional methods.

COLL 368

Synthetic lipids for liposome derivatization, targeting and triggered release towards drug delivery applications

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Liposomes provide a promising platform for drug delivery through the encapsulation of medicinal compounds. The ability to dictate the self-assembly properties and surface decoration of liposomal membranes is desirable to control drug targeting and release. Herein, we will present novel synthetic lipid analogs designed to facilitate liposome functionalization, targeting and release. In particular, liposome decoration and cell targeting through click chemistry reactions will be discussed. Additionally, photocleavable lipids for light-triggered liposome release will be presented.

COLL 369

Interfacial carbene reactions on hard and soft material interfaces

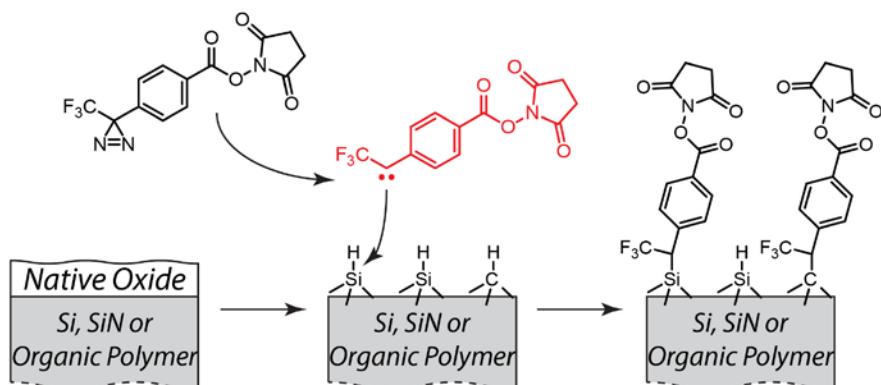
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We will discuss an interfacial carbene insertion on hard and soft material interfaces. Interfacial carbonylation can lead to the development of a molecular layer deposition technique, capable of functionalizing diverse materials (inorganic, organic, polymeric including flat, curved, rough or nanostructured interfaces) with uniform and stable monolayers of functional organic molecules. Instead of using self-assembly and ordering to form stable monolayers, we utilize active carbene precursors to enable rapid

liquid or vapor-phase formation of thermodynamically and kinetically stable surface bonds. Such chemisorption produces dense and uniform monolayers that do not require extensive intermolecular interactions for stability.

Recently, we demonstrated that a novel, vapor-phase carbonylation strategy can be used to form dense monolayers of functional organic molecules on passivated hard and soft interfaces. These monolayers are attached to the surfaces via non-hydrolytic Si-C and C-C bonds making them less prone to hydrolytic cleavage than typical SAMs on oxides and metals. However, due to their non-symmetrical structure, they do not have self-assembled phases and have slightly lower molecular surface coverage than the traditional aliphatic SAMs. Nonetheless, due to their exceptionally strong surface attachment, the stability of such monolayers is primarily determined by the reactivity of the underlying substrates, and not by the attachment chemistry. We demonstrated, that the carbonylation method can serve as a complementary technique to the traditional SAM methodology in applying functional molecular coatings on the substrates, which are typically incompatible with the traditional molecular self-assembly.

Interfaces with Si-H or C-H bonds



COLL 370

Carboranethiol self-assembled monolayers on gold surfaces

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Here we studied mixed SAMs of three carboranethiol (CT) isomers on Au(111) surface with distinct dipole moment vector directions in order to investigate the effect of dipole-dipole interactions on the film properties. We systematically changed concentration ratio of these isomers in the growth solution in order to correlate their solution ratio to film ratio and morphology, by means of wettability, ellipsometry and atomic force microscopy (AFM) measurements. In addition we studied the effect of gold surface roughness on the film properties by using two different type of Au (111) surfaces with different morphologies (Au(111) on mica and template stripped Au (111)). Finally, co-deposition of one of the CT isomers with mercaptoundecanol [HS(CH₂)₁₁OH, MUD) and

decanethiol [HS(CH₂)₉ CH₃, DT] was performed in order to investigate how CTs interact with alkane thiols with polar and nonpolar end-groups.

COLL 371

On the influence of electric fields on the adsorption dynamics of bio-polyelectrolytes at solid-liquid interfaces

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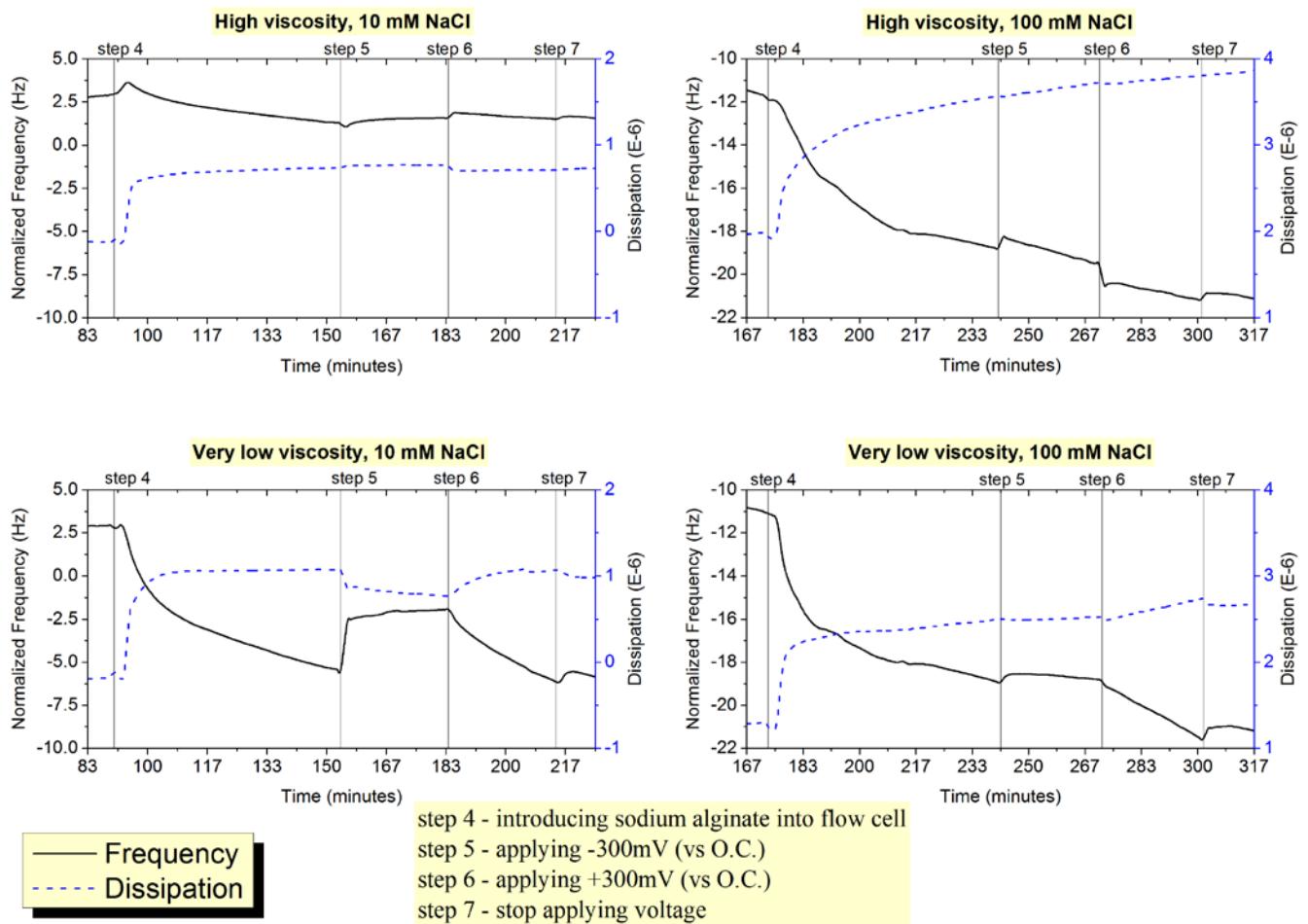
The range of environments in which microorganisms thrive is wide and in most cases, the presence of biofilms formed by them is regarded as undesirable. In processes that involve membranes, electrodes and other surfaces, the formation of a biofilm on surfaces hampers their proper functioning. The adverse effect of biofilm is mainly caused by limiting mass and heat transport properties.

In this study, a model system – alginate, common in *P. aeruginosa* biofilms – is studied using Quartz Crystal Microbalance with Dissipation (QCM-D) with an electrochemical flow cell. Alginate is adsorbed on a resonating gold coated electrode/sensor before an external voltage is applied on the sensor.

Adsorbed high viscosity alginate (**HVA**) exhibits small responses to applied voltage, in contrast to very low viscosity alginate (**VLVA**) that shows interesting behavior. Both solutions (10mM/100mM NaCl) of VLVA show increased adsorption when a positive voltage is applied, which is expected due to the negative charge of alginate. A result of important consequence is the reaction of the 10mM VLVA to a negative voltage. Under these conditions there is an almost-immediate desorption of alginate. This is due to the decreased electrostatic shielding occurring in the weaker ionic atmosphere.

Additional work was done with chitosan, positively charged, with samples of varying MW. Our results indicate that both ionic strength and MW have a large influence on the amount of attached molecules and even formation of multi-layers under certain conditions. Further research under conditions of external electric fields, and usage of a combined electrochemical-AFM is currently being done to further increase our understanding of the interactions between polymer molecules, and inside adsorbed layers.

Our results show clear dependence of the behavior of adsorbed alginate and chitosan, on both the ionic atmosphere and molecular weight. We show that under conditions that are accessible in water treatment systems it is possible to cause desorption to a certain extent.



COLL 372

Interfacial stress induced metal thin film surface reorganization

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Co-deposited multi-metal thin films have been widely used in many applications. However, in most applications, assumptions were made that the properties of the first deposited film do not significantly change upon deposition of a second layer. Interfacial stress on co-evaporated films, however, is well documented especially in epitaxial film growth. Growth of bimetallic films (hetero-epitaxy) involves deposition of a thin layer of metal (M1) on a host substrate, often silicon (111), followed by the growth or deposition of a second metal (M2) to create three interfaces, viz; M1/substrate, M1/M2, M2/air interfaces.

We demonstrate that in bimetallic film growth involving non-reactive metals (such as gold), the strain in the plane of the hetero-interface (M1/M2) can be estimated from the lattice mismatch, but the magnitude of the shear component of the strain depends on

the faceting of M1, inter-diffusion and propensity to reorganize. With this film reorganization, ultra-flat gold surfaces (lowest root-mean-square roughness achieved: 1.8 Å) were revealed after a template stripping procedure. The surfaces, M1/M2 interface and the film were fully characterized by AFM, STM, SEM, XPS, TEM, X-ray diffraction, nano-indentation and were also studied by simulations. Ultraflat surfaces has wide applications in optics, spectroscopy, biological tests, and materials of low dimensions, such as self-assembled monolayers and 2D materials.

For more reactive metal, reorganization of host thin film is affected by both a mechanical energy dissipation and a chemical adsorption energy penetration. Due to the reorganization orientation, the revealed templated stripped surface in most case has higher roughness, contrary to gold. The ability to tune the surface roughness/morphology without contaminating/scratching the surface leads to opportunities to study correlation between the surface structure and corresponding material chemistry and more.

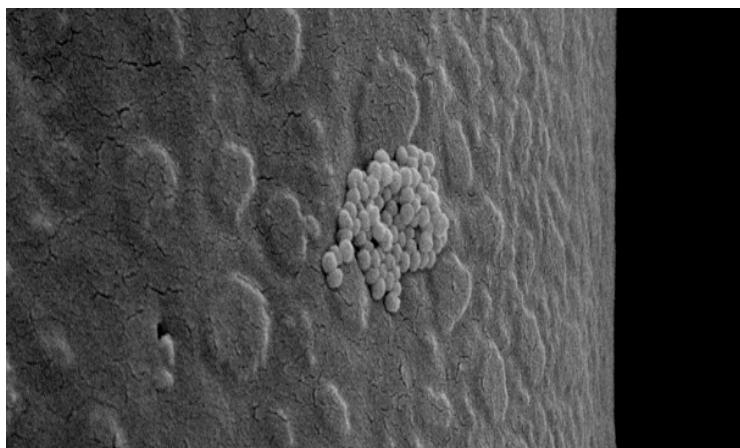
COLL 373

Size and aging effects on antimicrobial efficiency of silver nanoparticles coated on polyamide fabrics activated by atmospheric DBD plasma

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This work studies the surface characteristics, the antimicrobial activity and the aging effect, of plasma pre-treated polyamide 6,6 fabrics (PA66) coated with silver nanoparticles (AgNPs), with the aim to identify the optimum size of nanosilver exhibiting antibacterial properties suitable for manufacturing of hospital textiles. The release of bactericidal Ag⁺ ions from the 10, 20, 40, 60 and 100 nm AgNPs-coated PA66 surface were function of the particles size, number and aging. Plasma pre-treatment promoted both ionic and covalent interactions between AgNPs and the formed oxygen species on the fibers, favoring the deposition of smaller in diameter AgNPs that consequently showed better immediate and durable antimicrobial effect against Gram-negative *Escherichia coli* and Gram-positive *Staphylococcus aureus* bacteria. Surprisingly, after 30 days of aging, a comparable bacterial growth inhibition was achieved for all the fibers treated with AgNPs of <100 nm in size. The Ag⁺ in the coatings also favored the electrostatic stabilization of the plasma-induced functional groups on the PA66 surface, thereby retarding the aging process. At the same time, the size-related ratio Ag⁺/Ag⁰ of the AgNPs between 40 and 60 nm allowed for controlled release of Ag⁺ rather than bulk silver. Overall, the results suggest that instead of reducing the AgNPs size, which is associated to higher toxicity, similar long-term effects can be achieved with larger NPs

(40-60 nm), even in lower concentrations. Since the antimicrobial efficiency of AgNPs larger than 30 nm is mainly ruled by the release of Ag⁺ over time and not by the size and number of the AgNPs, this parameter is crucial for the development of efficient antimicrobial coatings on plasma-treated surfaces, and contribution to the safety and durability of clothing used in clinical settings.



COLL 374

Hot Splash Coating (HSC): A method to create thin layers of doped carbon on metal surfaces

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Heteroatom doped carbon materials surged recently as prominent candidates as catalyst for several charge transfer reactions, mainly of them related to renewable energy technologies. The method of synthesis of carbon materials normally employs the syntheses of powdered material that are them deposited on electrode surfaces using polymer binders, usually Nafion®, to stick the catalyst particles to the electrode surface. The quality of interfaces in electrochemical system plays important roles in the overall efficiency of the electron transfer process. Therefore, integrating electrocatalysts layers on the surface of metal electrodes can be a step forward on the field of electrocatalysis. In addition, the proposed method creates from amorphous to graphitic carbon in a very fast process, literally the process time spam is as longer as a time of a splash. The chemical nature of the carbonaceous materials as well as the presence of metal phases in the deposited layer can be easily controlled. The method consists in heating a metal electrode to a very high temperature (1500 to 1800°C) and them leave the hot metal piece falls into aqueous solutions containing organic compounds, that will serve as carbon precursors, and transition metal salt dissolved. When the hot metal touches the aqueous solution, the dissolved species are thermally degraded while the metal is still hot. Since the metal are cooled very fast, the amount of species that react with the surface is limited. The product of thermal decomposition sticks to the metal surface, forming a modifier layer. the method allows the control over the amount of carbon

deposited, for instance increasing the solution concentration the amount of species that encounter to the metal surface while it is still hot is higher. Other parameters in the synthesis process provide several advantages for the novel Hot Splash Coating (HSC) method in comparison to all other methods reported in the literature.

COLL 375

Control of surface energy to optimize post CMP cleaning efficiency for microelectronics fabrication

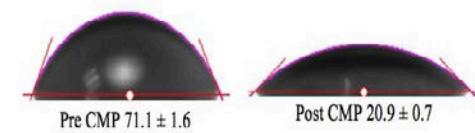
*Sebnem Ozbek¹, Travis W. Walker², G. Bahar Basim¹, bahar.basim@ozyegin.edu.tr.
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Chemical mechanical planarization is a well-established process in semiconductor manufacturing utilized for planarization of deposited metal or dielectric films to enable photo-lithography and multi-layer-metallization (MLM). The wafer surface is held by a holder and exposed to a polymeric pad under applied pressure as the head and the platen carrying the polishing pad rotate within a mismatch velocity. In the meantime, polishing slurry is flown on the pad surface, which is made of nano-meter sized abrasive particles and chemical agents to activate the wafer surface chemically. Hence, CMP has both mechanical and chemical components to achieve planarization and material removal spontaneously. The wafer surface is cleaned from the excessive chemicals and the slurry particles post CMP operations through utilization of the fundamentals of colloids and surface chemistry. The problem of attachment of the slurry particles on the wafer surface is becoming a more severe problem with the microelectronic device dimensions decreasing continuously. Therefore, this study focuses on the correlation of the changes in the surface energy to the CMP slurry particle count remaining on the wafer surface for the shallow trench isolation (STI) CMP. Hence, the surface roughness, contact angle, surface energy, and surface charge measurements of the silicon, silica, and nitride wafers were measured and compared to the particle count on the wafers post CMP clean application. In order to study the particle retention on the surface, particle removal experiments were conducted in a rinsing flow cell and a siphoning flow cell by implementing impinging jet (rinsing) flow and siphoning flow, respectively. Consequently, better post CMP cleaning formulations are suggested for the STI CMP applications with optimal surface energy conditions fulfilled.

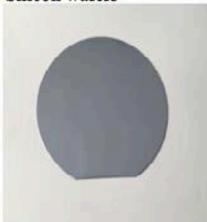
Desktop CMP set up



Contact angle for CMP treated silica glass



Silicon wafers



COLL 376

Self-propelled ionic gel at air-water interface

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We report on our recent finding of self-propelled gel at air-water interface. Our gel is composed of an ionic liquid and a polymer, 1-ethyl-3-methylimidazolium-bis(trifluoromethylsulfonyl)imide (EMIM-TFSA) and poly(vinylidene fluoride-co-hexafluoropropylene). When a piece of the gel with dimensions of approximately 0.5 x 1 x 8 mm is floated on distilled water in a petri dish, it immediately starts rotational motion. By the analyses of images taken by high-speed camera system (1000 frames per second), it becomes evident that the rotation center is a one end of the long gel piece and the rotational speed is about 8Hz. Thus the velocity of the other end of the gel piece reaches ~400 mm/s. This is, as far as we know, the fastest motion among the other self-propelled soft material thus far reported. The motion often accompanies the translation in addition to the rotation, especially at the initial stage of the motion.

The rotation continues 500~1000 s with gradual deceleration, after which it still shows a slow and nonlinear motion. The rotation motion immediately stops when a small amount of surfactant is added on the distilled water surface. It does not move when the gel piece is fully immersed in distilled water (which means the specific gravity of the gel is greater than that of water). The gel immersed in a water overnight does not contain EMIM-TSFA, which is confirmed by Raman spectroscopy. Thus EMIM-TSFA is released into water, and probably participates in generating the force.

We think that one possible explanation of the origin of self-propelled motion of our gel is Marangoni effect, known for driving "camphor boat". In the boat system, camphor forms a monolayer at air-water interface on one side of the boat. It yields the difference in surface tension between the heading direction and the back direction, and yields a self-propelled motion. Camphor is readily sublimed, which is advantageous for its continuous motion. The material we used, however, is an ionic liquid. The ionic liquid is

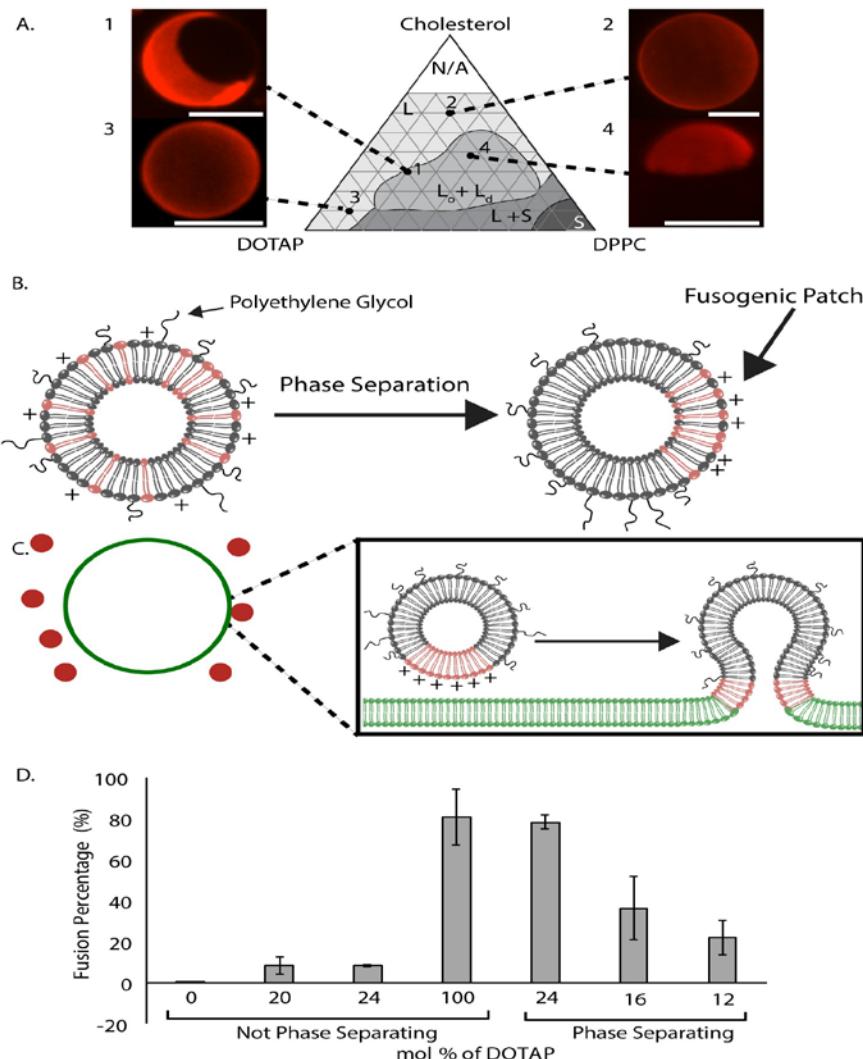
not sublimed and not reported to form monolayer at air-water interface. Further revision is necessary for the complete explanation of the mechanism.

COLL 377

Lipid phase separation enhances fusion

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Fusion of biological membranes is used by diverse biological systems, from viruses to organelles, to deliver macromolecules from one membrane-bound volume to another. Membrane fusion has also been investigated as a potentially efficient mechanism for the delivery of macromolecular therapeutics to the cytoplasm. However, a key limitation of current fusogenic liposomal systems is their relative inefficiency and lack of specificity for target cells. Here, we utilize lipid membrane phase separation to enhance fusion of liposomes to model membranes and cells. Specifically, we report that concentrating the fusogenic lipid, 1,2-dioleoyl-3-trimethylammonium-propane (DOTAP), within lipid domains dramatically increases the efficiency of membrane fusion. To demonstrate this concept, we created phase separating and non-phase separating liposomes with and without DOTAP, each labeled with a fluorescent membrane dye. These liposomes were incubated with target membranes of increasing molecular complexity including giant unilamellar vesicles, giant plasma membrane vesicles, and HeLa cells. In each case, target membranes incubated with phase separating liposomes containing DOTAP exhibited increased membrane fluorescence when compared to membranes incubated with non-phase separating vesicles containing DOTAP and control vesicles lacking DOTAP. These data demonstrate that phase separation can enhance membrane fusion by locally concentrating fusogenic lipids. We anticipate fusogenic, phase separating liposomes will be a key first step toward building an efficient and specific system for delivery of macromolecules to the cytoplasm. In particular, our ongoing work incorporates targeting ligands into phase separating liposomes, such that phase separation and subsequent membrane fusion can be triggered by specific interactions between liposomes and the target cell population.



A. The DOTAP phase diagram with examples of phase separated (1 and 4) and not phase separated (2 and 3) DOTAP Giant Unilamellar Vesicles. **B.** Phase separating liposomes.

C. Cartoon of phase separating liposomes fusing to Giant Unilamellar Vesicles. **D.** Fusion percentage is increased in phase separating liposomes. Scale bars are 5 μm .

COLL 378

Molecular interactions between model cell membranes and nanoparticles

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Nanoparticles have been extensively researched as nanomedicines, drug delivery vehicles, and bio-imaging agents. It is necessary for nanoparticles to enter into cells to realize their functions. Some nanoparticles can strongly interact with cell membranes and enter into cells by penetrating through the cell membranes. In this study, sum frequency generation (SFG) vibrational spectroscopy has been applied to investigate molecular interactions between model cell membranes and Au, Ag, as well as polymer nanoparticles. It was found that Au and Ag nanoparticles can cause lipid flip-flop. The interactions between the model cell membrane and Au nanoparticles are independent of

the particle size, but strongly dependent on the surface coatings of Au nanoparticles. SFG results indicate that Ag nanoparticles can also induce lipid flip flop, and can aggregate while interacting with the lipid bilayer. The interactions between the polymer nanoparticles and cell membranes are greatly influenced by the polymer nanoparticle charge.

COLL 379

Phospholipid flippases of the human erythrocyte

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The asymmetric organization of phospholipids in biological membranes is created and maintained by a combination of vectoral lipid synthesis, slow spontaneous transbilayer movement and the action of a variety of phospholipid transporters. These transporters comprise three distinct functional classes. Flippases catalyze ATP-dependent import of phospholipids and belong to the P-type superfamily. Floppases are ATP-dependent exporters of the ABC transporter family. Scramblases facilitate the bidirectional dissipation of the asymmetry gradient, often upon cell activation. The regulated disruption of phosphatidylserine (PS) asymmetry by scramblase activation and flippase inhibition results in PS exposure on the cell surface. This early indicator of apoptosis is a recruitment mechanism for engulfment and digestion by macrophages.

The simplicity, limited number of transporters, and minimal lipid metabolism of the human red blood cell has made it a useful system for the study of lipid transporters. As a result, red blood cell PS flippase activity has been well characterized. Transport of PS to the cytofacial surface of the plasma membrane is MgATP dependent, is sensitive to vanadate, Ca²⁺, and sulphydryl modification and is highly selective for the structure of the lipid substrate. Modification of the amine, carboxyl, or phosphate groups of PS diminishes transport significantly. An important recognition element is the stereochemistry of the C2 carbon of the glycerol backbone; only the *sn*-1,2 isomer is a productive substrate. Purification of the enzyme responsible for flippase activity based on vanadate-sensitive, and stereoselective, PS-stimulated ATPase activity has yielded a fraction enriched in an 85-90 kDa protein. The prominent ATPase in this preparation is the ABC-transporter ABCB6, a mitochondrial importer of the heme precursor coproporphyrin III. Other ATPases also copurify with PS-stimulated ATPase activity, including the P₄-ATPases ATP8A1 and ATP11C. Studies by our group and others have shown that recombinant ATP8A1 possesses PS-specific ATPase activity similar to the red blood cell flippase and, when reconstituted into liposomes, supports flippase activity. Recent studies have also reported that disruption of ATP11C expression results in physiological responses consistent with defective PS flippase activity. Evidence supporting a role for ABCB6 and the P₄-ATPases in the activities of the PS flippase and the purified PS-stimulated ATPase will be discussed.

COLL 380

Exploring the interactions of transition metal ions with lipid membranes

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Transition metal ions such as Cu²⁺ can bind tightly to lipids containing free amines. This includes binding to phosphatidylethanolamine (PE) and phosphatidylserine (PS). In the former case, PE lipids need to already be deprotonated to afford binding. In the latter, Cu²⁺ can displace a proton on the amine and change its apparent pK_A. The difference is related to the adjacent carboxylate moiety in PS, which assists in the binding process. Moreover, the apparent dissociation constant for Cu²⁺ to PS is dependent on its concentration in the membrane, while binding to PE is only weakly dependent on its concentration. Once bound to the surface, copper can undergo Fenton chemistry in the presence of oxidants like hydrogen peroxide, because it is a redox active ion. Experiments, show that the rate of double bond oxidation within the membrane can be sped up by almost an order of magnitude when lipids containing Cu²⁺ binding sites are present compared to the case where they are not.

COLL 381

Model system for separating viral membrane binding and fusion

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Enveloped viruses must bind to a receptor on the host cell membrane to initiate infection. Membrane fusion is subsequently driven by a conformational change in the viral fusion protein. We have developed a method to disentangle the two processes of receptor binding and fusion using synthetic DNA-lipid conjugates to bind enveloped viruses to target membranes *in the absence* of receptor. We demonstrate this method by binding single influenza virus to target vesicles and measuring the rates of individual fusion events using fluorescence microscopy. Influenza fusion kinetics are found to be independent of receptor binding. This approach can be used to study viruses where challenging receptor reconstitution has previously limited single-virus fusion experiments (e.g., HIV, Ebola and Zika).

COLL 382

Stochastic molecular mechanisms in membrane traffic

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Membrane traffic, an essential cellular process that plays a role in many human diseases, requires key biophysical steps including formation of membrane buds, loading of these buds with specific molecular cargo, separation from the parent membrane, and fusion with the target membrane. The prevailing view has been that structured protein motifs such as wedge-like amphipathic helices, crescent-shaped BAR domains, curved coats and constricting dynamin rings drive these processes. However, many proteins that contain these structural motifs also contain large intrinsically disordered protein (IDP) domains of 300-1500 amino acids, including most clathrin and COPII coat components. While these IDP domains have been regarded primarily as flexible biochemical scaffolds, we have recently discovered that IDPs are highly efficient physical drivers of membrane budding. Further, our work demonstrates that IDP domains serve as strong drivers of membrane fission. *How can molecules without a defined structure drive membrane budding and fission?* Our results support the idea that disordered domains generate entropic pressure at membrane surfaces, which is critical to overcoming key biophysical barriers to membrane traffic. IDPs are particularly efficient generators of entropic pressure owing to their very large hydrodynamic radii, potential for electrostatic repulsion owing to high net charge, and the substantial entropic cost of extending them. More broadly our findings suggest that *any* protein, *regardless of structure*, can contribute to membrane remodeling by increasing entropic pressure, and paradoxically, that proteins that lack a defined secondary structure, IDPs, may be among the most potent drivers of membrane traffic. Our ongoing work focuses on understanding how entropic pressure influences membrane traffic, and designing biophysical tools for manipulating receptor recycling and signaling.

COLL 383

Blue fluorescent amino acid for studying membrane protein structure and dynamics

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The discovery of green fluorescent protein (GFP) has fundamentally transformed biological spectroscopy and imaging, allowing a wide range of biochemical and biophysical processes and interactions to be studied at the cellular and molecular level. However, the stringent conditions required for the fluorophore of GFP (and its derivatives) to mature can limit its applications. In this talk, we will describe a blue fluorescent amino acid (BFAA) that does not require a specific environment and additional time to form, has a large fluorescence quantum yield, long fluorescence lifetime, and good photostability. Specific examples will be discussed, showing the potential utility of this BFAA for investigating the structure and dynamics of membrane proteins via single-molecule spectroscopy or microscopy.

COLL 384

Novel application of cellulose paper as a platform for fabricating giant liposomes

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Giant liposomes — through the entrapment of enzymes, ribosomes, DNA, and cytoskeletal components — are useful *in vitro* models for cells. Giant liposomes are also accessible structures to study biophysical processes, such as in-plane phase segregation of lipid molecules and membrane proteins, the budding of membranes, and the transport of molecules across membranes. Here we report a facile and scalable method to fabricate biomimetic giant liposomes by using a cellulose paper-based platform. Termed PAPYRUS for Paper-Abetted liPid hYdRation in aqUeous Solutions, the method is general and can produce liposomes in various aqueous media and at elevated temperatures. Liposomes produced through PAPYRUS are free of residual solvents and are not exposed to electric fields during the growth process. Due to cellulose's poor solubility in aqueous solvents, even at elevated temperatures, giant liposomes with binary and ternary lipid mixtures with high transitions temperatures can be formed with high yield. Furthermore, the porosity of paper allows gentle fluid flow normal to the paper, i.e. such as flow provided by hydrostatic pressure, to free giant liposomes into the bulk for further manipulation. Fluorescent labeling and analysis of the cellulose fibers demonstrated, as expected, no contamination of the giant liposomes mixture with soluble cellulose. We find that giant liposomes can be formed in various aqueous media such as ultrapure water, physiologically relevant ionic buffers such as phosphate buffered saline, Tris buffered saline, and in sugar solutions such as sucrose. Giant liposomes with appropriate binary and ternary lipid compositions demonstrate the expected phase behavior when quenched to temperatures that favor phase-coexistence. The ease of manipulation of paper makes practical massive parallelization and scale-up of the fabrication of giant liposomes, demonstrating for the first time the surprising usefulness of paper as a platform for macromolecular self-assembly.

COLL 385

Investigating the mechanism of electromechanical coupling in voltage-gated ion channels by time-resolved x-ray & neutron interferometry

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Although x-ray crystal structures exist for several voltage-gated ion channel (VGIC) proteins, the mechanism of coupling voltage dependent conformational changes in the voltage sensor domains to opening and closing the pore domain remains controversial.

This situation persists because the usual physical techniques for protein structure determination cannot access the dependence of their structures on a transmembrane voltage. As a result, less direct experimental approaches and sophisticated computational techniques have been utilized to develop consensus models of the voltage-dependent conformations responsible for electromechanical coupling in VGIC proteins. Alternatively, we have developed two methods for vectorially-orienting VGIC proteins within single phospholipid bilayer membranes at the solid-liquid interface within electrochemical cells designed for the investigation of the scattering-length density (SLD) profile structures of these membranes by x-ray and neutron reflectivity. The spatial resolution, or sensitivity to detail within the profile structure, can be dramatically enhanced using interferometric techniques. We have employed time-resolved “pump-probe” techniques to investigate changes in both the x-ray and neutron SLD profile structures of the isolated voltage-sensor domain of a voltage-gated potassium channel as a function of the applied transmembrane voltage. The changes in each of these two independent SLD profile structures were found to be consistent with molecular dynamics simulations of the voltage sensor domain within a fully-hydrated phospholipid bilayer investigated as a function of the transmembrane voltage. This agreement allowed us to relate the voltage-dependent changes in the SLD profile structure to the conformational changes in the 3-D atomic level structure of the voltage sensor. These approaches are now being applied to the complete homotetrameric VGIC proteins wherein each subunit contains a voltage sensor and ¼ of the pore domain. This is more complicated because unlike their isolated voltage sensor domains, the complete VGIC proteins typically exhibit inactivation upon prolonged exposure to depolarizing voltages, with respect to the resting transmembrane voltage, which requires the cyclic application of polarizing and depolarizing voltages of much shorter duration on the order of milliseconds. Recent results employing time-resolved neutron interferometry will be reported.

COLL 386

Enriching Ag nanocrystals with gold

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Silver nanocrystals have fascinating optical properties known as localized surface plasmon resonance, which is essential to applications such as sensing and imaging. For example, Ag nanocubes embrace surface-enhanced Raman scattering (SERS) properties with enhancement factors up to 10^6 at visible excitation wavelengths for highly sensitive detection of chemical or biological species. Unfortunately, elemental Ag is highly susceptible to oxidation under conditions that involve oxidants, halide ions, and acids. Such chemical instability often results in changes to the morphology of Ag nanocrystals, particularly at corners and edges with high energies, and ultimately compromises their performance. Additionally, the toxicity of the released Ag^+ ions also limits the potential applications of Ag nanocrystals in a biological system. One potential solution to improve the chemical stability of elemental Ag is to form alloys with a more

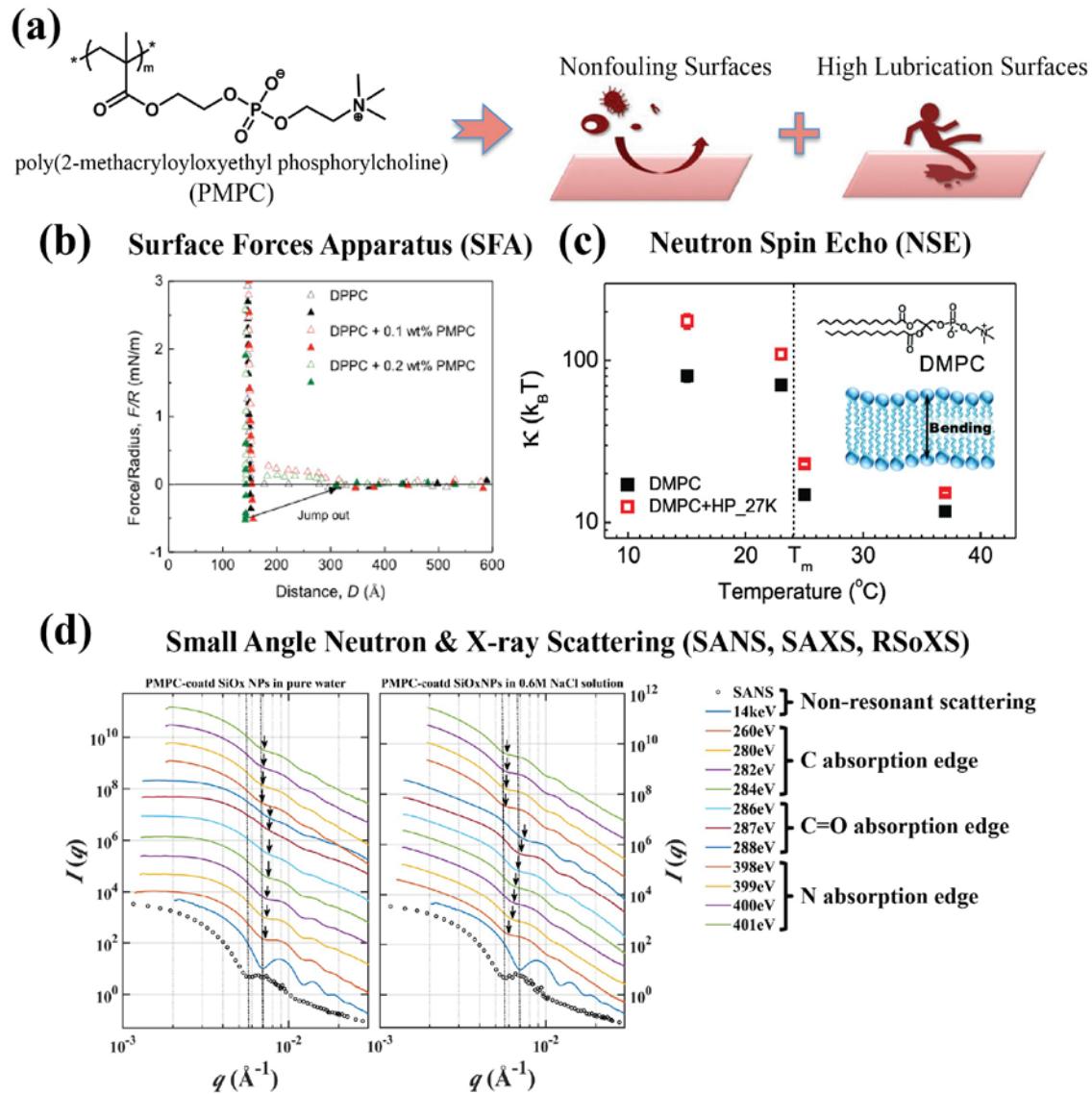
stable metal such as Au or protect the Ag nanocrystals with ultrathin Au shells. However, it is difficult to form Ag-Au alloys by reducing their precursors simultaneously in a solution phase due to their substantial difference in reactivity. It is also challenging to coat Ag nanocrystals with Au shells due to galvanic replacement. In this talk, I will report our recent developments in addressing these challenges. We have demonstrated the syntheses of Ag-Au bimetallic nanocrystals with greatly enhanced plasmonic properties and improved chemical stability for chemical and biological sensing and imaging.

COLL 387

Configurational behavior and charge correlation of Zwitterionic brushes at the solid-water interface

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Zwitterionic polymers (ZWP), on which each monomer segment bears both a positive and a negative charge, are an understudied class of polyelectrolyte macromolecules, most of which are simple polyelectrolytes (SPE) that bear a single sign of charge on each monomer. As each monomer has no net charge, the chains are not in extended configurations at low salt concentrations. In contrast to SPE, they expand when salt is added since the local attractions between positive and negative ions are screened, thereby producing a rich science base in understanding the configurations, ionic distribution, and in interfacial interactions of ZWP brushes in a variety of relevant and important ionic environments. The technical opportunity stems from observations that ZWP surface layers are particularly resistant to the colonization of microorganisms, with the consequent production of biofilms, on these surfaces. Here we thoroughly characterized the configurational behavior and lateral charge correlation of poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC) polymer brushes (Fig. 1a) at interfaces under a variety of ionic (mono- and multivalent) conditions with different concentrations. PMPC polymers only weakly interact with biomembranes via van der Waals forces as seen in force and neutron spin echo measurements, indicative of the nonspecific binding nature of PMPC polymers (Fig. 1b and c). The ion-induced changes of PMPC chain configurations are not apparent, in contrast to common polyelectrolytes and other ZWPs, such as poly(carboxybetaine) and poly(sulfobetaine) (Fig. 1d). This, in turn, establishes structure-property relationships between surface chemistry and the ability of a thin film to resist foulant adhesion for the design and optimization of antifouling materials.



COLL 388

Shape switchable patchy particles

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A facile method to synthesize shape switchable patchy particles was developed. The patch shape of the particles can switch reversibly between concave and convex feature upon external stimuli. The concave patchy particles are synthesized directly via a cluster encapsulation method, which can further shapeshifting to convex one when gradually absorbs organic solvent. The particles spontaneous assemble together into

chained, branched, zigzag and cyclic colloidal structures in a highly site-specific manner via surface liquid bridging.

COLL 389

General strategy for assembling metal chalcogenide capped semiconductor nanocrystals into open, mesoporous films with precisely controlled properties

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Mesoporous nanocrystal based thin films can be synthesized by block copolymer templating of cationic ligand stripped “naked” nanocrystals, followed by thermal treatment to remove the polymer template. This is a robust method to make high surface area structures from many nanocrystal building blocks including metal, metal oxide, metal fluoride, and metal chalcogenide nanocrystals. To date however, there have been no reports of using metal chalcogenide complex (MCC) capped nanocrystals as building blocks for mesoporous thin films. Such MCC capped nanocrystal based mesoporous films are desirable because they add an additional degree of chemical tunability to optimize materials properties for specific applications. For example compositionally matched molecular “solders” have recently been used to achieve the highest recorded mobility of solution processed semiconductors. Considering these advantages, we have developed a strategy to form mesoporous films of MCC capped semiconductor nanocrystals with precisely controlled properties. In our strategy, MCC capped nanocrystals are co-assembled with either a soluble polymer colloid or a pluronic surfactant template to form an organic-inorganic composite. Next, the reactivity of the MCC ligand is targeted to link the nanocrystals into a robust inorganic network by either exposing the films to a solution of soft metal ions which links the MCC ligands together, or the MCC ligands are thermally decomposed at mild temperatures to form a robust network of nanocrystals and the parent metal chalcogenide. Finally, the pore template is gently dissolved to open up the mesopores. These films show homogeneous and, in some cases ordered, porosity as observed by scanning electron microscopy, and they maintain the initial nanocrystal size, as determined by X-ray diffraction and ultraviolet-visible absorption spectroscopy. We further show that these materials can be chemically converted to other metal chalcogenides by sequential cation exchange without loss of pore structure. Finally, we show a strategy to conformally coat our mesoporous films with compositionally different semiconductor nanocrystals, opening a pathway for making well defined bulk heterojunctions between two different semiconductors. The combination of tunable porosity, high surface area and precisely controlled optical properties make these materials interesting for a variety of optoelectronic applications such as photovoltaics and photocatalysis.

COLL 390

Reversible self-assembly of monodisperse gold nanoparticle clusters in aqueous solution via pH-tunable interactions between surface ligands

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Metal nanoclusters composed of primary nanoparticles are of great interest in various advanced applications, including biomedical imaging, catalysis, and imaging subsurface reservoirs. Recently, we demonstrated a new colloidal synthesis to make reversible monodisperse self-limited clusters of nanoparticles in the range of 20-100 nm in less than a minute from 5 nm GSH-capped Au NPs by balancing short-ranged attraction against long-ranged repulsion. The size of the clusters could be tuned simply by controlling the pH, primarily to vary the short-ranged attraction between the glutathione molecules on the surface rather than the long-ranged repulsion between particles. For example, as the pH is lowered from 5.4 to 3.8, partial protonation of GSH anions to form a mixture of anions and zwitterions increased the hydrogen bonding between GSH markedly resulting in an increase in the hydrodynamic diameter of the clusters from 20 to 100 nm. This change is far greater than would be expected from the change in long-ranged electrostatic repulsion, given a small change in the zeta potential. The clusters fully dissociate to primary Au NPs upon raising the pH to 7 to break the hydrogen bonds between the GSH molecules, but on a slower time scale of ~ 1 hour. The slower time scale for dissociation versus association may be attributed to greater attraction between a nanoparticle and a cluster versus that between two nanoparticles.

Although the low zeta potential of the GSH-capped Au clusters (<10mV) was enough to provide long-ranged repulsion for self-limited growth at time scales less than several hours, the electrostatic repulsion between the clusters was too weak to prevent aggregation between clusters at longer time scales. With the addition of small amount of amounts of charged citrate to the GSH coated nanoclusters (for example 1/1 CIT/GSH), the time scale of cluster-cluster aggregation was lengthened, such that the hydrodynamic diameter of the clusters was constant for 1 day. This greater stability of the clusters may be explained by the greater charge (electrostatic repulsion) of the clusters and reduced GSH-GSH interactions upon adsorption of citrate.

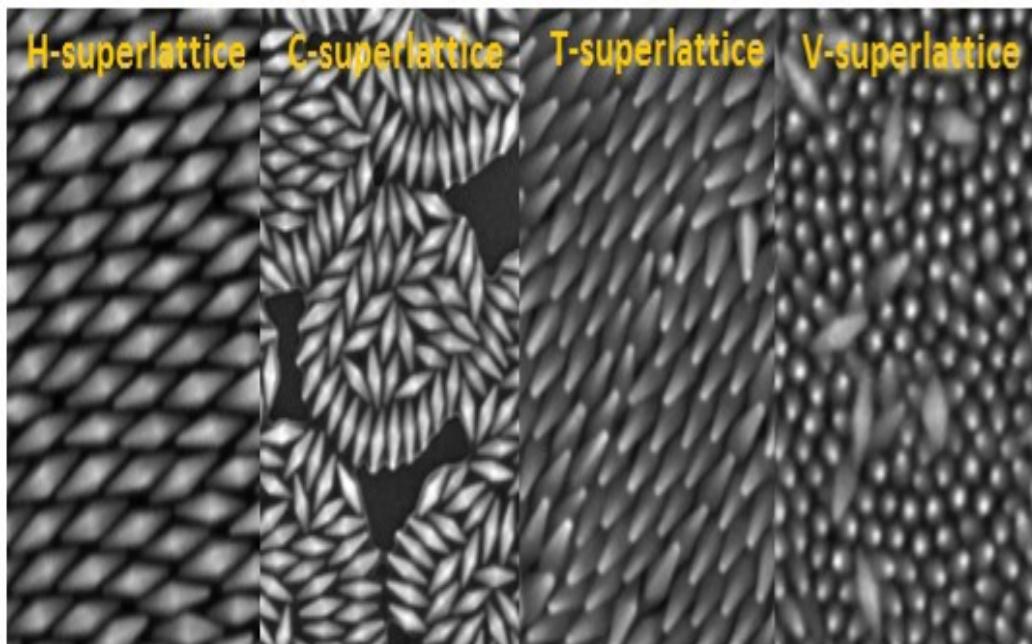
COLL 391

Two-dimensional bipyramid plasmonic nanoparticle superstructure with four distinct orientational packing orders

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Nanoparticle superlattices represent a new class of advanced metamaterials which have exhibited unusual optical, electrical, plasmonic, magnetic and mechanical properties. In particular, two-dimensional (2D) ordered plasmonic nanoparticle arrays can take full advantage of the shape-dependence, spatial arrangement, and directional properties of the nanoparticle. The properties of these superlattice sheets can be adjusted by controlling the nanoparticle size and adjusting the interparticle spacing, changing the shape of the constituent nanoparticles and further tuning their orientations. In principle, any plasmonic particles in the “artificial nanoparticle periodic table” could be used as constituent elements towards the fabrication of superlattice solids. However, only a few plasmonic nanoparticles have been successfully utilized in nanosheets fabrication due to the extreme difficulties in controlled self-assembly, limiting the further application of 2D superlattice.

Here, by using a new plasmonic element – gold nanobipyramid (Au NBP) as building blocks, we fabricated a new type of plasmonic nanoparticle superlattice, which showed four distinct orientational packing orders, corresponding to horizontal alignment, circular arrangement, slanted alignment and vertical alignment of constituent particle building elements. The orientational packing ordering directly influenced plasmonic coupling strength and modes, hence, determined the surface-enhanced Raman scattering (SERS) enhancements of plasmonic superlattices. In particular, vertical alignment structures showed the highest Raman enhancement factor, which was about 77-fold greater than the horizontal alignment arrays and about 19-fold greater than circular arrangement. The results reveal the nature and significance of orientational ordering in controlling plasmonic coupling and SERS enhancements of ordered plasmonic nanoparticle arrays.



Four distinct packing orders from nanobipyramid superstructure.

COLL 392

Watching nanoparticle growth with tandem *in situ* SAXS-XAS

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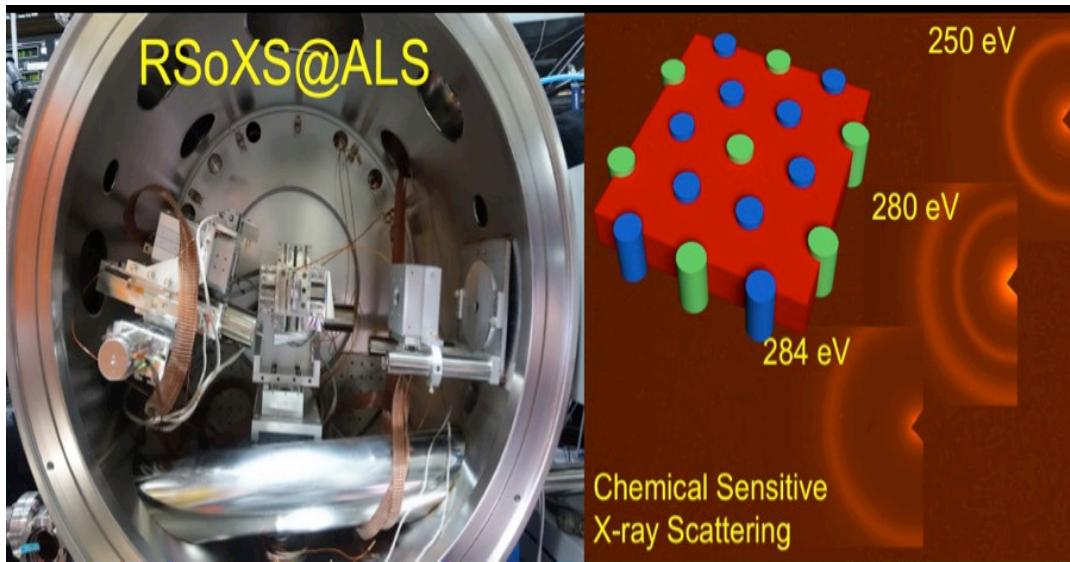
Nanoparticles have been applied in a variety of fields such as catalyst, medicine, and sensor. Controlling their growth and assembling them into hierarchical structures will be crucial for the applications. Current understanding of the nanoparticle growth and their assembly mostly derive from the characterization after they are synthesized. It will be interesting and important to have the atomic-level understanding of mechanism of the nanoparticle formation and assembly during the synthesis. The tandem *in situ* SAXS-XAS will be a unique way to achieve this goal. In this talk, I will talk about nanoparticle growth using SAXS-XAS.

COLL 393

Multimodal resonant soft x-ray scattering for soft materials

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Recent development of resonant soft x-ray scattering (RSoXS) at the Advanced Light Source (ALS) has enabled its applications to many critical research areas of materials research. Combining conventional x-ray scattering with soft x-ray absorption spectroscopy, RSoXS is a unique chemical sensitive structure probe that provides a novel route to unambiguously decipher the complex morphologies of mesoscale materials. Tuning x-ray photon energies to match the absorption spectrum of the different chemical components, the scattering contributions from the different components can be selectively enhanced, enabling a glimpse into these complex morphologies with unprecedented details. Applications of RSoXS have been extended to the areas of structured polymer assemblies, organic electronics, functional nano-composites, as well as liquid crystals. The overarching challenge now across various disciplines is to investigate the interfacial phenomenon of new and complex materials in their operational conditions, including batteries, catalysts, gas separations, fuel cells and water desalination, and bio-hybrid systems. In order to achieve comprehensive understanding of the *in-operando* process, we need multimodal research tools that provide information from different perspectives in order to discover, understand, and control the interfacial phenomena and architectures. This will require combining different *in situ* probes, such as x-ray scattering and electron microscopy, simultaneously in the same operating condition. We will discuss the recent development of customized instrumentation, multimodal characterization methods, as well as comprehensive theory for the extraction of the chemical distribution and spatial arrangement at multiple length scales in the application of soft materials.



COLL 394

Self-assembly of two-dimensional nanoparticle superlattice membranes: A study by synchrotron x-ray scattering

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Critical photonic, electronic, and magnetic applications of two dimensional (2D) nanoparticle superlattices often require special structural states such as the often desired perfect single crystal phase with long range orderings and limited defects. Self-assembly of nanoparticles at liquid/air and liquid/liquid interfaces has emerged as a simple yet efficient way to create 2D superlattices with tunable properties. Although microscopic mechanisms for the self-organization of ligand stabilized nanoparticles have been widely explored, the macroscopic patterns as a consequence of the inter-particle interactions on large length scales vary drastically under different assembly environments. Even for a simple case of evaporating a colloidal droplet of nanoparticles on a surface, a variety of patterns have been reported, ranging from ordered 2D, three dimensional (3D) nanoparticle superlattices, and fractal-like aggregates to percolated networks. Having such vastly different structures of nanoparticle superlattices hinders the identification of their physical properties thus creating obstacles for their device applications. It is therefore essential to further understand and control the nanoparticle self-assembly mechanism. X-ray scattering based techniques provide a unique *in-situ* and time-resolved tool to study the nucleation and growth kinetics of these superlattices at the assembly interfaces. With X-ray scattering, we were able to track the superlattice phase evolution of the droplet evaporated nanoparticle colloidal suspensions. Recently, we also showed that nanoparticle membranes formed at air/water interfaces exhibit a small (sub-nm) but significant ligand distribution asymmetry on nanoparticle surface. Molecular dynamics simulations elucidate the roles of ligand coverage and mobility in

producing and maintaining this asymmetry. Understanding this Janus-like membrane asymmetry opens up new avenues for designing nanoparticle superstructures.

COLL 395

Investigations of water structure at lipid interfaces

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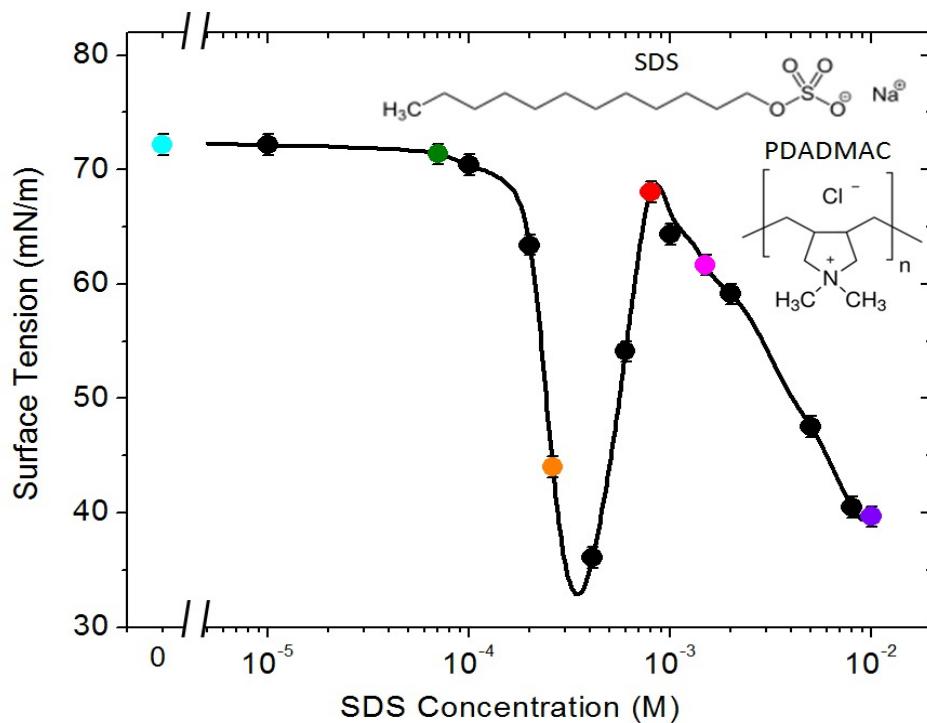
Vibrational sum frequency spectroscopy (VSFS) is employed to investigate interfacial water structure and lipid order at the water/air interface with Langmuir monolayers of phospholipids. The two-dimensional pressure of the monolayer is controlled in a Langmuir trough. The physical behavior of the monolayer can also be varied by controlling the alkyl chain and lipid head group chemistry. Divalent metal ions such as Ca²⁺ and Mg²⁺ can interact with phosphate and carboxylate moieties on lipid head groups through electrostatic interactions. These interaction are fairly weak for zwitterionic lipids like phosphatidylcholine, where a positive charge is also present. They become considerably stronger when negatively charged lipids like phosphatidylserine is employed (Kd values approximately 1 mM in the later case). The introduction of Ca²⁺ will specifically change the VSFS spectrum in the OH stretch region by displacing interfacial water molecules and attenuating the surface change. Interestingly, the situation changes when Cu²⁺ binds to phosphatidylserine membranes. In this case, much less change is noted in the 3200 cm⁻¹ peak as the net charge at the interface is not significantly altered by cation binding.

COLL 396

Interactions of surfactants and polyelectrolytes at water surface studied by surface tension and phase-sensitive sum frequency generation

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Surface tension has been the most popular measure of a molecule's surface activity. However, in many cases the complex behaviors of the surface tension are difficult to interpret. For example, the aqueous solution of sodium docecylo sulfate (SDS) and poly(diallyldimethylammonium chloride) (PDADMAC) shows a dramatic change in surface tension when the concentration of SDS is increased. We found that the dramatic surface tension change is a result of a surface charge reversal. The decrease of surface entropy resulting from a better ordering of surface water molecules has a significant contribution to the change of surface tension.



COLL 397

Biomedical surface analysis: Recent advances and opportunities for characterizing immobilized proteins and functionalized gold nanoparticles

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Biomedical surface analysis has undergone significant and numerous advances in the past 40 years in terms of improved instrumentation, introduction of new techniques, development of sophisticated data analysis methods, and the increasing complexity of samples analyzed. Comprehensive analysis of surfaces and surface immobilized biomolecules (peptides, proteins, DNA, etc.) with modern surface analysis instrumentation provides an unprecedented level of detail about the immobilization process and the structure of the immobilized biomolecules. Results from x-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS), near edge x-ray absorption fine structure (NEXAFS), surface plasmon resonance (SPR) and quartz-crystal microbalance with dissipation (QCM-D) biosensing, atomic force microscopy, and sum frequency generation (SFG) vibrational spectroscopy combined with computation methods such as molecular dynamic (MD) simulations provide important information about the attachment, orientation, conformation, etc. of biomolecules. However, even with the advances that have been achieved with these powerful surface analysis techniques, there still remain many significant challenges for biomedical surface analysis. These include characterizing the surface chemistry and structure of nanoparticles, determining the atomic level structure of protein bound to surfaces, 3D imaging of cells and tissue sections, and maintaining biomolecules and

materials in a biological relevant state when using ultra-high vacuum based analysis techniques.

This talk will discuss the recent results and current challenges in biomedical surface analysis as it relates to characterization of both immobilized proteins and functionalized gold nanoparticles, as well as what is being done to address these challenges.

COLL 398

Surface-modified nanoparticles for biomedical imaging

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We will report some of our recent developments in the advanced imaging systems. We will discuss how to use various surface modified nanoparticles for bioimaging including quantum dots and mesoporous nanoparticles. By various surface functionalization schemes, it is possible to control the location of nanoparticles both *in vitro* and *in vivo* allowing the measurement of chemical environments inside cells and tumors. For *in vitro* imaging, we have developed a novel ratiometric pH sensor design using water-soluble, dual-emission, Mn²⁺-doped quantum dots (Qdots) decorated with *D*-penicillamine (DPA-MnQdots). In contrast to more commonly used ratiometric pH-sensing schemes that rely on the coupling of two fluorophores, our design uses only a single emitter, which simplifies ratiometric sensing and broadens the applications of the sensor. Our single-emitter DPA-MnQdots exhibit two emission bands, at 510 nm (green) and 610 nm (red), which are respectively attributable to exciton recombination and emission of the Mn²⁺ dopants. The emission intensity ratio (I_{510}/I_{610}) of the DPA-MnQdots linearly depends on surrounding pH values within physiological conditions (from pH 4.5 to 8.5). Moreover, the biocompatible DPA-MnQdots were used for long-term monitoring of local pH values in HeLa cells.

As for the *in vivo* imaging, we have developed multi-photon microscopy using clearing reagent. It has been shown that blood vessels in the mouse whole brain can be imaged simultaneously. The penetration depth of multi-photon microscopy using clearing reagent can be as deep as 4 mm. On the same platform, it is possible to measure the movement of blood cells in living mouse at a frame rate higher than 100 frame/s. Such platform can also be used in imaging disease model and tumors.

COLL 399

Structure and function of surface immobilized peptides and enzymes in air

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Surface immobilized peptides and proteins are widely used in many important applications such as antimicrobial coatings, biosensors, biochips, and nano-electronics. In many of such applications, surface immobilized peptides and proteins are used in air without the presence of bulk water. Peptides and proteins may lose their functions in air

due to their structural changes. In this study, we systematically investigated molecular structures of surface immobilized peptides and proteins in air using sum frequency generation (SFG) vibrational spectroscopy, attenuated total reflectance (ATR) – FTIR, circular dichroism spectroscopy, and molecular dynamics simulations. We successfully elucidated structure-function relationships of surface immobilized peptides and proteins in air with no bulk water. We also successfully developed co-immobilized hydromimetic functionalities with peptides and proteins, which retained peptide/protein structures in air and greatly enhanced their functions in water-free environments.

COLL 400

In-situ surface spectroscopy and imaging: From electrocatalytic to live cell interfaces

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While many surface spectroscopies offer unprecedented precision and surface sensitivity, they can only be applied under somewhat restrictive environments such as high vacuum. Here, I describe two studies which combine surface vibrational spectroscopy with novel instrumentation to enable the dynamic molecular analysis of interfaces of importance to science and technology. One study involves the use of in-situ SFG to investigate electrochemical oxidation of different alcohols on platinum, while the other involves the use of mechanical traps for SERS analysis and 3D imaging of the plasma membrane of single live cells. These studies highlight the importance of in-situ techniques for investigation of important problems in surface science.

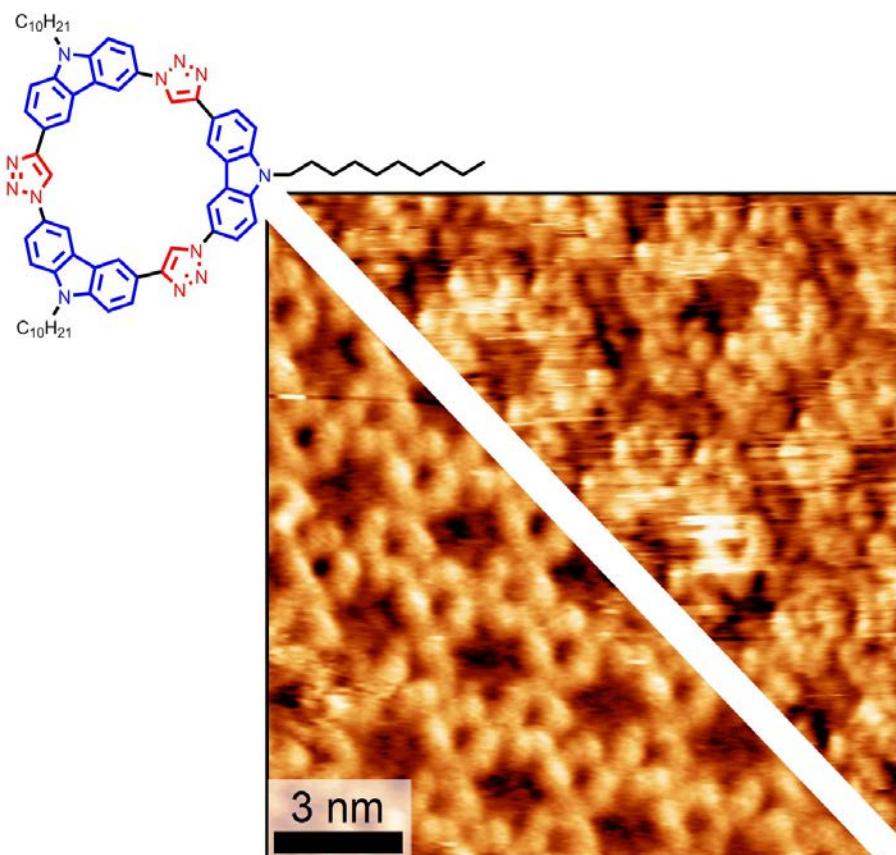
COLL 401

Hierarchical self-assembly of functionalized tricarbazolo triazolophane macrocycles at the liquid-solid interface

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Small molecule self-assembly at surfaces offers an efficient route to highly-ordered organic films that can be programmed with function for a variety of chemical and electronic applications. However, the success of these materials depends on our ability to program intermolecular interactions that will lead to excellent ordering at the surface and subsequent stacking into a thin film. Here, we demonstrate new results toward this goal of intelligent, bottom-up molecular design of a prototypical molecular platform of tricarbazolo triazolophane macrocycles (tricarb). Building on this macrocycle framework, we program peripheral alkyl units and other functional groups to steer 2D packing and

3D stacking. The supramolecular assembly is characterized by scanning tunneling microscopy at the solution-graphite interface. Using this approach, the 2D assembly can be steered by molecular design and synthesis between two different architectures that differ in packing density. Each architecture is assembled through hydrogen bonding and close-contact van der Waals interactions. We have also applied these design strategies to achieve ordered 3D growth into multilayers, which also depends strongly on the programming of functional moieties in the molecule that can be tuned to block or limit growth away from the surface. Initial electrochemical studies suggest that highly ordered tricarb multilayers may serve as a platform for electron transport in thin film applications.

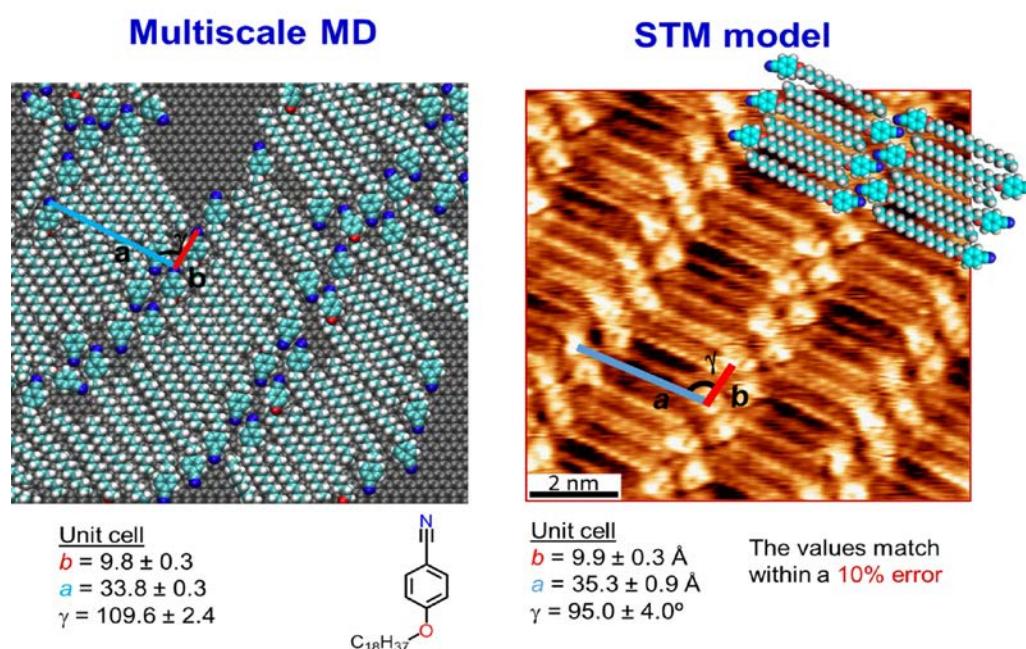


COLL 402

Predicting crystalline structures of organic photovoltaic materials involving alkoxybenzonitriles via multiscale computer-aided design

John M. Espinosa Duran, johespin@indiana.edu, Henry D. Castillo, James Dobscha, Sibali Debnath, Steven L. Tait, Amar H. Flood, Krishnan Raghavachari, Peter Ortoleva. *Chemistry, Indiana University, Bloomington, Indiana, United States*

Self-assembly of alkoxybenzonitrile molecules on graphite is simulated via an atom-resolved multiscale approach. Results show good agreement with STM observations for the alkoxybenzonitrile molecules in octanoic acid on graphite (HOPG). In particular, prediction of different stable crystalline structures for the various lengths of alkane tails evaluated align with observations. This comparison is uniquely enable via an all-atom multiscale approach implemented our custom version of Gromacs 5.0.4 and an in-house *ab initio* generated Charmm-compatible force field. Starting with a random or semi-equilibrated array of alkoxybenzonitrile molecules in octanoic acid or vacuum, the longtime evolution to surface-localized crystalline structures is made feasible and therefore can play a role in the computer aided design of nanomaterials (e.g. those for organic photovoltaics). The multiscale simulations are up to 10 times faster than conventional MD simulations.



Multiscale simulation result and STM image for alkoxybenzonitrile-18 in octanoic acid on HOPG

COLL 403

First-principles modelling of supramolecular organic assembly driven by electrostatic interactions

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The key importance of controlling supramolecular organic assembly for nanodevice fabrication has been clear since the early 90's i.e., soon after the dawn of experimental nanotechnology. Most of the earlier modeling work in this field aimed to rationalise the

experimentally observed two-dimensional assembly into increasingly complex nanostructures. More than two decades later, modeling techniques now start being able to *predict* supramolecular assembly with some degree of confidence. Besides significant theoretical advances and increased computing power, this has been enabled by pragmatic approaches that initially rely on experimental feedback to calibrate theoretical tools, and later allow proposing the fabrication of novel structures with desired functionalities to synthetic chemists and STM experts.

In this talk I will exemplify the above by describing various instances of 2D self-assembly of organic supramolecular structures supported by metal substrates, focusing on the role played by electrostatic interactions. I will discuss how these structures can be obtained by irreversible as well as reversible molecular charging, achieved by deprotonation or electron transfer, respectively, making it possible to fabricate peculiarly complex, or “tunable”, low-dimensional supramolecular assemblies. A typical application may e.g. start with appropriate choice/synthesis of molecules that will charge up upon adsorption on a target substrate, and extend to predicting the role of co-adsorbed linkage atoms to yield a charged organic salt adlayer with a desired work function value. If time allows, recent attempts of combining DFT calculations, classical molecular dynamics and Monte Carlo techniques to rationalise the results of co-adsorbing more than one chargeable organic species will also be presented, as well as efforts to design thicker organic structures with novel electronic properties.

COLL 404

Electronic effects in the self-assembly of strong donor/acceptor mixtures on metal surfaces

Roberto Otero, *roberto.oteru@uam.es. Universidad Autónoma de Madrid, Madrid, Spain*

Mixtures of organic molecules with donor and acceptor character are of paramount importance for the development of electronic and optoelectronic devices. When such organic films are contacted with metallic electrodes, charge transfer between the electrode and the organic active material affects considerably their physical and chemical properties. In particular, charge transfer from the substrate can potentially hinder intermolecular charge transfer, as seems to be the case in previous works. In this talk I will describe experimental and theoretical investigations demonstrating that intermolecular charge-transfer can still take place at metal/organic interfaces provided that the electron affinity of the acceptor is large enough and the ionization potential of the donor remains low. Moreover, we will show that the stoichiometric flexibility achieved for donor/acceptor mixtures on solid surfaces enables an extremely accurate method to control the charge state of the electroactive species.

COLL 405

Playing with electrons: How physics meets organic chemistry in the engineering of molecular interfaces

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Advances in the precision and the temperature range of experiments at surfaces and interfaces have led to a wealth of new science over the past few years. In particular the ability to use the whole breadth of organic synthesis for the creation of specific molecules and molecular epitaxy as well as surface engineering to modify the physical properties of the molecular systems practically at will have expanded the range of results dramatically. This development, it turns out, leads to a huge variety of experimental results which is sometimes hard to assign to a particular effect or property. Here, theoretical simulations, which have also substantially improved over the last years, turn out to be essential. We shall, on a number of model systems and for a number of effects like Kondo resonances, vibrations, chiral adsorption, and molecular rotations show that this variety and precision make it possible today to use molecular interfaces like lab benches and to perform detailed experiments on individual electrons and spins.

COLL 406

Electronic structure of two-dimensional pi-conjugated networks: Impact of lattice symmetry

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In this presentation, we will discuss the results of recent electronic-structure calculations and molecular-dynamics simulations on:
monolayers of two-dimensional polymer networks (covalent organic frameworks); here, we will detail how the symmetry of the repeat units (i) including three-arm and four-arm cores— and of the lattice influences the nature of the electronic bands (either totally flat or dispersive) at/near the Fermi energy; and
(ii) interfaces between such two-dimensional conjugated-polymer monolayers and substrates such as gold or boron nitride; in particular, we will describe the energy-level alignments at these interfaces.

COLL 407

Tuning charge transport in supramolecular assemblies of porphyrins on Au

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Molecules offer exceptional capabilities for the design of organic electronic components, as well as integrated elements of CMOS based technologies, due to the ability to readily tune their electronic states through designed synthetic modifications. Among the many challenges in implementing molecular/organic electronic devices, perhaps the most significant is understanding the correlation between chemical structure and the resulting conductive characteristics of a molecule assembled on a surface. Recently we have explored how nearest-neighbor interactions can be used to afford charge delocalization in supramolecular assemblies to shift transport out of the tunneling regime into the more chemically tunable charge-hopping regime. Here, the transport properties of a series of free-base and zinc coordinated tri-pyridyl and tri-phenyl porphyrin thiols inserted into a dodecanethiol matrix on Au(111) were studied using scanning tunneling microscopy (STM). For single molecules, the tunneling efficiency and I-V behavior was found to be dominated by through bond tunneling. However, when these same molecules were driven to assemble into islands of ~ 10 nm in dimension (e.g. through pi-stacking), distinct changes in their charge transport properties were observed, whereby a reduction in the charge confinement energy facilitated the transition from a purely tunneling mechanism to a charge-hopping mechanism. Directing such assemblies into pre-designed architectures however, still represents a significant challenge, and to address this we have explored the use of click-chemistry have been employed to enable the construction of better controlled supramolecular structures. The fabrication and assembly process, and its impact on the electronic properties of the materials will be discussed.

COLL 408

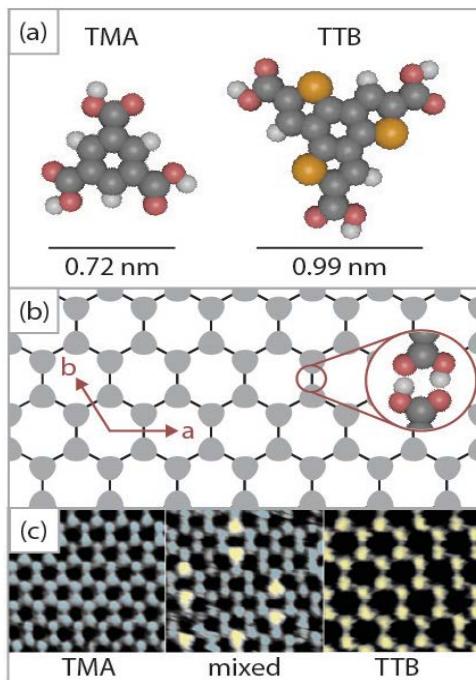
Entropic intermixing in a binary molecular system: A two-dimensional hydrogen-bonded molecular substitutional solid solution

Jennifer MacLeod^{3,2}, jennifer.macleod@qut.edu.au, **Josh Lipton-Duffin**^{4,2}, **Dmitrii F. Perepichka**^{1,5}, **Federico Rosei**^{2,5}. (1) Chemistry, McGill University, Montreal, Quebec, Canada (2) Centre for Energy, Materials and Telecommunications, INRS, Montreal, Quebec, Canada (3) Chemistry, Physics and Mechanical Engineering, Queensland University of Technology, Brisbane, Queensland, Australia (4) Institute for Future Environments, Queensland University of Technology, Brisbane, Queensland, Australia (5) Centre for Self-Assembled Molecular Structures, McGill University, Montreal, Quebec, Canada

Two-dimensional (2D) molecular self-assembly leads to the formation of well-defined supramolecular layers with tailored geometrical, compositional and chemical properties. To date, random intermixing and entropic effects in these systems have been associated with glassy phases and imperfect crystals. Here, we describe a 2D crystalline molecular self-assembled system that incorporates random substitutional defects. The system comprises two C₃-symmetric hydrogen bonding units with different sizes: terthienobenzenetricarboxylic acid (TTB) and 1,3,5-benzene tricarboxylic acid (TMA). Both of these molecules are well-studied, and self-assemble on highly oriented pyrolytic graphite (HOPG) surfaces to form hydrogen-bonded porous meshes. When

combined, the TTB and TMA can spontaneously form an intermixed lattice, where a lattice comprising predominantly TMA also includes a small number of TTB-substituted sites. This system is analogous to the substitutional solid solutions formed in some alloys of metals.

By combining density functional theory (DFT) calculations with Monte Carlo simulations, we are able to elucidate the thermodynamics of the system. This work provides insight into minimization of Gibbs free energy in an epitaxial molecular system, where molecule-substrate interactions, molecule-molecule interactions and the multiplicity of the available lattice configurations all play an important role.



(a) Molecular structures of TMA and TTB. (b) General scheme for the chickenwire mesh formed by cyclic dimeric association (shown at inset) between threefold symmetric carboxylic molecules. The mesh is hexagonal with a two molecule basis. For pure TMA, $a=1.61$ nm. For pure TTB, $a=2.37$ nm. (c) Scanning tunneling microscopy images showing the TMA, mixed, and TTB lattices. Each image is 10 nm × 10 nm.

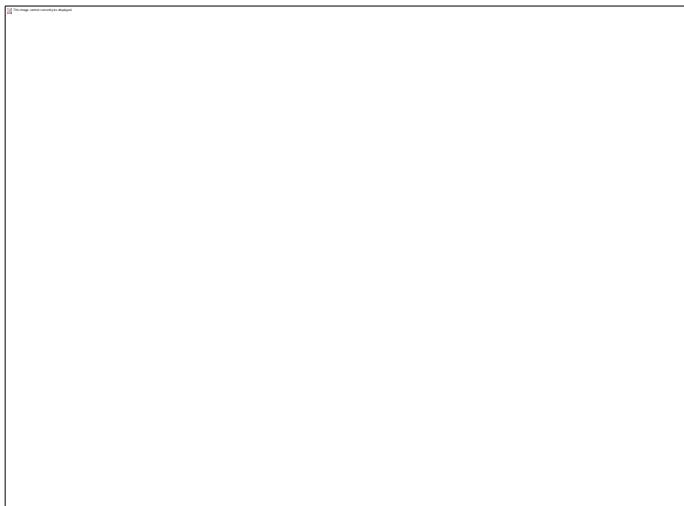
COLL 409

Self-assembly under confinement: Nanocorral for understanding fundamentals of 2D crystallization

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Supramolecular self-assembly under confinement opens the door to investigate elementary aspects involved in 2D crystallization. Until now, such studies have been

ample, mainly due to the limited possibilities to confine the assembling molecules within well-defined nanocompartments. Here, we demonstrate the formation of nanocompartments, called corrals, on graphite with nanoscale control over size, shape and orientation, and discuss how corral parameters impact the resultant self-assembly. Nanocorrals are created by scanning probe lithography, where the tip of a scanning tunneling microscope (STM) is employed to locally expose areas of free graphite on an otherwise densely grafted surface. Upon exposure of the graphite surface, molecules dissolved in an organic liquid above the surface undergo supramolecular self-assembly selectively within these corrals, as observed by STM. However, as opposed to self-assembly on bare graphite, the gradual surface revelation has a pronounced effect on nucleation and growth events. This is reflected by a strong bias of the assembly orientation and domain size. A systematic study on corral size, shape and orientation reveals the importance of geometric and kinetic constraints placed on the self-assembly during the initial stages of corral formation. These constraints eventually allow control over “seeding and growth” processes. The principles discussed in this work are believed to be invaluable tools for future studies on the thermodynamic and kinetic parameters involved in 2D crystallization.



COLL 410

Build-up and breakdown of a cytoskeleton in complex coacervate synthetic cells

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Simple and complex coacervate microdroplets are attractive models of membrane-less synthetic cells and compartments. However, efforts to shape and strengthen them have lacked ways to incorporate structures that can bear loads and exert forces. Here we show that dissipative self-assembly can take place in complex coacervates of cationic polypeptides and NTPs or RNA, enabling the dynamic formation and degradation of protein filaments inside the coacervates. In the intrinsically crowded environment of the coacervates filaments further assemble into bundles that are able to strongly deform the

coacervate droplets as long as chemical energy is supplied. At sufficiently high precursor concentrations the filament can induce fragmentation of the coacervate compartments, dividing them into multiple daughter cells. These experiments could help explain how structure formation was favored in crowded protocells and open the way for experiments aimed at controlling the shape and rigidity of membrane-less synthetic cells.

COLL 411

Actin encapsulation and assembly in polypeptide coacervates

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Biomolecules typically exist and do the work of the cell in crowded environments, whether in the cytoplasm, membrane-bound organelles, or non-membrane-bound phase-separated complexes. This is in stark contrast to the dilute solution limit traditionally used to study biomolecular properties and interactions, and begs the question of how crowded environments with plentiful weak interactions impact biologically important molecular reactions. Building on recent success in encapsulating proteins in the crowded interior of liquid polyelectrolyte-complex coacervates, we employed polypeptide coacervates as a platform to examine the electrostatically-driven self-assembly of the ubiquitous protein actin into linear filaments. Remarkably, in spite of the high concentration of strongly charged molecules in the coacervate interior, we observed actin assembling into micron-long filaments. Moreover, the rate of actin self-assembly was enhanced > 50-fold inside coacervates, and, consistent with an increase in the local protein concentration in coacervates, encapsulated actin assembled below the critical concentration of bulk solution. In contrast to the uniform distribution of the non-reactive protein bovine serum albumin (BSA) inside coacervates, actin filaments were found strongly peripherally localized. While the polycationic component of these coacervates, poly-L-lysine, is known to nucleate actin filaments in solution, we did not observe the hallmarks of lysine-mediated nucleation in coacervates, suggesting a different mechanism for coacervate-facilitated actin assembly. Together, these results highlight the variations in protein-protein interactions from dilute to crowded solutions and demonstrate the importance of direct measurements in physically crowded environments.

COLL 412

Cell-like structures by coacervation: Polymer microcapsules with addressable inner compartments that can harbor biomolecules, colloids or microbial species

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Eukaryotic cells have an architecture consisting of multiple inner organelles such as the nucleus and mitochondria, each surrounded by a membrane and having unique internal contents. Consequently, each organelle has a distinct function within the cell. In this study, we create biopolymer microcapsules with a compartmentalized architecture as in eukaryotic cells. To make these capsules, we present a biocompatible method that solely uses aqueous media (i.e., avoids oil phases), requires no sacrificial templates, and employs a minimal number of steps. Our approach exploits the coacervation of oppositely charged polymers dissolved in aqueous media. Specifically, droplets of an anionic biopolymer are generated using a home-made microcapillary device, with the droplets being sheared off the capillary tip by pulses of gas (air or nitrogen). The liquid droplets are then introduced into a reservoir whereupon they encounter multivalent cations as well as a cationic biopolymer; thereby, a solid shell is formed around each droplet by coacervation. In the next step, a discrete number of these capsules are encapsulated within a larger outer capsule by repeating the same process with a wider capillary. Our approach allows us to control the overall diameter of these multicompartment capsules (MCCs) (~ 300–500 μm), the diameters of the inner compartments (~ 100–300 μm), and the number of inner compartments in an MCC (1 to > 5). More importantly, we can encapsulate different payloads in each of the inner compartments, including colloidal particles, enzymes, and microbial cells. A hallmark of biological cells is the existence of cascade processes, where products created in one organelle are transported and used in another. As an initial demonstration with our MCCs, we study a cascade process involving two strains of bacteria, which communicate through small molecules known as autoinducers. In one compartment of the MCC, we cultivate bacteria that produce autoinducer 2 (AI-2). The AI-2 then diffuses into an adjacent compartment within the MCC wherein a reporter strain of bacteria is cultivated. The reporters imbibe the AI2 and in turn, produce a fluorescence response. Thus, the action (AI-2 production) and response (fluorescent signal) are localized within different compartments in the same MCC. We believe this study is an important advance in the path towards an artificial cell.

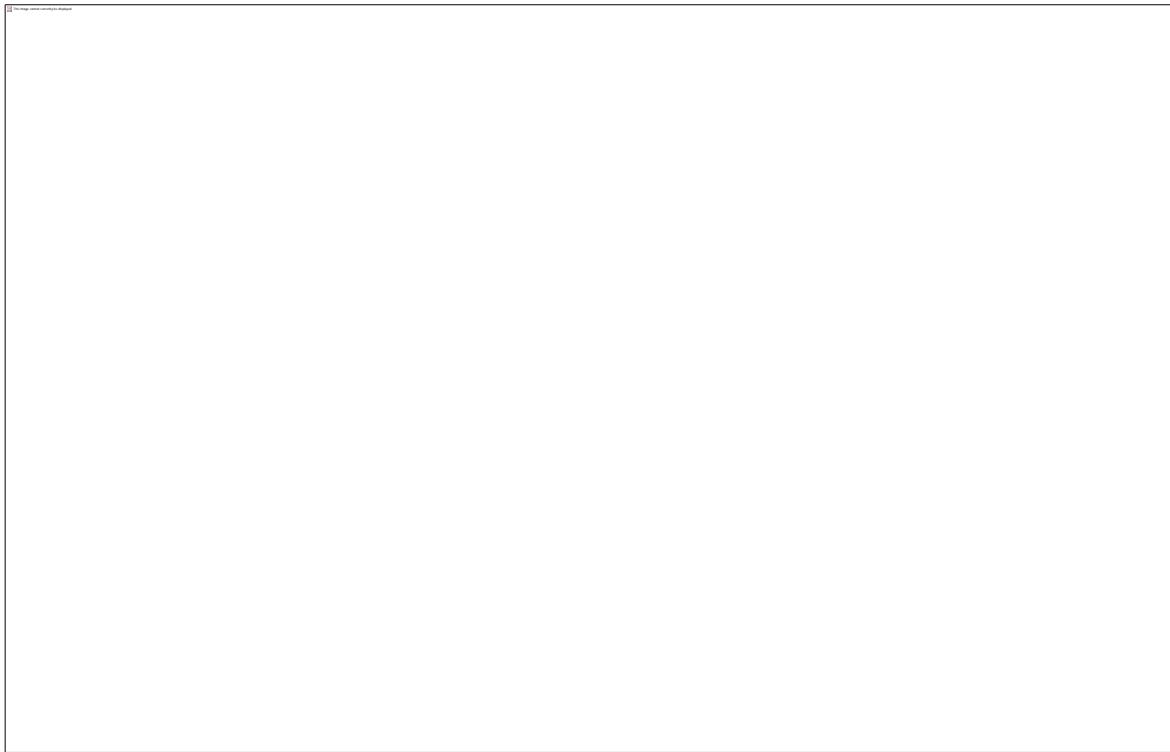
COLL 413

Protein coacervation in the processing of biomolecular composites

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Coacervation has received renewed interest in the past decade. Protein-based coacervates have notably been recognized to be involved in the formation of wet-resistant adhesives, which is related to their unique combination of physico-chemical characteristics: low viscosity, non-dispersity in water under specific pH and ionic strength, extremely low interfacial energy, and shear-thinning behaviour.

The role of protein coacervation in the formation of the squid beak will be presented. The squid beak exhibits a remarkable mechanical gradient from its soft base to its hard tip and is solely made of organic components, namely chitin and proteins with the latter the dominant phase at the tip. Combining RNA-Seq with proteomics, we have shown that the beak contains two protein families, namely chitin-binding proteins (DgCBPs) as well as modular histidine-rich proteins (DgHBPs). DgHBPs form concentrated protein coacervates that can spontaneously spread and infiltrate the nanoporous chitin scaffold. These process generates spatially controlled desolvation, resulting in the impressive biomechanical gradient. Such findings provide molecular-scale strategies for designing gradient materials, which could be used to create polymer-matrix composites using aqueous-based chemistry. Latest efforts to characterize DgHBPs coacervates by Small-Angle X-ray Scattering (SAXS) and 2D protein NMR will also be presented.



Proposed model for jumbo squid beak gradient formation (from Ref. [4])

COLL 414

Alternative solvent for biology

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Membraneless organelles, though less famous than their lipid encapsulated counterparts are important and ubiquitous cellular compartments. A number of these bodies have been observed to have characteristics of liquid droplets, and that their formation can be understood as a polymeric phase separation.

The protein Ddx4 is associated with nuage, membraneless organelles in germ cells. We have quantitatively studied the formation of membraneless organelles by this protein both inside cells and *in vitro*. Through rigorous thermodynamic analysis, we determine that the mechanism of formation arises through its disordered tails, and that specific cation-pi interactions between blocks of arginine and phenylalanine residues provide sufficiently strong interactions to cause the protein to phase separate. The behaviour is well described by Flory-Huggin's theory, a model that considers the phase separation of disordered polymers. We determine that the formation of the bodies is regulated by, for example, physiologically relevant methylation of the arginine residues. Notably, the dielectric of the interior of the droplets is more similar to organic solvent such as DMSO rather than bulk water.

The bodies are effectively concentrated solutions of polymer, and that the interior dielectric is very different to that of water: these membraneless organelles are regions of organic solvent, inside cells. In a manner akin to an organic chemist in a synthesis lab, biology has harnessed the properties of organic solvents for biochemistry.

We demonstrate this by showing the bodies have novel biochemical properties. Proteins are taken up, or excluded by the bodies in a manner that reflects their amino acid sequence, revealing they have predictable solubilities in these blobs of organic solvent. Moreover, we demonstrate that double stranded DNA is effectively melted when it moves inside these bodies. Thus the interior of the Ddx4 organelles behave as a passive helicase. These results indicate that cells have developed membraneless organelles as a means for altering the environment for biochemical reactions.

COLL 415

Measuring the intracellular dew point: Phase transitions in cells

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Phase transitions are increasingly recognized as playing an important role in intracellular organization, and its dysfunction in protein aggregation diseases. I will

discuss our work showing that membrane-less RNA and protein rich organelles, known as RNP bodies, represent condensed liquid phase droplets, which assemble by liquid-liquid phase separation. The nucleolus is one such nuclear RNP body, which is important for cell growth and size homeostasis. Using the reductive cell divisions of early *C.elegans* embryos, we've shown that a simple phase threshold model explains striking features of the intrinsic coupling of nucleolar assembly to cell size. Moreover, the dynamics nucleolar assembly can be quantitatively understood using a classical theoretical framework based on the Cahn-Hilliard formalism. We've also shown that the internal subcompartments of the nucleolus arise from multi-phase coexistence, with important consequences for sequential RNA processing. I will also discuss how phase transitions can be dynamically controlled within living cells, yielding rich insights into the link between intracellular liquids, gels, and the onset of pathological protein aggregation.

COLL 416

Designing bio-functionalised colloids for biosensing

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This talk will cover our group's research into the use of a variety of biofunctionalised nanoparticles including quantum dots and plasmonic particles for ultrasensitive biosensing. I will highlight the use of amplified biosensing strategies and strategies for intracellular delivery.

COLL 417

Functionalizing iron oxide with genomic DNA: Materials for drug capture

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Chemotherapy agents are well known for producing severe side-effects. One approach to mitigating this off-target damage is to deliver the chemotherapy directly to the tumor via transarterial chemoembolization, or similar procedures, and then sequestering any chemotherapeutic that enters systemic circulation. Materials capable of such drug capture have yet to be fully realized. We report the synthesis of genomic DNA-functionalized iron oxide nanoparticles, which we used to capture three common chemotherapy agents (doxorubicin, cisplatin, and epirubicin). Drug capture was studied in biologically relevant solutions including phosphate buffered saline, human serum, and porcine whole blood. The efficacy of these nanomaterials indicates that drug capture is a viable strategy for mitigating the harmful side-effects associated with chemotherapy.

COLL 418

Silica coated ferrimagnetic nanoparticles in trace glycoprotein recovery for LC-MS

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Glycan profiling is a promising area for biomarker discovery, but many protein candidates are present at ng/ml levels or lower. This makes direct glycoprotein profiling via LC-MS impossible. Immunoprecipitation methods can be used to increase analyte concentration, but all suffer from nonspecific binding. In an effort to perform glycan profiling on prostate specific antigen serum samples, ferrimagnetic nanoparticles were coated with silica using a modified Stöber process. After further surface modification, activator generated electron transfer atom transfer radical polymerization was used to grow a chromatographic quality acrylamide copolymer surface. The high density copolymer reduced biofouling and increased active antibody binding 5x over Dynabeads. Nanoparticles were characterized using transmission electron microscopy and a superconducting quantum interference device.

COLL 419

Synthesis, characterization and functionalization of inorganic, water soluble nanoparticles

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An essential ability that nanoparticles (NPs) must possess for applications in biologic systems is water solubility. A viable method for the phase transfer of hydrophobic synthesized NPs into aqueous solution is to coat the NPs with an amphiphilic polymer. When synthesizing inorganic NPs within organic solvents, the stabilization in solution is usually achieved by surfactants comprising *n*-alkane chains. By using a polymer for coating the NPs carrying hydrophobic side chains (*n*-alkyl chain of the same length) plus a hydrophilic backbone, the NP can be transferred to an aqueous milieu. Along with the coating procedure comes the formation of different sized micelles of polymer. Former studies showed that using size exclusion chromatography (e.g. gel electrophoresis), micelles with equal size like the coated NPs remain in solution. Using ultracentrifugation (in case of smaller NPs) as work up procedure leads to micelle free conditions, but along comes a loss in colloidal stability of NPs. Investigations for surface functionalizations indeed need to be tuned. A collection of synthesis, phase transfer and characterization of a variety of inorganic NPs thus provides the foundation for future investigations.

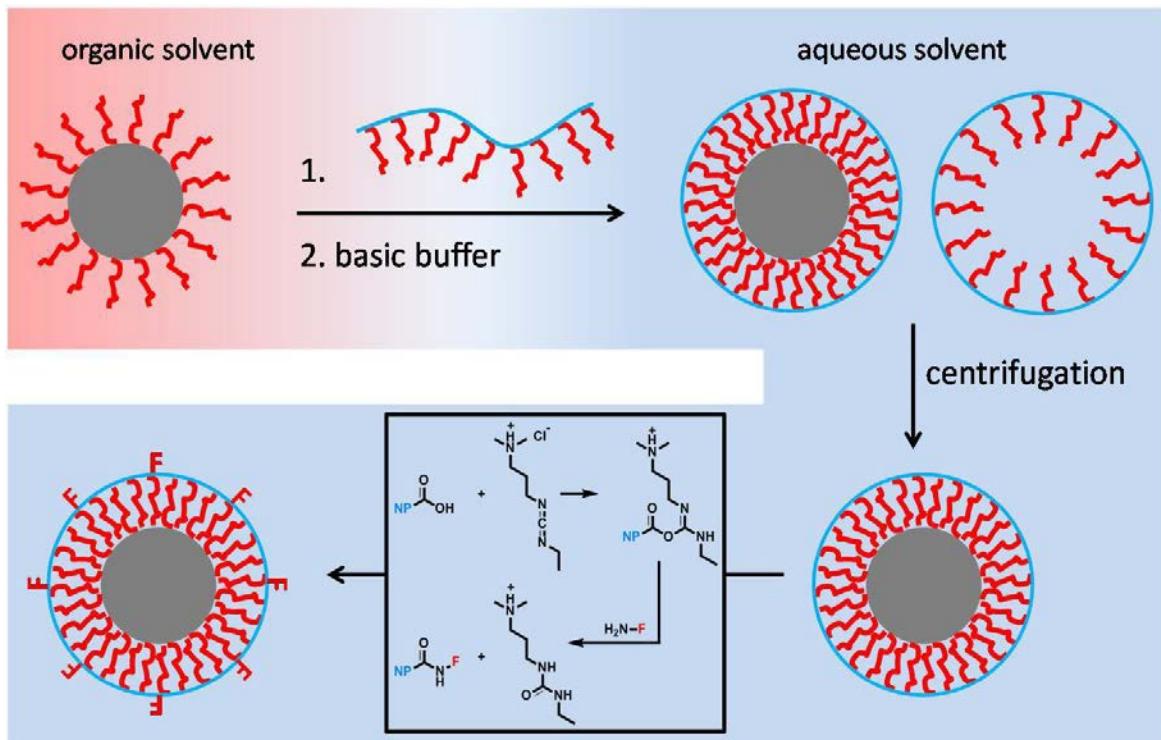


Figure 1. Based on the hydrophobic synthesis of inorganic NPs the phase transfer is performed using an amphiphilic polymer which provides the water solubility after increasing the pH via hydrolyzed maleic anhydride rings located on the polymers' backbone. The resulting carboxylates not only provide the NPs' negative surface charge, they also serve as foundation for further modification via coupling reactions with functional molecules (**F**) based on the formation of amide bonds.

COLL 420

Interpreting sensing mechanisms in nucleic acid-wrapped nanotube sensors through computational approaches

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Molecular nanosensors can be used for sensing of minute concentrations and spatial distributions of neurotransmitter molecules released by neuron cells. Here, we present our collaborative studies of polymer-carbon nanotube (CNT) conjugates used as optical sensors of neurotransmitters, with particular focus on polynucleotide polymers. The sensing mechanism is examined in detail in the recently developed dopamine nanosensor, based on DNA-(GT)_n-wrapped CNTs. Sensing of neurotransmitters added to the solution of the above conjugates usually relies on intensity increase in CNT

fluorescence, likely due to modulations induced in exciton relaxation rates in semiconducting CNTs. Our joint experimental and computational studies show that variations in polynucleotide sequence, sugar backbone conformation, and polynucleotide length can lead to large changes in the conformational stability of the polynucleotide CNT wrapping and CNT fluorescence. We propose a novel mechanism of the CNT fluorescence change within DNA-(GT)_n-CNT conjugates upon addition of dopamine, originating in modulations of the electrostatic environment of the exciton, which influences its relaxation rate. Furthermore, atomistic simulations performed provide detailed insight into dopamine interactions with the studied sensors, which can be correlated with the optical activity of CNTs.

COLL 421

Fluorescent nanodiamond labelled with gold nanoparticles for enhanced optical and electron microscopy imaging

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Fluorescent nanodiamonds (FND) with non-photo bleachable fluorescence from their nitrogen vacancy centers(NV), are an emerging class of material in bioimaging. FND in optical imaging can provide real-time living cell images, and was applied for long term in vitro or in vivo imaging as well as single molecular tracking. In this work, FND labelled with gold nanoparticles (AuNPs) were prepared by protein coating and purified by analytical ultracentrifugation sedimentation. The surface plasmon resonance effect of AuNP significantly decreased the lifetime and improved optical emission of NV centers, which allowed the reduction of laser power, and consequently, minimized the irradiation time required for FND excitation, thus making the FND-Au hybrids well-suited for decreased photo-toxicity in optical imaging.

Electron microscopy images with down to nanometers resolution, provide more detailed information even for subcellular organelles study. While the contrast of TEM images is dependent of sample density, thus the carbon crystal of FND cannot provide good contrast. The FND-Au hybrids were well-distinguishable from the dense subcellular background with high contrast due to the labeling with AuNPs thus facilitating detailed investigations by TEM. In this way, FND-Au cellular distribution and penetration of endosomal membranes was studied by TEM, and a unique flickering behavior of the FNDs was recorded by 3D scanning transmission electron microscopy (STEM) for the first time. Due to their excellent optical features, high contrast in electronic microscope imaging, their capability of endosomal escape, and high biocompatibility, the FND-Au hybrids reported herein represent a powerful platform for studying cellular activity and functions with single particle resolution.

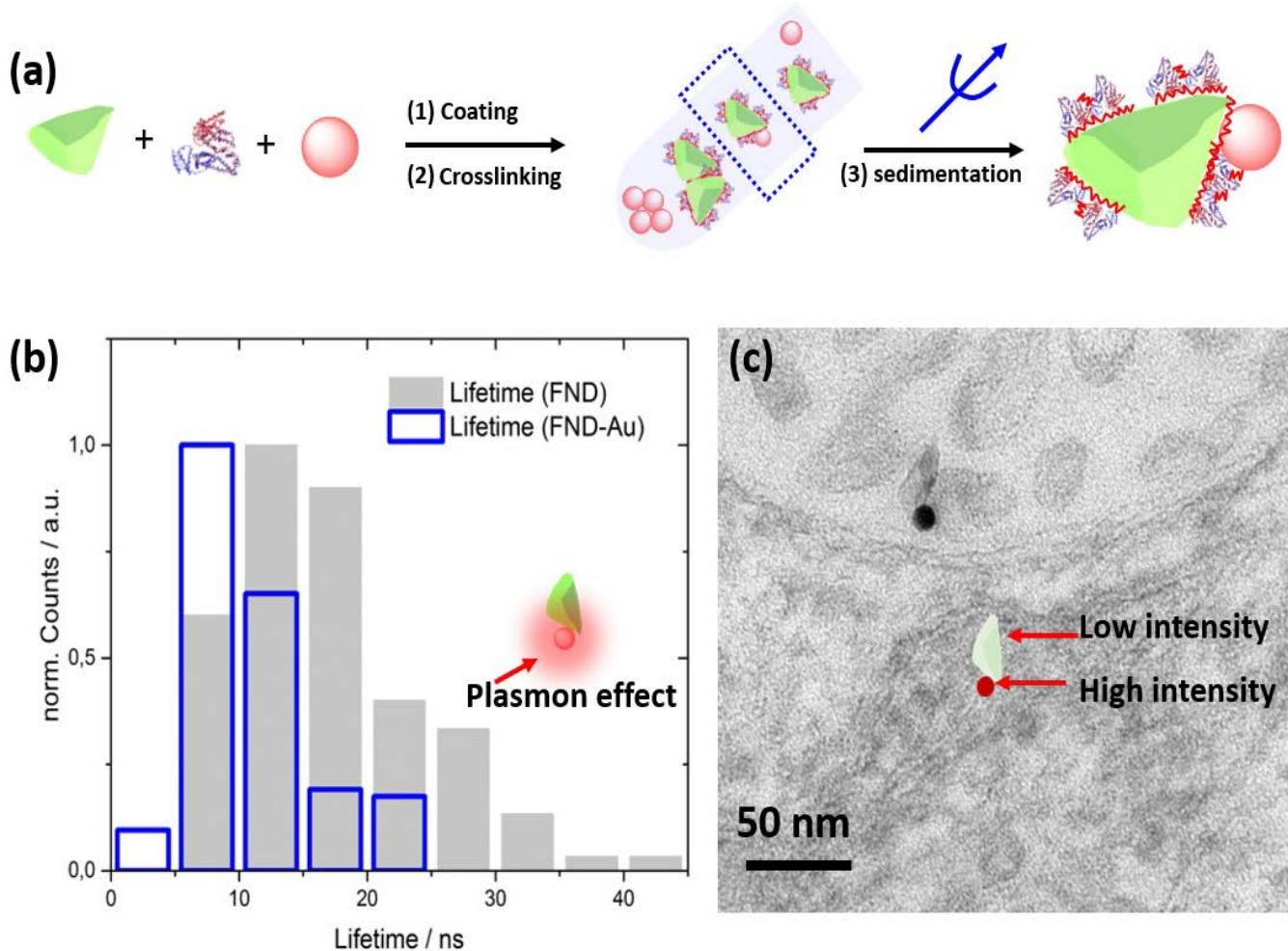


Fig. 1a FND-Au preparation and purification, b lifetime comparison of FND-Au and pure FND, c TEM of single FND-Au with enhanced contrast.

COLL 422

Understanding the interaction of nanoparticles and cells

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The use of nanotechnologies involving materials has increased in the recent years. The novel properties of the micro- and nanoparticles (NPs) make them attractive for a wide range of applications. Importantly, in order to use NPs in the context of medicine (nanomedicine) is essential to understand how NPs interact with cells in a relevant environment and their possible effects. Today, a complete understanding of the interaction of NPs with biological systems still remains a challenge. Indeed, their stability, uptake efficiency and mechanism, as well as the cell cycle of NPs including their life span fate and degradation in biological systems is not fully understood.

Therefore, a deeper understanding in these areas will help us to design new materials with more control properties, desirables for many medical applications. We will discuss and provide an overview of the biocompatibility studies of NPs and cells, and present in brief, strategies to assess and evaluate the interaction of nanomaterials with biological systems, for that, different techniques will be outlined.

COLL 423

Amphiphilic block copolymers at the oil-water interface

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Amphiphilic block polymers of the poly(ethylene oxide)-block-poly(propylene oxide) (PEO-PPO) family, commercially available as Pluronics or Poloxamers and approved for pharmaceutical use, offer prime examples of self-assembling systems that find diverse applications. The presentation will utilize research findings from our group and others to highlight how the fundamental aspects of amphiphilic block copolymer self-assembly in media consisting of water and an immiscible oil inform the formulation of Poloxamers applied to emulsions, colloidal dispersions, and drug delivery. The molecular conformation attained by the polymer amphiphiles around the oil-water interface will be compared to that of low-molecular weight nonionic surfactants, and this information will be connected to the macroscopic phase behavior and structure.

COLL 424

Dynamic and thermodynamic factors controlling transient Marangoni flow at the oil/water interface under convective diffusion surfactant adsorption conditions

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Surfactant solution flow over an initially bare oil surface produces a spatiotemporal gradient of surfactant adsorption rates, resulting in a transient interfacial tension gradient that drives Marangoni flow. The interfacial velocity can be several orders of magnitude larger than the velocity existing for flow of surfactant-free water along the interface. Marangoni flow during adsorption is in the direction of the bulk aqueous flow, while it acts opposite the bulk aqueous flow direction when an equilibrated adsorbed surfactant layer is rinsed with surfactant-free water. These flows entrain adsorbed particles and can be a significant mechanism for interfacial particle transport. Achievable Marangoni velocities and net displacements depend on thermodynamic and dynamic factors. The latter include bulk flow conditions, diffusion coefficients and adsorption or desorption rate constants. This presentation will consider the distinct

influences of varying dynamic parameters and equilibrium interfacial tension isotherms, as well as the potential to manipulate both Marangoni velocities and net displacements by addition of polyelectrolytes that associate with surfactants to produce complexes with varying interfacial activity.

COLL 425

Dynamics of oil-water interfaces: Adsorption, polymerization, and transport

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Oil-water interfaces play the key role in a wide range of scientific, technological, industrial, and chemical processes. Despite their importance, the varied transient processes that occur at these interfaces have remained extremely challenging to study. Motivated by several applications within this broader space, we have developed new tools to probe these dynamic processes, which we will discuss along with the insights they provide. First, we have developed ferromagnetic microbuttons to probe the interfacial rheology of oil-water interfaces that develops as asphaltenes adsorb. Such asphaltene layers are believed to stabilize oil/water interfaces, making water/oil emulsions difficult to break. By directly visualizing asphaltene layers under stress, we find the mechanical properties of these interfaces to show substantial heterogeneity. These heterogeneities appear to be common to evolving interfaces, and may provide opportunities for manipulation and control. Second, we have developed a microfluidic interferometry method to measure concentration fields as they evolve in space and time. In addition to measuring diffusion and partition coefficients, we use this technique to track interfacial polymerization reactions as they proceed, providing unprecedented insight into the kinetics of these reactions.

COLL 426

Formation of multi-nanoemulsions for colloidal synthesis

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In recent years, complex emulsions – *i.e.*, droplets with internal structure – have generated great research interest due to their potential applications in materials, foods, cosmetics, pharmaceuticals, and chemical separations. Microfluidic methods have already demonstrated the ability to create micron- and larger scale complex emulsions with breathtaking sophistication and control, as well as compartmentalize encapsulation of molecules within them. However, scaling the size of such droplets to the nanoscale has been extremely challenging due to limitations on the devices and energies required to produce nanoscale droplets, *i.e.* nanoemulsions. Here, we report the ability to fabricate complex water-in-oil nanoemulsions of various morphologies, and use them as

templates for forming complex structured nanoparticles. To produce complex morphologies, we combine high-energy emulsification methods with co-surfactant pairs possessing highly asymmetric molecular geometry. The former aids the generation of nanoscale droplets, whereas the latter influences their morphology through nearly zero surface tension and frustrated spontaneous curvature, resulting in the reproducible generation of nanoscale core-shell and multi-core shell morphologies. The size, stability, internal morphology and chemical compartmentalization of these complex nanoemulsions have been quantified using a combination of scattering, optical microscopy and cryogenic-transmission electron microscopy techniques. We show that complex droplet morphologies are retained upon the addition of various material precursors, and that the droplets are stable over the time scales required for material chemistry, thereby enabling their use as templates for complex nanoparticles.

COLL 427

Exploring the interfacial synergy between polymers and surfactants

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Surfactant/polymer combinations are well known to be important in emulsification, industrial, environmental, and biomedical applications. It has long been known that combinations of polyelectrolytes and charged surfactants exhibit tunable synergy and increased interfacial behavior. What remains unknown is the molecular detail that leads to this synergy at the interface. The studies to be presented examine the interfacial molecular properties involved in the co-adsorption of the ubiquitous surfactant cetyltrimonium bromide (CTAB) with the model polymer poly(acrylic acid) (PAA) at an oil/water interface. Vibrational sum frequency spectroscopy is used to measure the vibrational features of the surfactant and polymer at the interface, complemented with additional surface tension, zeta potential and dynamic light scattering studies. The results show charge-screening between CTAB and PAA causes interfacial layering and surface coverage. Slow reorientation eventually leads to a highly ordered structure over long timescales.

COLL 428

Pickering nanemulsions using bespoke sterically-stabilized diblock copolymer nanoparticles

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Pickering nanoemulsions comprise particle-stabilized droplets of 200-500 nm diameter. In principle, such formulations offer a range of applications in cosmetics, drug delivery,

agrochemicals etc. However, in practice they typically suffer from instability via an Ostwald ripening mechanism. Recently, we have used polymerization-induced self-assembly (PISA) to design a wide range of diblock copolymer nano-objects. More specifically, we have used RAFT aqueous emulsion polymerization to prepare sterically-stabilised spherical nanoparticles of 20-25 nm diameter. Such nanoparticles can be used to stabilize conventional oil-in-water Pickering macroemulsions comprising n-dodecane droplets of 50 µm diameter. Such precursor macroemulsions can be converted into nanoemulsions using high-pressure microfluidization using commercially-available equipment (LV1 Microfluidizer, Microfluidics). Optimization of the processing conditions affords access to final droplet diameters as low as 130 nm. Remarkably, such Pickering nanoemulsions do not seem to suffer from Ostwald ripening: DLS studies indicate no change in the mean droplet diameter after three months storage at 20°C.

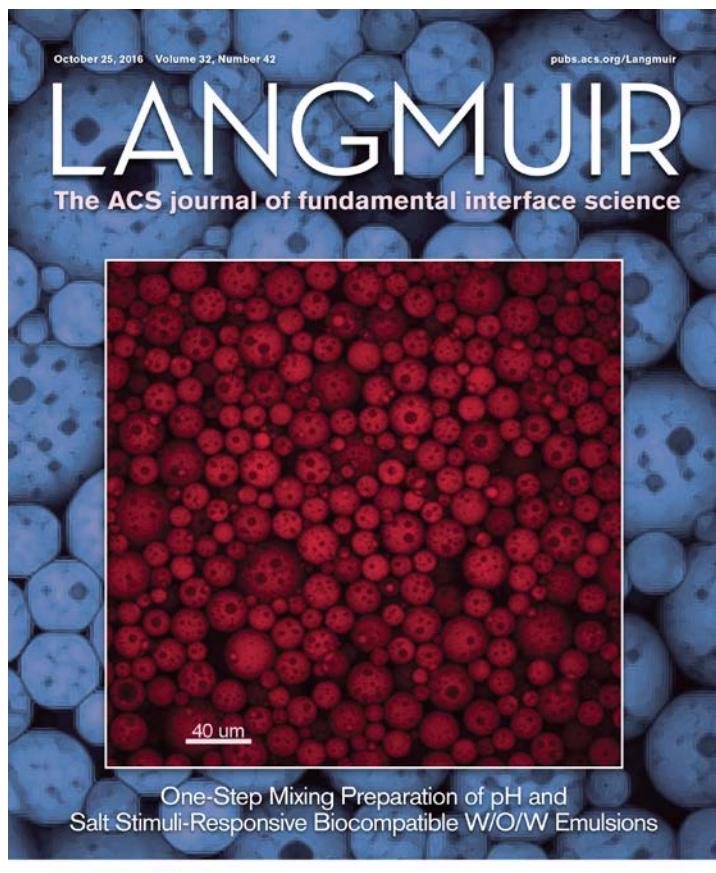
COLL 429

One-step formation of stable multiple emulsions

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Stimuli-responsive multiple emulsions formed in a one-step mechanical emulsification process are shown to be stable for months. These emulsions are stabilized by amphiphilic copolymers synthesized by atom transfer radical polymerization (ATRP). Depending on pH, ionic strength and temperature, different emulsion types are obtained, including water-continuous (W/O/W) and oil-continuous (O/W/O) multiple emulsions.

In particular W/O/W emulsions can be formed with biocompatible molecules like poly(dimethylsiloxane)-*b*-poly(dimethylaminoethyl methacrylate) copolymer and Miglyol® 812 as an oil phase. These emulsions enable the encapsulation and controlled release of hydrophilic species with the three stimuli: pH, ionic strength and temperature. Furthermore, we studied the formation conditions of multiple water – toluene – polystyrene-*b*-poly(styrene-*st*-dimethylaminoethyl methacrylate) emulsions. The conformation of the polymer adsorbed at the water – oil interface was probed using an original neutron reflectivity set-up. Our results evidence a correlation between emulsion type and polymer conformation. More precisely, the formation of multiple emulsions is promoted by a decrease in the curvature of the microemulsions formed in water, in agreement with cryo transmission electron microscopy and small angle neutron scattering. Finally, we exhibit predictive criteria for the formation of multiple emulsions based on interfacial tension and polymer partitioning measurements.



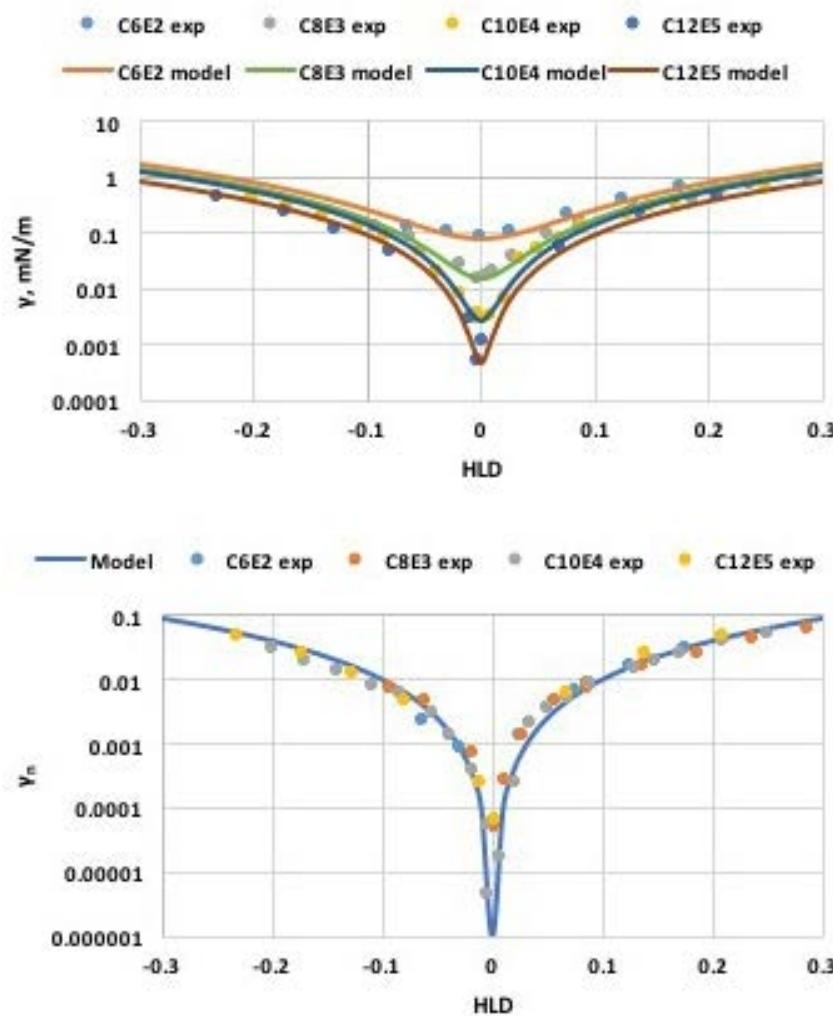
COLL 430

Microemulsion interfacial tension and characteristic length scale model using a microscopic curvature approach and the HLD concept

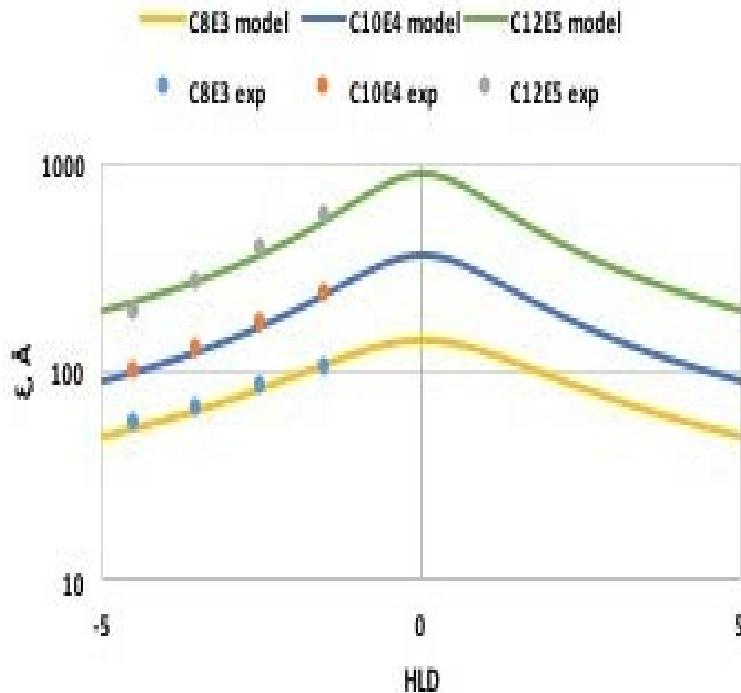
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In this paper we introduce a model for the oil-water interfacial tension as a function of surfactant affinity in the three-phase region, as captured by the hydrophilic-lipophilic deviation (*HLD*), which relies on film bending energy arguments and empirical relationships for the microscopic curvatures. Following a similar approach, we present a model for the characteristic length scale. After an appropriate normalization, the interfacial tension is related to the characteristic length scale using a simple expression. Finally, we introduce models for the oil-microemulsion and microemulsion-water interfacial tensions using phase boundary condition arguments, which are extended to account for compositional changes using the appropriate limits. All models are compared against experimental data to demonstrate their validity, and for the data examined the results give excellent fits. The approach has the potential to predict

two- and three-phase interfacial tension for changes in HLD input parameters, such as T, P, and overall composition.



Interfacial tension between the oil and water phases (top) and normalized interfacial tension (bottom) as a function of for different water—n-octane—C_iE_j systems. Experimental data from Leitao et al. (1996).



Characteristic length scale as a function of for different water—n-alkane—C_iE_j systems.
Experimental data from Sottmann et al. (1997).

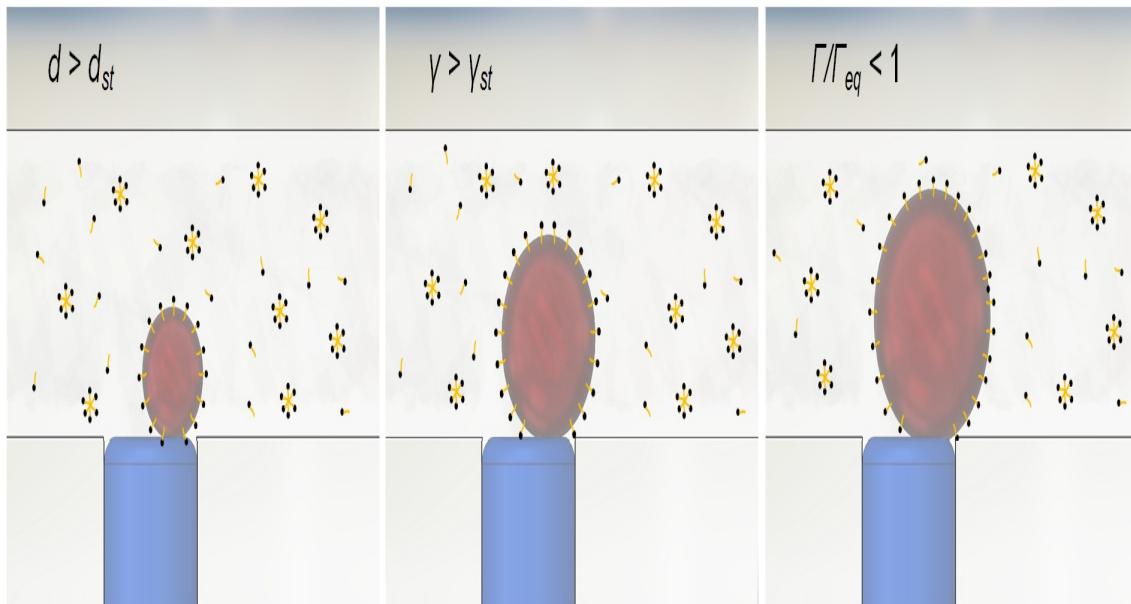
COLL 431

Determining the dynamic interfacial tension during droplet/bubble generation using T-junction and co-flowing microchannels

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The dynamic interfacial tension caused by surfactant adsorption or mass transfer during droplet/bubble generation process is an interesting issue for the development of interface science and technology. This phenomenon exhibits the variation of interfacial tension with operating conditions for the composition variation in the interface. The presentation gives a summary of our previous studies focusing on the determination of dynamic interfacial tension during droplet/bubble generation using T-junction and co-flowing microchannels, including two determination methods based on the droplet size and the pressure drop measurement, and the variation laws of interfacial composition with absorption and mass transfer. The working systems include microflow emulsification, liquid-liquid extraction and gas-liquid adsorption. Experimental results showed increase of decrease in the interfacial tension from the static interfacial tension with equilibrium of phases, especial in the droplet generation process with high generation frequency. Some models of dynamic interfacial tensions are suggested

based on the mass transfer analysis, which will be helpful for in-depth understanding multi-phase flows.



Droplet generation in a surfactant solution

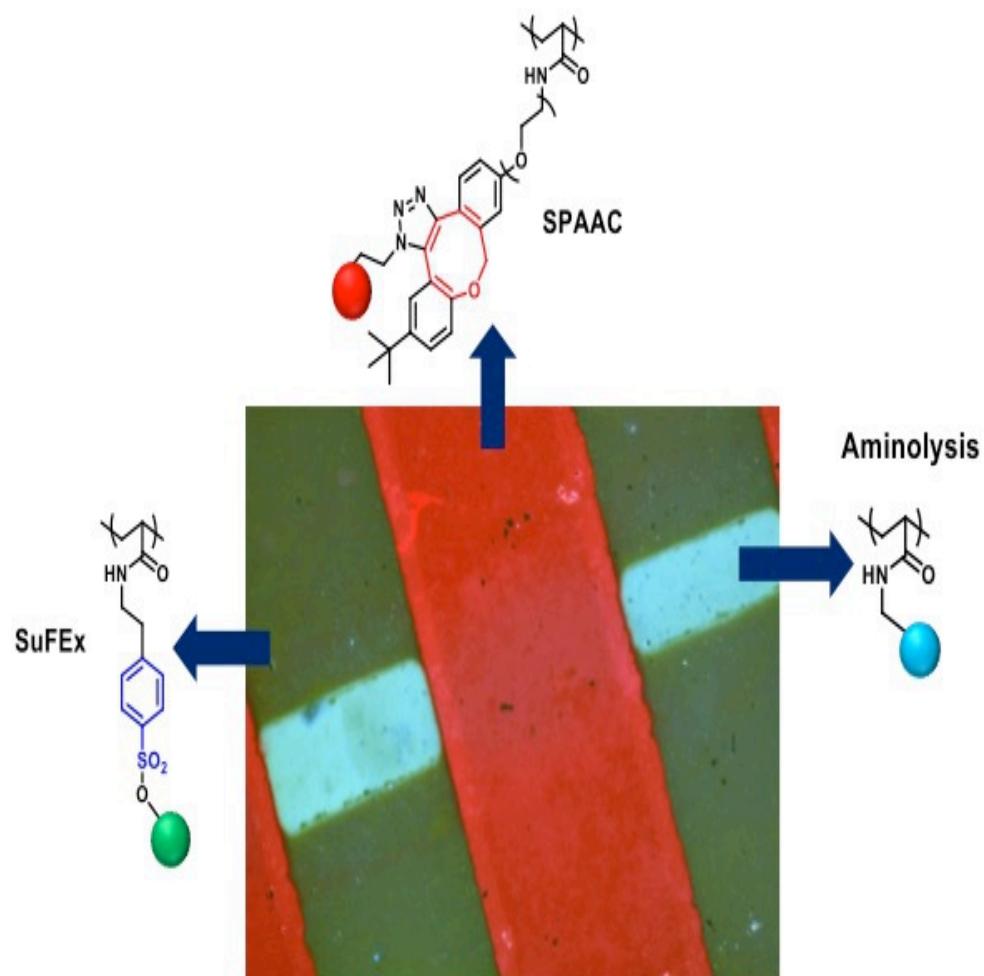
COLL 432

Generation of patterned multifunctional surfaces using orthogonal click chemistries

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Click chemistry combined with post-polymerization modification of reactive polymer brushes can result in a wide array of surfaces, differing in chemical functionalities and morphologies. In this talk, a tri-reactive surface is fabricated that can undergo three click reactions in one-pot with high fidelity and no cross-contamination. Using reactive microcapillary printing, poly(pentafluorophenyl acrylate) brushes, which react rapidly with primary amines, can be partially patterned with other click functionalities with excellent spatial control, including strained cyclooctyne derivatives and sulfonyl fluorides. This trireactive surface can then react selectively with high fidelity in a one pot reaction via three orthogonal chemistries at room temperature: activated ester aminolysis, strain promoted azide–alkyne cycloaddition, and sulfur(VI) fluoride exchange, all of which are tolerant of ambient moisture and oxygen. Furthermore, we will demonstrate how these surface reactions can also be used to create areas of

morphologically distinct features on the nanoscale, by inducing creasing in the films and grafting reactive nanoparticles. This approach allows for the development of highly complex surface motifs patterned with different chemistries and morphologies.



COLL 433

Bioinspired interfaces with controlled anisotropic wetting at scales

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Designing and fabricating nanostructured 3D interfaces with multiple layers (e.g. nanoscale transistor elements and phase-segregated block copolymer films for organic photovoltaics) is critical in the development of nanoscale device architectures.

Formation of nanoscopic thin films requires controlled interfacial wetting to prevent defects (e.g. pinholes, delamination, and line edge roughness) that impact device performance. Wetting properties change significantly at micron and nanometer scales due to the dramatic increase in surface area-to-volume ratios at very small droplet

sizes, raising challenges in designing interfaces with features at scales < 10 nm. However, nature routinely utilizes nanoscopic wetting control to build interfaces of striking geometric precision and functional complexity, suggesting the possibility of leveraging similar control in synthetic materials. Here, we take advantage of a set of bioinspired building blocks to generate a precisely patterned interface with nanoscale wetting orthogonality at the 5-nm scale, and examine differences in wetting geometry at scales approaching molecular dimensions.

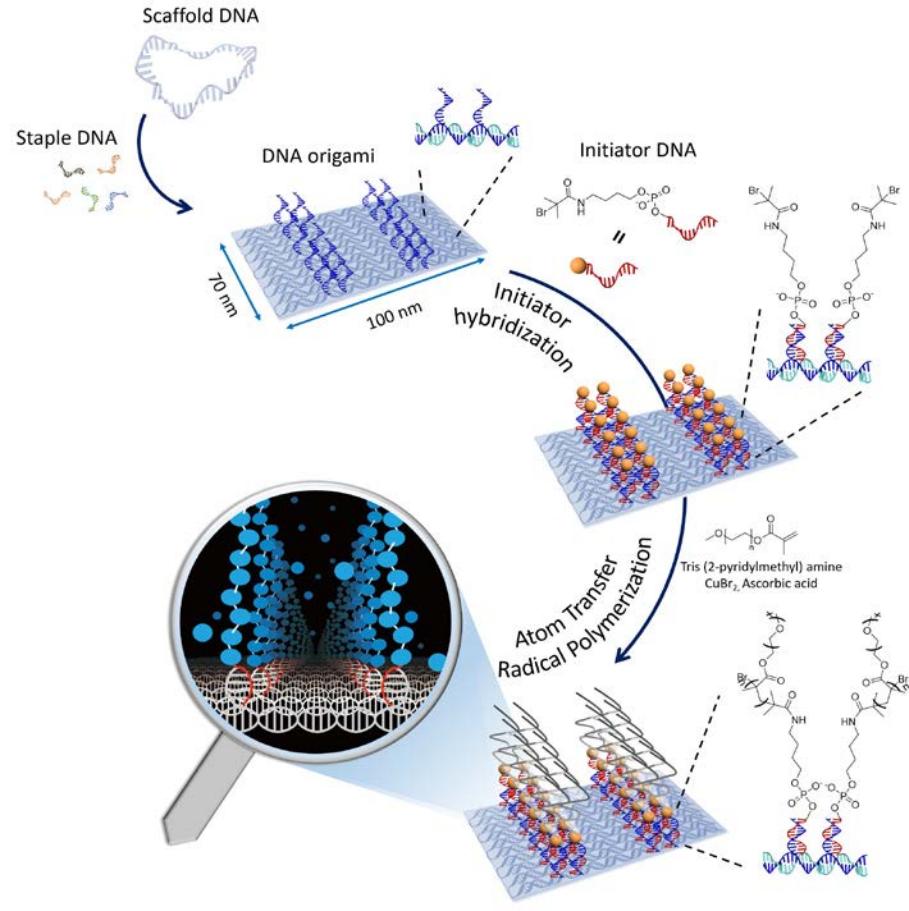
COLL 434

Programming polymer nanoarchitectures by DNA origami technology

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Bottom-up strategies to fabricate patterned polymers in nanoscale represent an emerging field in the development of advanced nanodevices, such as biosensors, nanofluidics, and nanophotonics. However it is still highly challenging to fabricate patterned polymers by existing bottom-up approaches with low nanometer resolution. DNA is a class of biopolymers and the molecular recognition by Watson-Crick base pairing enables a rational design of DNA nano-architectures in 2D and 3D with defined size and shape, so called, “DNA origami” which present manifold opportunities for functionalization with functional materials (nanoparticles, proteins, fluorophores, and so on) at the nanoscale with the highest precision.

Herein, we propose a novel technique for bottom-up fabrication of nanopatterned polymer surface on DNA origami scaffold via atom transfer radical polymerization (see Figure). Control over different nanopatterns, lengths of polymers, and composition of monomers, was achieved by tuning each single polymer growing position in a few nanometer precision on DNA origami. Our approach paves the way to the bottom-up fabrication of a large variety of nanoscale-patterned polymers with high density and flexibility, and offer various opportunities, such as the chance for crosslinkers to fix the polymeric nanostructures to remain intact even after removal of DNA origami.



Scheme of bottom up fabrication of polymer nanopatterns on DNA origami by surface initiated atom transfer radical polymerization

COLL 435

Polymer pen chemical lift-off lithography

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We combine chemical lift-off lithography (CLL) with large arrays of polymer pens with sub-20-nm tips, developing polymer pen chemical lift-off lithography (PPCLL). We demonstrated the feasibility of PPCLL with experiments using v-shaped polymer pen arrays and associated simulations. Simulation results show a nanometer-scale quadratic relationship between the contact linewidth and two variables: base linewidth of the polymer pen and vertical compression. We invented a supporting arm system and designed a series of v-shaped polymer pens with known height differences to control precisely the relative vertical position of each polymer pens at sub-20-nm scale, which mimicked a high-precision scanning stage. In this way, we successfully obtained linear array patterns with linewidths from sub-50-nm to sub-500-nm with minimum sub-20-nm linewidth increment tunability. The CLL pattern linewidth perfectly matched the simulations. These results suggest that through the proper design of the supporting arms to suitable positions and the base linewidth of the polymer pen arrays, one can completely eliminate the need for the scanning stage system in PPCLL to increase the throughput and to reduce cost. We also showed that PPCLL can be used to design and to fabricate DNA microarrays efficiently by backfilling the patterns after PPCLL with probe DNA, and subsequently hybridizing with complementary target sequences.

COLL 436

Nanoimprint lithography using DNA nanostructure templates

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This talk describes a fabrication of polymer stamps using DNA nanostructure templates. This process creates stamps having diverse nanoscale features with dimensions ranging from several tens of nanometers to microns. DNA nanostructures including DNA nanotubes, two-dimensional (2D) DNA brick crystals with three-dimensional (3D) features, hexagonal DNA 2D arrays, one-dimensional (1D) λ -DNA, and triangular DNA origami served as masters to transfer patterns to poly(methyl methacrylate) (PMMA) and poly(L -lactic acid) (PLLA) with high fidelity. The resulting polymer stamps were used as molds to transfer the pattern to the acryloxy perfluoropolyether (a-PFPE) polymer. This approach opens up new opportunities for using self-assembled DNA templates as masters to fabricate polymer stamps with diverse nanoscale features for applications of soft lithography.

COLL 437

Bottom-up approach to high density array of patterned polymer brushes

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Surface anchored polymer chains provide a stable and versatile route to modifying a range of interfacial properties. These include biological, electronic, optical or frictional

properties. However, the wide-scale usage of polymer brushes is limited by the scalability of the synthetic methodologies. We have developed a highly versatile universal approach to grow polymer brushes from a variety of substrates with high grafting density by using a single-component coating. We describe a random copolymer which consists of a polymerizable initiator, copolymerized with a thermal crosslinker by reversible addition–fragmentation chain transfer polymerization. The chemistry of the coating is modified to implement a bottom up approach to fabricate nano-patterned polymer brushes. By self-assembly of a block copolymer film on top of the coating, nanopatterned brushes are grown after selective removal of one domain from the block copolymer. The initiator containing cross-linkable copolymer can be viewed as a single component ultra-thin polymeric coating which is applicable to a range of substrates to grow high chain density polymer brushes. The ease of synthesis, chemical tunability, homogeneity of composition, stability in organic solvents and applicability by simple spin-coating to a wide range of substrates makes this a versatile approach to create functionalized interfaces. Further, we show the utility of this chemistry to examine mixed monolayers and the effect of confinement on brush morphology.

COLL 438

Surface assembly and packing preferences of fibrinogen mediated by the periodicity and alignment of block copolymer nanodomains

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The ability to control the specific adsorption and packing behaviors of biomedically important proteins by effectively guiding their preferred surface adsorption configuration and packing orientation on polymeric surfaces may have utility in many applications such as biomaterials, medical implants, and tissue engineering. We examine the distinct adhesion configurations of fibrinogen (Fg) proteins and the different organization behaviors between single Fg molecules that are mediated by the changes in the periodicity and alignment of chemically alternating nanodomains in the thin films of polystyrene-block-polymethylmethacrylate (PS-b-PMMA) block copolymer (BCP). *Via* direct visualization by high resolution imaging, the distinct adsorption and packing configurations of both isolated and interacting Fg molecules are determined as a function of the BCP template-specific nanodomain periodicity, domain alignment (*random versus fully aligned*), and protein concentration. During surface packing, the orientation of the protein backbone is largely governed by the periodicity and alignment of the underlying PS-b-PMMA nanodomains whose specific direction is explicitly resolved relative to the polymeric nanodomain axis. We have successfully created fully Fg-decorated BCP constructs analogous to two-dimensional Fg crystals in which aligned protein molecules are arranged either side-on or end-on, depending on the BCP template. Our results demonstrate that the geometry and orientation of the protein can

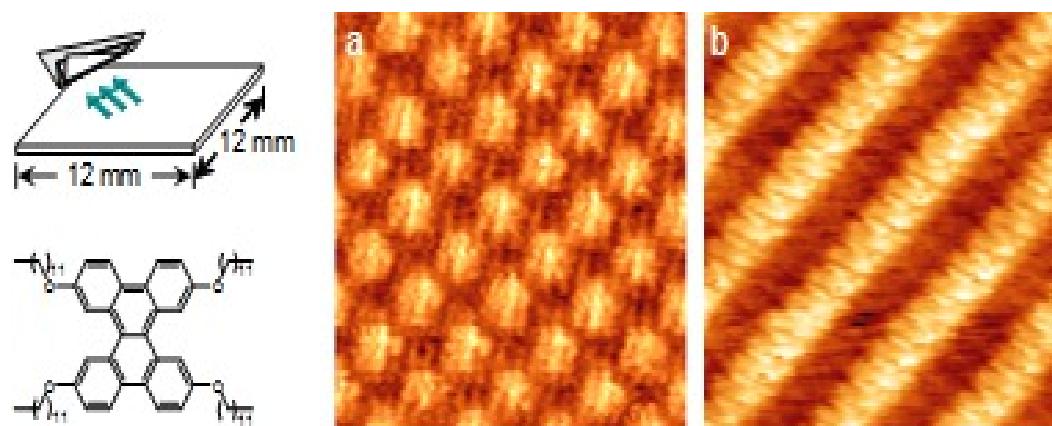
be effectively guided during Fg self-assembly by controlling the physical dimensions and orientations of the underlying BCP templates.

COLL 439

Monolayer assembly of polyaromatics by shear-induced alignment and by 2D porous networks

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The control of spatial arrangements of molecular building blocks on surface opens the foundational step of the bottom-up approach toward future nanotechnologies. The domain size of monolayers exhibiting crystallinity generally falls in the submicron scale. Reported herein are two methods that conveniently prepare aligned discotic compounds by shear flow and patterns by electrical pulses. For the first one, polyaromatics and rod-shaped oligomers can be aligned for as long as ~7 mm, simply by placing a piece of folded tissue against the substrate to draw a shear flow of the deposition solution. The preparation scheme is similar to the Couette flow where the laminar flow takes place between two concentric walls, one of which rotates and creates viscous drag proven useful to align macromolecules. The method can induce an edge-on orientation for alkyl-decorated polyaromatics and unsubstituted coronene which would otherwise adopt the face-on arrangement on graphite. For the method of electric stimuli which can be readily delivered by an STM tip, electrical pulses (3~5 V/10 ms) make accessible the structural transformation of the molecular assembly in a controllable manner. The model compound is an alkoxylation discotic nematogen. Upon the stimuli of 3, 4, and 5 V, the assembled patterns become hexagonal, bilayer, and nanoporous, respectively. This phenomenon is attributed to the deposition of tip-induced polarized molecules to the oppositely charged substrate whose local charge redistributes upon activating the stimuli.



Scheme illustrating how the monolayers are aligned by placing the tissue vertical to of HOPG.

(a) Without and (b) with the shear treatment, the monolayers are lying down with face-on and aligned with edge-on orientation, respectively. Image size: 12x12 nm.

COLL 440

Actuatable DNA origami-nanoparticle composites for energy harvesting and storage

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Nanoparticles have tremendous potential in energy applications, such as harvesting and storage. However, a significant difficulty at the nanoscale is controlled assembly of these materials. Nanoparticles synthesized in solution must be precisely ordered to achieve specific effects, such as plasmonic interactions. However, this can be difficult because of their small size. Here, we describe a method to assemble nanoparticles, including gold nanoparticles, magnetic nanoparticles, and semiconducting quantum dots, using three-dimensional (3D) deoxyribonucleic acid (DNA) origami “hinge” constructs as a template. Templating permits nanoparticles to be assembled with precise orientations in 3D space. We evaluated the energy landscapes as a function of nanoparticle location from the hinge vertex, demonstrating a reduction of energy states.

In contrast to many 2D patterning approaches, these templates also have the potential to dynamically alter their shape in response to external stimuli. However, prior work primarily relies on actuation by the addition of complementary DNA strands, a slow process with actuation times of tens of minutes to hours. We investigated the potential for heat to actuate devices, showing that bulk heat delivery can easily actuate structures on the minutes time scale. Further, we explored the possibility for actuation via heat delivered by the nanoparticle itself. Gold nanoparticles can harvest optical energy from the environment converting it to heat. Local heating can melt single stranded DNA connections on the origami structure leading to actuation (opening) of the origami hinge. Thus, energy can be stored, released, and transmitted at the nanoscale, noninvasively via this approach.

COLL 441

Studies of electrochemical reactions at individual nanostructures via combined electroanalytical and optical methods

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Analytical methods utilizing correlated electroanalytical and optical measurements are presented which enable detailed studies of the electrochemical properties of individual nanostructures. Scanning electrochemical microscopy is employed to directly measure the rate of electrochemical reactions at individual nanoparticles, while optical spectroscopy is used to probe the structure of these particles *in situ*. This enables the correlation of electrochemical kinetic data with particular particle structures, providing valuable insights into structure-function relationships for a given electrochemical process. Additionally, *in situ* spectroscopic measurements facilitate investigations into the mechanisms responsible for transient changes in electrochemical reactivity (e.g., catalyst deactivation). Initial studies applying the described methods to model electrocatalytic systems are presented.

COLL 442

Nanoelectrochemical techniques for high-resolution imaging and characterization of catalytic nanostructures

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This paper is concerned with two complementary approaches to studying electrochemistry of catalytic nanostructures: nanoscale imaging of topography and reactivity with a tip of the scanning electrochemical microscope (SECM) and monitoring the collisions between single catalytic nanoparticles or metal clusters and a nanoelectrode. The former technique can provide spatially resolved information about electron transfer properties and catalytic activity under steady-state conditions. Collision experiments yield information about particle interactions with the electrode surface and its dynamics on the microsecond time scale. The combination of nanoelectrochemical tools with high resolution TEM and computer simulations was used for quantitative analysis of the experimental data.

COLL 443

Detecting small molecule binding with membrane proteins

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Measuring small molecule interactions with membrane proteins on cells is critical for the understanding of cellular communication processes, validation of biomarkers, and screening of drugs. Despite the importance, developing such a capability has been a difficult challenge. In this presentation, we will describe a new label-free detection technology to quantify the interactions of both large and small molecules with membrane proteins on the cell surface in real time. The technology is based on

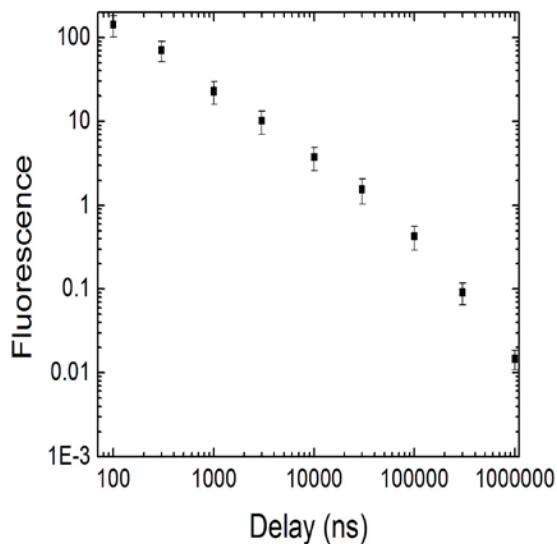
detecting molecular binding-induced mechanical deformation in the cell membrane with a sensitive optical imaging and tracking system. In contrast to the existing technologies, the present technology does not require extraction, purification, labeling or immobilization of the proteins on a surface, which is thus particularly significant for studying membrane proteins that are difficult to extract and purify, or unstable after purification

COLL 444

Gold nanoparticle assisted delayed luminescence in conjugated polymers

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The charge recombination process is integral to the operating mechanism of organic light-emitting diodes (OLEDs). In particular, the fraction of recombination events resulting in singlet excited states sets an upper limit on operating efficiency. Furthermore, one explanation of the effects of small magnetic fields on the efficiency of OLEDs involves magnetic effects on the recombination process. Here, we use the common phenomenon of delayed luminescence in fluorescent conjugated polymers due to recombination of photogenerated charge pairs as a tool to investigate the recombination process. By deliberate addition of small gold nanoparticles, we are able to measure both fluorescence and phosphorescence in the long-lived emission of F8BT (Poly[(9,9-di-n-octylfluorenyl-2,7-diyl)-alt-(benzo[2,1,3]thiadiazol-4,8-diyl)] films that persist after the directly photogenerated singlet state has decayed. We observe power law decay of the fluorescence on the microsecond timescale due to charge pair recombination and study its excitation pulse energy and magnetic field dependences. Taking advantage of spin-orbit coupling provided by gold nanoparticles incorporated into the conjugated polymer film, we are also able to track the dynamics and magnetic field dependence of the phosphorescence. Our data support an overall picture where charge recombination must be mediated by a charge transfer state.



COLL 445

Growth of highly fluorescent gold and silver nanoclusters

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We have developed a one phase reaction route to grow hydrophilic metal nanoclusters (NCs) with greatly promising fluorescence properties. The clusters are stabilized with lipoic acid and poly-(ethylene glycol)-modified lipoic acid (LA-PEG) ligands. The growth of the NCs involves the reaction between metal precursors (e.g., HAuCl₄) and ligands, and it can be carried out either in the presence of photo- or borohydride-reduced ligands. We find that when the reaction is combined with photo-chemically transformed LA-PEG ligands the strategy yields Au nanoclusters with red or blue emission, depending on the exact structure of the ligand used. We also find that when using lipoic acid as ligand, doping a few Au atoms into magic size Ag nanoclusters substantially enhances their fluorescence quantum yield and long term colloidal stability. We detail the growth and characterization of the various nanocluster materials using absorption, fluorescence, TEM and DOSY NMR spectroscopy. We also explore integration of these materials with biology.

COLL 446

Competitive partial charge transfer interactions with hydrogen-bonded solvent networks

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The presence of noncovalent interactions such as hydrogen bonding with solvent molecules can affect how organic molecules interact with nanostructured metal surfaces in significant ways. Nitrogen-containing conjugated molecules are extremely sensitive to such interactions and exhibit partial charge transfer with both metal surfaces and with hydrogen-bonded water networks in a competitive fashion. Here, this competition is discussed in the context of surface enhanced Raman spectroscopic (SERS) experiments and in energy-related device applications.

COLL 447

Colloidal assembly in alchemical space

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Leading nanoscientists like Nicholas Kotov have demonstrated the richness of colloidal assemblies through their discoveries of self-assembled structures in one, two, and three spatial dimensions. What is the role of the simulator in predicting and explaining colloidal self-assembly phenomena? In this talk, we discuss recent advances in theoretical and computational methods for the prediction of colloidal assemblies thermodynamically optimized for target structure and/or function. We discuss applications of digital alchemy and machine learning, achieving chirality, and we elaborate on the recently proposed idea of alchemical space in the context of colloidal assembly and its importance for prediction and understanding. Using these various concepts and tools, we make predictions that can be tested by experiments.

COLL 448

Control of DNA-functionalized nanoparticle assembly

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Directed crystallization of a large variety of nanoparticles, including proteins, via DNA hybridization kinetics has led to unique materials with a broad range of crystal symmetries. The nanoparticles are functionalized with DNA chains that link neighboring functionalized units. The shape of the nanoparticle, the DNA length, the sequence of the hybridizing DNA linker and the grafting density determine the crystal symmetries and lattice spacing. By carefully selecting these parameters one can, in principle, achieve all the symmetries found for both atomic and colloidal crystals of asymmetric shapes as well as new symmetries, and drive transitions between them. A scale-accurate coarse-grained model with explicit DNA chains provides the design parameters, including degree of hybridization, to achieve specific crystal structures. The model also provides

surface energy values to determine the shape of defect-free single crystals with macroscopic anisotropic properties.

COLL 449

Large-scale nanocrystal arrays

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Nanoscale semiconductor and metal nanocrystals exhibit size dependent absorption, scattering and emission spectra. While there are many applications for these materials as ensembles, increasing interest has focussed on the potential optoelectronic applications for single nanocrystals in molecular sensing, high density information storage, high-throughput DNA screening and plasmonic imaging. Typically, nanocrystals are spin-coated from solution onto substrates at random, which makes analysis and archiving tedious. Such nanocrystals cannot be routinely addressed by the user. To utilise these novel materials in optical or electronic devices, methods are needed for assembly of single nanocrystals into ordered structures.

In this talk, we will present the first work demonstrating quantitative self-assembly and patterning of single nanocrystals from the nanometre lengthscale to the centimetre lengthscale. We will discuss several methods including capillary force assembly, chemical assembly and electrophoretic assembly. The third of these is particularly flexible. A polymer coated substrate is patterned using EBL, photolithography or nano-imprint lithography to generate a template. The substrate must be conducting. Particles are deposited either anodically or cathodically depending on their charge. We demonstrate that a wide range of particle types, particle shapes and particle sizes can be deposited. We present the first optical image created from single nanoparticles. Up to 10^{10} particles may be put down over a square centimetre substrate with fidelity > 95%.

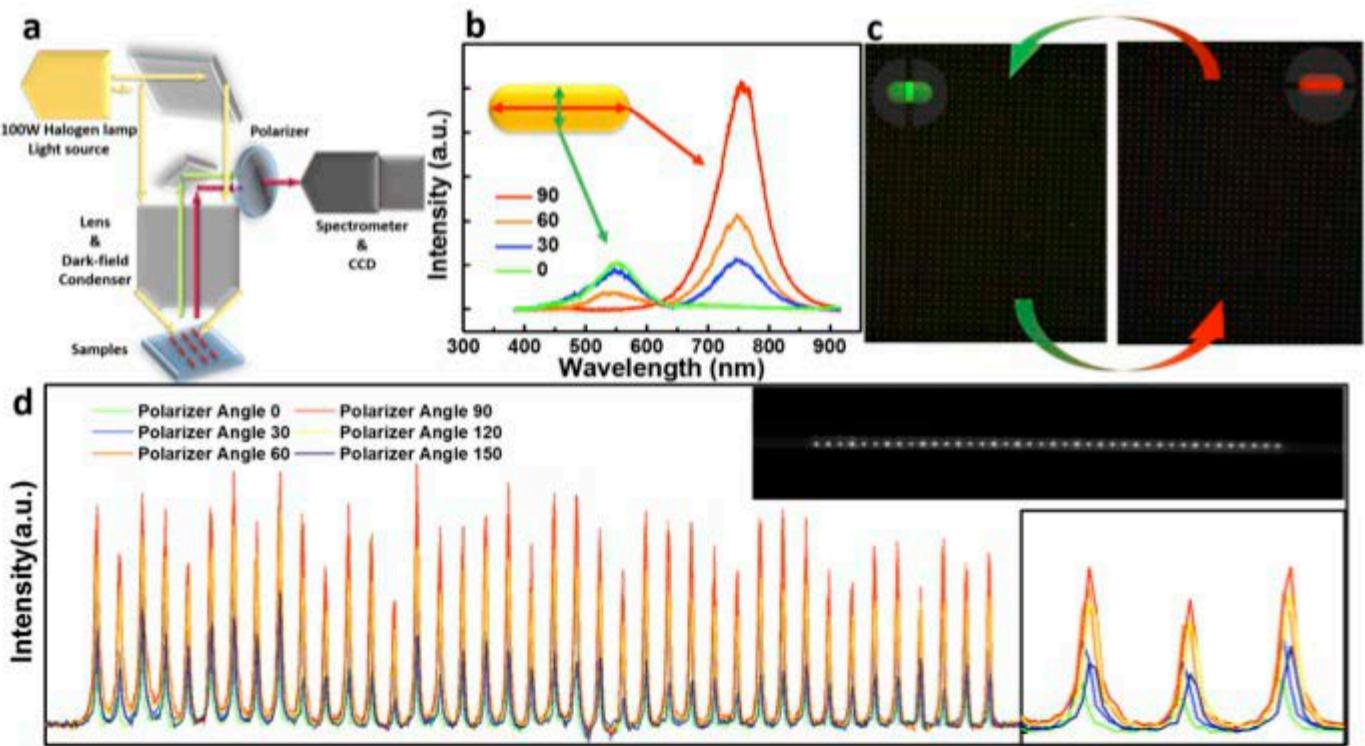


Figure. 1 Left- Experimental dark-field microscope set-up for single particle spectroscopy. Top Right: Deposited gold rods are aligned and exhibit ensemble-averaged polarisation-dependent scattering spectra. Bottom: Intensity map across a row of gold rods as a function of polariser angle showing uniform alignment.

COLL 450

Surface patterning of nanoparticles with polymer patches

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Patterning of colloidal particles with chemically or topographically distinct surface domains (patches) has attracted intense research interest. Surface-patterned particles act as colloidal analogues of atoms and molecules, serve as model systems in studies of phase transitions in liquid systems, behave as ‘colloidal surfactants’ and function as templates for the synthesis of hybrid particles. The generation of micrometre- and submicrometre-sized patchy colloids has currently reached the state of the art, however surface patterning of inorganic colloidal nanoparticles with dimensions of the order of tens of nanometres remains a challenge. Such nanoparticles exhibit size- and shape-dependent optical, electronic and magnetic properties, and their assemblies show new collective properties. Currently, nanoparticle patterning is limited to the generation of two-patch nanoparticles, and nanoparticles with surface ripples. Here we demonstrate nanoparticle surface patterning, which utilizes thermodynamically driven segregation of

polymer ligands from a uniform polymer brush into surfacepinned micelles following a change in solvent quality. Patch formation is reversible but can be permanently preserved using a photocrosslinking step. The methodology offers the ability to control the dimensions of patches, their spatial distribution and the number of patches per nanoparticle, in agreement with a theoretical model. The versatility of the strategy is demonstrated by patterning nanoparticles with different dimensions, shapes and compositions, tethered with various types of polymers and subjected to different external stimuli. These patchy nanocolloids have potential applications in fundamental research, the self-assembly of nanomaterials, diagnostics, sensing and colloidal stabilization

COLL 451

Can particles mimic atoms and molecules?

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Realizing the enormous potential of nanoparticles in such as energy, biomedical, and optoelectronic fields requires the organization of these particles into larger or hierarchically ordered structures with defined macroscopic properties. Inspired by molecular self-assembly into structures with astonishing complexities and functions in living organisms or synthetic systems, we and others are striving to achieve programmable self-assembly of nanoparticles as “molecule equivalents”. The ability to do so holds great promises to manipulate matter at nanoscale scale and to exploit the emergent properties of nanoparticle ensembles. However, unmet challenges still remain at this frontier. In this talk, I will present our efforts to develop nanoparticles that can mimic conventional molecules to assemble into hierarchical structures with programmable architectures, and to understand the similarity and differences between these nanoparticles and molecules. Specifically, two systems will be discussed, including i) the precise positioning of nanoparticles into supracolloidal molecules with defined valence using non-biological molecules, and ii) the assembly and liquid crystal behaviors of nonconventional colloidal nanorods (e.g., bent nanorods).

COLL 452

Stimuli-responsive materials by nanoscale assembly and disassembly

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Self-assembly and directed assembly have been employed as very powerful methods for fabricating functional materials from nanoscale building blocks. New properties unavailable from individual nanoparticles are often created through the collective effects such as interparticle coupling and structural ordering. An important consequence of the formation of such secondary structures is that the properties of nanoparticle ensembles

can be dynamically controlled by manipulating the assembly and disassembly behaviors, making them excellent candidates for constructing stimuli-responsive or smart materials. In this presentation, I will use a number of examples recently developed in my group to demonstrate that dynamic assembly and disassembly processes can be utilized as powerful tools to construct functional optical materials that can effectively respond to stimuli such as temperature, chemical environment, and electric and magnetic fields.

COLL 453

Development of a porous photocatalytic matrix for encapsulation of membrane-bound proteins

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Using sol-gel methodology, we developed a porous titanium dioxide matrix, or gel, for the encapsulation of membrane-bound proteins for the purpose of enhanced photocatalysis for water-splitting in visible light. To prevent damaging the encapsulated proteins, ethanol content within the gels was restricted to 30vol% or less with water content ranging from 70 to 100vol%. Photocatalytic activity of the gels was determined by monitoring the concentration of a model molecule, methylene blue, within the gel as it is known to degrade when in close proximity to the titanium dioxide water-splitting process. Under UV light, gels containing no protein were proven to degrade methylene blue at a rate comparable to commercial P25 titanium dioxide nanoparticles with over 98% methylene blue concentration loss after five hours of irradiation. Additionally, in order to sensitize the titanium dioxide gels for photocatalysis in visible light, we successfully encapsulated bacteriorhodopsin within the pores of titanium dioxide gels during synthesis. Absorption spectra of these gels was collected during the span of several weeks to confirm the stability of the bacteriorhodopsin within gels over time.

COLL 454

Time-resolved second harmonic microscopy of molecular transport through living cell membranes

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Nonlinear light scattering in the form of Second Harmonic Generation, due to its symmetry properties, has been proven effective for characterizing molecular transport through the membranes of living biological cells with membrane specificity and real time resolution. Second Harmonic Light Scattering (SHLS) has even been demonstrated as

a label free method so that transport rates of molecules, with or without nonlinear polarization, can be determined. Our studies based on SHLS have shown dramatic differences in transport rate due to differences in molecular structure and membrane modification. In this report, we show our effort in developing SHLS as a microscopic tool for imaging molecular transport through living biological cells with time and spatial resolution.

COLL 455

Chemical imaging of the lipid composition at the site of influenza budding

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The influenza virus acquires its lipid envelope when it buds from the host cell's plasma membrane. Intriguingly, the influenza viral envelope is enriched with cholesterol and sphingolipids, and depletion of either cellular cholesterol or sphingolipids is detrimental to influenza virus replication. These observations led to the long-standing hypothesis that the influenza viral proteins are recruited to ordered cholesterol- and sphingolipid-enriched domains in the plasma membrane for virus particle assembly and budding. Though this hypothesis is well supported by indirect evidence, whether cholesterol and sphingolipids are enriched at the site of influenza budding has not been decisively tested due to the difficulty of simultaneously imaging cholesterol and sphingolipids within the plasma membrane. We have overcome this obstacle by developing a secondary ion mass spectrometry (SIMS) approach to image metabolically incorporated, stable isotope-labeled lipids in the plasma membrane with a lateral resolution of ~100 nm. Here we have imaged metabolically incorporated ¹⁵N-sphingolipids and ¹⁸O-cholesterol as well as immunolabeled viral envelope proteins on the surfaces of influenza-infected MDCK cells, and assessed their co-localization. The results of this decisive test of the long-standing hypothesis that the influenza virus buds from cholesterol- and sphingolipid-enriched membrane domains will be presented

COLL 456

Modulating effects of small molecules on the structure and dynamics of lipid-membranes

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The interaction of small molecules with lipid membranes and the detailed knowledge of their binding site and bilayer distribution are of great biological and biomedical importance. In this talk, I will first discuss how partition of small molecules to the

membrane may influence the structure and dynamics of the membrane. MD simulations of interactions of an anticancer drug tamoxifen (TAM) with lipid membranes will be presented, which, in conjunction with a variety of spectroscopic and neutron experiment, shed new light on membrane mediated anticancer mechanisms by TAM. I will then present MD results on how the hydrophobic thickness mismatch and the phase behavior of the lipid bilayers modulate the distribution and orientation of carotenoids within the membranes. Finally, I will discuss mechanisms by which small molecules, e.g., α -tocopherol, traverse a cell membrane as revealed by MD simulations using advanced sampling techniques. Detailed knowledge of these mechanisms will have significant implication for understanding physiological distribution, pharmacokinetics and resistance of drug molecules.

COLL 457

Crowding-induced mixing of lipid bilayers: Examination of mixing energy, reversibility, and dynamics

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We use fluorescence microscopy to examine the crowding-induced mixing transition of liquid ordered (L_o)-liquid disordered (L_d) phase separated lipid bilayers when proteinaceous particles of increasing size bind to either the L_o or L_d phase. These particles contained histidine-tags, which were phase targeted by binding to iminodiacetic acid (IDA) head groups, via a Cu^{2+} chelating mechanism, of lipids that specifically partition into either the L_o phase or L_d phase. The degree of steric pressure was controlled by varying the size of the bound particle (10-240 kDa) and the amount of binding sites present in the lipid bilayer. A Boltzmann distribution was applied to mixing statistics within giant unilamellar vesicle (GUV) populations (i.e. percentage of mixed and unmixed GUVs). It also incorporated the steric-pressure contribution to free energy via the Carnahan-Starling equation of state. Values for the free energy of mixing were determined for various lipid compositions; its value decreased as a critical/mixing composition was approached, thus validating the thermodynamic model. We also applied a mass transfer-based diffusional model to analyze the observed L_o phase domain dissolution in supported lipid multibilayers – that along with visual observations and activation energy calculations, provides insight into the sequence of events in crowding-induced mixing.

COLL 458

Effects of defects on lipid biomembranes

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“Defects” on biomembranes can be induced by hydrocarbon chain mismatch, lateral segregation of lipids on the bilayer (e.g., lipid domains or lipid “raft”), and the onset of phase transitions (locally immiscible of the lipid). These defects significantly affect the characteristics of the systems. This presentation will focus on the fundamental understanding (at molecular level) of the recent findings in the defect-enhanced lipid transfer and defect-induced hydrophobic molecules’ insertion. Both phenomena suggest that the interface area between ordered and disordered domains plays a key role in dictating the spontaneous transfer of lipid and the hydrophobic interactions between foreign molecules and the membrane host.

COLL 459

Super-resolution stimulated emission depletion-fluorescence correlation spectroscopy reveals nanoscale membrane reorganization induced by pore-forming proteins

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Membrane–protein interactions play a central role in a wide variety of cellular processes.

The primary virulent pathway for the action of antimicrobial peptides and pore forming toxins (PFTs) are initiated by protein binding, oligomerization and pore formation. The dimensions of the transmembrane pores typically range from 10 - 30 nm depending on the nature of the pore forming toxin. Detecting local perturbation to the lipid dynamics around these pore complexes and correlating these changes to the nature of the protein and membrane composition is challenging due to the small length scales involved.

Using a combination of super-resolution stimulated emission depletion nanoscopy with fluorescence correlation spectroscopy (STED-FCS) we unravel the emergence of nanoscale lateral heterogeneity in supported bilayer membranes made up of 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC) and cholesterol upon interaction with the PFT, listeriolysin O (LLO). Using the shift in the length scale from a Brownian to a non-Brownian diffusive regime (< 150 nm) as a signature, we correlate pore formation with cholesterol induced sequestration in bilayers with varying cholesterol content. Bilayers prepared with labeled lipids present in either the proximal or distal leaflet allow us to track the dynamical perturbation in a leaflet-dependent manner upon LLO incubation. From the differences in the extent and intensity of the dynamical crossover as observed

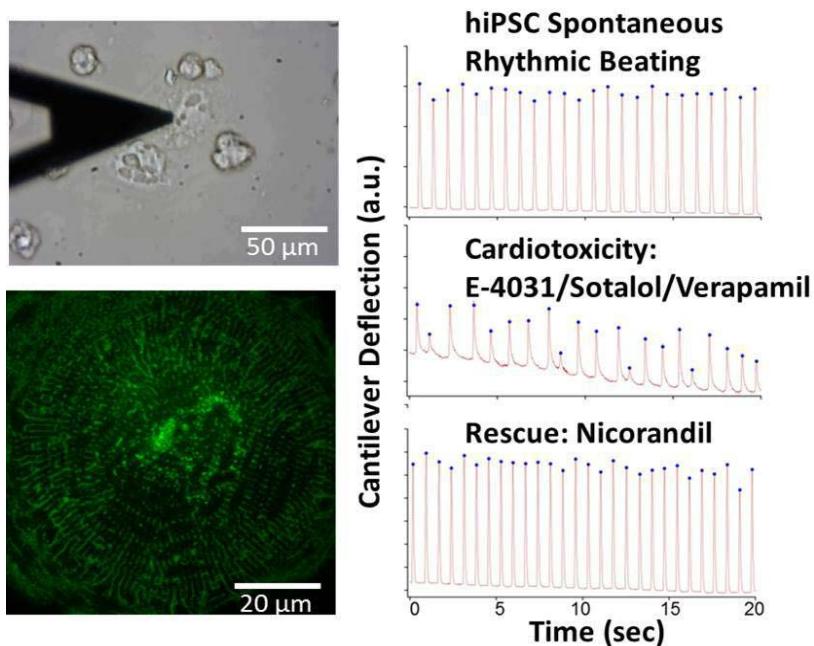
with STED-FCS, these experiments reveal that the affinity for cholesterol in the membrane binding motifs of the LLO subdomains induce cholesterol and lipid reorganization to a greater extent in the distal (upper) leaflet when compared with the proximal (lower) leaflet. From STED-FCS measurements on POPC and DMPC membranes incubated with LLO, the pore forming efficacy and resulting pore morphology is related to the degree of fluidity in the lipid bilayer.

COLL 460

Nanosafety and toxicity assessment by using spontaneous beating cardiomyocytes

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Nanoenabled smart and innovative products and processes have created a tremendous growth potential for a large number of industry sectors. At the same time, many questions have been raised relating to the potential impact on human health and on the environment of these materials. The real concern is the lack of systematic studies on hazards of or exposure to nanomaterials. Cellular systems are a fundamental element of living biological systems. It is likely that monitoring toxic response of cellular model systems to nanoparticle exposure will provide insight in to the “modes-of-action” of nanoparticles and which of them need to be further investigated for risk assessment. An AFM-based approach to investigate compound induced ion channel effects in spontaneous beating cardiomyocytes is developed for prescreening drug development and serves as a cellular system for nanosafety studies. Cell assay based approaches to assess toxicity, localization and accumulation of nanomaterials will be discussed.



An AFM-based approach to investigate compound induced ion channel effects in spontaneous beating cardiomyocytes is developed for prescreening drug development and serves as a cellular system for nanomaterial risk assessment.

COLL 461

Epitaxially connected quantum dot superlattices

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Connecting quantum dots into epitaxially connected superlattices is a new and exciting route to novel two-dimensional materials. The ability to control the atomic structure of the quantum dot building block (*i.e.*, size, shape and composition) and the geometry of the superstructure creates fertile opportunity space to synthesize and study new classes of 2D materials. Theoretical calculations on these systems predict interesting phenomena including topological states and Dirac cones. We present recent advances in our group to fabricate atomically connected quantum dot superlattices with structural coherence approaching a single atomic bond length.

Despite the high degree of structural coherence, surprisingly charge carriers are strongly localized, as shown by the first charge transport measurement in an atomically coherent quantum dot device. Before theoretically predicted properties can be probed, outstanding knowledge gaps concerning the formation of epitaxially connected superlattices need to be resolved. The formation of superlattice polymorphs (*e.g.*, square or honeycomb lattices) is related to the preferred orientation of constituent nanocrystal building blocks and the rate of assembly. Understanding and ultimately controlling the transformation of the nanocrystal assembly into an atomically coherent superlattices hinges on establishing deeper insights into the fundamental transformation mechanism and the complex interplay of transport and reaction dynamics of the chemical trigger near the nanocrystal surface. We discuss recent efforts in our group to disentangle these effects. To better understand how polydispersity of the quantum dot building blocks impacts long-range order in the 2D assembly, we developed analytical methods to quantitatively characterize the propagating disorder in terms of a paracrystal model; this approach underscores the dramatic impact of angstrom scale translational disorder on structural correlations at hundreds of nanometers.

COLL 462

Nanocube superlattices of CsPbBr₃ perovskites and pressure-induced phase transformation at atomic and mesoscale levels

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Device application of lead-halide perovskites requires serious consideration of structural improvement and property enhancement. Using pressure processing of assembled perovskite nanocubes (NCs) with *in situ* small/wide angle X-ray scattering and photoluminescence probes, we studied the detailed evolution of CsPbBr₃ perovskite nanocrystal superstructures under external pressure. Through control of solvent evaporation, CsPbBr₃ perovskite NCs spontaneously assemble into a *simple cubic* superlattice. Upon increase of compressional magnitude to 17.5 GPa, the perovskite undergoes pressure-induced phase transformations at both atomic and meso-scales. After complete release of pressure, the newly nucleated perovskites not only have an improved crystal structure, but also display an enhanced optical property as compared to the starting NCs. A detailed examination and overall analysis reveal a stress-induced attachment and fusion of NCs into highly ordered 2D nanoplatelets that have uniform thickness and single crystallinity. It is proved that the pressure processing of NC assembly represents one novel and efficient approach for fast conversion of lead-halide perovskites into a stable structure with enhanced properties for applications.

COLL 463

Self-assembly of actinyl peroxide nanoclusters with cationic surfactant

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The interaction between surfactants of different chain lengths with an actinyl peroxide cage Li_{48+m}K₁₂(OH)_m[UO₂(O₂)(OH)]₆₀(H₂O)_n (m≈20 and n≈310) (U₆₀) in aqueous solution is reported. The U₆₀ clusters will self-assemble into vesicular structures when interacting with surfactants. The sizes of assembled products keep increasing before reaching equilibrium, indicating the fusion of these assembled structures. The long chain surfactant (CTAB) can interact stronger with U₆₀ than short chain surfactant (DTAB). Both electrostatic interaction and hydrophobic interactions are playing an essential role in regulating the size of the assemblies. Laser light scattering, TEM and AFM measurements were applied to characterize the solutions and assembled structures.

COLL 464

Stimuli-responsive colloidal architectures and porous membranes by melt-shear organization

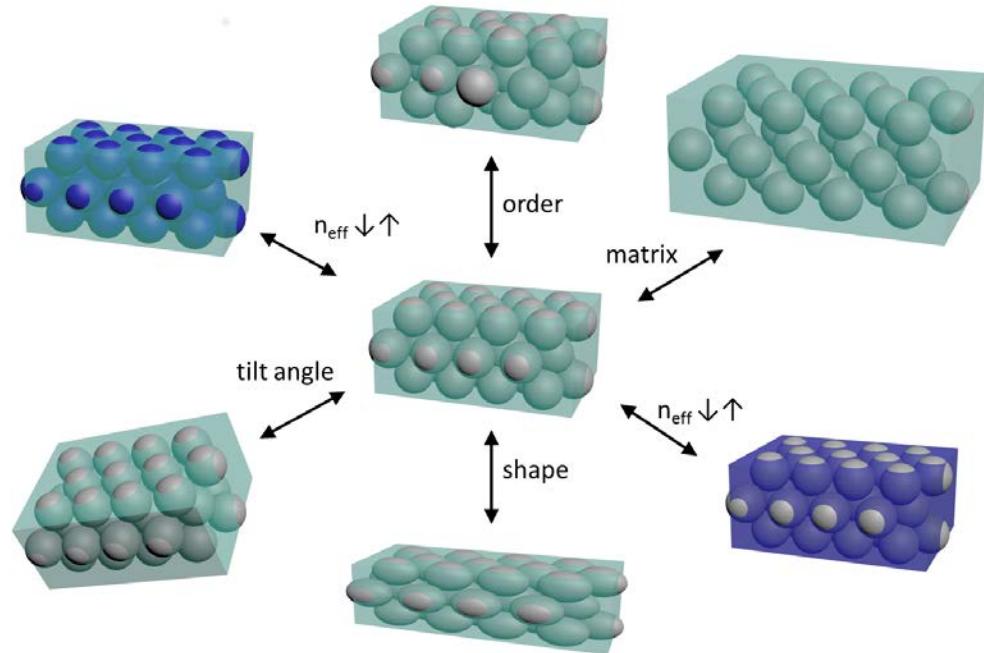
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Highly ordered 3D colloidal architectures provide access to a rapidly growing field for various applications, e.g., sensing, photonics or membrane technology. A promising technique for the preparation of colloidal crystal films is the so called melt-shear organization technique. As a basic prerequisite the preparation of tailor-made core-shell particles is essential. During melt-shearing which comprises an increase in temperature under application of moderate pressures, a radial flow profile for the polymer mass is induced and the core particles will merge into a colloidal crystal structure inside the viscous polymeric shell material. The advantage of this technique compared to other processes is the possibility to create flexible and large-scalable films without a dispersion medium.

The synthesis of the core-shell particles follows a stepwise emulsion polymerization, which allows the incorporation of different functional and stimuli-responsive monomers that can be triggered by e.g. temperature, light, mechanical stress, redox chemistry or solvent. The resulting polymer film then comprises the intrinsic capability of a color change by these triggers. These stimuli-responsive polymer films offer highly attractive applications in photonics, sensing or as security features.

Additionally some of the obtained structures can be converted into highly ordered (porous) ceramics.

The use of bifunctional silane monomers offers the capability of self-crosslinking the entire hybrid material during processing or in a subsequent step. Due to the hybrid crosslinking strategy, the thermal stability of the matrix-building shell material is considerably increased. Finally, a porous ceramic structure can conveniently be achieved after thermal treatment of the hybrid polymer film.



COLL 465

Framework stability vs. collapse: Quantifying the role of nearest-neighbor nanocrystal bonding as a key factor in determining order in mesoporous colloidal nanocrystal frameworks

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Recognizing the factors that contribute to the stability of mesoporous films assembled from ligand-stripped (or "naked") doped metal oxide nanocrystals and amphiphilic block copolymer architecture-directing agents is vital to their fabrication into films for low-cost, solution processable devices. Here, we present our recent efforts in the quantitative analysis of order-disorder transitions, framework stability, or conversely framework collapse, by systematically varying nanocrystal weight fraction relative to the block copolymer for a variety of block copolymer sizes. Using image analysis techniques for top-down and cross-sectional SEM, along with analysis by GISAXS and a 3-D representation of the framework from STEM tomography, we can provide a greater understanding of the role nanocrystal-nanocrystal contacts contributes to well-controlled assemblies and precise framework architectures across multiple length scales.

COLL 466

Assembly of free-standing, flexible, citrate-capped gold nanoparticle films at the air-water interface

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Colloidal noble metal nanoparticles, due to their size and optical properties, have been used extensively in the field of plasmonics. Arranging noble metal nanoparticles into films is a growing area of research that shows much promise in developing flexible plasmonic sensors. Often, nanoparticle films are made through laborious methods such as electron beam lithography or the use of a complicated solvent system. We have developed a simple procedure to produce nanoparticle films that uses citrate-capped gold and silver nanoparticles and a simple solvent system to induce nanoparticle film formation. This formation process involves adsorption of gold nanoparticles on a functionalized substrate, followed by a delamination process of the particles from the

substrate at an air/water interface to form a film. During film formation, the localized surface plasmon resonance (LSPR) characteristics of the film change as the dispersed particles appear red in solution and then take on a more metallic appearance when arranged into a macro-sized, monolayer film. The effects of surface chemistry, surface energy, and solvent in film formation will be discussed. The films have been captured onto substrates that have varying topological features while still remaining intact. Because the films possess nanovoids, surface enhanced Raman spectroscopy (SERS) measurements were explored. The films are candidates for development as versatile, flexible sensors to detect chemical and biological targets.

COLL 467

Complex superparamagnetic particle architectures: Obtaining novel properties by controlled assembly and combination of nano-building-blocks to nanostructured entities

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In the recent years, the art of synthesising and tailoring nanoparticles with distinct properties has attracted tremendous interest and has been explored very well. The next step further is to consider these particles as nano-building blocks which shall be combined bottom-up, to form again particles, but now complex, nanostructured particles. The aim is to achieve novel functional particles with interactive properties that can only be obtained from the smart assembly of nano-building blocks to combined entities.

In this talk, two examples of such complex particle entities using nano iron oxides with superparamagnetic properties as building blocks will be shown.

The first example is about the formation of hollow microballoons derived from superparamagnetic iron oxide nanoparticles with silica patches. Using patchy iron oxide nanoparticles is the key towards being able to create hollow micron sized entities which evolve from a lifelike Pickering-emulsion process. Ultimately, it is possible to obtain a magnetically steerable particle system with a density of less than 0.2 g/cm³.

The second example is about a smart optical composite material with isotropic and anisotropic optical properties by combination of luminescence and high reflectivity which enables switching between both depending on an applied wavelength of light. The composite is formed as anisotropic core/shell particles by coating superparamagnetic iron oxide-silica microrods with a layer of the luminescent metal-organic framework and can be rotated by an external magnet. The integration and control of light emission modes within a homogeneous particle dispersion marks a new type of smart optical material, addressing fundamentally new directions for research on switchable multifunctional materials.

COLL 468

Nanoparticles, nanorods and shish-kebabs with precisely controlled dimensions, compositions, and architectures

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In this talk, I will elaborate general routes to a rich variety of functional nanoparticles, nanorods, and shish-kebabs with precisely controlled dimensions, compositions and architectures by using nonlinear block copolymers as templates. Our approach enables the facile synthesis of organic solvent- and water-soluble monodisperse nanoparticles, nanorods, and shish-kebabs with desired dimensions, compositions and architectures, including plain, core/shell and hollow nanoparticles, plain and core/shell nanorods, and nanotubes, by capitalizing on a set of rationally designed nonlinear block copolymers as nanoreactors. These organic solvent-soluble and water-soluble monodisperse nanoparticles and nanorods include metallic, ferroelectric, magnetic, luminescent, semiconductor, and their core/shell structures, which represent a few examples of the kind of nanocrystals that can be produced using this technique. The applications of these functional nanocrystals in solar energy conversion (i.e., dye-sensitized solar cells, perovskite solar cells, and photocatalysis) will also be discussed.

COLL 469

Synthesizing dual-emitting quantum dots on indium phosphide cores

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Heterostructured semiconductor nanoparticles synthesized with increasing complexity impart advanced functionality to the resulting quantum dots (QDs) for applications in sensing, solid state lighting, and photovoltaics. Adding semiconductor shells to InP core materials is an effective way to protect the easily oxidized core as well as engineer the bandgap structure of the particle. Under certain conditions where partial oxidation of the core is observed, however, the defect layer acts as a hole tunneling barrier, creating a particle that emits both as a core/shell quantum dot and as a quantum well or Inverted-Type I QD. The relative intensity of the two emission peaks can be adjusted through control of the oxidation of the core and emission colors dictated by the shell composition and thickness. The dual functionality of these particles for combined imaging and photochemistry is demonstrated.

COLL 470

Biomimetic catalysis in green organic transformations

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We have developed selective oxidative palladium-catalyzed borylative and arylative carbocyclizations of enallenes, allenynes, and bisallenenes as well as C-H activation/carbocyclization of arylallenenes. These reactions have been used in a number of useful cascade reactions. Many of these cascade reactions employ molecular oxygen as the oxidant in a biomimetic approach.

In another approach to biomimetic catalysis, enzymes have been combined with racemization catalysts for dynamic kinetic resolution. An example of the latter approach is the development of a biomimetic hybrid catalyst that works as an artificial metalloenzyme.

COLL 471

Fischer-Tropsch synthesis on cobalt catalysts-on the effect of water revisited

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Water is an inherent component in Fischer-Tropsch Synthesis on Co catalysts. One molecule water is formed for each molecule CO that is converted. Water may affect the selectivity, activity, deactivation and state of the catalyst. Small Co particles may oxidize by exposure to the reaction mixture, particularly in the initial stages of the reaction. However, oxidation should not be associated by the observed deactivation during steady-state conditions. Although many rate equations do not contain water as a term, the activity may increase or decrease depending on the catalytic system as a result of increasing content of water. The selectivity of C₅+, however, will always increase with increasing content of water and it follows that the selectivity increases with conversion and comparisons between different studies should therefore be based on constant conversion. The effect of water on the selectivity is independent of its origin, i.e. adding water to the feed has the same effect as water produced by the reaction. The effect of water depends on the catalyst properties such as the support, the particle size and the promoter. As an example it has been shown that small pore γ-Al₂O₃ is less efficient at high water content than large pore γ-Al₂O₃. Several theories and mechanistic explanations have been proposed to explain the effect of water in Fischer-Tropsch synthesis. Most probably it is the active CH_x carbon inventory that is the key factor. Different experimental evidences of the effect of water with emphasis on alumina and aluminates will be presented together with a discussion of possible mechanisms.

COLL 472

Aspects of the Fischer Tropsch reaction mechanism in the light of chemical transient kinetics

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Despite extensive studies of Fischer Tropsch (FT) catalytic CO hydrogenation, a detailed understanding of the reaction mechanism leading to long-chain hydrocarbons is still missing. C-C coupling and CO-insertion remain the main mechanisms of the reaction. The present contribution is aimed at scrutinizing which of the mechanistic suggestions are compatible with the experimental results obtained by quantitative Chemical Transient Kinetics (CTK), as developed in our group over the past few years. Chemical transients provide relaxation-type information on the response behavior of catalysts relative to abrupt changes of the gas phase composition. Our studies with Co/MgO, as well as pure Co and Ni model catalysts, allowed the atomic amounts of carbon, oxygen and hydrogen during the “build-up” to be evaluated for the CO hydrogenation under atmospheric pressure conditions. It was shown that the monolayer limit was surpassed even before reaching the steady state, with the amounts of O atoms always exceeding those of C atoms. Thus, the catalyst surface did not provide metallic sites under steady state conditions. Furthermore, for the above catalyst systems, chain-lengthened hydrocarbons appeared in sequence with considerable delay times when switching to reactive FT conditions. Chain lengthening was not observed under conditions of irreversible CO chemisorption. Instead, gaseous CO was necessary for this to occur. This behavior was interpreted as being in agreement with a CO insertion mechanism. This interpretation was supported by the finding that during back-transients to non-reactive conditions, CO was being evacuated from the reactor with the same time constant as Ar reference gas. Plotting the Anderson-Schulz-Flory” chain lengthening probability α for hydrocarbons in the build-up stage clearly showed proportionality to the CO pressure but non-monotonous behavior as a function of accumulating carbon (or CH_x) as would be expected if CH_x insertion or C-C coupling were occurring.

Time-dependent infrared measurements showed the formation of surface formate species. We will discuss the question for the role of such species as intermediates in hydrocarbon chain lengthening and the general validity of the CTK/IR measurements by inspecting more complicated catalyst systems. In particular, we will discuss the performance results for Co/Mn₅O₈ catalysts which show high selectivity for the formation of long-chain oxygenates, besides paraffins and olefins, under FT conditions.

COLL 473

Selective hydrocarbon oxidation catalysis by Au atomic and nanoclusters

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In recent years, the important role of metal-support interface in Au catalysis has been documented for various reactions, ranging from CO oxidation, selective hydrocarbon oxidation, to alcohol decomposition. Recently, Au atomic clusters stabilized by intermediates formed in the reaction are found to be important in selective liquid phase hydrocarbon oxidation. Interestingly, for these reactions, the function of Au is not the traditional lowering of the activation barrier for the transformation of reactant to product, but in facilitating the formation of an initiator for the catalytic cycle that may occur without participation from Au. Examples from our laboratory illustrating these two modes of operation of Au clusters will be presented.

COLL 474

Probing the role of particle size in nickel phosphide hydrotreating catalysts

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Transition metal phosphides show excellent promise for heteroatom removal reactions and the most active phosphides have exhibited higher hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) activities than commercial sulfided Co-Mo/Al₂O₃ and Ni-Mo/Al₂O₃ catalysts. Among metal phosphide catalysts, oxide-supported nickel phosphide (e.g. Ni₂P/SiO₂) has demonstrated particularly strong potential, but the role of particle size in determining hydrotreating activity and selectivity is not well understood. Using mesoporous silica encapsulated nanoparticles (Ni₂P@mSiO₂) prepared by solution phase methods and Ni₂P/SiO₂ catalysts prepared by temperature-programmed reduction (TPR), the deep HDS properties of Ni₂P have been probed over the 3-16 nm size range. The catalysts have been characterized by a range of methods including transmission electron microscopy (TEM), CO chemisorption and infrared spectroscopy, while the HDS of 4,6-dimethylbenzothiophene (4,6-DMDBT) was used to investigate catalytic properties. HDS measurements were carried out using a model feed of 1000 ppm 4,6-dimethylbenzothiophene (4,6-DMDBT) in decalin over the temperature range 513-573 K. A strong dependence of HDS activity on Ni₂P particle size was observed, with the smallest particles exhibiting the highest activities. The correlation of 4,6-DMDBT HDS activity and selectivity with particle size, surface area and CO chemisorption capacity will be discussed.

COLL 475

Competing forces in chiral surface chemistry: Enantiospecific adsorption versus enantiomer self-aggregation

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The enantiospecific adsorption of chiral molecules on chiral surfaces is dictated by two competing forces: the enantiospecificity of adsorption energetics and the propensity of enantiomers to disproportionate into homochiral (conglomerate) or heterochiral (racemate) clusters. These phenomena have been studied by measuring the surface enantiomeric excess, ee_s , of chiral amino acid mixtures adsorbed on Cu single crystal surfaces and in equilibrium with gas phase mixtures of varying enantiomeric excess, ee_g . Alanine adsorption on Cu{3,1,17}^{R&S} surfaces is non-enantiospecific, $ee_s = ee_g$, because alanine enantiomers do not interact with either the surface or with one another enantiospecifically. Aspartic acid adsorbs enantiospecifically on the Cu{3,1,17}^{R&S} surfaces; $ee_s \neq ee_g$, even during exposure to a racemic mixture in the gas phase, $ee_g = 0$. Exposure of the achiral Cu{111} surface to non-racemic aspartic acid, $ee_g \neq 0$, results in local amplification of enantiomeric excess on the surface, $|ee_s| > |ee_g|$, as a result of homochiral aggregation. Finally, in spite of the fact that the Cu{653}^{R&S} surfaces are chiral, the adsorption of aspartic acid mixtures yields $|ee_s| > |ee_g|$ indicating that homochiral aggregation dominates enantiospecific adsorbate-surface interactions. All of these types of behavior are captured by a Langmuir-like adsorption isotherm that includes competition between enantiospecific adsorption and both homochiral (conglomerate) and heterochiral (racemate) clustering of chiral adsorbates.

COLL 476

Hot electron-mediated surface chemistry on solid-gas and solid-liquid interfaces

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The detection of hot electrons and understanding the correlation between hot electron generation and surface phenomena are challenging questions in the surface science and catalysis community. Hot electron flow generated on a gold thin film by photon absorption (or internal photoemission) appears to be correlated with localized surface plasmon resonance.

In this talk, I will show strategy to quantify the non-adiabatic energy transfer and detect hot electron flux during the elementary steps of the surface reactions occurring at solid-gas and solid-liquid interfaces. To detect and utilize the hot electron flows, the nanodiodes consisting of metal catalyst film, semiconductor layers, and Ohmic contact pads were constructed. It was shown that the chemicurrent or hot electron flows were well correlated with the turnover rate of CO oxidation or hydrogen oxidation separately measured by gas chromatography, suggesting the intrinsic relation between catalytic reaction and hot electron generation. We show a novel scheme of graphene catalytic nanodiode composed of a Pt NPs array on graphene/TiO₂ Schottky nanodiode, which allows detection of hot electron flows induced by hydrogen oxidation on Pt NPs. By analyzing the correlation between the turnover rate (catalytic activity) and hot electron current (chemicurrent) measured on the graphene catalytic nanodiodes, we demonstrate that the catalytic nanodiodes utilizing a single graphene layer for electrical connection of Pt NPs are beneficial for the detection of hot electrons due to not only atomically thin nature of graphene but also reducing the height of the potential barrier

existing at the Pt NPs/graphene interface. I will show that hot electron flow generated on a gold thin film by photon absorption (or internal photoemission) is amplified by localized surface plasmon resonance. We report results obtained using metal/n-Si nanodiodes which show creation and transfer of hot electrons in the course of a catalytic decomposition of aqueous hydrogen peroxide (H_2O_2) on the surface of Ag, Pt and Au catalysts. The chemicurrent yield, the number of hot electrons detected per oxygen molecules, reaches values up to 0.1. Finally, The effect of surface plasmons on the catalytic and photocatalytic activity on metal–oxide hybrid nanocatalysts is also highlighted. These phenomena imply the efficient energy conversion from the photon energy to the chemical energy, with the potential application of hot electron-based photocatalytic devices.

COLL 477

Chemisorption impacts on physisorption: Perturbations of 2D self-assemblies at the liquid-solid interface

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Patterning two-dimensional (2D) surfaces with self-assembled arrays of functional molecules has been pursued for its potential to manipulate the remarkable materials properties of substrates like graphene, MX_2 , and other novel 2D surfaces. Demonstrations of controlled self-assembly processes by tuning either intrinsic variables (molecular design and symmetry) or extrinsic properties (temperature, concentration, solvent, capillary flow, and substrate) are well documented. Here, we investigate the impact of chemisorbed species on the self-assembly of different molecules on the graphite surface. We demonstrate how chemisorbed molecules on graphite surface can impede molecular self-assembly at the liquid-HOPG interface. Chemisorption is facilitated through aryl radical attack of the graphite surface after electrochemical activation of diazonium species. The resultant sp^3 hybridized sites act not as nucleation points but as barriers to obstruct the self-assembly processes. Self-assembly obstructions include the creation of domain boundaries, stacking faults, and poor/no assembly in laterally confined areas ($\sim 8 \times 8 \text{ nm}^2$). Annealing treatments demonstrate the ability of the self-assembly to minimize the perturbations created by the defects. Selective removal of the covalent defects via *in situ* nanolithography provides a handle to control Oswald ripening. This work represents a generalized platform for fundamental perturbations studies on nucleation, growth, and ripening processes within 2D physisorbed self-assemblies.

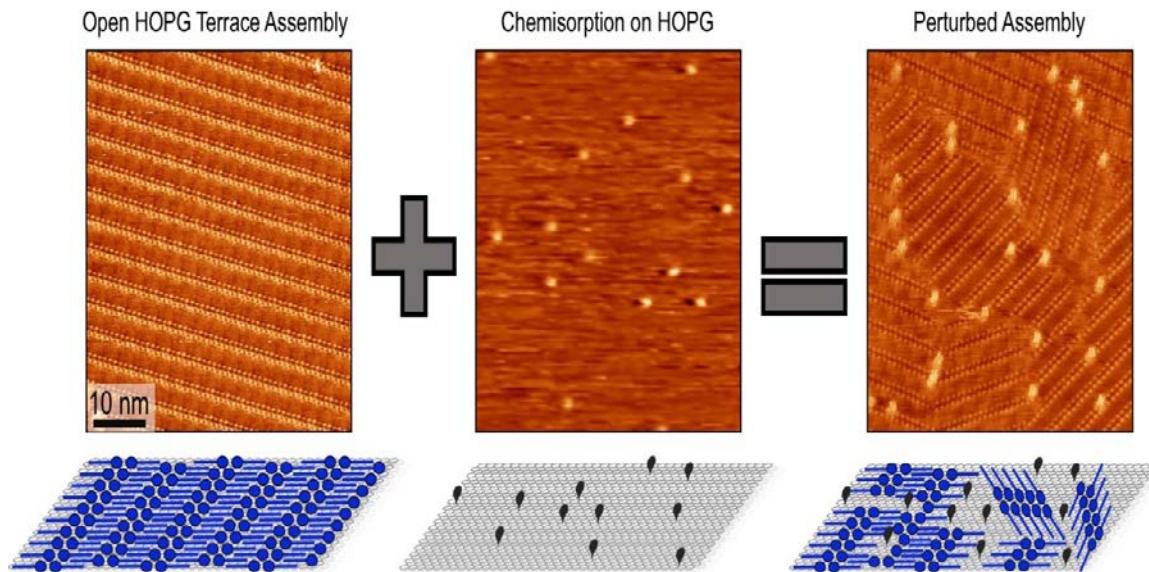


Figure 1. STM images and schematic models showing the self-assembly of 5-octadecyl-isophthalic acid (ISA-OC₁₈) on open terraces, the chemisorption of 3,5-tertiarybutylphenyl chemisorbed on HOPG, and the resultant perturbed structure that the chemisorption has on the self-assembly of ISA-OC₁₈.

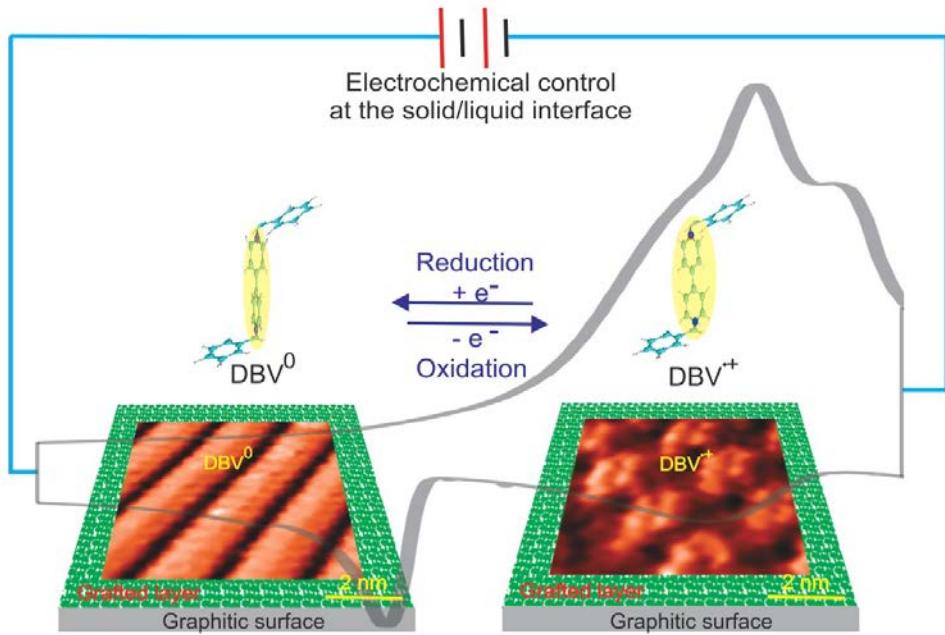
COLL 478

Nanoconfined self-assembly on a grafted graphitic surface under electrochemical control

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Graphene has been the subject of intense research efforts on account of the remarkable properties it possesses; these include ultrahigh electron mobility, ballistic transport, ambipolar charge carriers, and high thermal and electrical conductivity. Despite the exceptional qualities, some inherent characteristics of graphene, such as the zero-band gap, prevent its widespread use in technological applications. Molecular functionalization of graphene is a promising approach to address these challenges and widen the scope of its applications. In the present work, both non-covalent and covalent functionalization protocols were employed for functionalizing graphene/graphite surfaces under electrochemical control. The efficiency of the functionalization process and the stability of the grafted films as a function of electrode potential are investigated using a combination of cyclic voltammetry and electrochemical scanning tunneling microscopy (EC-STM). Furthermore, we show that it is possible, under electrochemical control, to locally remove the grafted species via EC-STM tip based nanomanipulation.

The as-formed *nanocorals* of pristine graphitic surfaces serve as size-limiting platforms for the molecular self-assembly of guest molecules, i.e. n-doping reduced dibenzyl viologen (DBV). The experimental finding opens new avenues to investigate supramolecular self-assembly of n-/p-doping molecules in nanoconfined spaces under electrochemical control towards bottom-up creation of nanoconfined n-/p-doped 2D materials for nanoscale electronics applications.



The self-assembly of reduced dibenzyl viologens within nanocorals at different substrate potentials

COLL 479

Surface-confined molecular nanostructures: Influencing molecule-surface interactions as well as electronic surface properties

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The interest in studying organic nanostructures on surfaces emerges from their prospective usage as nanoscale functional materials in applications ranging from electronics to spintronics and catalysis. By making use of molecular recognition processes based on non-covalent interactions, well-ordered 1D and 2D molecular structures can be formed on surfaces. Understanding the interplay of the underlying intermolecular and molecule-substrate interactions, and processes on the atomic and molecular scale is the key for being able to deliberately tune the functional properties of organic nanostructures.

In my presentation I will focus on three topics. (i) For the same porphyrin derivative adsorbed on Au(111), the effect of changing the intermolecular interactions (H-bonded

vs. metal-coordinated) on molecule-substrate interactions has been investigated. (ii) In order to reduce the molecule-substrate interactions, we studied the effect of introducing a graphene layer between the molecules and the metal substrate and compared the observed self-assembled structures. (iii) To influence the electronic surface properties, we made use of quantum confinement by adsorbing a self-assembled H-bonded porous molecular network on Au(111).

COLL 480

Hierarchical assembly of Xe atoms in an atomically precise array of quantum boxes

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Quantum boxes (QBs) have been arranged in extended 2D arrays by the self-assembled formation of a porous on-surface coordinated network. These boxes provide a particular environment to study the condensation of atoms and small molecules. The electronic states contained in these arrays can be configured in an atom-by-atom manner. The localized perturbation is controlled by the targeted filling level of the individual QBs with Xe atoms after Xe repositioning. It is shown that specific filling patterns of the network of QBs which are coupled in an inherently precise way by self assembly specifically perturb, and thus modify the localized and delocalized quantum box states (QBSs). In particular the energy levels of the QBSs and their coupling across the 2D QBarry is modulated which provides an analogy to a breadboard as it is used in the design and testing of electronic circuitry.

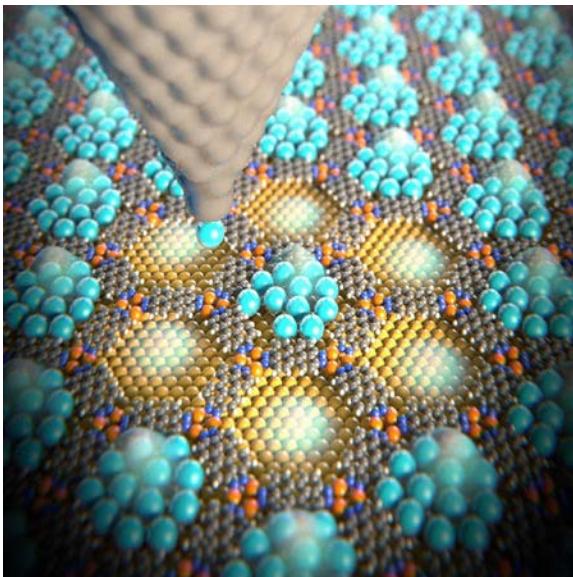


Fig 1: Model of a porous network being configured by removal of Xe atoms from the quantum boxes. A quantum box filled with 11 Xe atoms in the center is surrounded by six empty quantum boxes in a plane of full boxes.

COLL 481

Templated 2D supramolecular assembly of fullerenes on graphite by five-coordinate gallium–porphyrin monolayers

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The development of methods for the bottom-up fabrication of hierarchical assemblies that incorporate nanostructured carbon is integral to the rational design of electronic materials that implement their useful properties. We report studies that probe the application of patterned monolayers of five-coordinate gallium porphyrins as templates that direct the organization of fullerenes on highly oriented pyrolytic graphite (HOPG) under ambient conditions. Gallium octaethylporphyrins of the type $\text{Ga(OEP)(C}\equiv\text{CR)}$ ($\text{R} = \text{Ph}$, 3-thiophene, 1-pyrene, 2-pyrene, 9-trptycene, 9-anthracene) self-assemble into ordered monolayers on HOPG upon deposition from solution, as determined by STM imaging. The monolayers present a pseudo-hexagonal lattice in which the $\text{C}\equiv\text{CR}$ ligands are perpendicular to the surface, forming corrals with dimensions that are appropriate for accommodating C_{60} . Addition of solutions of C_{60} and its derivatives to $\text{Ga(OEP)(C}\equiv\text{CR)}$ monolayers results, for specific R groups, in the formation of bilayer structures comprised of the original porphyrin monolayer and an adlayer of fullerene. The R groups were chosen to allow systematic investigation of the effects of their C_{60} binding constant, contact point, and orientation upon the extent of fullerene incorporation. For example, $\text{Ga(OEP)(C}\equiv\text{CPh)}$ monolayers are not observed to coordinate C_{60} , consistent with the low solution affinity of its R group. Monolayers of the

higher-affinity R = pyrene derivatives exhibit inclusion of fullerenes across a range of concentrations, and the thiophene derivative produces a unique multilayer structure. The factors that control the formation and structures of these assemblies will be discussed.

COLL 482

Supramolecular control of interfacial structure in organic semiconductors

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This presentation will review our recent studies of the role of hydrogen bonding and other supramolecular interactions in controlling self-assembly of functional semiconducting molecules. Using a combination of STM, AFM, X-ray crystallography and DFT calculations, we explore the complex interplay of intramolecular, molecule-molecule and molecules-surface interactions in defining the supramolecular structure at the interface. The discussed case-studies will include hydrogen-bonding assembly of naphthalenediimides (NDIs)n in monolayers and thin films on conducting and insulating surfaces, the effect of aromatic rings in diketopyrrolopyrrole oligomers, and assembly of fullerene and its derivatives on thiol-based monolayers.

COLL 483

Hierarchical self-assembly of novel organic polycyclic aromatic molecular systems into 1D and 2D nanomaterials

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Crafting the structure and function of organic materials using the strategies of self-assembly and supramolecular chemistry has progressed over the past two decades in materials chemistry. A variety of systems have been engineered where function is directly linked to non-covalent interactions, such as ionic, hydrophobic, van der Waals, hydrogen, and coordination bonds. They also influence solid-state self-organization to produce an organized structure at any scale, ranging from the nano and micrometer scales to microscopic dimensions. Here we present a fused-arene based molecular dyads and triads with polarizable functional groups to serve as a comprehensive guide for designing next generation of 1D and 2D functional materials. We utilize strong $\pi-\pi$ stacking interactions of the polycyclic, planar, rigid aromatic rings and electrostatic interactions, mainly sigma-hole (σ -holes) interactions of the polarizable groups as an effective approach to fabricate versatile 1D and 2D assemblies. The building block molecules include four different planar aromatic molecules: perylene tetracarboxylic diimide (PDI), anthracene, pyrene, and carbazole. A derivative of PDI forms a class of

n-type semiconductor and later three are of *p*-type character. Studying both types of semiconductors will provide well rounded, integrated understanding of the optoelectronic properties of fused arene-based organic materials and the potential applications in nanoscale devices.

COLL 484

Adsorption of n-alkanes on the surface of h-boron nitride: A thermodynamic and molecular dynamics study

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Molecular adsorption on surfaces is fundamentally important in a variety of scientific and technological processes. Surface adsorption plays a key role in catalysis/catalytic supports, optoelectronic devices, lubrication and adhesion, wetting phenomena, and separations. We present the results of a comprehensive investigation of the first ten members of the homologous series of *n*-alkanes (methane-decane) adsorbed on the basal plane of hexagonal boron nitride using high-resolution, volumetric adsorption isotherm measurements (more than 30 separate temperatures per molecule). The experimentally determined heats of adsorption vs. carbon chain length follow the well-known “odd-even” behavior of the *n*-alkanes. While this may not be surprising we will illustrate additional potential surface configurations that can lead to an increase in entropy. Potential phase transitions are identified using changes in the 2D-compressibility. In addition, we describe the results of companion molecular dynamics modeling to provide microscopic insight to the wetting behavior as a function of alkane chain length and film thickness. Concentration profiles were calculated normal to the surface to illustrate the interface broadening as a function of film thickness and temperature. A comparison with the behavior of the same *n*-alkane set on MgO and graphite will also be included. These studies can serve as the basis for developing accurate, robust models of the potential energy surfaces and can be used for future investigations of the microscopic structure and dynamics of these adsorbed films using neutron/x-ray diffraction and neutron spectroscopy.

COLL 485

Multiscale and hierarchical organic materials by design, synthesis, and self-assembly

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Molecular building blocks with electronically active p-systems are being envisioned for the creation of ordered nanostructures needed in organic electronics applications. We know that the electronic properties of these molecules derive from the internal chemical bonding patterns and can be readily modified using synthesis. Those same synthetic tools can, in principle, be used to program a molecule's external bonding patterns; the ones that support the non-covalent contacts directing self-assembly. However, we do not yet know the rules (structure patterning and ranges of intermolecular forces) that govern the resulting hierarchical organization of such assemblies. For this reason, we are investigating with multiscale theory and experiments how atomic and molecule-level interactions drive the hierarchical 2D tiling and 3D stacking of molecular building blocks into patterned organic materials. We focus on creating ordered versions of bulk heterojunctions by the ordering of flat organic molecules at graphite-solution interfaces and their observation using scanning tunneling microscopy (STM). Examples will be presented that highlight the hierarchical ordering of macrocycles and small molecules, and the rules of assembly that they bring to light.

COLL 486

Resistance to cold cataract in the eye lens proteins of a cold-adapted fish

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The $\beta\gamma$ -crystallin fold that is ubiquitous in the structural proteins of the vertebrate eye lens is an ancient structural motif found in diverse organisms from all three domains of life. In organisms without eyes, e.g. archaea, bacteria, tunicates, and sponges, $\beta\gamma$ -crystallins serve as calcium-binding proteins. In vertebrates, they are primarily found in the eye lens, where they play an important role in controlling the refractive index gradient of this specialized tissue. The ubiquitous $\beta\gamma$ -crystallins of the vertebrate lens are believed to have descended from an ancestral single-domain Ca^{2+} -binding crystallin by a process that included gene duplication resulting in two copies of the double Greek key domain per chain, as well as selection for high refractive index. Because the lens has negligible protein turnover, the crystallins must remain stable and soluble for the lifetime of the organism despite their extremely high concentrations. In particular, we are interested in the resistance to phase separation of the cold-adapted crystallins of the Antarctic toothfish, *Dissostichus mawsoni*.

The eye lens of *D. mawsoni* is evolutionarily adapted to function in the permanently sub-freezing waters of the Southern Ocean. This is in contrast to temperate and tropical fishes, and endothermic mammals, the lenses of which undergo liquid-liquid phase separation at low temperatures. Mammalian lenses phase separate at temperatures

between 10 °C and 20 °C – well above the Antarctic's sub-zero marine environment. The ability of the toothfish lens to maintain transparency in this frigid environment is particularly remarkable given that fish lenses have a high concentration of constituent proteins $\geq 1000 \text{ mg * mL}^{-1}$). We hypothesize that γ -crystallin isoform heterogeneity coupled with cold selective evolutionary pressures contribute to the clarity of the toothfish lens. Here we report the thermal stabilities and phase diagrams of seven key γ -crystallin lens proteins, prepared recombinantly in *E. coli*. The implications of our findings with respect to the roles of frustration, ionic interactions, and protein flexibility liquid-liquid phase separation will be discussed.

COLL 487

Design and optimization of polyphosphate coacervates for use in biomedical devices

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Linear polyphosphates (PP), and in particular the coacervates that can be formed through subsequent cationic interactions, represent an interesting class of biomaterials for biomedical device development. Such coacervates have potential utility in a variety of clinical applications, including embolization procedures that may be used to block blood flow to tumors, or in localized drug delivery by way of microencapsulation. In this presentation, detailed studies on the processing and resulting physical properties of polyphosphate coacervate systems derived from NaPP and divalent cations – namely calcium, strontium and barium – are described in relation to targeted device optimization. Generally speaking, these polyphosphate coacervates degrade and dissolve at a fast rate, losing half of their original mass in a week and transforming to mainly pyrophosphate after 4 weeks. This burst dissolution phase occurs earlier for coacervates prepared from very short chain polyphosphate, although longer polyphosphate chains do not increase coacervate longevity significantly. In contrast, cation type and NaPP degree of polymerization (D_p) can be shown to profoundly impact viscoelastic properties, with high D_p yielding predominantly elastic characteristics; high D_p coacervates also demonstrate generally greater hemostatic properties overall. Using a design of experiments approach, a radiopaque liquid embolic agent synthesized from Ca(Ba,Sr)PP coacervates was optimized with respect to viscosity, radiopacity and cell viability, and subsequently validated in an animal model. Efforts to enhance the overall versatility of these coacervate-based systems through processing modifications are also described. Initial studies have revealed that introducing low levels of trivalent ions (Ga, Al) can modulate the degradation and cohesive characteristics of these *in situ* forming CaPP coacervates. Using polyphosphate coacervate precursors, a low temperature emulsion / solvent extraction technique has also been employed to generate therapeutically loaded phosphate glass microspheres. Sustained *in vitro* release of minocycline over a 7-day period was observed, suggesting potential utility of this

approach for treating periodontitis. Overall, PP coacervate-derived biomaterials offer potentially innovative solutions to challenging clinical applications.

COLL 488

Complex coacervate for cardiac regeneration

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Cardiac repair and regeneration is a critical challenge. There are multiple research thrusts aimed at promoting regeneration and healing rather than pathological remodeling with the hall mark of excessive fibrosis. We pursue the use of proteins for potentially faster clinical translation. Clinical translation of protein therapies faces multiples challenges; the most significant is how to maintain bioactivity so as to lower dosage and reduce off-target effects. My lab uses heparin and biocompatible polycations to form an injectable coacervate that preserves the bioactivities of heparin-binding proteins. The delivery system is self-assembled from aqueous solutions. We explore several growth factors, cytokines and morphogens. I designed the delivery vehicle to mimic the interaction among fibroblast growth factor-2 (FGF2), heparin and FGF receptor. The effectiveness of the coacervate delivery system is demonstrated using multiple proteins (FGF2, SDF, VEGF, HGF, HB-EGF, IL10, TIMP3, Shh, PDGF, NGF among others) in multiple animal models (mice, rat, pig). Here I will describe the use of this coacervate to provide spatial and temporal control of the release of TIMP3, FGF2, and SDF-1 α in a rat cardiac infarction model. This combination leads to steady recovery of cardiac function after one week, while the same amount of proteins failed to induce long lasting effect and showed the same deterioration of function as saline control. We show that the proteins can be detected 28 days after injection, an order of magnitude longer than free proteins. The released proteins exert their effects through binding to the receptors to reduce ECM degradation, modulate inflammation, activate angiogenesis, and recruit progenitor cells. Taken together, this shows that complex coacervate is an appropriate vehicle for therapeutic proteins.

COLL 489

Discovery of a family of new LCST peptide polymers: Coacervation behavior and self-assembly

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Proteins and synthetic polymers that undergo aqueous phase transitions mediate self-assembly in nature and in engineered material systems. Despite this widespread interest, little is known about how phase behavior of a protein is encoded in its amino acid sequence to specify lower critical solution temperature transition (LCST) phase behavior. To address this lacuna, we synthesized intrinsically disordered peptide

polymers to test motifs that we hypothesized would encode phase behavior and show that, consistent with predictions, they exhibit tunable LCST behavior in physiological solutions. These data also provide heuristics to design new LCST exhibiting peptide polymers that consist of biologically active peptide repeats. A subset of the newly discovered LCST polymers also show significant thermal hysteresis in their cloud point behavior. CD studies as function of temperature suggested that the origins of hysteresis may lie in the emergence of secondary structure upon desolvation of the more hydrophobic, hysteretic blocks. To test this hypothesis, different fractions of (Ala)₂₅ helical domains were encoded into an ELP that show no thermal hysteresis. Consistent with our hypothesis, these polymers display varying degrees of thermal hysteresis (T_t -cooling < T_t -heating) that is likely driven by inter-chain hydrogen bonding of the structured domains. We have also synthesized diblock copolymers with a hysteretic and non-hysteretic block, and have found that they show temperature triggered self-assembly into rod-like nanoparticles that retain their shape upon cooling for extended periods of time. This shape memory effect strongly depends on the degree of hysteresis exhibited by the core-forming block and persists upon prolonged incubation at temperatures below the critical assembly temperature.

COLL 490

Engineering Pickering emulsions using protein/polysaccharide complexes

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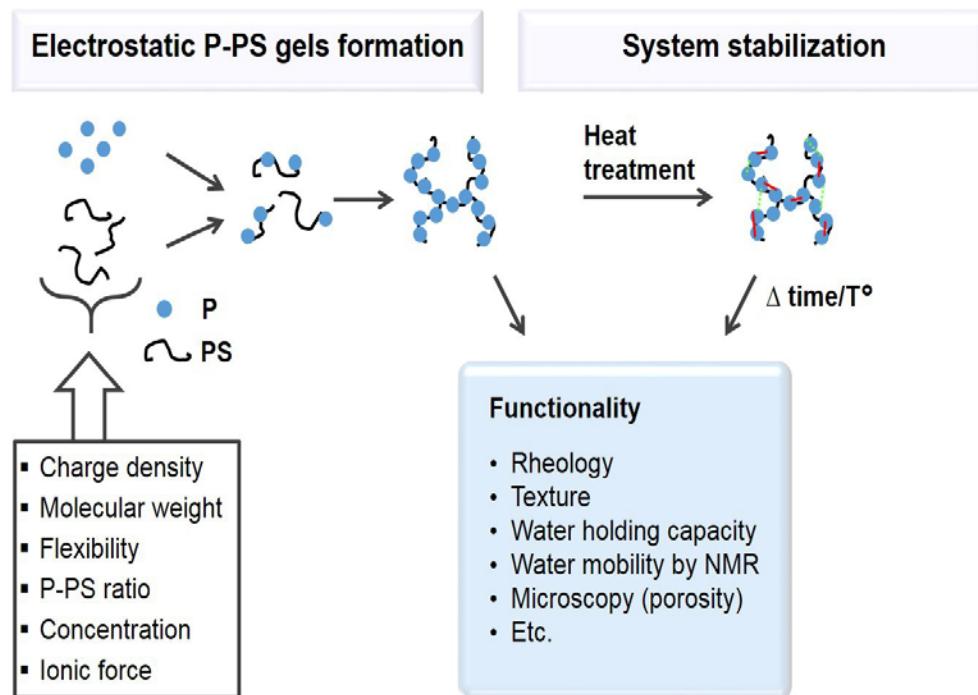
Particle size and surface wettability play leading roles in the distribution of particles on the oil-water interface and the stability of emulsions. The present work utilized nanocomplexes assembled from gelatin and tannic acid to stabilize Pickering emulsions, whose particle sizes and surface wettability were further regulated by using a polysaccharide. The sizes of nanocomplexes, which ranged from 205.8 nm to 422.2 nm, increased with the addition of polysaccharide, while their contact angles decreased from 84.1° to 59.3°, revealing hydrophilic nature. Fluorescence microscopy and cryo-scanning electron microscopy (cryo-SEM) results indicated that the nanocomplexes were located at the oil-water interface. Interfacial shear and dilatational rheological results exhibited a fast and irreversible adsorption behavior, which differed from rearrangement of gelatin molecules at the oil-water interfaces. The minimum concentration of nanocomplexes for emulsion stabilization was 0.1 wt%. Our results demonstrate that protein/polyphenol/polysaccharide nanocomplexes can be applied to form stable surfactant-free food emulsions for nutraceutical delivery.

COLL 491

Functionality of protein-polysaccharide hydrogels

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Foods are complex systems where proteins (P) and polysaccharides (PS) play a major role as structural and nutritional agents. Their structural organization in food determines the textural and sensory qualities of foods. In addition to the intrinsic properties of P and PS (molecular weight, structural conformation, charge, etc.), interactions with other constituents in the food also direct their assembly and influence their functionality. Coupled gels were made with β -lactoglobulin (β Ig)-xanthan gum (XG) or Lysozyme (Lys)- XG with in situ acidification with glucono delta-lactone (GDL) (reaching pH 4.4 or 7 respectively), in quiescent condition. The gel strength, microstructure (porosity) and water holding capacity were determined for several biopolymer concentrations and ratios. At similar concentration and ratio (0.3 wt%, ratio 0.5), both gels exhibited different gel strengths. Softer gels were found for Lys-XG compared to the β Ig-XG (76 vs 342 Pa). The residual net charge at pH 7 is -20 mV for LYS-XG compared to -50 mV for β Ig-XG. Both gels can retain high amounts of water (> 300g / g biopolymer). The gelation mechanism was identified for the β Ig-XG system where β Ig aggregates along the XG chains and could be considered as a crosslinking agent. The main limitation of these systems being a gel dissolution at neutral pH due to disruption of electrostatic interactions. Heat treatment stabilization was investigated and allowed to introduce these gels in neutral pH systems. The spectrum of P and PS functionality may be broaden using associative interactions and this will enable food scientist to design products with desired structure and texture.



COLL 492

Using coacervation to achieve surface-selective particle deposition

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Modern personal care and detergent formulations should not just clean the surface but also, at a later stage, deliver certain benefit agents, such as perfumes or conditioning agents, onto the surface. At the next level of performance, these benefit agents should be deposited selectively at intended target surfaces. Using in-situ null-ellipsometry we have studied the surface deposition of hydrophilic or hydrophobic model particles from aqueous polymer– surfactant formulations onto anionic hydrophilic, or hydrophobized, model silica surfaces. The model particles were anionic silica particles or silicone oil droplets, respectively, both with hydrodynamic radii in the range 15-20 nm. The polymer-surfactant formulations contained anionic sodium dodecylsulfate (SDS) and a cationic polymer. Surface deposition from the formulations was induced by controlled dilution of the formulations into the coacervation region, and was monitored with time by ellipsometry. The dilution simulated a rinsing process in a typical application. In all cases a steady-state surface layer remained after extensive dilution. An enhanced deposition from the silica-containing formulations was found on the hydrophobized silica surface, indicating a substantial co-deposition of silica particles. The opposite trend, enhanced co-deposition onto hydrophilic silica, was found in similar experiments with hydrophobic silicone oil droplets as co-deposants. The amphiphilic cationic polymers evidently favor a “mismatched” co-deposition of anionic particles to hydrophobic surfaces, or vice versa. The findings suggest a strategy for surface-specific delivery of particles to surfaces.

COLL 493

Super Temporal-Resolved Microscopy (STReM) for measuring fast interfacial dynamics

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Protein dynamics at interfaces are crucial to a wide range of applications including disease inception, drug delivery, and separations science. Recent efforts by our group and others have shown the promise of applying single molecule methods to link mechanistic detail about protein adsorptions to macroscale observables. However, although the best super-resolution methods achieve high spatial resolution, the temporal resolution remains low. We report Super Temporal-Resolved Microscopy (STReM) to improve the temporal resolution of 2D super-resolution microscopy by a factor of 20 compared to the traditional camera-limited frame rate. This is achieved by rotating a phase mask in the Fourier plane during data acquisition and then recovering the temporal information by fitting the PSF orientations. The feasibility of this technique is verified with both simulated and experimental 2D adsorption/desorption and 2D emitter transport. When STReM is applied to measure protein adsorption at a glass surface, previously unseen dynamics are revealed.

COLL 494

New luminescence nanothermometers in different biological windows

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High-resolution thermal sensing and bioimaging at the cellular level and in animal models (in vivo applications) is interesting for both early diagnosis and controlled treatment via photothermal conversion. Despite excellent in vitro results have been obtained with visible emitting luminescent nanothermometers, their application for in vivo studies is very limited due to the reduced penetration depth of visible light in biological tissues. This can be overcome if materials with emission and absorption bands lying in the so-called first and second biological windows, corresponding to the 650-950 and 1000-1350 nm spectral ranges, respectively, where tissue scattering and absorption are minimized.

Here we present the last results we obtained in luminescence nanothermometry and bioimaging in the first and second biological spectral windows using specially oxide-based materials, such as monoclinic double tungstates and tetragonal Gd vanadate nanoparticles doped with Tm^{3+} , Ho^{3+} , and Nd^{3+} , in some cases sensitized with Yb^{3+} . The results show that high thermal sensitivity can be obtained in the first biological window with Tm^{3+} , Yb^{3+} : $GdVO_4@SiO_2$ nanoparticles using up-conversion excitation mechanisms, and that the inert shell plays an important role in improving the thermal sensitivity and resolution. We will also show that Nd^{3+} : $KGd(WO_4)_2$ capped with APTES molecules can be used for luminescent thermometry with good sensitivity in both the first and second biological windows. Furthermore, these nanoparticles can also be used for bioimaging specially in the first biological window, achieving a penetration depth of ~1 cm. Tm^{3+} , Ho^{3+} : $KLu(WO_4)_2$ nanoparticles have been explored also as luminescent thermometers and bioprobes in these spectral ranges. The results achieved indicate that these nanoparticles can also be used as photothermal agents. In this field, we used an integrating sphere to determine in an easy and fast way the photothermal conversion efficiency of photothermal agents, including Au nanoparticles and graphene derivatives.

COLL 495

Improving surgery via selective detection of ovarian tumors using fluorescent nanoparticles

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Surgery is the frontline therapy for ovarian cancer and has two purposes. The first is to remove as much of the disease as possible – this is called debulking. The second is to stage the cancer – to see how far the cancer has spread from the ovary. Surgery is critical to patient outcomes with survival linked to the degree of tumor removed from the abdomen. The amount of residual disease at the end of surgery is very subjectively

reported with inherent surgeon bias. Therefore, there is a clinical need for more precise objective detection techniques during surgery, to enable surgeons to identify smaller tumors. The ability to fluorescently detect tumors during surgery that are too small to see with the naked eye would greatly enhance the surgeon's capabilities. We have developed nanoparticles that selectively label ovarian tumors in mice when injected IP. Little to no signal is seen in healthy tissue. This phenomenon has been confirmed in freshly excised patient samples. We are now optimizing the particles in preparation for clinical translation.

COLL 496

Liver specific MRI contrast agents based on Mn²⁺ containing nanoparticles

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Contrast agents have become essential and critically important in liver MR imaging for accurately diagnosing liver lesions with high confidence. While there have been attempts to diversify contrast agents with various materials, Gd³⁺ complexes, which are effective for both lesion-detection and -characterization in T₁-weighted MRI, remain the only available MRI contrast agents for diagnosing liver lesions. However, since the possibility of nephrogenic systemic fibrosis as a result of the release of Gd³⁺ ions is becoming a serious issue, an urgent need has re-emerged to develop safer contrast agents based on less-toxic materials that can take over the role of Gd³⁺ complex-based contrast agents.

In this presentation, I will discuss our strategy of developing Gd³⁺-free (low toxicity) contrast agents for liver MRI with high contrast-enhancing efficiency in T₁-weighted MRI and lesion differential dynamic MR imaging properties, based on Mn²⁺-containing nanoparticles such as Mn²⁺-doped silica nanoparticle (Mn-SiO₂) and hollow manganese silicate nanoparticle (HMS), by exploiting the characteristics of nanoparticles and cell-specific uptake and diffusion of released Mn²⁺ ions. Especially, I would like to share the details of the time-sequential and tissue-differential change in Mn-SiO₂- and HMS-enhanced liver MRIs that detect difference among tissues in vascularity and existence or modification among particular cells in Mn²⁺-uptake and -excretion capability and may enable increase in the ability to distinguish among various hepatic tumors according to origin, vascularity, and cell viability.

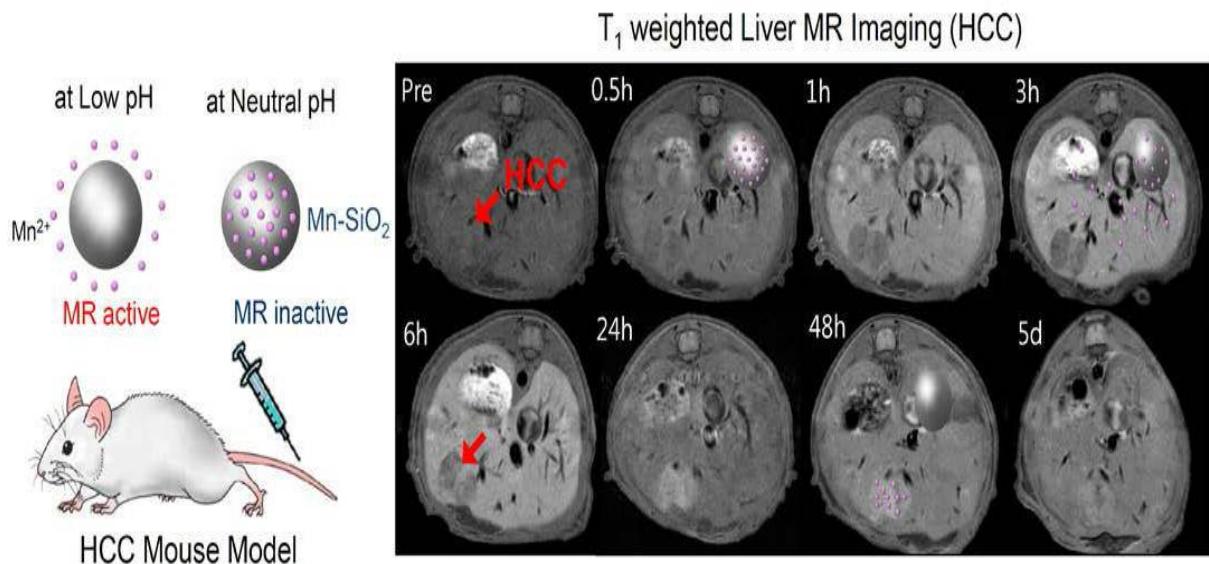


Figure 1. Mn-SiO₂-enhanced ^T₁ weighted liver MR images of an orthotopic xenograft mouse model of human hepatocellular carcinoma.

COLL 497

Targeted sensing and drug delivery using smart nanoparticles

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Nanoparticles are of importance in biomedical applications due to their intrinsic properties. The ligand coating of the nanoparticles is critical for colloidal robustness and nanoparticle function and the chemical composition/morphology of the inorganic core is important in defining/tuning the optical, electrical and magnetic properties of the nanoparticulate system. As the chemical synthesis of nanoparticles and nanoparticle functionalization techniques advance during the years, the design of nanoparticulate systems become more sophisticated facilitating multitasking nanoparticle roles.

In this presentation I will discuss recent progress in our group concerning the design of nanoparticles and their incorporation in biological systems to facilitate sensing, drug delivery and accurate manipulation. My talk will focus on a new class of nanoparticles that can accommodate synergistic actions of sensing and drug delivery in cells. These multitasking particles are able to selectively release their therapeutic payload in response to specific mRNA signatures and selectively kill model cancerous cells as opposed to healthy cells.

COLL 498

Strategies for making smart foams, emulsions and multiphasic gels stabilized by functional particles

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We will discuss strategies for making novel responsive classes of soft matter and nanomaterials by using multiphasic fluids and particle-controlled interfacial effects. One such class of materials can be formed when light or field-responsive particles are embedded into foams, emulsions and colloidal gels. In the first part of the talk we will present the design and characterization of a few types of very stable, yet stimuli-responsive, Pickering foams. These foams are stabilized by rod-like polymer particles or ones made from hydrophobically modified cellulose. By addition of carbonyl iron particles into the matrix, these Pickering systems can be made photo- as well as thermally sensitive, resulting in novel photo-thermo-magneto responsive foams. In the second part of the talk, we will describe a new smart multiphasic gel system containing ultraflexible chains assembled from magnetically responsive nanoparticles bound by liquid lipid bridges. The initial application of an external magnetic field aligns the superparamagnetic nanoparticles into chains, where they become bound by the soft attractive potential induced by the surface-condensed lipid. The liquid bridges allow for particle rolling and sliding, and the resulting chain flexibility was measured to be orders of magnitude higher than any other linear structures reported to date. The nanoparticles binding through soft, "snappable" liquid bridging provides a facile means of creating self-repairing gel networks. Such flexible responsive multiphasic structures can be used in applications such as switchable assemblies of patchy particles, and novel colloidal inks for 3D printing. Finally, we will discuss the development of scalable, rapid and efficient processes for synthesis of functional nanomaterials by precipitation under shear in biphasic systems. The ultralow interfacial tension between oil droplets and shear medium enables the formation of high surface area liquid structures, which can serve as templates for the formation of diverse classes of polymer and biopolymer materials, at least one characteristic dimension of which may be on the nanoscale. Our "shear nanospinning" technique opens the way to scalable manufacture of nanofibers and a broad range of polymer nanomaterials.

COLL 499

Probing hydrophobic interactions at solid/water/oil/air interfaces and surface interaction mechanisms of deformable emulsion droplets

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Hydrophobic effects play important roles in a wide range of natural phenomena and engineering processes such as coalescence of oil droplets in water, air flotation of mineral particles, folding and assembly of proteins and biomembranes. The intermolecular and surface interactions at solid/oil/water/bubble interfaces play critical roles in many industrial processes such as oil production. In this talk, I will review some of our recent experimental attempts to reveal the physical origin of hydrophobic effects by directly quantifying the hydrophobic interactions on both solid/water and fluid/water interfaces, and then report our recent progress in probing the interaction mechanisms of deformable W/O and O/W emulsion droplets and air bubbles using state-of-the-art nanomechanical techniques such as surface forces apparatus (SFA) and atomic force microscopy (AFM) coupled with bubble/drop probe technique. Micropipette and in-house built 4-roll mill fluidic device were applied to monitor the stability of both pipette-supported and freely suspended emulsions in the presence of interfacially active chemicals (e.g. asphaltenes, the heaviest component in bitumen and crude oil) under quasi-static and dynamic flow conditions, respectively. The interaction forces between O/W or W/O emulsion drops were directly measured using droplet probe AFM and analyzed using a theoretical model based on Reynolds lubrication theory and augmented Young-Laplace equation by including the effects of disjoining pressure. A long-range “hydrophilic” attraction was found between water drops and polyelectrolyte surfaces in oil. Our results provide new insights into the fundamental understanding of hydrophobic interactions and interaction mechanisms of deformable emulsion droplets and bubbles in complex fluids.

COLL 500

Ion specific effects in Winsor III microemulsions

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A Winsor Type III microemulsion is a separate, surfactant-rich phase that forms in equilibrium with excess oil and water. Varying the amount of an added simple electrolyte can induce the formation of a Type III microemulsion from an oil/water/surfactant system. The concentration of sodium chloride at which equal volumes of oil and water partition into the middle phase is called the optimal salinity. We observe large changes in optimal salinity when varying the cation of an added salt. Potassium, calcium, magnesium, cesium, rubidium and lithium chloride salts are investigated. Observed shifts in optimal salinity are consistent with the Hofmeister series. For example, potassium, the weakest chaotrope, reduces the optimal salinity, while lithium, the strongest kosmotrope, increases the optimal salinity. Results suggest that microemulsions might be surrogates for future studies of the mechanism of the Hofmeister effect.

COLL 501

How molecular structure of surfactants determine the dynamics and viability of wettability alteration

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Only about 35% of oil in place is recovered from carbonate reservoirs through primary and secondary flooding because of oil wet surfaces and resulting unfavorable capillary pressures. Surfactants can improve oil recovery significantly by altering wettability of surfaces. However, the process of selecting an effective surfactant for wettability alteration is dependent on a number of factors, including mineral type, temperature, salinity, and nature of adsorbed oil and ultimately how the molecular structure of the surfactant interacts with all of these. Here we present an experimental study of the effectiveness of surfactants with different hydrophobic groups and different lengths of a hydrophilic oligomer. The surfactants selected alter the wettability of the rock primarily by acting on the water-rock and oil-rock interfaces and have minimal effect on the interfacial tension of the oil-water interface. The dynamics of wettability alteration is measured by the evolution of contact angles of oil-drops on initially oil-wet surfaces and film coverage for surfactant-induced dewetting of oil-films. The hydrophobic groups are found to determine which surfactants primarily act on rock interfaces. The rate and degree of wettability alteration are strongly controlled by the length of the hydrophilic oligomers. Shorter oligomers lead to faster and greater wettability alteration and are least sensitive to the effects of temperature and salt concentration. Experimental observations are efficiently summarized by a few thermodynamic and kinetic parameters. A theory is presented to describe the dynamics and provide a framework to extract rate constants for the adsorption and desorption of the surfactants to the rock interfaces. These rate constants and the surfactants effect on contact angle are used in a pore-scale model for imbibition in the presence of surfactant to determine which surfactants structures are practically viable for wettability alteration in oil-wet carbonate reservoirs.

COLL 502

Effects of salinity on oil recovery: Experimental and theoretical studies of crude oil-water-calcite surface restructuring and associated physical and (electro)chemical interactions

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We have measured crude oil-brine-mineral surface (calcite) interactions using a variety of dynamic techniques including contact angles, Surface Forces Apparatus (SFA), AFM, interfacial tension, XPS and other physical and chemical surface characterization techniques. Different brine (ionic electrolyte) solutions and temperatures were investigated, as well as dynamic (time-dependent) effects. The primary aim of the experiments was to investigate the “dilution effect”, where dilution of the ionic concentration of the fluid injected into oil wells is found to enhance oil recovery. Ionic strengths were varied from 350,000 ppm to pure water; and temperature varied from 20 to 75°C. We conclude that the “dilution effect” is due to a combination of colloidal (electric double-layer, hydration and van der Waals) forces, based on well-established theories for these interactions. In addition, our experiments reveal electro-chemical reactions involving dissolution, adsorption, and restructuring of the calcite surfaces, which increases their roughness (cf. the geological process of Pressure Solution). Both the colloidal forces and surface roughening and restructuring act to reduce the adhesion of the crude oil-brine interface to the calcite-brine interface (across the thin aqueous film) which in turn reduces the water contact angle (increasing the water-wettability and, presumably, oil recovery) with increasing dilution. These two processes appear to be essential for the dilution effect to be effective at all solution concentrations from formation water to pure water. We also find that three different processes occur that have very different time scales: (1) the initial, rapid (seconds – minutes) physical ion exchange with the surfaces that *locally* changes the surface charge/potential and hence the double-layer and hydration forces, (2) the *local* electro-chemical dissolution and restructuring of the surfaces (minutes – hours), which is also often accompanied by the adsorption of an organic-ionic layer on the mineral surface that comes off as visible flakes with the oil, and (3) large-scale, long-times, diffusion-rate controlled restructuring leading to *macroscopic* changes in rock morphology.

COLL 503

Simple-to-apply wetting model to predict the thermodynamically stable and the metastable contact angles on textured/rough/pattered surfaces

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The effects of roughness/textured/patterned surfaces on the apparent contact angles, i.e., on the ‘apparent’ adhesion energy between liquids and solid surfaces, have been studied extensively in the last decade. Although existing models allow for *a priori* predicting the apparent thermodynamically stable and metastable contact angles, they require extensive mathematical manipulations, and are therefore not commonly used by the scientific community. Instead, the classical and simple to apply Cassie-Baxter and Wenzel models are commonly used to *a posteriori* analyze contact angle

measurements on rough/textured/patterned surfaces.

Recently, we derived a more general simple-to-apply wetting model and equation that (1) allows for *a priori* predicting the thermodynamically and metastable contact angles on textured/rough/patterned surfaces; (2) combines the classical Cassie-Baxter and Wenzel wetting models/equations; (3) includes the effect of surface texture that is outside of the droplet on the apparent contact angle; and (4) can be used to engineer textures that would yield any desirable macroscopic contact angle for a given solid material and two liquids, e.g., oil-water-mineral surface.

During the talk, the wetting model will be presented and demonstrated by experiments with crude-oil/brine/core-rock, which is a relevant system for the oil industry. In addition, applications of the model to thermodynamically unstable/metastable states and its relation to contact angle hysteresis and the ability of the system to reach the thermodynamically stable contact angle on textured surfaces will be discussed.

COLL 504

Molecular and colloidal phenomena at aqueous interfaces of structured oils

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Molecular and colloidal self-assembly at aqueous interfaces of isotropic oils have been widely explored due, in part, to their central role in phenomena such as the spreading of fluids and emulsion stability. This presentation will move to consider structured oils, and the question of how the presence of long-range order within the oil can impact the organization of molecular adsorbates and colloidal assemblies at aqueous interfaces. In particular, I will describe how elastic stressed associated with long-range order in nematic oils can induce phase separation in monolayers of either soluble or insoluble amphiphiles. In addition, for colloidal adsorbates, the presence of topological defects induced by insertion of the colloid into the oil interface will be shown to lead to inter-colloidal forces that result in organized assemblies with unusual symmetries. The results of studies performed at planar interfaces and curved interfaces of oil droplets will be discussed.

COLL 505

New dimensions in patterning: Placement and metrology of chemical functionality at all scales

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We place single molecules and assemblies into precisely controlled environments on surfaces. The inserted assemblies and the monolayer matrices that contain them can be designed so as to interact directly, to give stability or other properties to functional supramolecular assemblies. New families of highly symmetric molecules are being

developed to yield even greater control and are enabling elucidation of the key design parameters of both the molecules and assemblies. These design elements, in turn, enable controlled chemical patterning from the sub-nanometer to the centimeter scales. We simultaneously develop metrology tools for these methods to give unprecedented insight on the structures, function, and properties of these assemblies.

COLL 506

Construction of highly ordered surface molecular nanostructures: From non-covalent interaction to covalent bond

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The formation of nanostructures with concomitant patterns and functions is of utmost importance in the field of surface molecular engineering and nanotechnology. With the carefully designed peripheral functional groups to facility intermolecular interactions, the sophisticated nanoporous structures with ordered pattern on solid supports can be tailored, which could serve as template to regulate surface orientation and distribution of functional molecules and nano-objects. In this presentation, recent advances toward molecular engineering of molecular nanoporous networks with defined size and periodicity on solid supports will be discussed. We demonstrated that the complementary hydrogen bond partner recognition has been utilized to construct two-component nanoporous network with alkyl chains as spacers between network nodes. Beyond weak intermolecular interaction, the nanoporous networks interconnected through covalent bond have attracted great attention due to their graphene-like topology and the associated properties. the key challenge urgent to address for synthesis of high quality sCOFs is how to obtain desired topological structures with perfect structural uniformity. Recently, we have demonstrated that the high quality large scale sCOF synthesis can be achieved by tuning the thermodynamic equilibrium and growth kinetics. This presentation will focus on the synthetic methodology for the on-surface fabrication of high quality sCOF materials.

COLL 507

Chemical orthogonality at the molecular limit: Structural lessons from the membrane applied to layered material interfaces

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The recent explosion of research into noncovalent functionalization of layered materials has created a resurgence of interest in molecular monolayers based on lying down phases of functional molecules that create striped or networked functional patterns at the few nanometer scale. While interfaces functionalized in this way present significant challenges in terms of ensuring robustness, they also offer a striking degree of flexibility

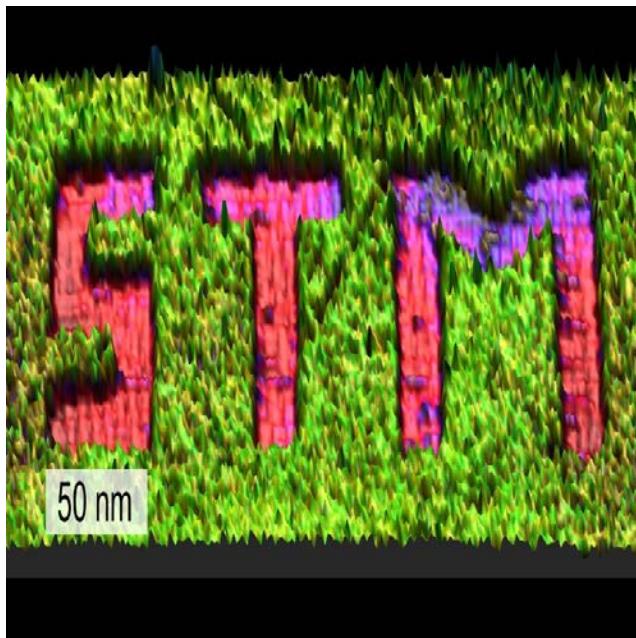
in terms of designing interactions with other materials. Here, we discuss lessons that can be learned by making analogies to functional strategies adopted within the cell membrane, ranging from lysine snorkeling in transmembrane helices to the formation of lipid rafts.

COLL 508

Controlling molecular self-assembly on graphene and graphite at the nanoscale: Combining bottom-up and top-down strategies

Steven De Feyter, steven.defeyter@kuleuven.be. Chemistry, KU Leuven - University of Leuven, Leuven, Belgium

In this presentation, I'll focus on different strategies developed in our group to control molecular self-assembly at the nanoscale on graphitic substrates such as graphite and graphene. Various stimulus activated strategies to control or influence pattern formation at the liquid-solid interface will be presented, including those involving light, temperature, and electric fields. Furthermore, we will illustrate how by liquid flow at the macroscale and by local nanolithography approaches the directionality of self-assembly processes can be tuned. In addition, strategies to control pattern formation in case of competing self-assembly pathways will be revealed.



STM based nanolithography

COLL 509

Surface mass spectrometry and STM characterizations of compositionally patterned monolayers and their post-assembly chemical modifications

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Compositionally patterned monolayers with a variety of designed structures have been shown to self-assemble by physisorption on planar substrates. STM and other scanning probe methods often provide adequate characterization of these monolayers' composition and morphology. Post-assembly chemical modification is one strategy for stabilizing and using compositionally patterned monolayers to direct further nanoscale assembly. Not all monolayers transformations are amenable to characterization by STM. This presentation will discuss combined applications of surface mass spectrometry and STM to characterize complex monolayers formed by self-assembly and by post assembly chemical modification.

COLL 510

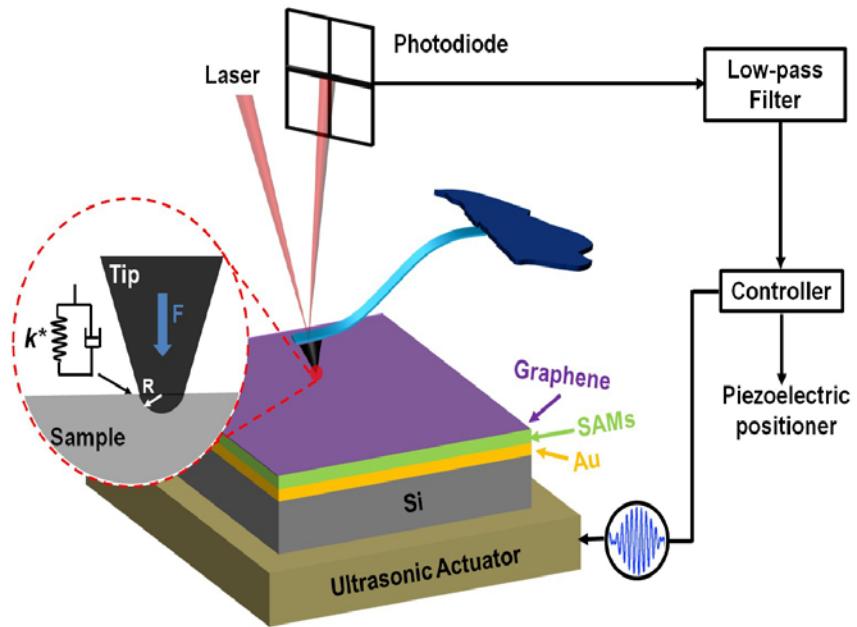
Subsurface structure fingerprint of 2D materials and heterostructures by their nanomechanical response

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Here, we demonstrate that contact resonance atomic force microscopy (CR-AFM) can yield a quantitative, subsurface-structure sensitive, mechanical fingerprint of 2D layered materials. First, we show a new method that combines *ab initio* and continuum modeling approaches to deconvolute the experimentally measured, aggregate contact stiffness and to quantify the nano-mechanical stiffness contributions from each material layer. We demonstrate the power of our method on epitaxially monolayer (MLG), bilayer (BLG), trilayer graphene (TLG), grown on silicon carbide, *i.e.*, a system for which well-defined structure models exist. The experimental method can clearly distinguish, nanometer-sized, subsurface domains of oxygen-intercalated graphene grown on SiC(0001).

Next, we apply CR-AFM to study how the head-group chemistry of self-assembled monolayers (SAMs) affects the interfacial mechanical properties of graphene on SAMs. Variations in these properties affect the stress transfer between substrate and the supported graphene and thus the performance of the graphene-based devices. We show that the changes in interfacial mechanical properties can be characterized through out-of-plane elastic properties measurements. Combining CR-AFM experiments with Molecular Dynamics (MD) simulations we show that the head group chemistry of the SAMs can have a significant effect on the out-of-plane elastic modulus of graphene on SAMs through the interfacial interactions. The MD simulations clearly show that water molecules located at the FLG-SAM interfaces mediate the interaction between graphene and the SAM and are the key factor for the observed stiffness difference between graphene on hydrophobic and hydrophilic SAMs. Our approaches are able to extract, in addition to topographic information, also chemical information from buried

interfaces in 2D layered materials by unravelling the origin of mechanical subsurface-structure "fingerprints" with high lateral resolution.



Schematic showing contact resonance AFM applied to interrogate graphene on a self assembled monolayer.

COLL 511

Quantitative connections between Raman spectroscopy and scanning tunneling microscopy in chemisorption on graphite

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Heterogeneous reactions between solid substrates and solution phase reactants have seen increased interest in an effort to manipulate the properties of material surfaces and two-dimensional (2D) substrate materials. Such reactions result in covalently bound molecular species to the surface, where the surface properties become tunable based on the nature and concentration of molecular adsorbates. Control over degree of chemisorption on 2D substrates requires not only spatial characterization from local scanning probe microscopy methods (Fig.1 A&B), but also chemical characterization methods such as Raman spectroscopy to verify bond formation to the surface (Fig.1 C&D), using the D-band intensity at $\sim 1334 \text{ cm}^{-1}$. Here, we establish a quantitative link between these two characterization methods using electrochemically activated aryl diazonium chemistry (Fig.1 F). The degree of chemisorption on the graphite surface is altered by varying the concentration of species and the electrochemical activation

parameters. High-resolution characterization with scanning tunneling microscopy provides quantitative reaction characterization at the surface, while Raman spectroscopy is employed to verify the chemisorbed nature (Fig.1 E). A quantitative model linking the spatial information (average inter-defect distance) and chemical information (D-band to G-band intensity ratio) is constructed. This work provides a fundamental contribution to characterization and understanding of chemically patterned surfaces.

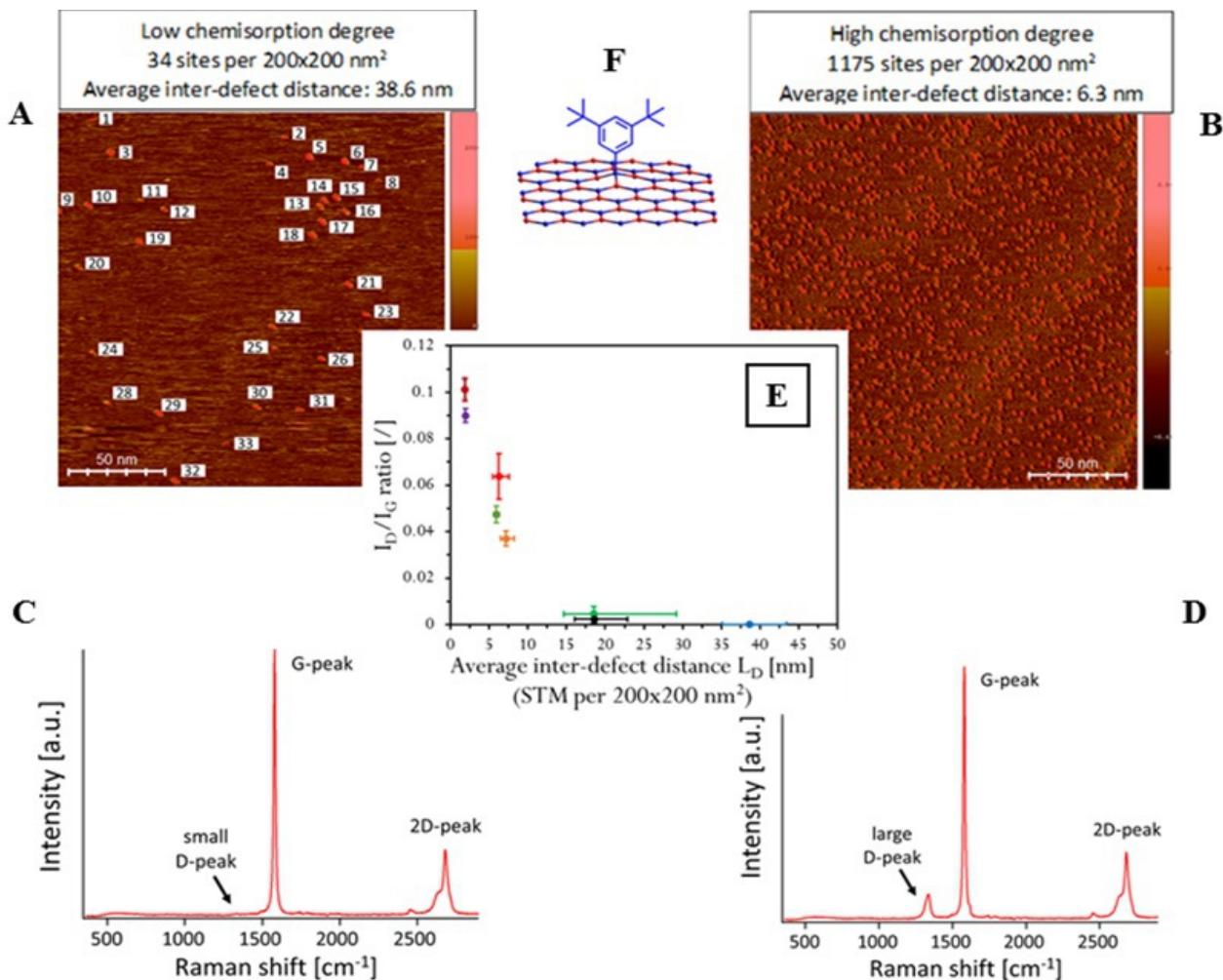


Fig.1 The analysis of varying degree of chemisorption (i.e. low (A&C) and high (B&D) degree) by STM (A&B) as well as Raman spectroscopy (C&D), resulting in a quantitative link between spatial and chemical information of diazonium chemisorption (F) at the graphite surface (E).

COLL 512

Chemisorption on graphitic substrates imaged at the single molecule level

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Heterogeneous reactions between solvated reactants and solid substrates have emerged as a promising method to tailor surface structure and composition. Naturally, the rational design and control over different reactions (diels-alder, fluorination, oxidation) with surfaces has seen considerable attention in recent years. Here, we focus on the scanning probe microscopy characterization of diazonium induced radical attack reactions for chemisorption on graphite surfaces. High-resolution scanning tunneling microscopy (STM) images alongside density functional theory (DFT) simulations support the assignment of individual chemisorbed molecules on the graphite surface. Calculated rotation barriers and experimentally determined surface alignment preferences are shown. STM topography and current image comparisons made between physisorbed and chemisorbed species at the surface indicate an elevated nature of the chemisorbed molecules. In light of this elevated vertical orientation, STM imaging artifacts including double tip effects are discussed. Broadly, this work contributes to the theme of the heterogeneous reaction product characterization at the nanoscale.

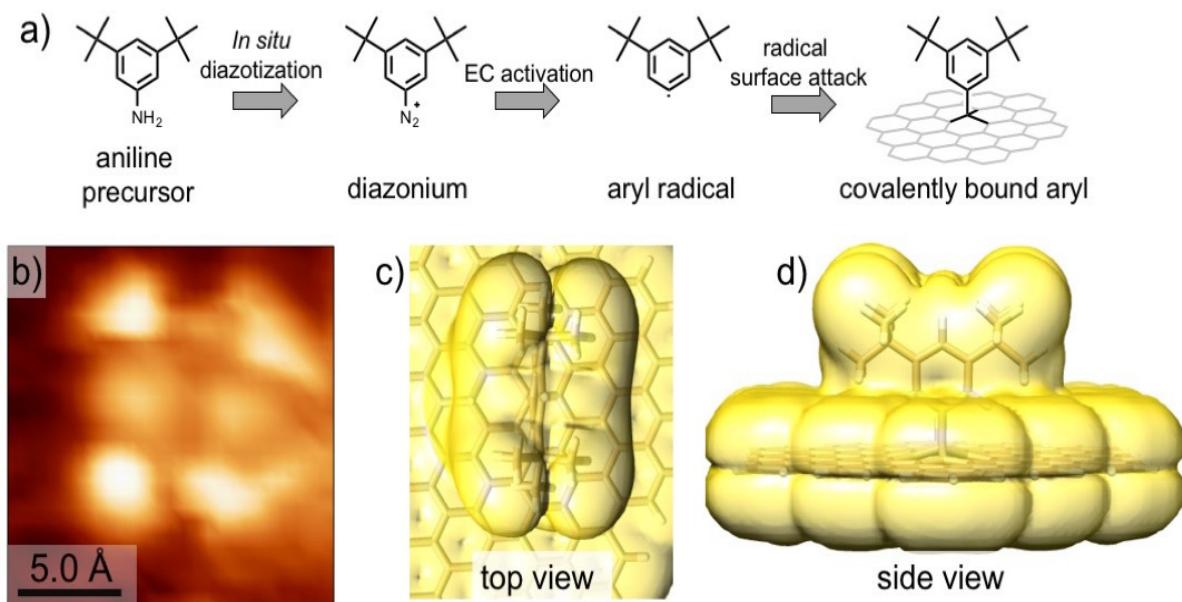


Figure 1a) Reaction scheme for diazonium radical attack reaction. **b)** High-resolution STM of 3,5-tertiarybutylphenyl chemisorbed on the graphite surface. **c)** top view and **d)** side view of a DFT simulation of 3,5-tertiarybutylphenyl chemisorbed on a small graphene sheet. (B3LYP/6-311+G(2d,p) level with the Tersoff Hamman approximation)

COLL 513

Optically transparent ultramicroelectrode for studying local electrochemical events of single Au nanoparticle using combined methods of electrochemistry and dark field scattering microscopy

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Plasmonic active metal NPs are broadly used in cleaning energy conversion and electrochemical and optical sensing of molecular recognition events. However, it is extremely challenging to resolve chemical and physical transformation at single NP level using conventional optical and electrochemical methods for resolving their local structure-function relationship. A spectroelectrochemical method with combined optical and electrochemical techniques are used in our study to resolve electrocatalytic property of single Au NPs. Combined methods of photolithography and electrodeposition are used for fabricating Au NP modified indium tin oxide ultramicroelectrode (ITO UME). Dark field scattering (DFS) microscopy and scanning electron microscopy (SEM) were used to characterize NPs on the surface of ITO UME. Dark field spectroelectrochemical study of hydrazine oxidation at planer ITO and ITO UME confirmed the formation of small bubbles on NPs surface. The formation of nitrogen bubbles on the surface of Au NPs and induced change of DFS will be presented and discussed.

COLL 514

Structural plasmonics studied using ultrafast spectroscopy beyond the diffraction limit

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Plasmonic nanoparticle transducers offer unique opportunities for using light amplification to improve optical microscopy measurements. Here, experimental outcomes in key areas critical to understanding nanoscale-structure-specific light-matter interactions are described, including structure-dependent plasmon coherence times and plasmon-mode-specific 3-D spatial localization of electromagnetic energy to nanoscale volumes. Interferometric single-particle second harmonic generation (SHG) and two-photon photoluminescence (TPPL) imaging techniques developed in our lab provide high spatial accuracy and precision along with femtosecond time resolution for examining nanoparticle assemblies. Femtosecond time-resolution is achieved by employing a sequence of phase-locked laser pulses to examine the nanostructures. These imaging methods have been employed to quantify plasmon coherence times for assemblies of nanospheres and nanorods. Determination of plasmon coherence times provides a quantitative measurement of mode-specific quality factors, which are

important for assessing the efficiency of nanostructures for using electromagnetic energy. Based on our coherence data, one-dimensional nanorods are promising building blocks of nanoparticle networks for using electromagnetic energy at the nanoscale. The effectiveness of the nanorods results from the inherent length-to-diameter aspect-ratio-dependent tunability of the longitudinal plasmon resonance (LSPR) frequency. The LSPR of high aspect ratio nanorods can be energetically decoupled from interband relaxation channels, which are a major source plasmon decoherence, thus explaining the experimental results. Indeed, preliminary interferometric nonlinear optical studies of nanorod trimers indicate the plasmon coherence time can be increased by approximately 100% for nanoparticle networks of specific symmetries. Translation of these coherence time increases to improved 3-D spatial accuracy will be demonstrated.

COLL 515

Directional charge-separation in organic semiconductor nanowire crystals

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This talk will focus on optical probes of directional interactions in ordered assemblies of organic semiconductors. Using tools of single-molecule spectroscopy, our approach is based on isolated crystalline nanowires where the nanowire itself plays a material role analogous to a single molecule, and optical polarization (in either absorption or emission) can be referenced to specific crystallographic directions. Of particular interest are timescales for mixing transverse and longitudinal polarizations which encode information on the (directional) interaction of different intermolecular coupling modes in the assembly. We will highlight recent work on isolated crystalline nanowires of an interesting small-molecule semiconductor called 7,8,15,16-tetraazaterrylene (TAT, for short) which display several unusual and exciting properties with applications to organic opto-electronics.

COLL 516

Long-range catalytic communications within and between single nanocatalysts

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Enzymes often show catalytic allostery in which reactions occurring at different sites communicate over a distance up to a few nanometers. Here we report that phenomenologically similar, but mechanistically distinct, effects also exist in nanoparticle catalysts, which are non-biological catalysts. We achieve this by analyzing the correlation between temporally subsequent reactions occurring at different locations *within* single metal nanocatalysts, resolved spatiotemporally using single-molecule fluorescence localization microscopy. This intraparticle catalytic communication, a first-

of-its-kind discovery, occurs in multiple metal based nanocatalysts and in multiple distinct catalytic reactions, and the communication reaches over hundreds of nanometers with a temporal memory of $\sim 10^1$ to 10^2 seconds, leading to positive cooperativity among surface sites *within* a single nanocatalyst. We further observe a similar phenomenon *between* individual nanocatalysts with communication distances of many microns, but this interparticle communication is limited to certain reactions. Using a range of experimental manipulations, we show that the interparticle catalytic communication, if occurring, operates via a molecular diffusion mechanism. In contrast, the intraparticle catalytic communication operates via a distinct mechanism, likely through surface hole hopping. This intraparticle catalytic communication, phenomenologically similar to enzyme cooperativity, represents a new conceptual paradigm in understanding nanocatalysts.

COLL 517

Observation of local redox events at individual plasmonic nanoparticles using spectroelectrochemistry methods

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Plasmonic nanoparticles such as Au nanoparticles (NPs) exhibit interesting light scattering and local field enhancement capability. These photophysical properties allow us to study local redox activities of single plasmonic nanoparticles. Dark field scattering, photoluminescence, and electrogenerated chemiluminescence (ECL) are used to probe local redox reactions such as catalyzed oxidation of tripropylamine (TrPA), hydrazine oxidation for nanobubble generation, and metal nanoparticle formation. Our study shows that these optical responses at individual plasmonic NPs are strongly dependent on particle size, and are affected by the local chemical and charge transfer environment of the NPs. These optical detection schemes can allow one to study the local redox activities of single nanoparticles with improved spatial and spectral resolution. Particularly, ECL at single Au NPs shows slight temporal variations in intensity attributed to the oxidation and reconstruction of small clusters on the Au surface during ECL generation. Quantitative agreement between calculations and experiment concerning the effect of particle size and electrode potential on spatial and transient ECL profiles will be presented.

COLL 518

Photophysical investigation of electron ejection efficiencies of novel organic near-IR absorbing dyes into TiO₂ based semiconductor surfaces for dye-sensitized solar cell applications

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States (2) Chemistry and Biochemistry, University of Mississippi, University, Mississippi, United States

Organic dyes capable of significant absorption in the near-IR (NIR) have become a promising area of research as a result of their application as dye sensitizers in solar cells. Major factors limiting the ability of dye-sensitized solar cells (DSSCs) from converting solar energy into usable electricity are the inability of these dyes to absorb low energy photons in the NIR and IR window and poor electron injection efficiencies. Unfortunately, these two problems are intimately related and improving NIR absorbance often comes with a decreased injection efficiency. Since the NIR and IR window makes up a significant portion of the photons emitted by the sun, shifting and broadening the absorption of these dyes to lower energy is seen as necessary before DSSCs can become a commercially viable source of alternative energy. Here, the photophysical properties and injection efficiencies of a series of novel NIR absorbing dyes are investigated on different TiO₂ based substrates and at the single molecule level.

COLL 519

Mechanistic insights into multiple blinking states in small core-shell and core-multishell quantum dots

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Adding shells to core quantum dots (QDs) is known to affect the blinking behavior in complex ways. We recently reported that varying the inner and outer shell materials and thicknesses of core-multishell QDs significantly affects both the quantum yield and blinking, although they were usually not correlated with each other (Bajwa et al. ChemPhysChem (2016) 17, 731-740; Omogo et al. ACSNano (2016) 10, 4072-4082). Although the majority of papers describe QD blinking in terms of binary “on” and “off” behavior, some recent papers have identified the presence of at least one more state – the so-called “grey” state. This state has been proposed to result from trions, but only some QD blinking reports shows its presence while others do not, and it is not yet clear what factors affect it. We have performed a systematic study of the grey and on state populations and dynamics as a function of controlling the shell material and thickness in order to better understand the underlying principles behind the multiple states and to postulate a mechanistic model describing our results. We hope that developing such a model will help provide a framework in which blinking can be more easily and accurately controlled for spectroscopy and imaging applications, especially while maintaining as small a QD size as possible.

COLL 520

Organometal Halide (OMH) Perovskite Quantum Dots (PQDs): Effective surface passivation using peptides

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Organometal halide (OMH) perovskites have shown great promise for various applications including photovoltaic solar cells due to their unique optical and electronic properties. However, device and material degradations caused by factors such as light, oxygen, water, temperature, and oxide layers used in devices present a major challenge for practical applications. We use OMH perovskite quantum dots (PQDs) as a good model system to understand the origin of the materials instability and have developed strategies to enhance stability using surface passivation with special molecular ligands to reduce surface defects or trap states. In particular, we have found that bifunctional peptides can serve as bidentate ligands for effective surface passivation in a manner that is simple to implement. This study demonstrates that surface chemistry approaches are highly promising for stabilizing OMH perovskites.

COLL 521

Non-additive interactions at chemically and structurally complex interfaces

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The interactions between charged colloids immersed within aqueous electrolyte solutions have been widely explored. The concept of an electrical double layer is often used to describe the interactions. Non-polar domains of colloids are typically classified as “hydrophobic” and assumed to promote self-association within aqueous solutions. This presentation will discuss experimental measurements of intermolecular interactions mediated by heterogeneous interfaces. Measurements performed with two experimental systems will be described. First, measurements of forces using single-molecule methods will be used to demonstrate that whether or not a non-polar domain mediates a “hydrophobic interaction” depends strongly on the proximity of immobilized charges. The net interactions mediated by these heterogeneous interfaces do not reflect additive contributions of forces measured at non-polar or charged interfaces. This non-additivity will be shown to be evident in the self-assembly of amphiphilic species in solution. Second, measurements will be presented that suggest that the strength of hydrophobic interactions depend strongly on the dynamics and order of the molecules comprising non-polar interfaces. Overall, these observations identify a number of unresolved issues related to intermolecular interactions mediated by water.

COLL 522

Programmable materials from DNA bonds and nanoparticle atoms

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An ideal material synthesis strategy would allow one to systematically tune the strength, specificity, and symmetry of interactions between material building blocks without altering the intrinsic properties of the building blocks. Although it is exceedingly difficult to control the complex interactions between atomic and molecular species in such a manner, interactions between nanoscale components can be encoded, independent of the nanoparticle structure and composition, through the ligands attached to their surface. Our group, in particular, has shown that nucleic acids can be used as highly programmable surface ligands to control the spacing and symmetry of nanoparticle building blocks in structurally sophisticated materials. These nucleic acids function as programmable “bonds” between nanoparticle “atoms” and can be analogized to a nanoscale genetic code for assembling materials. The sequence and length tunability of nucleic acid bonds has allowed us to define a powerful set of design rules for the construction of nanoparticle superlattices with more than 30 unique lattice symmetries, over one order of magnitude of interparticle distances, tunable defect structures, and several well-defined crystal habits. Materials can even be programmed to dynamically respond to external biomolecular and chemical stimuli, allowing structure and properties to be tailored on demand. This control allows for the predictable crystallization into, and reversible transformation between, thermodynamic states with different crystal symmetries, particle stoichiometries, thermal stabilities, and interparticle spacings. Notably, this unique genetic approach to materials design affords functional nanoparticle architectures that can be used to catalyze chemical reactions, manipulate light-matter interactions, investigate energy transfer between nanostructures, and improve our fundamental understanding of crystallization processes.

COLL 523

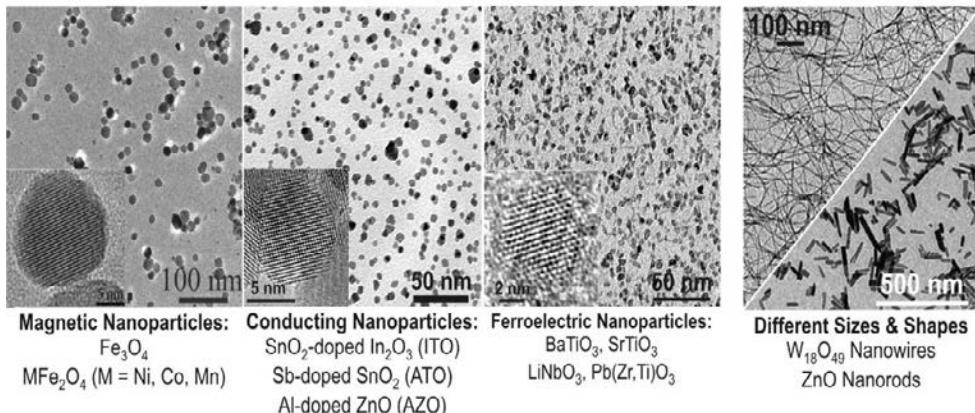
Nanoparticle assembly: Bridging size scales and dimensionalities

Markus Niederberger, *markus.niederberger@mat.ethz.ch. ETH Zurich, Zurich, Switzerland*

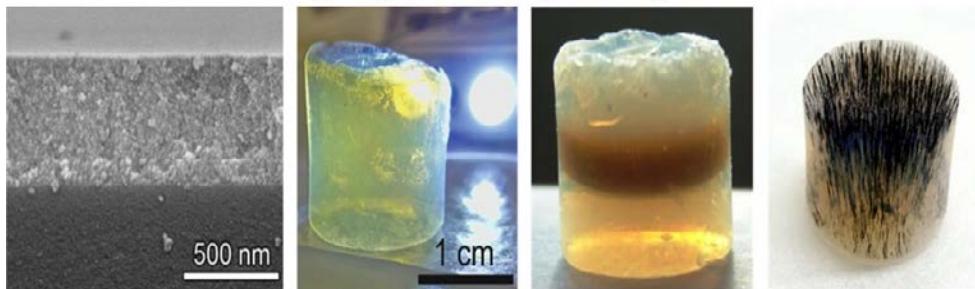
Nanoparticles offer a broad range of size- and shape-dependent properties and are thus the ideal building blocks for the bottom-up fabrication of functional materials. However, to produce macroscopically sized materials, the nanoparticles have to be arranged over several orders of length scales.

The talk will cover the synthesis of various types of nanoparticles, mainly metal oxides, with different sizes and shapes by nonaqueous sol-gel chemistry (Figure, upper part). Different strategies will be presented, how nanoparticles, nanowires or nanosheets can be assembled and processed into 2- and 3-dimensional geometries, including films and aerogels (Figure, lower part). A major effort is directed towards achieving monolithic bodies with macroscopic size, however without losing the nanoscale properties of the initial building blocks. Co-assembly of different types of nanoparticles enables subtle tuning of the properties of the final materials, optimizing them for specific applications in gas sensing, photocatalysis or in energy storage.

Well-defined nanoparticles as building blocks



Macroscopic (multicomponent) materials



COLL 524

Making all the puzzle pieces fit: Shape directed assembly of anisotropic nanocrystals into multi-component superlattices

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This presentation will focus on the shape-controlled synthesis and assembly of anisotropic nanoscale building blocks. Semiconductor nanocrystals, metal nanoparticles and nanorods, and rare earth doped lanthanide nanophosphor plates create a library of shape-controlled nanoparticles to explore fundamental assembly processes. Shape directed assembly at the nanoscale allows both single component systems and collections of complementary shapes to be explored. Experimental procedures for the synthesis and structural characterization of monodisperse nanospheres, nanorods and

nanoplates and assemblies of these will be shared. Specific examples of binary self-assembly of two and three anisotropic nanoparticle building blocks mediated by shape complementarity will be presented as a case studies. We will focus on liquid interfacial assembly techniques that allow the formation of self-assembled single component as well as the formation of binary superlattices from two anisotropic nanocrystals over a micrometer length scale and discuss progress on templated assembly of smaller discrete structures. Recent efforts to explore periodic and aperiodic structures will also be shared.

COLL 525

Synthetic methodology for colloidal synthesis of inorganic nanomaterials: Limitations and opportunities

*Vishwas Srivastava, Igor Fedin, Hao Zhang, Dmitri V. Talapin,
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Colloidal chemistry has revolutionized the synthesis of inorganic nanomaterials. The field has evolved tremendously, both in the fundamental understanding, and in the ability to provide a toolset for the preparation of functional materials with precisely engineered structure, size and shape. However, the current methodology has several general limitations.

The lack of atomic precision in the synthesis of functional nanomaterials restricts the ability to harness all the power of this broad and diverse class of materials. Real nanomaterials always vary in size to a certain extent. This variation introduces inhomogeneous broadening of the absorption and emission spectra and reduces charge carrier mobilities in nanocrystal films. The polydispersity originates from a weak size dependence of the free energy related to the addition or removal of individual atoms to/from a nanoscale object. Currently size distribution can only be controlled by kinetic factors and it would be difficult to further improve the homogeneity of kinetically controlled reaction products. We discuss a paradigm-shifting approach toward nanomaterials with minimal, ideally no, size distribution. The goal is to establish means to thermodynamically control nanomaterials synthesis using a sequence of two complementary *self-limiting* surface reactions. This concept is inspired by the success of gas-phase atomic layer deposition (ALD) widely used in microelectronics and other fields. Our studies show that the ALD concept can be implemented in solution and, when applied to colloidal nanomaterials, enables layer-by-layer growth of crystalline lattices with true atomic precision.

The other general limitation of traditional colloidal chemistry is related to thermal stability of organic solvents at high temperatures required for some hard-to-crystallize materials. Very few organic substances remain liquid above 400°C, and solvent or ligands decomposition becomes a serious problem at even higher temperatures. The use of inorganic salts as solvents eliminates this issue and brings new opportunities. As an example, colloidal synthesis of GaAs nanocrystals was unsuccessful for over 20 years. We found that GaAs NCs synthesized in organic solvents generally have a high

concentration of vacancies and antisite defects. Annealing of the colloid in a molten salt at 500°C eliminated these structural defects without NC sintering. We envision multiple exciting opportunities for colloidal chemistry in molten salts.

COLL 526

Building materials from colloidal nanoparticles

Ludovico Cademartiri, *lcademar@iastate.edu. Iowa State University, Ames, Iowa, United States*

We reported an approach to produce nanostructured polycrystals in the form of films by first crystallizing the “grains” first as ligand-capped nanocrystals synthesized in solution as colloids, then depositing them by self-assembly, and finally removing the ligands by plasma processing (i.e., “nanocrystal plasma polymerization”, NPP). Since this approach bypasses stochastic bulk nucleation, it can form polycrystals with uniform, nanoscale grain sizes, but the evolution of the structure, composition, and cohesiveness of the films during the removal of the ligands is unclear. For example, it is not known whether trace amounts of carbon remain behind between the particles, whether bonds are formed between the particles, and how the plasma successfully removes organics from the inside of these films.

We will describe the structural, chemical, and mechanical evolution of films of colloidal nanoparticles upon exposure to an O₂ plasma (500 mTorr, 7 W, 6 h to 168 h of exposure). The particles in the arrays are initially separated by organic ligands (trioctyphosphine oxide, TOPO) that bind to the particle’s surface through the phosphine oxide group. The plasma removes the alkyl tails of the ligands over the course of several hours (carbon concentration is 1.3 ± 0.5 at. % after 168 hrs). Before finally settling into an all-inorganic polycrystal, the arrays go through an intermediate, highly porous state (~0.5 void fraction) where the particles are joined by necks of ligand molecules. This highly porous state obtained after ligand removal result in high surface area materials with 100% crystallinity, good mechanical properties, and bare inorganic surfaces that could be very attractive for any application involving interface processes (e.g., energy storage, photovoltaics, catalysis) and the study of these processes as a function of material structure.

Cracking during ligand removal by plasma processing (down to 0.6 at%) is entirely controlled by the structure of CNAs: while close-packed ordered CNAs cracked after self-assembly or ligand removal, disordered CNAs up to 440-nm-thick remained crack free after ligand removal and sintering. The process is demonstrated with particles of different composition, ligands, size, and shape, as well as with binary polycrystals. Films produced by this approach have conductivities comparable to those of bulk crystals over more than 1 cm (1.370 S/cm for PbS films).

COLL 527

Pattern recognition of membrane images to deduce cellular signaling status

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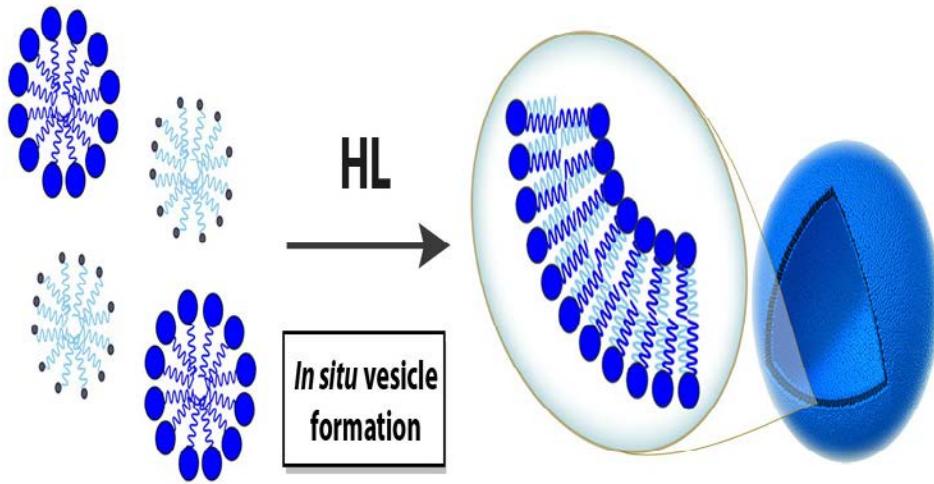
The morphology and membrane features are directly correlated to the biological status and function of a cell, such as activation, spreading, motility, malignancy, and death. Modern bioimaging technology enables visualizing cellular membranes with high spatial resolution in real time. These high resolution images have been frequently used empirically to identify characteristic features and deduce the cellular behavior. This presentation reports our initial attempt to deduce cellular signaling processes by quantifying correlated cellular morphology and membrane - features of cells from high-resolution images acquired using scanning electron microscopy and atomic force microscopy. Using a multi-stage pattern recognition system on images of immune cells, particularly mast cells as an example, we are able to determine the cells discrete activation status as well as the degree of activation (or allergy). The methodologies presented here shall be of generic importance for harnessing quantitative information from high resolution images of cellular membrane and revealing biological status and function of individual cells.

COLL 528

Spontaneous phospholipid membrane formation by histidine ligation

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A major challenge for the construction of artificial lipid membranes is the development of simple and robust methods for mimicking natural phospholipid membrane generation. Here we describe a nonenzymatic and chemoselective approach that relies on histidine ligation to form phospholipids de novo from water-soluble amphiphilic precursors. The resulting phospholipids can spontaneously self-assemble into micron-sized vesicles and encapsulate small charged molecules and biomacromolecules. Such approach can be useful in bottom up construction of an artificial cell.



COLL 529

Hydrogel-assisted membrane protein reconstitution for studying GPCR dependence on lipid composition

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The lipid composition of cell plasma membranes varies radically with tissue type and can be altered in an individual by disease, diet, and pharmaceuticals. Variation in lipid composition represents a potentially important physiological control over membrane protein function, and modulating lipid composition provides a potential route for treating diseases related to the function of membrane proteins. We have developed a hydrogel-based system for reconstituting G protein-coupled receptors (GPCRs) in the membranes of giant unilamellar lipid vesicles (GUVs) of controlled composition. Along with the receptor, the GUVs include downstream reporter systems that provide a fluorescent signal in response to receptor activation. Varying the composition of the GUVs and measuring the activity of the receptor upon introduction of agonist allows for the lipid dependence of the protein to be probed.

We have investigated the lipid dependence of both the human serotonin 5-HT_{1A} receptor (5-HT_{1A}R) and the adenosine 2A receptor (A_{2A}R). Generally, both proteins are more active in membrane compositions with higher degrees of lipid order. This dependence is apparent regardless of whether membrane order is modulated by varying cholesterol concentration or by introducing non-human sterols, indicating that it is a function of bulk membrane properties rather than specific protein-cholesterol interactions. 5-HT_{1A}R also shows an increase in activity in the presence of phosphatidylethanolamine (PE) lipids, indicating that increasing membrane curvature stress favors active receptor conformations. Finally, in phase-separating liquid-ordered/liquid-disordered membranes, the phase segregation behavior of A_{2A}R depends on whether or not it is bound to a ligand. Ligand-bound A_{2A}R tends to partition to the

liquid ordered phase while unbound A_{2A}R tends to partition to the liquid disordered phase.

COLL 530

Dimerization of a GPCR in membranes investigated by SANS

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G protein-coupled membrane receptors (GPCR) are key molecules in signal transduction pathways that transmit signals of a variety of ligands such as hormones and neurotransmitters to the cell interior. They are also a major target of pharmacological intervention to aid recovery from disease. Receptor function is strongly modulated by homo-oligomerization of GPCR, hetero-oligomerization between different GPCR, as well as by interaction of GPCR with other membrane-associated proteins. The protonated GPCR bovine rhodopsin was reconstituted into proteoliposomes composed of perdeuterated lipids extracted from *E. coli* bacteria grown on fully deuterated medium. It was observed that intensity of small-angle neutron scattering (SANS) from entire proteoliposomes in 98% D₂O buffer, measured at angles q<0.008 Å⁻¹ reached a minimum at a protein/deuterated lipid molar ratio near 1/500, while yielding maximal scattering contrast for incorporated opsin (bleached rhodopsin) over the wider angular range of 0.008 Å⁻¹<q<0.3 Å⁻¹. A Guinier analysis of the SANS spectrum gave a radius of gyration of opsin in proteoliposomes of 30.8±2.0 Å and a molecular weight of 86.5±0.9 kDa, both consistent with formation of opsin dimers. Incoherent scattering of neutrons was very low due to overall low proton content of samples. This enabled determination of a structure factor of rhodopsin dimers at good resolution. The dimer shape fits a parallelepiped with the dimensions 108.1±2.6 Å by 25.6±1.6 Å by 61.8±1.8 Å. Reconstitution of membrane proteins into liposomes that match neutron scattering length density of D₂O makes SANS a powerful method for studying oligomerization.

COLL 531

Toward a quantitative continuum model for membrane shape fluctuations

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A Helfrich-like model for membrane energetics will be discussed. The model explicitly includes area compressibility and density fluctuations within the membrane and, when solved exactly numerically, yields quantitative agreement with particle-based toy models for thermal membrane behavior. This provides both some insight into longstanding

puzzles regarding the interpretaion of membrane tension and also some new questions that remain to be answered.

COLL 532

Interfacing proteins with *de novo* membrane formation

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We also have a strong interest in applying covalent coupling reactions to the formation and modification of phospholipid membranes. We have utilized chemoselective reactions, such as copper-catalyzed triazole formation or the native chemical ligation, to drive the *de novo* synthesis of phospholipid membranes. To interface synthetic membranes proteins, we have recently developed protein reactive membrane anchors utilizing SNAP-tags. Light driven spatiotemporal control over proteoliposome formation is possible using photocaged membrane anchors. We have also shown that transmembrane proteins can be spontaneously incorporated during *de novo* membrane formation. Recent studies have extended our work to GPCRs. Continued development of selective bioconjugation reactions will facilitate the interfacing of synthetic molecules with biological systems for new capabilities.

COLL 533

Hybrid model membrane combining micropatterned lipid bilayer and hydrophilic polymer brush

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Substrate-supported planar lipid bilayers (SPBs) are being utilized as a versatile model system of the biological membrane. However, functional assays of membrane proteins in SPB are limited due to the proximity between the solid support and the membrane. For controlling the substrate-membrane distance, we developed a hybrid membrane of SPB and hydrophilic polymer brush. A micropatterned SPB comprising polymerized bilayer and natural (fluid) lipid bilayer was lithographically generated. Hydrophilic polymer brushes of poly-2-methacryloyloxyethyl phosphorylcholine (poly(MPC)) was formed on the surface of the polymeric bilayer by *in-situ* atom transfer radical polymerization (ATRP). The polymeric bilayer acted as a stable scaffold for both the fluid bilayer and the polymer brush. The ATRP reaction could be conducted in the aqueous solution, in the presence of embedded fluid bilayers. The polymer brush terminals could be functionalized by forming a block copolymer of poly(MPC) and poly-

(2-aminoethyl methacrylate) (poly(AMA)) through successive ATRP reactions. A microbial rhodopsin from *Haloquadratum walsbyi* was reconstituted into the fluid bilayer to assess the effects of polymer brushes on the model membrane and incorporated proteins. The combination of micropatterned bilayer and polymer brush is an important step toward a model membrane that can mimic the two-dimensional and three-dimensional structures of the biological membrane, enabling to incorporate and assay membrane proteins in a truly biomimetic environment.

COLL 534

pH-dependent behavior of lipid bilayer coatings on mesoporous silica nanoparticles

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Nanoparticle drug delivery vehicles require a coating that is robust, biocompatible, and facilitates long circulation times in the biofluid but must efficiently uncloak to release the drug cargo upon reaching its target site. A lipid bilayer coated mesoporous silica nanoparticle, called the protocell, has been shown to release its contents of small molecule cargo upon lowering to acidic pH (~ 5) thus providing a route for cargo delivery via the endosomal pathway. The mechanism of cargo release, however, is currently unknown. We recently found that lipid bilayers on glass reorganize their structure upon lowering of solution pH to result in the formation of large pores. The pores form rapidly (within seconds) spanning out to several microns in diameter with irregular shape. Pore formation was further found to be general for PC lipids in either the fluid phase (e.g., POPC, DOPC) or the gel phase (e.g., DPPC), although the latter forms smaller pores (sub-micron). Through molecular models we find that a bilayer membrane under tension forms pores that are stabilized in the presence of lipids with positive spontaneous curvature. Using a novel wedge-shaped lipid prepared in our lab we were able to show the formation of large stable pores, thus verifying the latter portion of the modeling prediction. The generation of membrane tension through pH change of a supported lipid bilayer on silica as the driving force for membrane pore formation will be discussed.

COLL 535

Investigating electrostatic interactions between PIP₂ and the EphA2 receptor tyrosine kinase

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Receptor tyrosine kinases (RTKs) regulate many cellular processes and also play a critical role in the progression of cancer. RTK activation occurs through conformational changes of the receptor, which are normally induced by a ligand binding event. There is evidence from computer simulations that a cationic patch on the intracellular domain of RTKs interacts with anionic lipids in the plasma membrane (PM). Through such interactions, the plasma membrane could play an active role in RTK conformation and regulation. Experimental evidence for these interactions is difficult to achieve due to the complex structure and dynamics of the plasma membrane, but resolving the role of plasma membrane lipids in regulating RTK function could provide a novel route to developing more effective therapeutic interventions. Here we report on an experimental approach to quantify lipid-protein binding between the intracellular domain of the RTK EphA2 (EphA2ICD) and phosphatidylinositol (4,5) bisphosphate (PIP₂) lipids using pulsed interleaved excitation fluorescence cross-correlation spectroscopy (PIE-FCCS). By measuring the diffusion of purified EphA2ICD on asymmetric PIP₂-containing supported lipid bilayers, we observed collective diffusion of EphA2ICD and PIP₂ lipids indicating that they form a stable complex. We have also investigated EphA2ICD organization in live cells and are currently working to understand which regions of the intracellular domain are critical to these interactions. Our direct probe of electrostatic interactions between EphA2ICD and PIP₂ show that the PM could be directly involved in the regulation of this receptor and potentially other RTKs that share a similar domain architecture.

COLL 536

Designed nanoparticles architectures by self-assembly

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We use a high degree of addressability of nucleic acids and their structural plasticity to direct the formation of structures from nanoscale inorganic components. We have investigated the major leading parameters determining a structure formation in such systems and explores new concepts for creating targeted nano-architectures. The principles and practical approaches developed by our group allow for assembly of well-defined three-dimensional superlattices, two-dimensional membranes and finite-sized clusters from the multiple types of the nano-components. Our recent progress on the development of by-design assembly strategies will be illustrated by nanoparticle lattices with “engineered” crystallographic symmetries, and clusters with prescribed architectures. Finally, I will discuss approaches for the dynamical control of assemblies, which allow for reconfiguration and selective triggering of system transformations. Some examples of using this assembly approach for creating optically active materials will be provided.

COLL 537

Exploring plasmon-exciton coupling at the surface of TiO₂ nanorods

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Plasmon-exciton coupling in nanostructured materials has been a well-studied approach for generating unique optical properties. A Fano resonance is one type of optical phenomenon that may be generated by plasmon-exciton coupling. Our group recently demonstrated a strong Fano resonance in colloidal suspensions containing silver nanoplatelets coated with a thin layer of J-aggregate dye. As a follow on to this work, we recently initiated efforts to further explore the impact of plasmon-exciton coupling on the optical, catalytic, and charge injection properties of titanium dioxide. As a model nanostructure for studying this impact, we endeavored to fabricate a nanocomposite that contained titanium dioxide nanorods, silver nanoplatelets, and a J-aggregate dye. Hence, in this presentation we detail our efforts to fabricate titanium dioxide nanorods that are decorated with silver nanoplatelets and coated with a J-aggregate dye. Our approach for fabricating titanium dioxide nanorods is first described. Next, we describe a novel technique for growing silver nanoplatelets on the surface of the rods, followed by the electrostatic adsorption of a J-aggregate dye on the surface of the TiO₂/Ag nanocomposite. In terms of our attempts to elucidate the impact of plasmon-exciton coupling on the transfer of charge from the J-aggregate dye to the titanium dioxide, we detail results obtained from transient absorption and fluorescence measurements. Finally, we describe our initial efforts to characterize the catalytic behavior of the nanocomposite via the degradation of methylene blue, industrial toxins, and chemical agent simulants.

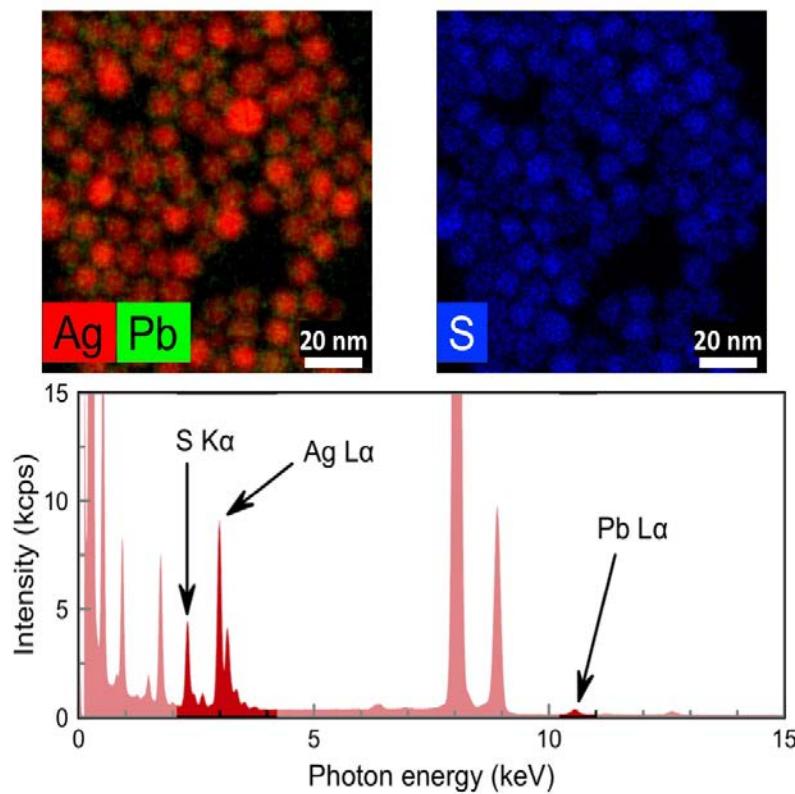
COLL 538

Room temperature, scalable cation exchange in PbS and CdSe quantum dots using a silver(I) complex

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Cation exchange represents a promising avenue to colloidal nanomaterials with previously unavailable combinations of size, shape, and composition. The method has so far been restricted both in scope and in scale due to limitations in reactivity, ion

mobility, and co-solubility of the nanoparticles and exchange reagents employed. In this presentation, we describe a cation exchange reagent permits rapid and highly efficient, room temperature exchange using both cadmium and lead chalcogenide quantum dots as starting materials. The reagent is based on a silver(I) complex that is prepared in situ and is soluble in toluene at concentrations up to 0.5 M. The reagent is air-stable and photostable for at least weeks on the shelf under fluorescent lighting. Optical spectra, elemental analysis, and TEM images provide evidence for rapid, room-temperature cation exchange using this reagent with CdSe and PbS quantum dots. Sizes of the resulting Ag₂S and Ag₂Se quantum dots are defined by the initial PbS or CdSe quantum dots. Partial exchanges are being explored as a path to mixed-metal species, with particular interest aimed at the spatial distribution of cations in these products. Finally, these silver-containing quantum dots are being employed in successive cation exchange reactions to achieve compositions not directly attainable from the original PbS and CdSe quantum dots at room temperature.



COLL 539

Controlled assembly of metallic nanoaggregates and their use in understanding cell uptake of nanoparticles

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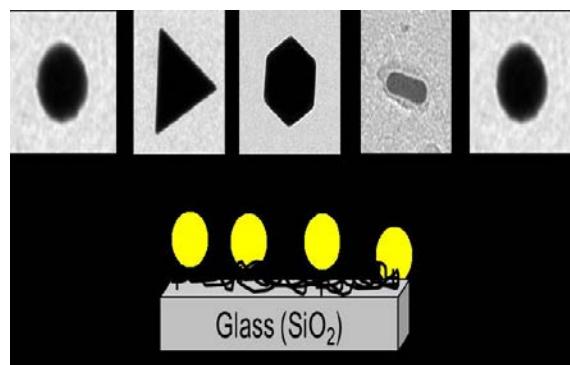
Controlling nanoparticle aggregation is an area of intense investigation. To date, many strategies make use of sophisticated linkers, such as DNA or long polymers. Here we demonstrate the preparation of gold nanoparticle aggregates using simple small molecule cross linkers. The aggregates can be prepared from a range of starting particle sizes and are formed with remarkably low polydispersity. For any given starting building block particle size, the resulting nanoaggregate size can be tuned. The nanoaggregates are readily surface functionalized. These nanoaggregates have unusual plasmonic properties and remarkably low cell uptake.

COLL 540

Synthesis and assembly of gold nanoparticles/polymers: Spheres, prisms, octahedra, and rods...oh my!

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Gold nanoparticles can be used in a variety of applications. To create stable and portable samples for these applications, multiple layers of polyelectrolytes and gold nanoparticles were assembled on glass substrates by electrostatic layer-by-layer methods. Four polymers (poly(diallyldimethylammonium chloride), polyvinylpyrrolidone, polyethyleneimine, and poly(sodium 4-styrene sulfonate)) with positive, negative, and neutral charge and four different size and shape gold nanoparticle (spherical, prismatic, octahedra, and rods) were used. Each polyelectrolyte was used to assemble LBLs with each gold nanoparticle shape. Gold nanoparticles and assembled layers were characterized via dynamic light scattering, UV-vis spectroscopy, transmission and scanning electron microscopy, and atomic force microscopy. Binding and sensing applications were detected by measuring the localized surface plasmon resonance of the GNPs.



COLL 541

Transforming layered to nonlayered two-dimensional materials: Cation exchange of SnS₂ to Cu₂SnS₃

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The transformation of two-dimensional (2D) layered SnS₂ to nonlayered Cu₂SnS₃ via cation exchange reaction was demonstrated. Cu₂SnS₃ nanosheets (NSs) maintain the overall morphology of their parents, few-layer SnS₂ templates. In specific, Cu₂SnS₃ NSs possess microscale size and have controlled thicknesses by varying the number of SnS₂ layers. Thus, existing layered materials can serve as templates for difficult-to-synthesize nonlayered 2D compounds using cation exchange, which provides a bridge between families of layered and nonlayered materials. New 2D systems are therefore accessible, which opens the door to future explorations of nanostructure optical and electrical properties.

COLL 542

DNA-assembled chain-like nanoparticle architectures with tailorable organizations

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DNA nanostructures have been widely used as templates and guiding agents to precisely control the position of nanoparticles and organize them into chain-like one-dimensional (1D) structures. The nanoparticle chain-like structures can facilitate the control over energy transfer, optical responses and they are considered for building magnetic and electrical materials. These functions highly depend on the structure, dimension and fidelity of the assembled chain organization. One of the challenges in building such 1D structures is devising methods for creating hetero-structures and error-forgiving assembly schemes. To address the challenge we developed a general method of assembling diverse nanoparticle linear architectures with internal organizations based on a simple DNA origami template. The resulting quasi-1D structure is composed of multilayered nanoparticle clusters. Adjacent layers of clusters are linked through the nanoparticle-DNA template hybridization. By rationally controlling the composition, size, number, and position of nanoparticles in each layer, a variety of nanoparticle linear structures can be assembled. The relative orientation of adjacent layers can be controlled by the position and sequence of anchoring strands. We demonstrate the utility of such structures for probing plasmonic effects on low-dimensional nanomaterials.

COLL 543

Fabrication and application of inorganic nanoparticle superstructures

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Fabrication of inorganic nanoparticle superstructures is one of the most important ways to realize the practical applications of nanomaterials in many fields, e.g., photonics, electronics and sensors. In this talk, I will introduce the recent progress in our group on this research topic, which include: (1) Fabrication of large-scale and hierarchy superstructures via manipulation of the physical interactions between inorganic nanoparticle building blocks; (2) Preparation of dynamic and reversible superstructures by design of Janus-type inorganic nanoparticles; and (3) Application of inorganic nanoparticle superstructures in the field of energy and catalysis. At the end of the talk, I will briefly discuss current challenge in our work.

COLL 544

Synchrotron-based x-ray techniques for in-situ superlattice discovery and processing of nanocrystal assembles

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Nanocrystals behave like atoms and have ability to spontaneously self-assemble into periodically ordered structures, in which these nanocrystal-packed solids are called as “supercrystals”. The supercrystals represent completely the new category of condensed matters, enabling manifestations of a variety of new phenomena and technological applications. To facilitate the discovery of assembled superlattice diagram and associated property, we developed a series of synchrotron-based techniques, which synchronize SAXS and WAXS as well as various spectroscopy together, to in-situ monitor the assembly process and property manifestation as well as structural reconstruction of nanocrystal superlattices with subsequent materials processing under various environments. I will introduce synchrotron-based X-ray techniques developed at CHESS, and highlight several scientific cases of nanocrystal assembles, which can stimulate the nanocrystal assemble community to take advantage of synchrotron x-rays to perform their breakthrough research towards fast discovery and controlled design of novel materials.

COLL 545

Functionalizing surfaces with polymeric layers

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Polymeric layers can bestow a number of useful properties to surfaces, including lubricity, resistance to protein adsorption, and hydrophilicity. They can be attached physically, of course, by means of spin-coating, but far more interestingly, they can be covalently grafted in the form of brushes and crosslinked systems, such as gels. Beyond this, the systems can be stratified, to incorporate functionality at fixed intervals within a 3-D structure; patterned, so as to allow spatial discrimination between different regions for cell studies, for example; or produced as gradients of specific properties such as molecular weight or grafting density, for research purposes. While the common laboratory approaches for fabricating such systems are challenging to implement on a large, industrial scale, recent alternative methods show promise for incorporating such surface-bound polymeric systems in a host of useful applications.

COLL 546

Alkyl-cyclens as effective sulfur- and phosphorus-free additives in engine oils for improved boundary lubrication

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Demands for improved fuel efficiency in transportation drive the development of more efficient engine lubricants. The present research explores a novel type of thermally stable, heterocyclic lubricant additive for engine oils. We have developed a series of sulfur- and phosphorus-free oil-soluble alkyl-cyclen-based molecules. Under boundary lubrication conditions, these additives reduce friction by up to 70 % and wear by 95 % from room temperature to 200°C. Molecular dynamics simulations indicate that these cyclen-based molecules adsorb strongly onto oxide surfaces (representative of practical steel surfaces), in an orientation that allows tethered hydrocarbon chains to protect asperities from direct contact in the boundary lubrication regime. The success of this approach suggests opportunities for the design of lubricant additives with functionalities that operate through the entire lubrication regime.

COLL 547

When surfaces get rough: Studies of the assembly and frictional properties of SAMs and graphene SAM-composites on surfaces with nanoscale roughness

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The energy losses associated with friction and wear have significant impacts on the economies of the world, but new 2D materials, such as graphene, have been shown to exhibit ultralow friction, making its use as a friction modifier of interest across a number of platforms. From previous studies, the effective frictional response of graphene has been seen to depend on the nature of the relative chemical interactions between the nanomaterial and the contacting interfaces, suggesting a means of tuning its friction response by precise control of the chemical forces at play. We have developed a model platform to investigate true nanoscaled asperity-asperity contacts using silica nanoparticles to form substrates with asperities of controlled radius of curvature (ca. 5 – 20 nm), matching those found in many machined interfaces. Molecular adlayers on silica, such as silane based self-assembled monolayers (SAMs), can dramatically reduce friction in such interfaces however, they are easily damaged during impact and shear. A challenge with these molecular adlayers is that nanoscale surface roughness impacts both the formation and quality of the SAMs, as compared to those on atomically smooth surfaces, decreasing film stability. To explore the complex interplay of chemical and mechanical forces at surfaces, we have employed a combination of AFM, IR and Raman spectroscopy, and MD simulations, to examine how high pressure, surface curvature and molecular forces come together to control friction at the atomic/molecular level for SAM and graphene-SAM composites on rough surfaces, with an eye toward tailored control of friction and tribochemistry.

COLL 548

Depositing nanostructures using electron beams: Insights from surface science

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Focused electron beam induced deposition (FEBID) is an increasingly popular nanofabrication technique, capable of creating a wide variety of size and shape selected metal-containing nanostructures using organometallic precursors, with applications in catalysis, plasmonics and mask repair for example. The need to develop organometallic precursors specifically for FEBID that can create deposits with higher metal contents than are current possible with existing chemical vapor deposition (CVD) precursors has provided the motivation for surface science studies. These experiments have shown that the electron-stimulated reactions of the adsorbed precursor during the FEBID process can be broken down into two sequential steps. In the first step, the electron induced deposition of surface bound organometallic precursor's proceeds through **desorption** of one or more of the ligands present in the parent compound. In situations where there are different types of ligands attached to the central metal atom, certain ligands (e.g. CO) appear to be "preferred" leaving groups. Following the initial deposition step, however, subsequent electron-stimulated reactions of the remaining ligands typically lead to ligand **decomposition** and it is this second step that is responsible for most of the organic contamination in EBID nanostructures. One notable exception to the ligand decomposition step involves metal-halogen bonds which are susceptible to electron-stimulated halide ion desorption. Thus, halogen atoms directly

attached to the central metal atom in organometallic complexes can be scrubbed by electron processing. Based on this information we have evaluated the potential of Pt(CO)₂Cl₂ to serve as FEBID precursor and create pure Pt nanostructures using FEBID.

COLL 549

Surface structure dependence in oxide catalysis: Comparison of methanol reaction on CeO₂ oriented surfaces and nano crystallites

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The effect of surface structure upon surface chemistry, as studied using model surfaces, has been a broad research theme that has been successfully pioneered by Prof. Somorjai. Role of surface structure in oxide catalysts is of continuing interest in determining the factors involved in controlling reaction selectivity and rates. Recently, both experimental and computational work has been aimed at determining how variation of the crystallographic facet affects reaction pathways catalyzed at CeO₂ surfaces. We and others have compared UHV studies of products evolved in temperature programmed reaction at single crystal faces with (111) and (100) orientations with reactor based examination of product distributions from shape selected CeO₂ oxide particles dominated by {100} or {111} facets. Recently we have examined methanol reactions to create a detailed understanding of how activity and product selectivity varies with reactor parameters temperature, methanol:O₂ ratio, contact time and especially how selectivity varies with preferred crystallographic orientation of the CeO₂ nanoparticles. In addition to its practical importance, methanol catalytic conversion is a fascinating test-probe reaction because multiple pathways can be accessed and the selectivity between them may be a subtle balance between site acidity/basicity, availability of oxygen from the reducible surface and surface atomic geometry. Such results form a basis for comparison of catalytic performance with UHV-based TPD and spectroscopic studies of surface adsorbates and their formation from methanol adsorption and computational studies of transition states and energetics. In this presentation, I will compare both UHV- and reactor-based experiments with computational studies to explore the role of surface structure in methanol reactions by CeO₂ catalysts as well as the challenges of comparing these methodologies.

COLL 550

Water speciation and mechanochemical reactions at/in multicomponent silicate glass surfaces

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Water adsorption and reaction on glass surfaces play important roles in chemical and mechanical durability of glasses. Compared to metals or crystalline oxide materials, the surface chemistry of multicomponent glasses in humid ambient is much less understood. This is in part because the adsorbed water can often be dissociated or diffused into the glass, especially in the case of alkali-containing silicate glasses; in addition, glass itself can have some hydrous species (hydroxyl and molecular water) in the subsurface or bulk. Since glass is in non-equilibrium state, glass composition, thermal history, surface treatment, and environment condition can also affect the water adsorption and reaction behavior. We employed vibrational SFG spectroscopy, and other spectroscopy techniques that provide complementary information, to investigate water adsorption and reaction at the multicomponent silicate glasses containing leachable alkali ions. These studies revealed a unique role of the alkali ion leaching and exchange on the activity of water at glass surfaces, which could be correlated with surface mechanical and mechanochemical properties of glass surfaces.

COLL 551

Topochemical synthesis of a two-dimensional polymer *via* [2+2] cycloaddition on the multigram scale

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We here report the convenient, inexpensive and large scale synthesis of a C₃-symmetric styryl pyrylium salt as a novel monomer for the topochemical synthesis of an organic two-dimensional polymer (2DP). The monomer self-assembles into a crystalline, layered arrangement, polymerizes and eventually delaminates into sheets of 2DP. This is the third ever case in which a single-crystal-to-single-crystal transformation and subsequent liquid-phase exfoliation yielding 2DPs could be achieved. The structure of both monomer and polymer crystals is confirmed by XRD, IR and ¹³C CP/MAS NMR.

The novel system provides outstanding possibilities:

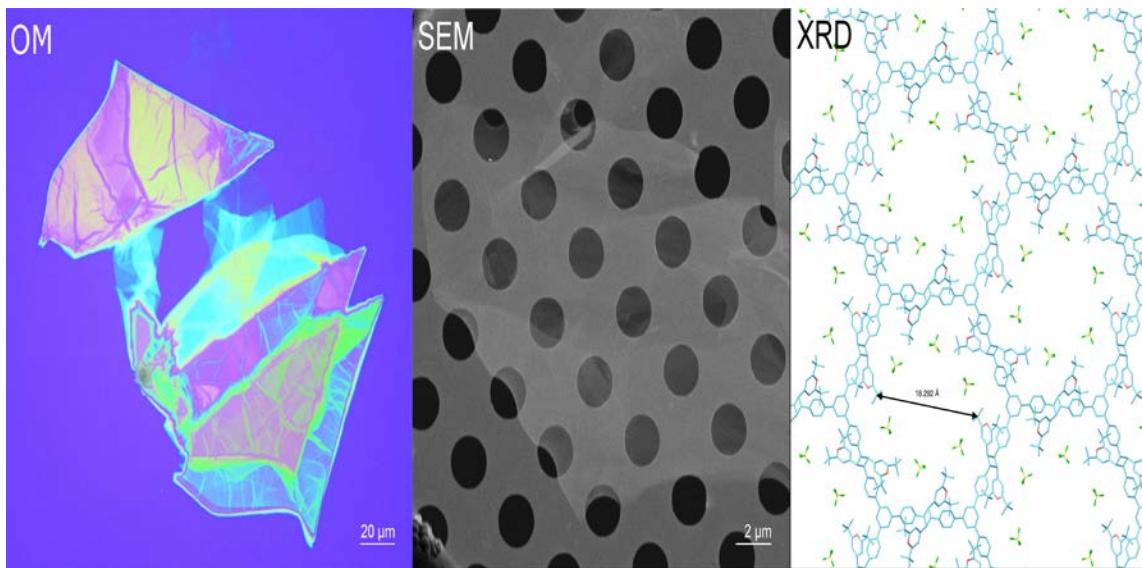
- > Easy accessibility (35 g prepared after single runs of a 4 step synthesis)
- > Crystals grow in sizes of up to 5 mm
- > Single and multi-layers of crystalline polymer by liquid-phase exfoliation within a few days

The 2DP may be regarded as a positively charged, planar and crystalline honeycomb-mesh. The negative counter-ions are supposed to encase the sheet from both sides. Properties of these organic materials are intrinsically different from their inorganic 2D counterparts, e.g. pores are rather large (18 – 28 Å) and the polymerization reaction is reversible at elevated temperatures (>150 °C). Therefore, spatially resolved post-

modifications under mild conditions or membrane applications are conceivable.

The timescale of exfoliation is unusually fast and yields large 2D polymers: large films of up to 10 µm in lateral size can be found already after 2 d. AFM measurements show apparent heights of 1.5 – 2.5 nm for the thinnest features, to which we tentatively assign monolayer character. These sheets are stable under ambient atmosphere and, apart from occasional tearing, endure the exfoliation conditions for months. Current research is directed towards improving the dispersity, whereby the final goal is to obtain fractions of homogenously thick sheets (ideally monolayers). Ultracentrifugation may prove a valuable tool here.

First trials have shown the polymer to be semi-conductive and electroluminescent. Prototype OLEDs have been manufactured by drop-casting a 2DP dispersion.



Zooming into 2D polymers from the macroscopic world to molecular dimensions

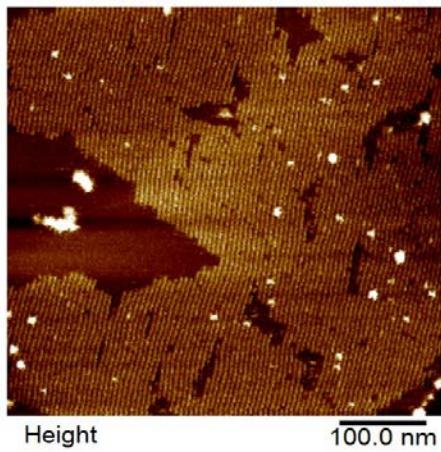
COLL 552

Structure elucidation of two-dimensional polymers synthesized at the air/water interface

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A two-dimensional polymer (2DP) is a polymer composed of topologically planar repeat units that are connected by covalent bonds. The resulting sheet is one monomer unit thick, free-standing and exhibits internal order. The underlying chemistry relies on topochemical photocycloaddition of trifunctional monomers. When synthesized at the

air/water interface, the main challenge lies in the characterization of the resulting sheets which are a mere nanometer thin. We have recently developed a method for monitoring the photopolymerization of the monomer film on solid substrates. Furthermore, we visualized crystalline domains within the film by high-resolution atomic force microscopy. Finally, a combination of computational modelling and tip-enhanced Raman spectroscopy allows mapping of the orientation of the thin film on the substrate down to the scale of 20x20 nm. These findings are important steps towards a full characterization of a two-dimensional polymer which encompasses proof of polymerization, characterization of the domains within the film, as well as the molecular structure within a domain.



High resolution AFM image of polymer film on HOPG, revealing crystalline domains over large areas.

COLL 553

Self-assembly and on-surface polymerization of bromine-functionalized pyrene derivatives on noble metal surfaces

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For around one decade, on-surface polymerization has been introduced as an alternative method to classical solution-based organic synthesis for constructing novel 1D and 2D materials. One of the intriguing materials, which can be reliably obtained through on-surface polymerization based on Ullmann coupling, are graphene nanoribbons. However, during the polymerization reaction, the presence of the split off halogen atoms on the surface may hamper the diffusion of the monomers and thus,

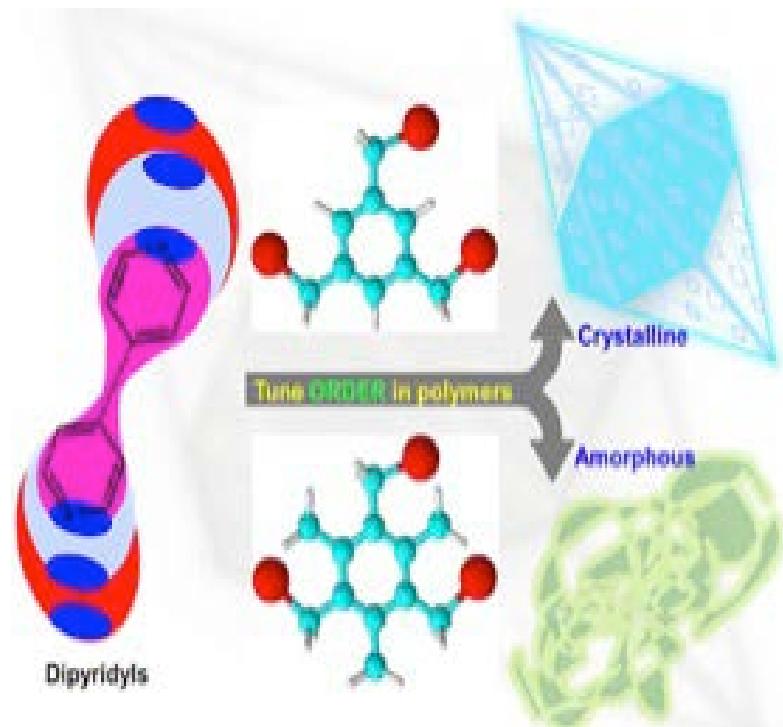
negatively influence the formation of well-ordered polymer structures. Here, we investigated both the self-assembly and on-surface polymerization of bromine-functionalized pyrene derivatives on Au(111) and Cu(111) surfaces under ultrahigh vacuum (UHV) conditions. Furthermore, we present a hydrogen dosing treatment to reduce the influence of the split off halogen atoms on the polymer formation. The combination of scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS) measurements and density functional theory (DFT) calculations enabled the detailed understanding of the well-ordered self-assembled arrangements as well as the intriguing polymer structures on Au(111) and Cu(111).

COLL 554

Charged induced formation of crystalline network polymers

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Order in purely organic network polymers is hard to achieve, as reversible, dynamic covalent bond formation is required. Strategies focused on thermodynamic controlled transformations, as kinetics would not seemingly favour reversibility. We recently reported formation of crystalline network polymers under kinetically favoured conditions by using quaternary ammonium salt linked networks. Charged bulky bridges align, even under fast reaction times (20 minutes) if the rotational freedom is granted. Adding vicinal methyl substituents block the ordering, hence form amorphous networks. Raman experiments and SEM images reveal stacking of 2D layers. Substituent effects and forced equilibrium conditions can lead to mismatched assemblies.



COLL 555

Exploring molecular assembly at surfaces

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The adsorption and self-assembly of organic molecules at surfaces has recently been investigated extensively, both because of the fundamental interest and for prospective applications in nanoelectronics. Molecule-molecule and molecule-substrate interactions can be tuned by appropriate choice of substrate material and symmetry. Upon molecular adsorption, surfaces typically do not behave as static templates, but often rearrange to accommodate different molecular species. We review recent experiments using Scanning Tunnelling Microscopy, providing new insight into fundamental properties such as molecular diffusion and self-assembly via surface templating and H-bonding driven by co-adsorption. Our approach is to modify surfaces providing suitable surface cues that may guide the assembly of adsorbates. Recent advances in using the substrate as catalyst for surface confined polymerization reactions will also be discussed.

COLL 556

Hierarchy of interactions and templation effects in supramolecular assembly at surface: From organic monolayers to thin films

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This talk will analyse the effect of an inorganic surface on the spontaneous organisation of molecular building blocks into complex architectures by considering forces between molecules and surfaces as a further ingredient in the complex hierarchy of interactions that govern supramolecular self-assembly. It will be shown that while surfaces clearly introduce bring an extra degree of complexity into this already intricate problem, they also represent a unique opportunity for understanding the fundamental processes at play because of the availability of extremely high resolution analytical techniques that allow to investigate and even visualise the assemblies down to the molecular and atomic scale.

A number of recent examples drawn from the collaboration between our laboratory and several theoretical groups will be presented, exemplifying cases where the surface has different degrees of influence. We will start from the instance where the effect of the surface is minimal, demonstrating that two-dimensional (2D) hierarchical supramolecular nanostructures can be programmed by molecular design. We will then move to the case when the substrate templating effect becomes more relevant, presenting recent efforts to develop a general, though simple and computationally inexpensive model with quantitative predictive capabilities, providing a comprehensive description of the ‘subtle interplay’ between intermolecular and molecule-substrate

interactions. Finally, we will deal with the question of how far the surface templating effect extends when moving from 2D to thin film growth, demonstrating that the answer critically depends on the differences between the monolayer and the molecular bulk crystalline structure. This last topic will also be used to discuss the importance of expanding our current, traditional surface science experimental techniques in order to analyse molecular films beyond the ultra-thin monolayer limit.

COLL 557

Sophisticated photoresponsive system made of supramolecular assembly of photochromic diarylethene at solid/liquid interface

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In order to apply photochromic compounds in practical use, especially in molecular electronics, assembly and arrangement of the molecules are very important. Therefore, supramolecular photochemistry in two-dimensional (2-D) assemblies is attracting interest. 2-D self-assemblies of photochromic diarylethenes were studied by STM at a liquid/solid interface at the single molecule resolution. We have successfully introduced cooperative model on 2-D assembly of a 2-thienyl-type diarylethene. The concentration dependence of surface coverage showed abrupt increase at certain concentration, but no ordering was observed for the closed-ring isomer at various concentrations. The adsorption behavior was explained by a cooperative self-assembly model by the Langmuir adsorption model incorporating the nucleation and elongation constants K_n and K_e . On the basis of this phenomenon, highly sensitive photochemical control of the assembly was successful. Extensive studies based on this cooperative self-assemblies will also be presented.

COLL 558

Understanding intermolecular interactions driving the self-assembly of alkoxybenzonitriles on graphene

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Soft molecular self-assemblies of organic-thin films tailored by weak interactions on a two-dimensional (2D) surface such as graphene display a range of versatile features in the field of organic electronic devices. To understand the associated molecular ordering and stacking patterns, it is important to gain a deep insight into the variety of intermolecular interactions driving the self-assembly of these molecules. Herein, we have adapted an efficient computational approach to investigate the intermolecular interactions between non-covalent dimers involving lateral (2D) and stacking (3D)

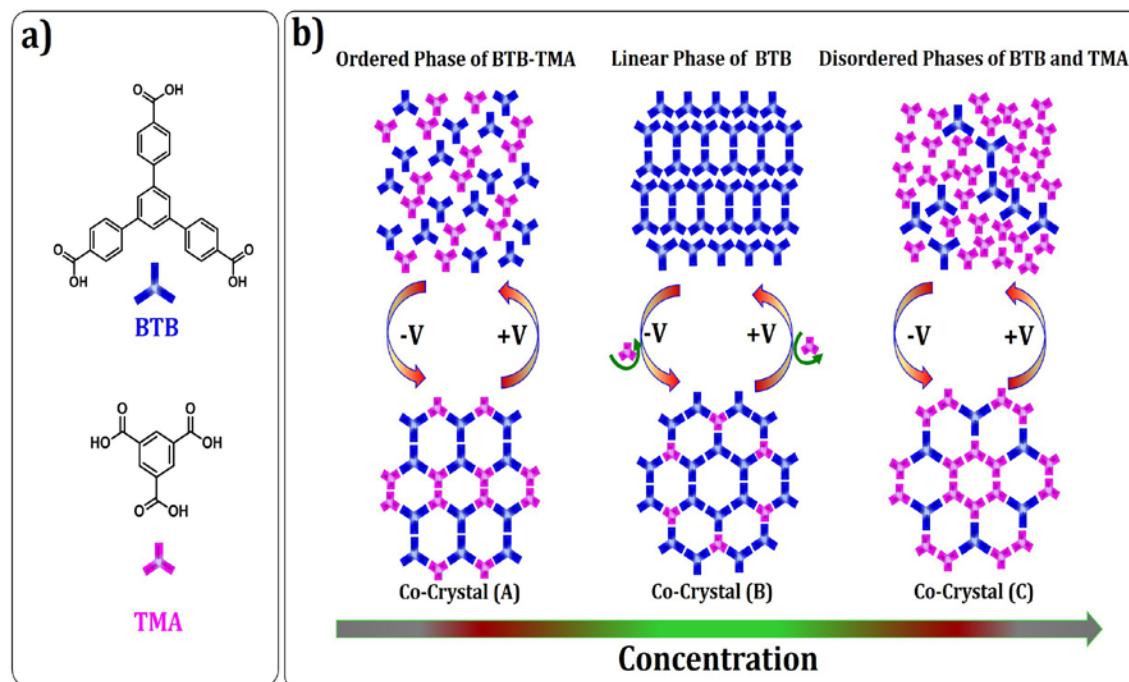
orientations of molecules such as alkoxybenzonitriles. Additionally, interactions of such molecules with the solvent, e.g., octanoic acid, have been studied to calculate distance-dependent intermolecular interaction energies over the full active range. We have performed energy decomposition analysis of these intermolecular interactions using symmetry adapted perturbation theory (SAPT) to derive a categorized and clear understanding of the target factors playing a decisive role in the self-assembly of alkoxybenzonitriles on a graphene surface.

COLL 559

Stimuli responsive phase behavior in hydrogen-bonded bicomponent supramolecular networks

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The present investigation demonstrates the effect of electric field on the phase behavior of surface adsorbed, hydrogen-bonded, bi-component supramolecular networks. Three types of low density supramolecular co-crystals were fabricated by varying the ratio of individual components in solution. Using scanning tunneling microscopy (STM) at the solution-graphite interface, we demonstrate that a reversible transition between a well-ordered co-crystalline and a disordered phase-separated state can be achieved by simply switching the polarity of the voltage applied to the substrate. The complex stimulus responsive phase behavior was found to critically depend on the solution stoichiometry. Such externally triggered reversible phase transitions in multicomponent systems may have potential utilities in the fabrication of functional organic thin films.



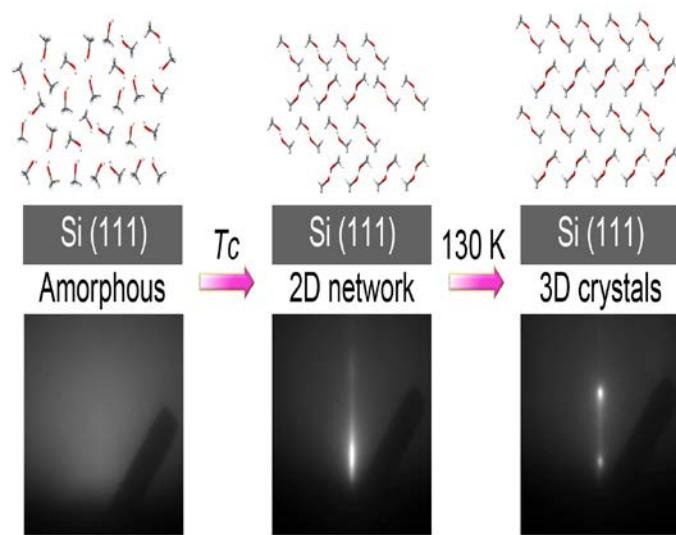
Scheme:(a) Molecular structures of 1,3,5-tris(4-carboxyphenyl)benzene (**BTB**) and trimesic acid (**TMA**). (b) Schematics of concentration dependent porous co-crystals (bottom) and electric field induced supramolecular multicomponent networks (top).

COLL 560

Structural transformations and self-assembly of interfacial methanol ice on hydrophobic surfaces

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Methanol continues to be a chemical of interest because of its importance as a common solvent and in various applications such as fuel cells and catalysis. Structurally and chemically, the existence of both a hydrogen-bond-forming hydrophilic group and a small hydrophobic methyl group leads to the molecule's rich behaviors, especially at interfaces. To distinguish the interfacial properties from the bulk ones, surface-sensitive or even specific methods are needed. Here, using reflection high-energy electron diffraction as a contactless, surface-specific technique for direct structure probing, the unique self-assembling behaviors of vapor-deposited methanol assemblies on hydrophobic surfaces were revealed for the first time. Hidden structural transformations were uncovered, which have been obscure in spectroscopic and other indirect measurements. Furthermore, thin methanol ice forms 2- and 3-dimensional, long-range ordered structures at different temperatures, depending on the annealing procedures used. These findings may reconcile the inconsistent previous reports for the crystallization of interfacial methanol, whose process is in fact far beyond a presumed single-stage description.



Two-stage structural transformations and self-assembly of interfacial methanol on H-terminated Si(111) (T_c , crystallization temperature).

COLL 561

Electroanalytical characterization of environmental chemical processes of engineered nanoparticles

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Applications of engineered nanoparticles in electronics, catalysis, solid oxide fuel cells, medicine and sensing continue to increase. Traditionally, nanoparticle systems are characterized by spectroscopic and microscopic techniques. This presentation will describe development of an electrochemical method based on nanoparticle impacts with a microelectrode for evaluating the fundamental surface properties, functionalization and reactivity of metal and metal oxide nanoparticles. We will demonstrate the potential of this method for the: 1) assessment of surface reactivity of redox active nanoparticles, 2) monitoring surface adsorption/desorption and speciation at single particle surfaces, and 3) as a method enabling rapid label free detection of biomolecular recognition targets. We will demonstrate capabilities of this method as a novel tool for assessing environmental chemical processes involving nanoparticles and for characterizing biomolecule-nanoparticle conjugates for biosensing design. Potential advantages and limitations of this approach as a method for the routine study of nanoparticles and nanoparticle systems will also be discussed.

COLL 562

Search for new properties and applications of micro- and nanohydrogels

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Several efforts were undertaken to extend and tune the properties of micro-, nano- and thin layer hydrogels responding to environmental conditions. The main accent was given to introduction of various crosslinkers to the PNIPA polymers. In the first try microgels based on pNIPA crosslinked with appropriate derivative of cystine (BISS) were synthesized by applying surfactant-free emulsion polymerization. AS a result, in addition to sensitivity to temperature, the microgels acquired the ability to degrade and sensitivity to pH. The introduction of three-segment oligonucleotide hybrids as crosslinkers to PNIPA-AAc nanogel networks led to a substantial increase in storing efficiency of intercalators, including anticancer drugs, compared to the nanogels with regular crosslinkers. Significant changes in volume phase transition temperature were obtained after modification of pNIPA hydrogels with a derivative of dopamine and Fe(III) cations. Sensitivity to several medium parameters, such as temperature, pH and ionic strength and electroactivity and conductivity were cumulated in one microcomposite by combining three components: PNIPA crosslinked with bisacryloylcystine microgel, PANI nanofibers and Au nanoparticles. By the combination of LCST-type thermally

responsive polymers a set of new core-shell microgels was obtained. It was possible to limit the swelling process of the composites to a narrow temperature range.

Thin hydrogel layers were anchored to regular- and microelectrode surfaces by using the electrochemically induced free radical polymerization. The deposition of nanogels, on the gold electrode surfaces, was also done by employing the interactions of disulphide groups in the crosslinkers with gold.

Quartz crystal microbalance was particularly useful in examination of responses of gel layers to changes in temperature. The swelling behavior of the gels and their structure and morphology were also investigated by doing dynamic light scattering measurements, thermogravimetric analysis and by employing SEM, TEM, voltammetry and Raman and NMR spectroscopies.

COLL 563

Quasi-adiabatic proton exchange membrane fuel cell fixture for automotive cold-starts

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Fuel cell subzero cold start remains a central issue prohibiting automotive fuel cell commercialization; however stack level testing is expensive. A quasi-adiabatic single-cell fuel cell fixture was designed, built, and validated to emulate cold starts at the stack level. Galvanostatic cold starts were attempted at 600 mA cm^{-2} ; however the tests were dominated by high membrane resistances. To improve controllability, potentiostatic+galvanostatic cold starts were performed: set to 0.1V until the current attained a value of 600 mA cm^{-2} . For the same water content and heater power, potentiostatic tests and galvanostatic tests resulted in comparable cold start profiles. Shorter times to reach 0°C were observed with higher initial water contents ($\lambda=6.2$ vs $\lambda=3.2$). Heat output data based on cell voltage, current, and heating pad power consumption was input into a finite element model in COMSOL and temperatures predicted by the model were compared to the temperatures measured during the cold starts.

cold-start testing is being evaluated using a quasi-adiabatic single cell fixture developed in-house, expanding upon the original proto-type designed at United Technologies Corporation. Heating pads were integrated into the fixture and powered at levels equivalent to 1x and 2x adjacent cells to compensate for non-adiabatic losses. Higher water content favorable impact initial performance, however at long time scales seems to insignificantly impact cold start probability. Cold start probability is significantly impacted by the heating pad condition indicating significance of bipolar plate and coolant thermal mass impact on ability for CL to self-heat to above 0°C .

COLL 564

Nanocarbon bowls: Functionalization, structures, applications

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Bowl-shaped polycyclic aromatic hydrocarbons that serve as prototypes of fullerene surfaces (and thus often referred to as buckybowls, fullerene fragments or *p*-bowls) and end-caps of carbon nanotubes constitute an important and unique class of curved carbon-rich compounds that is rapidly expanding over the last decades. Carbon bowls exhibit a range of special properties stemming from their open bowl-shaped molecular structures and nanosize dimensions. A great variety of such bowls ranging in size and curvature is now known. Through additional functionalization their structures, properties and reactivity can be further tuned. This controlled functionalization significantly expands this class of unique carbon-rich compounds and also allows tailoring their properties for specific applications. Selected highlights of our investigations of various curved carbon-rich aromatic systems will be presented focused on their unique structures and properties, self-assembly trends and potential as light-weight organic nanocarbon materials.

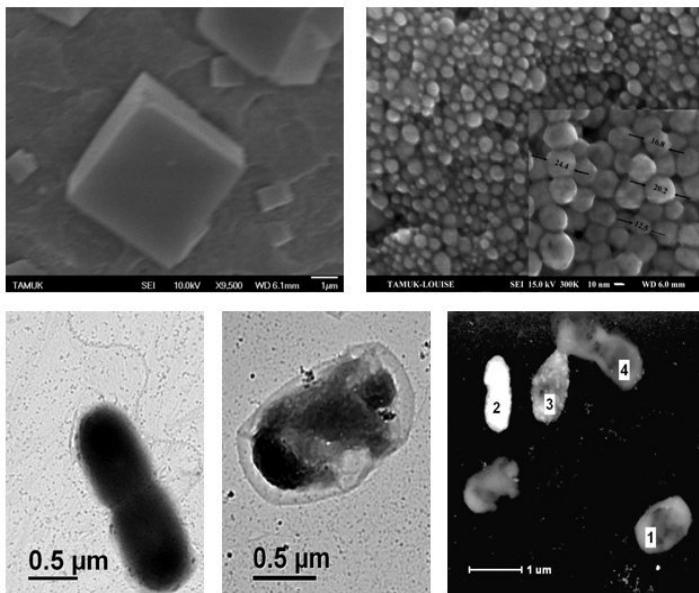
COLL 565

Functionalized porous organometallic compounds as inhibitor of cell division

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This research focused on development of a series of metal-organic frameworks (MOFs) and evaluate their cytotoxicity. It was found that these MOFs displayed high potential in delivery drugs and cancer diagnosis. A feasible hydrosolvo-thermal wet-chemistry approach was used to produce the MOFs with functionalization through ligand coordination. Tunable covalent (ligand) coordination frameworks in the fabrication of MOFs allow for high surface area, unique crystal geometry, ultrahigh porosity and controlled particle size. Transition metals centers were used to serve fluorescence platforms whilst the ligands and capping agents served as biocompatibility agents. Several state-of-the-art instruments were used to determine the crystalline phase, particle size, distribution, and crystallinity of MOFs. *In-vitro* toxicity data indicated that MOFs IC₅₀ (0.02 ppm) is comparable to, or lower than the current first-line drug formulations. At higher doses, the kinetics of action were approximately ten-fold higher. These biological effects may be attributed to the unique tetra-topic carboxylate ligand bridging to a bimeric $\mu_2\text{-H}_2\text{O}$ -centered cluster, in addition to high crystallinity and high aspect ratio. The latter factors lend themselves to high MOF-cell surface contact, which in turn leads to depolarization of the mitochondrial membrane from the lactate dehydrogenase assay.

SEM images of MOFs and NPs



Intact and damaged *E. coli*, and *S. aureus*

COLL 566

Relationship between phosphorous and metals in Lake Auburn

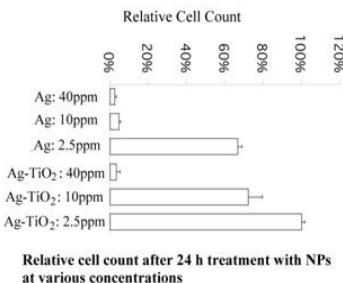
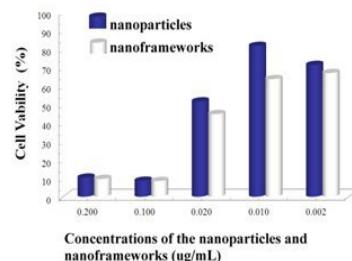
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Lake Auburn serves as the drinking water source for the towns of Lewiston and Auburn in Maine; Lewiston is the second largest city in the state. Lake Auburn is considered a pristine source, requiring only disinfection for treatment. However, in recent years algal blooms have become of concern. Phosphorous (P) is typically the limiting nutrient in most lakes. Previous research showed that when the P results from internal loading (i.e. from sediment in the lake) metals such as aluminum and iron are also present in specific molar ratios. The current project attempts to look at the relationship between the amount of P in the water column of Lake Auburn, and its relation to metal concentrations (such as iron and aluminum) in an effort to determine the origin of the P observed in the lake. This study contributes to the thesis of a senior chemistry student at Bates College, a small liberal arts college located in Lewiston. The project is in collaboration with an ecologist in environmental studies at Bates looking at the entire ecosystem, and with the water utility.

COLL 567

Characterization of three pathogenic L-ferritin mutants that cause neuroferritinopathy

Toxicity on CHO



Toxicity on NIH 3T3

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Ferritin is a 500 kDa iron-storage heteropolymer (HL) protein composed of two structurally similar but functionally different subunit types named H- and L-chains. The H-chain has a potent ferroxidase activity that catalyzes the oxidation of ferrous to ferric ions whereas the L-chain plays important roles in iron nucleation and protein stability. Pathogenic mutations on the L-chain lead to neuroferritinopathy, a neurodegenerative disease characterized by abnormal accumulation of ferritin and iron in the central nervous system. Here, we have characterized the thermodynamic stability, iron uptake, and iron release properties of three pathogenic L-ferritin mutants (L154fs, L167fs, and L148fs also known as Ln1, Ln2 and L442P) and one non-pathogenic variant (L135P). Overall, the data show an iron loading capacity for all ferritin samples ranging between 1800-2400 Fe/shell with Ln2 holding the least amount of iron. The order of stability of the ferritin samples is HL > H-chain > L135P > Ln2 > Ln1 > L442P. Iron oxidation appears to proceed mainly via a ferroxidation reaction with 2 Fe atoms oxidized by 1 O₂ molecule suggesting the production of H₂O₂. This ratio slowly increases to about 3 Fe per 1 O₂ at higher iron loadings. The non-pathogenic mutant (L135P) exhibited a local unfolding around the 3-fold axes and showed higher rates of iron release, suggesting an important role of these channels in iron mobilization. Ln1 and L442P had the highest rate of iron mobilization accounting for 100% iron release within 30 minutes of reaction, a result consistent with the onset of neuroferritinopathy.

COLL 568

Thread- and paper-based devices for use in enzyme assays for Point-of-Care (POC) diagnostic devices

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Microfluidics-based technologies continue to gain traction as alternatives to traditional techniques and have great potential in resource-challenged settings where access to more expensive instrumentation is not always possible. At present, particular need is in the healthcare area and in offering greater access to point-of-care (POC) devices. Herein, we describe the development of colorimetric-based assays utilizing microfluidic thread-based analytical devices (μ TADs) and paper-based analytical devices (mPADs). We demonstrate their integration as POC devices to assess acetylcholinesterase (AChE) activity, to quantify glucose using glucose oxidase (GOx) and horseradish peroxidase (HRP), and in the development of an ELISA to quantify rabbit IgG. The results obtained using these devices coincide to those obtained using traditional techniques. The ease of fabrication, low cost, variability in platform design, and educational value provided by the use of μ TADs and mPADs make them an appropriate vehicle for undergraduate research and demonstrate their great potential in a variety of disciplines. Continued advances in device designs that can improve upon traditional

methods of detection as well as sample handling and high-throughput, will embolden the use of these platforms for understanding and solving a myriad of global problems.

COLL 569

Modification of the paper-based NanoCerac antioxidant assay for high-throughput use: An analysis of twenty-four green teas for antioxidant activity throughout six consecutive infusions

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Background: Adaptations and improvements have been made upon the paper-based Nanoceria Reducing Antioxidant Capacity (NanoCerac) assay, in order to create a high-throughput (HTP) analysis method to be used on large sample sets. **Experimental:** Modification made to the NanoCerac assay include: utilization of smaller sample volumes, simultaneous preparation of samples, simultaneous deposition of samples, and utilization of a novel customized MatLab program for rapid, automated analysis of digital NanoCerac sensor images. Our HTP version of the NanoCerac was validated through analysis of the effect of re-infusion on the antioxidant capacity of twenty-four commercial green teas; a study, which involved 432 samples. The popular oxygen radical absorbance capacity (ORAC) assay was used alongside the NanoCerac in this study, as a comparator measure of antioxidant capacity. **Results:** The NanoCerac and ORAC assays correlated moderately ($R^2 0.80 \pm 0.19$). NanoCerac assay modifications resulted in increased speed of analysis as well as reduced material requirements. This HTP method, capable of analyzing roughly forty-eight samples per hour, acts as a drastic improvement to the original method, which required two hours for each sample analyzed. A novel measure of sustained antioxidant capacity, the total inherent antioxidant capacity (TI-NanoCerac or TI-ORAC) was named following measurement of six repetitive infusions of varietal green teas. The average first-brew NanoCerac, TI-NanoCerac, first-brew ORAC and TI-ORAC were: 0.73 ± 0.1 GAE/g tea; 2.4 ± 0.70 mmol GAE/g tea; 1.0 ± 0.3 mmol TE/g tea and 2.1 ± 0.71 mmol TE/g tea respectively. **Conclusions:** This HTP adaptation of the original NanoCerac assay offers advantages over the ORAC assay, including portability and rapid analysis. While NanoCerac sensors are capable of identifying specific antioxidant compounds, using the published database of reference colors (Sharpe, et. al. 2014), this high-throughput version of the NanoCerac assay is best suited for analysis of large sample sets for antioxidant activity. The demonstrated measurement of total-inherent antioxidant capacity (TI-AOX) of a sample that is infused repetitively, offers a new approach to analyzing botanicals that may commonly be reused as part of their medicinal applications.

COLL 570

Genome-wide DNA methylation variations upon engineered nanomaterials and their implications in nanosafety assessment

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Many engineered nanomaterials (ENMs) do not elicit detectable cytotoxicity using traditionally developed methods for bulk materials or chemicals, due to the low sensitivity of the methods. Thus, more sensitive methodologies are needed to evaluate their safety profiles. DNA methylation is an early sensitive parameter in response to a wide range of exogenous and endogenous stimuli including ENMs. However, there is limited understanding on this front, and, to address this issue, we performed DNA methylation sequencing at base-pair resolution in lung A549 and kidney HEK293T cells upon diverse ENM exposure. Exposure of silver nanoparticles and graphene oxide led to significant increases in global 5-mC level, which was however to a much less extent for gold nanoparticles, carbon nanotubes, nano-TiO₂ and nano-ZnO. Furthermore, physicochemical properties, such surface modification, affected ENM-induced DNA methylation variations. Through gene functional mapping, significant perturbations in cellular processes and signaling pathways could be ascribed primarily to DNA methylation alterations. Supported by gene expression and toxicological/physiological evaluations, adverse outcome pathways, adaptive cell survival and compensatory effects were identified due to the genome-wide DNA methylation changes. Thus, ENM-induced DNA methylation variations represent a more sensitive fingerprint analysis of their direct and indirect effects that may be overlooked by the traditional toxicity assays, and the understanding on the structure-activity relationship for DNA methylation changes induced by ENMs would open a new avenue for their safer design.

COLL 571

Catalytic enhancement of multienzyme cascades co-localized on colloidal quantum dots

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Enzymes and multienzyme pathways are of tremendous interest for the production of industrial chemicals and in the development of metabolic sensors. The utility of enzymes for industrial catalysis and biosensing can be increased by immobilization of the enzymes on a surface since this often enhances their stability and facilitates the purification and reuse of the enzymes from the reaction mixture. Unfortunately,

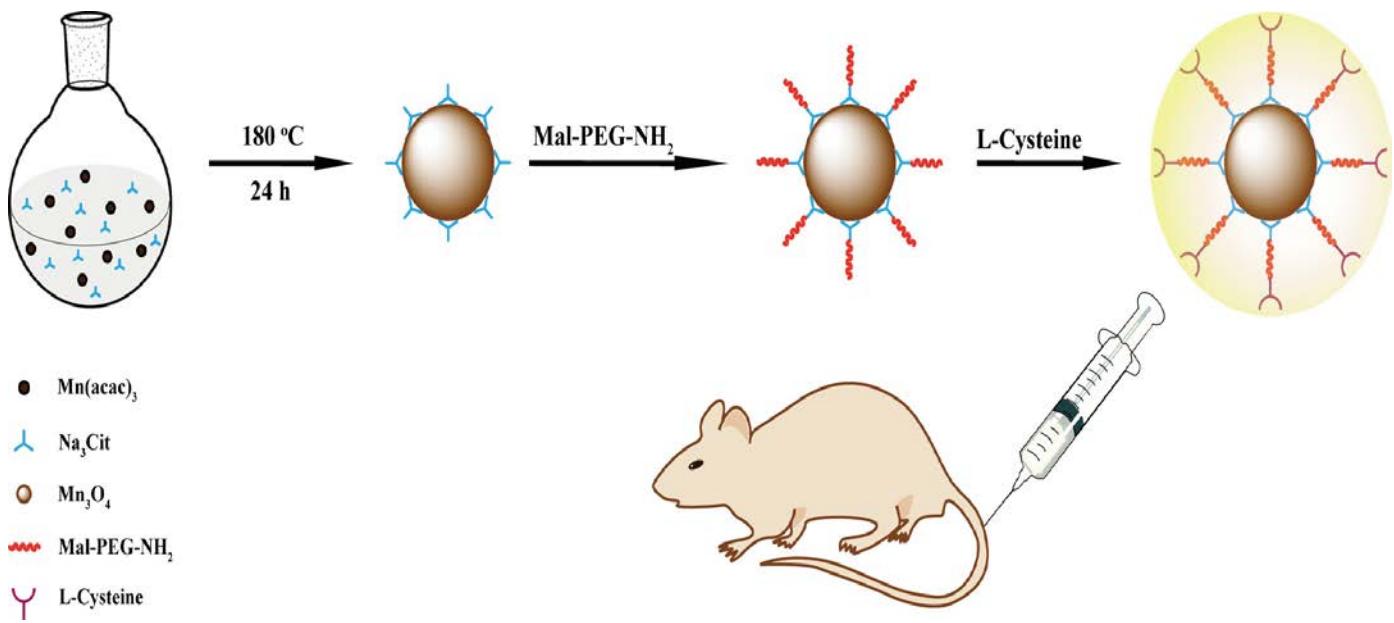
immobilization of enzymes on large planar surfaces often results in loss of enzymatic activity. Recently our group and others have demonstrated that immobilization of enzymes on nanoparticles can often result in enhanced enzymatic activity relative to the free enzyme in solution. In many cases, a single enzyme is insufficient to carry out the necessary chemical transformations. As a result, immobilization of multiple enzymes constituting a synthetic pathway is becoming increasingly common. Other groups have demonstrated that colocalization of enzymes within a pathway can lead to enhanced catalysis, presumably via a substrate "channeling" mechanism. Our most recent studies have involved the immobilization of multienzyme cascades on quantum dot surfaces in an attempt to harness both the enhanced activity of nanoparticle-bound enzymes as well as substrate "channeling" phenomena. We have demonstrated the ability of nanoparticle immobilization to greatly enhance the kinetics and product yield of multiple pathways containing up to 7 enzymes. Additionally, we observe enhanced kinetics of single bound enzymes (>50 fold increases) within the context of the immobilized pathways and use mechanistic analyses to uncover the mechanism of these enhancements. Finally, we provide strong evidence that the pathway enzymes are stabilized by nanoparticle binding and are able to effectively "channel" substrates between the colocalized enzymes.

COLL 572

Antibiofouling manganese oxide nanoparticles: Synthesis, characterization, and potential applications for T_1 -weighted MR imaging of tumors

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Herein, we report the functionalization of manganese oxide (Mn_3O_4) nanoparticles (NPs) with L-cysteine to create an antibiofouling zwitterionic surface for improved tumor magnetic resonance (MR) imaging applications. In this work, monodispersed trisodium citrate-stabilized Mn_3O_4 NPs were formed by decomposition of tris-(2,4-pentanedionato) manganese(III) *via* a solvothermal approach, followed by sequential conjugation with polyethylene glycol and L-cysteine. The final multifunctional Mn_3O_4 NPs were well characterized by different methods. We show that the formed Mn_3O_4 NPs with a mean diameter of 2.7 nm possess desirable water-solubility, colloidal stability, and cytocompatibility and hemocompatibility in a given concentration range. With the L-cysteine modification, the particles are able to be rendered with prolonged blood circulation time (28.4 h half-decay time in mouse), which is much longer than those without L-cysteine modification (18.5 h), and decreased macrophage cellular uptake. Thanks to the prolonged blood circulation time and the good r_1 relaxivity ($3.66\text{ mM}^{-1}\text{s}^{-1}$), the L-cysteine-modified Mn_3O_4 NPs were able to be used as a contrast agent for effective T_1 -weighted MR imaging of a xenografted tumor model *in vivo* *via* the passive enhanced permeability and retention effect. The as-prepared Mn_3O_4 NPs with multiple reactive surface groups can be further modified for different biomedical applications.



COLL 573

Quantum dot (QD)-fullerene (C_{60}) conjugates for imaging real-time changes in cellular membrane potential

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Cell membrane potential is associated with numerous normal and anomalous (driven by diseases or injuries) activities of mammalian neuron and muscle cells. Recently, significant interest has arisen in the development of new optical probes for the visualization of the membrane potential of large numbers (hundreds to thousands) of neurons simultaneously with single cell resolution. Ideally, such probes would overcome some of the limitations of current materials and techniques. Patch clamp, for example, is limited to single cell analysis while voltage-sensitive dyes and fluorescent proteins are plagued by photobleaching and intracellular instability. Semiconductor nanocrystals or quantum dots (QDs) offer superior optical properties for cellular sensing applications given their photostability, amenability to bioconjugation, and their ability to engage in efficient energy and electron transfer. We have developed a voltage-sensitive QD-based assembly comprised of a central QD scaffold around which is appended multiple copies of a peptide-fullerene (C_{60}) conjugate. The photoexcited QD engages in electron transfer to the fullerene electron acceptor and the rate of this transfer process is modulated by changes in cellular membrane potential. We show the ability to control the efficiency of electron transfer by ratiometrically controlling the number of fullerene electron acceptors arrayed around the QD as well as by controlling the distance of the

fullerene from the QD surface. In HeLa cells and in primary mouse cortical neurons, this optical construct efficiently reports on changes in cellular membrane potential induced by potassium chloride depolarization. The implications of this sensing modality on the ability to visualize the activity of neuronal cells, and other electrically excitable cells, will be discussed.

COLL 574

Cerium oxide nanoparticles as novel biosensing tools: Properties, sensing mechanism and applications

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Cerium oxide nanoparticles or nanoceria have a unique structure and interesting physicochemical properties and reactivity that vary with the size, shape and surface coating. These particles have been traditionally used in catalytic applications in automotive combustion engines, and solid oxide fuel cells, and more recently have been proposed as therapeutic agents in biomedicine. This presentation will discuss properties, characterization and novel applications of nanoceria particles in the biosensing field. These materials have tunable redox activity, optical and catalytic properties and can be used to transduce and amplify signals in chemical and biological detection schemes involving biomolecules. The resulting hybrid nanostructures integrate biorecognition, signal amplification and detection capabilities and can function as all-in-one biosensing devices. Through careful engineering design it is also possible to maintain both the functional nanoscale properties and bioactivity of these materials by printing. Design and performance characteristics of several types of nanoceria-based sensing platforms for point-of-care diagnosis, food quality control and personal exposure assessment as well as implantable and wearable biosensors for detection of physiological biomarkers will be discussed, with examples of applications. These sensors have been interfaced with portable databases and user-friendly signal transduction methods, have been mass-produced by printing and have demonstrated excellent analytical performance when used in the field.

COLL 575

GlycoNanoparticle barcodes for pathogen identification

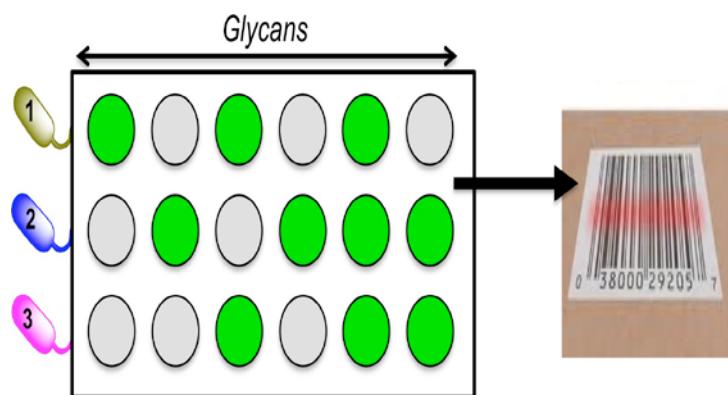
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Carbohydrates are ubiquitous in Nature, functioning as energy stores, providing mechanical strength and crucially as signaling/binding motifs in biochemical systems. For example, glycosylation of proteins is crucial to their folding and stability, and many pathogens exploit cell-surface sugars to invade their hosts. Reproducing glycans on nanoparticles could therefore enable the role of glycans in infection to be probed, but

also as new therapeutics or sensors. However, the synthesis of complex glycans is challenging and not easily scalable meaning simplified structures have to be used, which offer intrinsically lower specificity and affinity than Native glycans.

Here I will present the use of glycosylated gold nanoparticles as plasmonic (colour changing) sensors for pathogens triggered by particle aggregation on pathogen/toxin surfaces. The design rules to enable the formation of particles which are stable in complex media (buffer, urine, plasma, blood) using tailored polymer coatings will be shown. Secondly, the use of multiplexing, or 'barcoding' to improve discriminatory power of these sensors will be shown; rather than having a single channel sensors, which display promiscuity to several lectins (carbohydrate binding proteins) multiple particles are used in parallel with statistical algorithms to 'score' binding events and gives increased discriminatory power.

Such probes may find application to rapidly identify pathogenic bacteria, enabling correct usage of dwindling antibiotics as well as to track outbreaks.



Barcoding pathogens based on their binding profile to multiple simple glycans

COLL 576

Friction and lubrication from the nano (molecular) through the micro ($\mu\text{m-mm}$) to the macro (geological) scales, and over large time and velocity scales

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The traditional laws and models of friction, such as Leonardo da Vinci and Amontons' Laws of friction, and the Stribeck Curve for lubrication, were expounded many years ago (da Vinci in the late 15c). These pioneers of tribology introduced terminologies, such as the Coefficient of Friction (COF), mixed lubrication, and concepts or "laws" (like the velocity independence of the COF, and the "contact area" or film thickness) that break down or that do not apply or that cannot be measured in many practical tribological and especially lubrication situations, and where the length, load/pressure, time and rate (velocity) scales can vary by many orders of magnitude – for example, nm- μm contact diameters for particle interactions compared to >10 km in geological fault lines – a difference of 13 orders of magnitude in length (and much more in area).

Likewise, for slow ‘creeping’ sliding at nm/s – mm/s compared to >10 m/s in machines and engines. Additionally, stiction and stick-slip sliding and their implications for wear, sound generation, sensory perception and biolubrication, do not fit naturally into any of the original laws or concepts, yet these often are *the* major tribological parameter of many systems, for example, in generation surface damage (wear). The talk will review recent and not so recent experimental and theoretical (computational) examples of the “New Tribology”, illustrating how many different processes, such as those mentioned above, that cover large ranges of length and time scales, can be better understood within more general and unified theories and/or concepts.

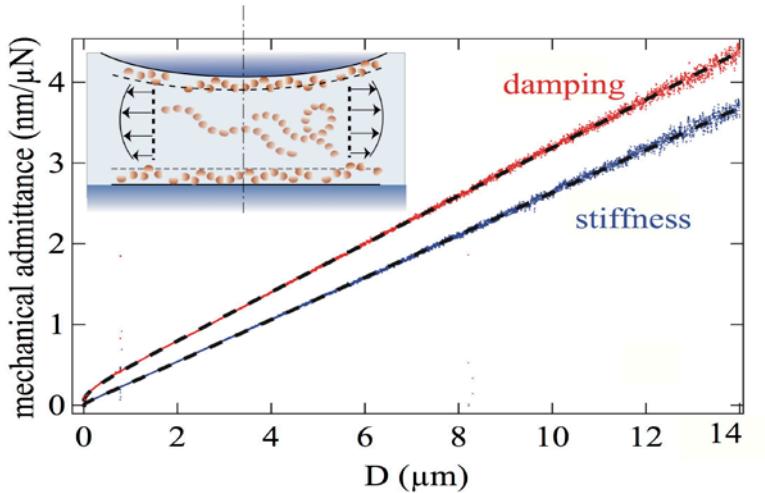
COLL 577

Nanorheology of complex fluids at interfaces: Bulk behavior and complex slip length

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Water solutions of high molecular weight polymer, made up of deformable objects in solution, are usually used for oil recovery applications. These viscoelastic fluids generally display an important interfacial slip which dominates their rheological properties at sub-micron scales. The understanding of this phenomenon is necessary to account for the behaviors observed during their flow within nanoporous mediums, such as oil tanks walls.

We study the interfacial hydrodynamics of polyelectrolyte solutions of high molecular weight thanks to nanorheology experiments carried out with a home-made surface force apparatus. During these experiments, the hydrodynamic boundary condition is investigated by studying the drainage flow of these confined solutions brought about by the approach of the confining solid walls. Confinement can be continuously modified from fifteen micrometers to the contact between the walls. The measurement of the normal viscoelastic forces exerted on the walls is interpreted using the theoretical model we develop. We show that the hydrodynamic boundary condition is complex and exhibits a complex slip length. When confinement is larger than the size of the macromolecules, these forces behavior gives us access to the viscoelastic properties of the solutions. Thanks to the study of these forces at sub-micron scale, we determine the microscopic origin for the apparent slip we observe.



the mechanical impedance is measured between 15 microns to the contact between walls. The behavior shows a complex slip length.

COLL 578

Binary and ternary systems with ionic liquids in confinement

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Imitating natural synovial joints, swollen polymer chains anchored on tribopairs have shown potential as lubricating systems. The fluid-like cushioning layer of solvated polymers effectively reduces friction. To fully leverage the lubricating feature of polymer brushes, a good solvent is needed to stretch the anchored polymer chains. Ionic liquids (ILs) are considered outstanding solvents, and thus, they could potentially serve as the swelling agent for neutral polymers and for polyelectrolytes. We, thus, propose to take advantage of the amphiphilicity of ionic liquids and of their high viscosity to optimize lubrication performance. In our studies we characterize the structural properties of binary and ternary systems with ionic liquids, including IL-swollen hygroscopic polymer brushes, and correlate these parameters to the lubrication performance. The surface forces in the proposed systems are investigated with an extended surface forces apparatus, and are correlated to solubility and structural studies of the bulk solutions. Friction force measurements help to understand the properties of the confined systems and provide guidance to establish design parameters for good lubrication performance via these complex systems.

COLL 579

Shear banding of piezoviscous fluids as a stability problem

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Recent experiments have shown direct evidence of shear banding in the flow of some fluids at high shear rates and pressures, a typical example being lubricants in elasto-hydrodynamic (EHD) contacts. Interestingly, the same fluids have been found to shear when in contact with certain materials but not when in contact with others under the same conditions. This indicates that shear banding is not a purely rheological phenomenon. Instead, it is a result of the mechanical and thermal interaction between the fluid and the confinement, as well as a result of the fluid properties and their sensitivity to shear, pressure and temperature. In this paper, a detailed analysis is performed to show that shear banding appears for piezoviscous fluids under appropriate boundary conditions if a coupled solution is sought to the elastic, thermal and hydrodynamic problem of flow in tribological systems. In particular, it is shown that shear banding arises from a stability problem formally similar to a buckling problem. The implications for friction and slip are discussed.

COLL 580

Local rheology of lubricants

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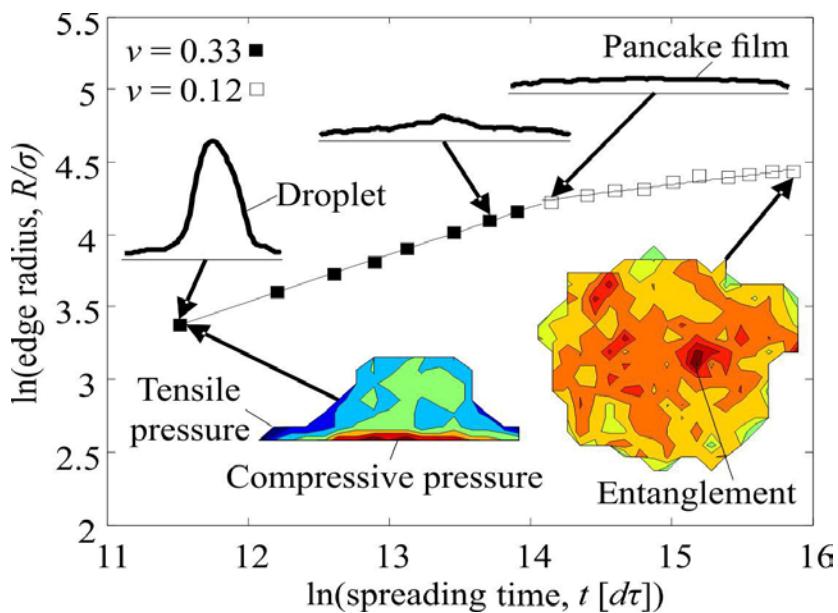
When fluids experience high pressure, such as one encountered by elastohydrodynamic (EHD) lubricants in ball bearings, their rheology may deviate from properties measured in ambient conditions. This may be due to pressure-induced glass transition, shear thinning and also thermal effects. To better understand how fluids behave in EHD contacts and their origins, local rheological information is necessary. In our group, laser-based techniques are used to investigate local rheology of lubricants in point contacts. Local rheological heterogeneity are detected. Depending on molecular structure of the liquids, and its pressure- and temperature-viscosity coefficients, shearing banding and shear thinning may occur. Several fluids are tested. It is hoped that through these experiments, a relationship between molecular structure, flow of lubricants and friction is established.

COLL 581

Anomalous spreading kinetics of polymer lubricant films

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Micro- and nanoscale devices and mechanisms are frequently covered with a thin film of a low surface energy polymer to protect against fouling and corrosion and to reduce adhesion and wear between contacting parts. When optimizing these films for lubrication, careful attention needs to be paid to the spreading kinetics of these molecular films as this determines how quickly the monolayer heals after being damaged during contact. Here, we report both experimental measurements of how fast lubricant films with a monolayer thickness spread over surfaces and molecular dynamics simulations of this spreading process. In contradiction to many previous studies, we show definitively that these polymers do not spread by simple diffusion, where the distance the film edge was predicted to move as distance $\sim (\text{time})^{1/2}$. Instead, the radius R of the area covered by the film spreading from a droplet is found to grow as $R \sim (\text{time})^v$, with $v \sim 1/3$ if a droplet is still present, and with $v \sim 0.1$ once the droplet has spread into a pancake shape. The figure shows an example result from our molecular dynamics simulations. Molecular dynamics simulations indicate that pressure within the droplet drives the flow into the precursor molecular film and that entanglement of polymers within the spreading film impedes this flow. These studies also provide important insights into how slip occurs at the molecular level at liquid–solid interfaces.



COLL 582

Quantitative analysis of Raman spectra of fatty acid lubricants under pressure

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Langmuir-Blodgett monolayers of zinc arachidate in a solid-solid contact have been studied by total internal reflection (TIR) Raman scattering in the pressure range of 3-6 kbar. The spectra show the retention of a high degree of chain order over this pressure range. The intensity of spectra acquired in the C-H stretching region with s-polarised

light decreases with increased pressure while p-polarised spectra in the same region increase in intensity with increased pressure, indicating a progressive increase in chain tilt with pressure. A quantitative model is presented for the interpretation of Raman intensities from thin films at interfaces based on integration of the electric field over the microscope objective, calculated using the Lorentz Reciprocity Theorem. This model is applied to the calculation of the tilt of the Zn arachidate chains under pressure, by analysis of the intensities of the symmetry and antisymmetric C-H stretches. The pressure is determined from the Newton rings and Hertz's theory of deformation. Hence the compressibility of the Zn arachidate monolayers under normal load can be calculated. The limitations of the model used to interpret the Raman spectra are discussed.

COLL 583

Controlling friction and adhesion using two-dimensional responsive microgels

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Adhesion and friction forces between two-dimensional (2D) colloidal arrays made of different particles were investigated. Soft-responsive and non-responsive hard particles of different size were used to create homogeneous 2D arrays. We showed that friction could be successfully modulated, with a friction coefficient varying by nearly *three orders of magnitude*, using covalently attached soft-responsive microgel particles. This important change in lubricating properties was correlated with the particle swelling behavior, i.e. the friction coefficient decreasing exponentially with increasing the swelling ability regardless of the particle size, degree of ionization of the particle and surface coverage. In addition, highly responsive and robustly attached microgel particles are able to sustain high-applied load (up to 600 atm) without significant surface damage. 2D arrays of non-responsive hard particles also gave rise to superlubricity due to particle rolling. Different mechanisms of lubrication for the different systems will be discussed.

COLL 584

Interfacial properties of fluid lubricants on bearing material surfaces

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This talk will highlight our research efforts towards understanding the interfacial properties of fluid lubricants on bearing steels and ideal material surfaces. Here we have used the blowoff technique to examine how an oil's dynamic viscosity (η) varies as a function of film thickness (h). To date, we have found that the strength and breadth of the $\eta(h)$ curve depends on the chemical composition of both the oil and the supporting surface. Comparatively, data also illustrates the central role lubricant additive packages

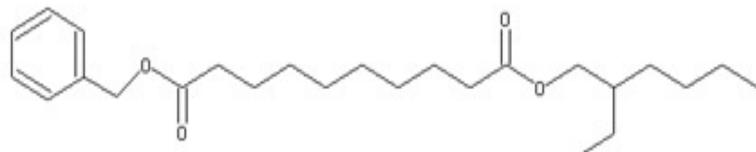
have as wetting agents. For unformulated oils, spontaneous dewetting is observed for both 440C and SiO_x surfaces, while formulated oils yield films that can, depending on film preparation method, be significantly more stable. Together, wetting stability and blowoff measurements suggest that an interfacial composition gradient is likely the origin of differences observed between the various formulations.

COLL 585

Formulation chemistry for ultra-stable ester-based oils

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Fluid dynamic bearing spindle motors are now ubiquitous in magnetic recording disk drives. Areas of continuous improvement for these motor bearings are limiting oil oxidation and minimizing the motor voltage and electric charge buildup in the oil. This talk describes the development of an ester oil formulation with antioxidants and a kinetic model for synergistic formulation of primary and secondary antioxidants. A kinetic model that includes the synergistic effects of primary and secondary antioxidants and metal catalyst on oil oxidation lifetime is employed to guide the formulation. Modeling of the elementary chemical kinetic reactions provides a significant benefit because it reduces the development cycle time and lowers the total cost to obtain improved motor lifetime. Novel polycyclic charge control additives have the potential to offer improved motor voltage stability as a charge conduction pathway parallel to the currently used aromatic amine antioxidants.



COLL 586

Relation between adsorption and nanoscale tribological performance of organic friction modifiers

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Although lubricant additives can be evaluated by dedicated engine tests, these tests are expensive, time-consuming and do not allow evaluating the mechano-chemical processes at the molecular scale. In this study we investigate the adsorption mechanisms of friction modifiers on steel surfaces using quartz crystal microbalance. The nature of the interaction, i.e. chemi- or physisorption, adsorption kinetics and

adsorbed mass on the steel surface was measured as a function of surfactant concentration in base oil, while the friction behavior of the layers was studied using lateral force microscopy in the absence of wear. The relationship between adsorption and friction force will be discussed for additives with different molecular structure.

COLL 587

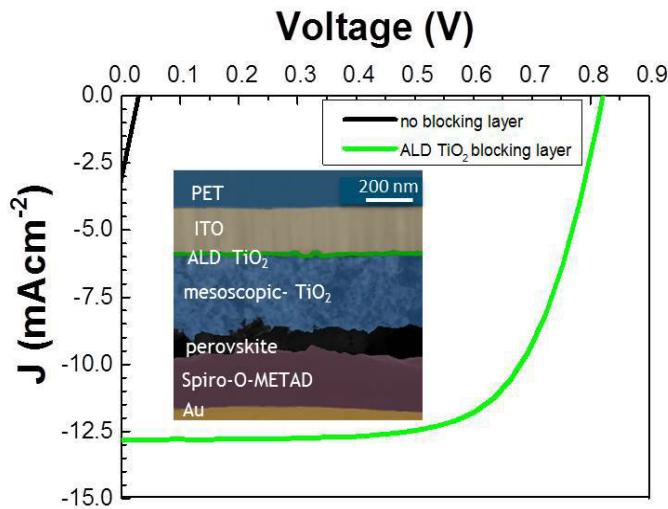
Plasma-assisted atomic layer deposition for energy conversion and storage devices

Mariadriana Creatore, m.creatore@tue.nl. Applied Physics, Eindhoven University of Technology, Eindhoven, Netherlands

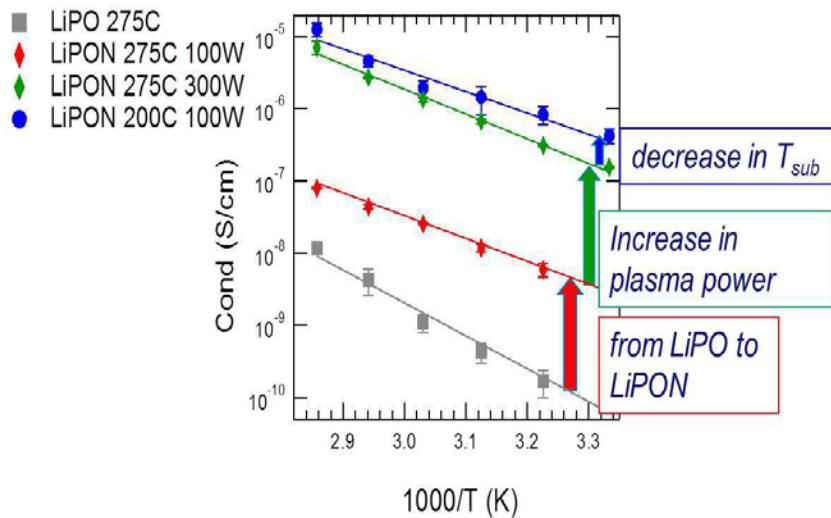
I will address the opportunities which atomic layer deposition (ALD) offers to the field of energy devices: control in (ultra-)thin film growth, compatibility with 3D-structures, suppression of charge carrier recombination processes at complex interfaces, and low temperature processing.

In the first case study, dedicated to organo-metal halide perovskite solar cells, I will describe the complex interface ITO/mesoscopic TiO_2 scaffold/ methylammonium mixed halide perovskite and I will focus on the application of low temperature plasma-assisted ALD TiO_2 (5-10 nm) on PET/ITO, as excellent blocking layer towards charge carrier recombination at the above-mentioned interface (Fig. 1). Furthermore, I will address the ALD deposition of ultra-thin (<< 1 nm) Al_2O_3 processed on the perovskite absorber, leading to an enhanced long-term device stability under humidity conditions ranging from 40% to 70%.

In the second case study, I will present plasma-assisted ALD as tool for nitrogen-doped lithium phosphate (LiPON) as solid electrolyte for 3D all-solid state Li-ion batteries. The optimized deposition process delivers a Li-ion conductivity of 5×10^{-7} S/cm at room temperature (Fig. 2), with good conformality on high aspect ratio pillars. Furthermore, a solid state battery device has been fabricated comprising a $\text{Li}_4\text{Ti}_5\text{O}_{12}$ cathode, a 70 nm thick ALD LiPON solid electrolyte and a metallic lithium anode, delivering a capacity of 0.3 Ah/cm³ and a stability of the LiPON layer versus Li, with no evidence of lithium dendrite formation.



I-V characteristics of perovskite solar cells with/out an ALD TiO₂ blocking layer. In the inset the cross-section of the perovskite solar cell is shown.



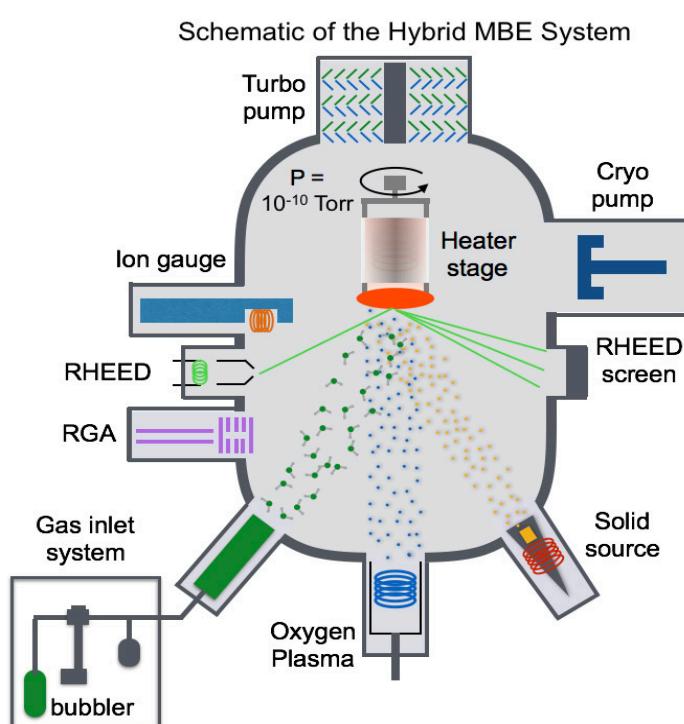
Li-ion conductivity of LiPON layers for different process parameters.

COLL 588

Tin alkyls as a tin source in hybrid molecular beam epitaxy

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The use of tin alkyls as precursors to epitaxial, single crystalline films of tin oxide and tin-doped perovskites in a hybrid molecular beam epitaxial system will be presented. With an rf-oxygen plasma as the oxygen source and tetraethyltin, three kinetic regimes corresponding to reaction-, flux- and desorption-limited growth were identified as a function of substrate temperature and tin precursor flux. Attempts to extend this process to the deposition of Sn-alloyed SrTiO_3 yielded relatively little tin incorporation. Switching the tin source to hexamethylditin, Sn_2Me_6 , allowed the growth of single crystal, epitaxial films with as much as 40 atomic % tin. To explore the extent of this unexpected effect, results from additional precursors including tetramethyltin will be presented. Computational studies aimed at understanding precursor chemistry in the high temperature region required to achieve single crystal films will be discussed.



COLL 589

Evidence for surface-plasmon-mediated precursor dissociation in ultrashort-pulsed-laser-induced surface chemistry

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Our group has designed a unique configuration of a SEM/focused ion beam (FIB) DualBeam system equipped with in-situ, coincident ultrashort pulse laser (UPL) capability. UPLs enable unprecedented temporal control over light with pulse durations in the picosecond to femtosecond regime. This allows incredibly high instantaneous power delivery over very short timescales. Due to ejection of material before energy can

be dissipated via phononic losses, it is thought nearly athermal ablation of materials.

Due to the coincidence of the SEM/FIB, the system lends itself well to the high resolution study of light interactions with surfaces. While many photon-induced chemical processes such as either direct photolysis or indirect light-driven pyrolysis have been studied for decades, the processes that might occur in the UPL regime are much less understood and studied. Here we report on use of this specialized system to investigate UPL-induced beam chemistry on a variety of surfaces.

We report on three distinct phenomena involving UPL-induced beam chemistry using a (trimethyl)methylcyclopentadienyl platinum precursor. Firstly, when sub-ablation-threshold laser intensity is used to irradiate surfaces in the presence of the precursor, it is possible to induce deposition with near IR wavelengths. Secondly, electron-beam-induced deposition (EBID) can be used to provide a nucleation layer, reducing the activation barrier for deposition. This has been demonstrated as an effective method for sub-diffraction limit laser induced deposition. Thirdly and most strikingly, the deposition morphology is highly ordered and periodic on plasmonically active substrates such as gold. The evidence presented indicates the possibility of a thermal pyrolytic process, a multiphoton-induced photolytic effect, or a combination of both on non-plasmonically active substrates. On plasmonically active substrates we hypothesize that the dissociation reaction is amplified by surface plasmon resonance and the boundary conditions imposed by the EBID nucleation layer.

COLL 590

Metalorganic chemical vapor deposition of 2D materials: Challenges and new approaches

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The spectrum of two-dimensional (2D) materials “beyond graphene” has been continually expanding driven by the compelling properties of monolayer films compared to their bulk counterparts. Device applications, however, require the ability to deposit single crystal 2D films over large areas necessitating the use of epitaxy techniques to control film orientation. Our studies have focused on the epitaxial growth of layered chalcogenide films, including WSe₂ and WS₂, by metalorganic chemical vapor deposition (MOCVD) on sapphire and related substrates. The choice of precursor has a significant impact on the nucleation and growth of 2D domains. When organic chalcogen sources are used, a thin defective graphene layer forms on sapphire during growth at elevated temperature (>700°C) which impedes W(Se,S)₂ nucleation and lateral growth. This problem was eliminated through the use of hydride sources such as H₂Se and H₂S thereby enabling single crystal monolayer and few layer films on sapphire.

We also developed a new graphene encapsulated growth process to synthesize ultra-

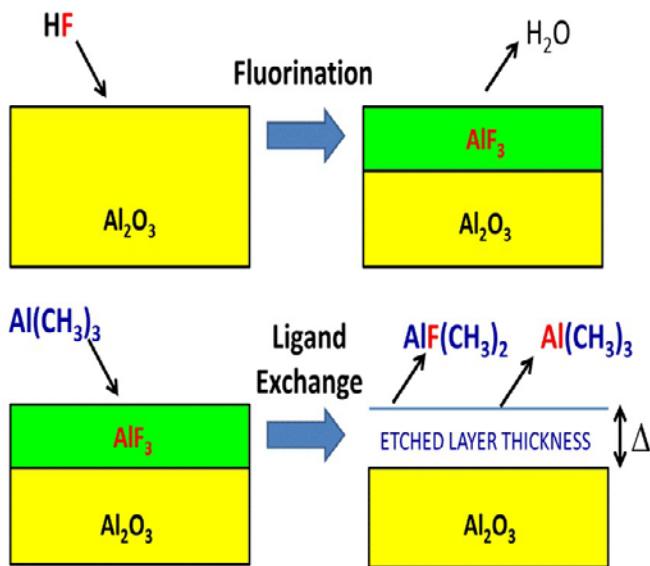
thin 2D layers of gallium nitride (GaN_x). In this process, MOCVD is used to deposit Ga atoms on the surface of epitaxial graphene formed on SiC. The Ga atoms intercalate beneath the graphene, diffuse along the graphene/SiC interface and are converted to gallium nitride via exposure to ammonia (NH_3). 2D GaN_x formed by this process exhibits a rhombohedral structure (R3m space group) in contrast to the wurtzite structure of bulk GaN. First principles calculations supported by optical spectroscopy measurements indicate that it is a direct gap semiconductor with a wide bandgap energy of ~4.8-4.9 eV making it of interest for heterostructure devices and UV emitters. Since many other elements can intercalate into graphene, it is possible that other 2D semiconductors that don't naturally exist as layered materials or are unstable and air sensitive can be synthesized using graphene encapsulated growth.

COLL 591

Atomic Layer Etching (ALE) using sequential thermal reactions: Atomic Layer Deposition (ALD) in reverse

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Atomic layer etching (ALE) is a thin film removal technique based on sequential, self-limiting surface reactions. ALE is the reverse of atomic layer deposition (ALD). This talk will discuss the gas-phase thermal ALE of metal oxides and metal nitrides using sequential fluorination and ligand-exchange reactions. HF and SF_4 are the reactants for fluorination. $\text{Sn}(\text{acac})_2$, $\text{Al}(\text{CH}_3)_3$, $\text{AlCl}(\text{CH}_3)_2$ and SiCl_4 are the metal precursors for ligand-exchange. The fluorination reaction converts the metal oxide or metal nitride to the metal fluoride. The metal precursor then accepts fluorine from the metal fluoride and donates one of its ligands to the substrate to produce volatile reaction products. Thermal ALE has been demonstrated for Al_2O_3 , HfO_2 , ZrO_2 and AlN. The etching rates are temperature dependent and are typically in the ~0.2-1.0 Angstrom/cycle range. The etching by thermal ALE is isotropic and surface roughness is observed to be lowered versus number of ALE cycles. In addition to other metal oxides and metal nitrides, thermal ALE should also be applicable to other materials such as metal phosphides, metal arsenides and elemental metals. One important application for thermal ALE is selective ALE. The ligands on the metal precursor for ligand-exchange can determine whether the metal in the metal fluoride can produce volatile reaction products. This talk will highlight Al_2O_3 ALE using HF and $\text{Al}(\text{CH}_3)_3$ and AlN ALE using HF and $\text{Sn}(\text{acac})_2$ as the reactants. Selective ALE will also be demonstrated for Al_2O_3 , HfO_2 , ZrO_2 , SiO_2 , Si_3N_4 and TiN using $\text{Sn}(\text{acac})_2$, $\text{Al}(\text{CH}_3)_3$, $\text{AlCl}(\text{CH}_3)_2$ and SiCl_4 as the metal precursors. Depending on time, results for ZnO ALE using HF and $\text{Al}(\text{CH}_3)_3$ will be presented that illustrate the new concept of "conversion-etch" where ZnO is first converted to Al_2O_3 prior to etching. The "conversion-etch" mechanism will enable the thermal ALE of a wider range of materials.



Al_2O_3 ALD Using HF & $\text{Al}(\text{CH}_3)_3$ as Reactants

COLL 592

Sequential infiltration synthesis for nanoscale patterning

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Sequential infiltration synthesis (SIS) is a technique for chemically modifying organic polymers using repeated, sequential exposures to a pair of precursor vapors. SIS is similar to atomic layer deposition (ALD), but whereas ALD results in dense, conformal films on a solid substrate, SIS infuses the bulk of an organic polymer to produce an organic/inorganic hybrid material with unique and tunable properties. SIS offers a number of exciting possibilities for advanced patterning and I will highlight these in my talk. For instance, aluminum oxide SIS dramatically enhances the plasma etch resistance of PMMA. Consequently, SIS on the PMMA allows dense, high-resolution (sub-20nm) patterns to be defined and transferred deeply into silicon, and increases the mechanical stiffness of the PMMA to prevent pattern collapse during wet development enabling the aspect-ratio patterning. Directed self-assembly (DSA) can also benefit from SIS technology. Block copolymers (BCPs) comprised of covalently linked, incompatible units such as polystyrene-block-poly(methyl methacrylate) (PS-b-PMMA) can spontaneously form ordered, periodic nanostructures and serve as etch masks. Unfortunately, the low etch resistance of polymers limits the utility of BCP films for lithography. However, by selectively infiltrating one of the polymer components using SIS, the BCP etch resistance can be greatly improved. For instance, trimethyl aluminum (TMA) will react preferentially with the carbonyl functional groups in PMMA, but will not

react with PS. In this presentation I will describe *in situ* measurements performed to study the selective chemistry that underlies SIS. These studies also have a direct bearing on selective ALD and CVD for the deposition of nanostructures.

COLL 593

Insight into the recombination kinetics of colloidal silicon nanocrystals

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Silicon nanocrystals offer tangible opportunities for advancing several technical fields in the photonics sector. The earth abundance and biologically benign nature of silicon suggest the potential for a green alternative to the metal-chalcogenides, yet a precise understanding of the complex nature of photoluminescence in silicon nanostructures has eluded scientists for more than two decades. In particular, a clear understanding of the interplay between quantum confinement and surface-passivation chemistry in an indirect band-gap material such as silicon has not yet been achieved. In this presentation, we will address these challenges by examining the various recombination channels using fluorescence spectroscopy. Specifically, we address the origin of both 'fast' (ns) and 'slow' (s) photoluminescence relaxation in precisely size-resolved colloidal silicon nanocrystals synthesized via both solution- and plasma-based methods.

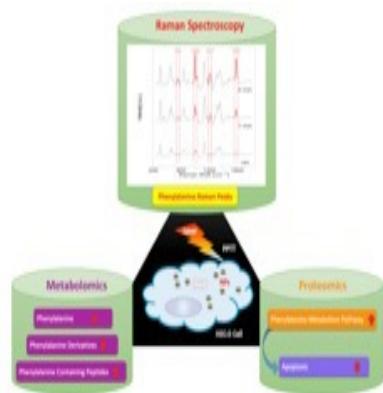
COLL 594

Simultaneous time-dependent surface enhanced Raman spectros-copy, metabolomics and proteomics reveal cancer cell death mechanisms associated with Au-nanorod photo-thermal therapy

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In cancer plasmonic photothermal therapy (PPTT), plasmonic nanoparticles are used to convert light into localized heat leading to cancer cell death. Among plasmonic nanoparticles, gold nanorods (AuNRs) with specific dimensions so as to absorb the near-infrared (NIR) laser light have been widely used. The detailed mechanism of PPTT therapy, however, still remains poorly understood. Typically, surface enhanced Raman spectroscopy (SERS) has been used to detect time-dependent changes in the intensity of the vibration frequencies of molecules that appear or disappear during different cellular processes. A complete proven assignment of the molecular identity of these vibrations and their biological importance have not yet been accomplished. Mass spectrometry (MS) is a powerful technique that is able to accurately identify molecules in chemical mixtures by observing their m/z values and fragmentation patterns. Here, we complemented the study of changes in SERS spectra with MS-based metabolomics and proteomics to identify the chemical species responsible for the observed changes in

SERS band intensities. Using PPTT, we observed that the bands at around 1000, 1207 and 1580 cm⁻¹ increase in intensity, which were assigned in the literature to phenylalanine with dispute. Our metabolomics results showed increased levels of phenylalanine, its derivatives and phenylalanine-containing peptides, providing evidence for more confident SERS peak assignments. To better understand the mechanism of phenylalanine increase upon PPTT, we combined metabolomics and proteomics results through network analysis, which proved that phenylalanine metabolism was perturbed. Furthermore, several apoptosis pathways were activated, via key proteins (e.g. HADHA and ACAT1), which are consistent with the proposed role of altered phenylalanine metabolism in inducing apoptosis. In conclusion, our study shows that the integration of the SERS with MS-based metabolomics and proteomics can assist the assignment of signals in SERS spectra, and further characterize the related molecular mechanisms involved in the cellular processes involved in PPTT.

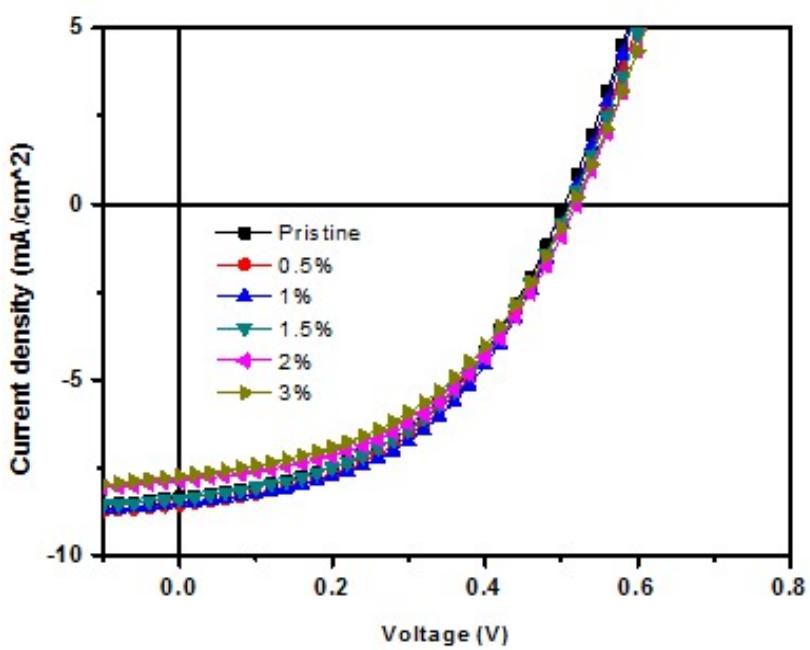
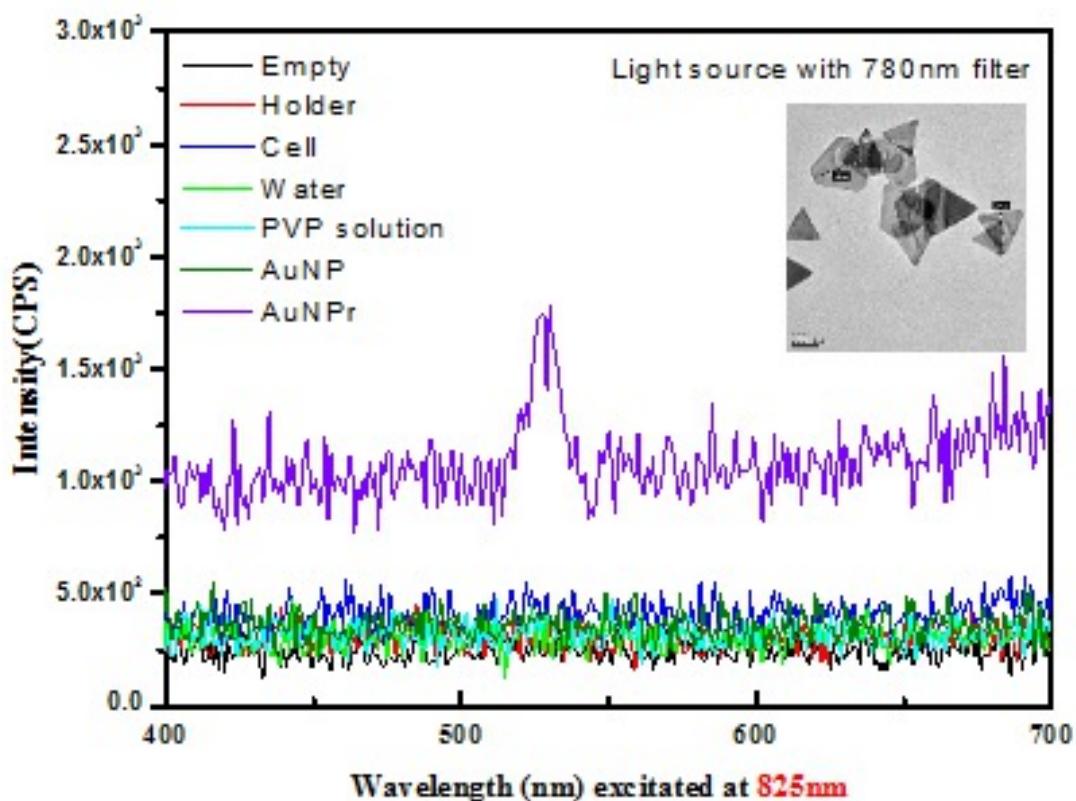


COLL 595

Synthesis of gold nano-prism with dual effects of plasmon resonance and non-linear optical property to improve the performances of organic solar cell

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We have developed a simple and versatile method to synthesize the gold nano-prism (AuNPr) by growing it through seed-mediation and thereafter separating it via sedimentation method. The grown AuNPr showed strong plasmonic resonance peak localized near NIR region. Apart from strong plasmonic effect, we also observed the non-linear optical behavior which has not been observed in metal nano-prism structure before. It was confirmed using photoluminescence(PL) spectroscopy where excitation wavelength of 825nm produced luminescence peak at around 525nm. To apply the dual properties of plasmonic effect and up-conversion emission, we fabricated various organic bulk heterojunction solar cells utilizing these AuNPr in different configurations.



COLL 596

Three dimensionally assembled gold nanostructures for visible light-driven water oxidation

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Plasmonic gold (Au) nanostructures are great attractive for visible-light-driven water splitting due to their excellent chemical stability and strong visible light absorption via localized surface plasmon resonance (LSPR). The absorbed light in the Au nanostructures can be converted to hot carriers via the decay of LSP that can be subsequently utilized for photocatalytic water splitting. Here we introduce a plasmonic photoanode comprising three-dimensional (3D) porous network of colloidal gold nanoparticles (AuNPs) coupled with an oxygen evolving catalyst. The 3D Au nanostructured photoanode is prepared by the layer-by-layer (LbL) assembly of negatively charged AuNPs and cationic polyethyleneimine (PEI) on a titanium oxide (TiO_2) thin layer. First, the hot carrier transfer in the photoanodes is investigated depending on the interfacial properties under visible light illumination. The photocurrents increase with the removal of the PEI layer by calcination because the PEI layer prevents the hot carrier transfer from AuNPs to TiO_2 . The multi-layered assembly varies the structural and optical properties of the Au nanostructures that are associated with the generation and injection of hot carriers. The unique 3D porous networks of the multi-layered Au nanostructures are retained during thermal annealing with a silica layer that is removed by a 30 % KOH solution, which absorb a broadband solar spectrum from visible to NIR region. Furthermore, IrO_2 hydrosols are assembled on the multi-layered Au nanostructures as water oxidation catalysts. Plasmonic photocurrents significantly increase with the increased number of AuNP layers under visible light illumination. The results indicate that the hot carrier generation in the Au due to the SPR increases with the enhanced light absorption. Our study suggests that the optimized plasmonic nanostructures based on AuNPs will provide a promising light-harvesting platform for sustainable and efficient solar water splitting in the visible region.

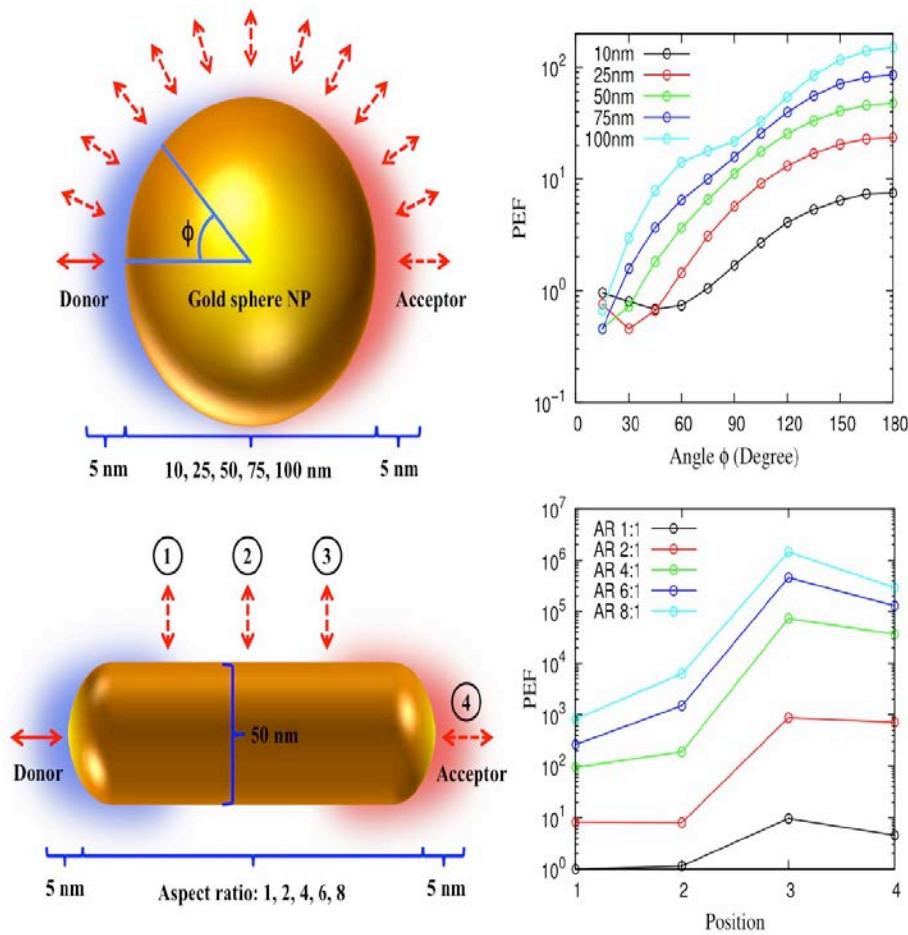
COLL 597

Plasmon-coupled resonance energy transfer: A real-space real-time computational electrodynamics approach

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Nanoplasmonics has significant influence on physical processes in molecular systems. One particular interest is the plasmon-coupled resonance energy transfer (PC-RET). Here, we present a study on such phenomenon using the time-domain electrodynamics

resonance energy transfer (TED-RET) method. This method is a real-space real-time computational approach based on classical electrodynamics, utilizing the finite-difference time-domain (FDTD) method to obtain the electric field generated by the donor molecule in the presence of nanoparticles. For method validation, we show that without the nanoparticles, our numerical results on the RET rate in homogeneous media, such as vacuum and water, are exactly the same as those obtained from the analytic solution of quantum electrodynamics. We then demonstrate that with the advantage of the plasmonic effect from gold nanoparticles, the RET rate between a pair of donor-acceptor molecules can be raised by a factor as high as 10^6 times. Meanwhile, the long-range decay of the RET rates can be significantly reduced, and the spacial "node" in RET rate can be shifted or possibly eliminated. Another interesting observation is the suppression of RET rate in certain regions near the nanoparticles, due to the local destructive interference between the electric field from the molecular donor dipole and the induced field from the nanoparticles. The results suggest promising future utilization of PC-RET in areas involving light harvesting or sensing, amongst other applications.



Demonstration of plasmonic enhancement factor (PEF) on RET rate through examples of nanospheres (*Top*) and nanorods (*Bottom*). In both cases, solid red arrows represent the transition

dipoles of donor molecules, while dashed arrows represent the possible locations of acceptors molecules.

COLL 598

Development and molecular understanding of Plasmonic Photothermal Therapy (PPTT) in combating cancer

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In cancer plasmonic photothermal therapy (PPTT), gold nanoparticles (AuNPs) are used to convert light energy into localized heat leading to cancer cell death. Among plasmonic nanoparticles, gold nanorods (AuNRs) have been widely used as they absorb near-infrared (NIR) laser light (safe to biological system). Herein, **1)** we developed a new AuNRs formulations techniques, yielding better generation of AuNRs, enhanced cancer cell targeting, and thus is more selective and efficient. On the other hand, the detailed mechanism of PPTT, still remains poorly understood. Thus, **2)** upon PPTT we used Surface Enhanced Raman Spectroscopy (SERS) to detect time-dependent changes in the intensities of the vibration frequencies of molecules. We complemented the study of changes in SERS spectra with metabolomics, proteomics, western blots through network analysis. It showed several apoptosis pathways (favorable death pathway compared to necrosis) were activated, which are consistent with the proposed role of altered phenylalanine metabolism in inducing apoptosis. **3)** Studying the AuNPs' effect on mechanical properties of cancer cells using high-resolution three dimensional imaging and atomic force microscope. ^[8] **4)** Moving from cells to animals, In Xenograft mice we explored the death pathway using proteomic analysis and immunohistochemistry in mouse tumor tissues, indicated that PPTT trigger cancer death via apoptosis with no remarkable toxicity to mice, even after 15 months from treatment. **5)** Furthermore, the feasibility of PPTT has been verified on natural tumors in dogs and cats without any relapse or toxicity effects even after 1 year of treatment. In conclusion, together these data on cells, mice, cats and dogs demonstrated that our AuNR-PPTT inducing apoptosis is effective and safe for cancer therapy provides a strong framework for application.

COLL 599

Assembly of ring-like nanostructure arrays via drop evaporation method

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Ring-like materials have received increasing attention due to their structural symmetry, unique properties and great potentials in a wide spectrum of technological applications such as data storage, photonic devices, and sensor. In this talk, we will present a simple

method to fabricate ring-like nanostructure arrays over regions of several tens of mm². Chemically functionalized gold nanoparticles are assembled via drop evaporation on a monolayer of silica colloids. The morphology of ring-like nanostructure can be controlled by the experimental parameters such as substrate temperature, nanoparticle concentration, packing of the colloids, and the ligands on the nanoparticles. In particular, the sizes of resulted rings are mainly determined by colloidal sizes and humidities during experiments. These ring structures with possible peculiar photonic properties might be widely utilized in a variety of optical applications.

COLL 600

Photo-oxidative degradation of single giant quantum dots

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Colloidal quantum dots have many applications in biological research, sensing technology, energy-saving device technologies, and high color quality devices; quantum dots are now ubiquitous in displays including HDTVs and computer monitors. Unfortunately, however, quantum dots are susceptible to photodegradation that reduces functionality over a long period of time. In displays, degradation is avoided by protective device architecture (such as polymer encapsulation), but an ideal cost-effective solution would involve development of air- and oxygen-tolerant single quantum dot structures. For this poster, we will detail time-resolved fluorescence studies of the degradation of quantum dots. Single quantum dot spectroscopy shows that thick-shell QDs display structure-dependent photostability; we will report our investigations into the mechanism responsible for this variation in photostability. Additionally, we have found that different quantum dot structures undergo distinct degradation processes. We will also compare single quantum dot results with ensemble measurements of quantum dot photodegradation to demonstrate the utility of performing degradation studies at the single particle level.

COLL 601

Highly sensitive surface-enhanced Raman scattering substrate of Ag thin film fabricated by gas-timing RF magnetron sputtering

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Surface texture and engineering of silver (Ag) thin films fabricated by sputtering technique are very attractive for several advanced technologies especially on surface enhanced Raman scattering (SERS) substrate. It has been known that crucial factors of highly-sensitive SERS substrate based on Ag thin films are depended on texture orientation and morphology of thin films. Although several research groups have demonstrated the controllability in the texture and surface morphology of sputtered Ag thin films, the external energy sources such as substrate bias voltage, heating the substrate during growth or post annealing and ionized magnetron sputter deposition (IMSD) are necessary to include. Such external additional techniques make a complex and high cost operation and are not available to fabricate sputtered Ag film at room temperature. Here we demonstrate a special technique to control a texture orientation of Ag thin films via using gas-timing (GT) RF magnetron sputtering. By utilizing GT technique, a dense structure and a high ratio of (111)/(200) of Ag films could be obtained without any applying additional energy sources. We found that the GT technique not only provides the ability to adjust the number of sputter species from the target, but also generates the self-energy assisted deposition which related to the atomic peening effect. Furthermore, we found that high (111)/(200) ratio of Ag films strongly affects on the SERS activity of Ag films due to hot spot effect. Our results highlight that the texture engineering of metal thin films could be accomplished by using GT technique.

COLL 602

ALD-protected polyoxometalate water oxidation catalysts immobilized on light-absorbing metal oxide thin films for enhanced durability and photocurrent density

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Fast and selective polyoxometalate (POM) water oxidation catalysts (WOC) have been previously shown to interact with metal oxide surfaces with cationic surface properties. The system with TiO₂ nanoporous films and Ru₄Si₂ has elucidated evidence of a strongly bound catalyst that retains water oxidation properties under UV-illumination. In this work, we have enhanced the stability of Ru₄Si₂ under turnover conditions using atomic layer deposition (ALD) while increasing the photocurrent density of the system with visible light absorbing hematite thin films. Characterization techniques including FTIR, XPS, EDX and voltammetric studies indicate that Ru₄Si₂ remains intact on the hematite surface with 4 nm of ALD protection.

COLL 603

Nanoparticles' interactions with viruses

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Viruses kill every day in large numbers especially in low-income countries. Any given day ~1600 children age 1 to 5 die of diarrhea (mostly due to rotavirus). More than 5000 people have died of Ebola in the last outbreak. On the other hand, viruses also save lives as vaccines; unfortunately, because of their thermal instability, vaccines need constant refrigeration. This generates a 'cold chain' need for vaccines that contributes to >50% of the costs of vaccination programs and generates significant logistic problems especially in developing countries. The 'cold chain problem' is considered among the top challenges for global vaccinations. In this talk, these problems will be addressed with the tools of nano-medicine. Results show that nanoparticles (and equivalent small or macro-molecules) can have a wealth of interactions with viruses. Depending on the particles' coating and on the specific virus, particles can (i) thermally stabilize viruses, (ii) inhibit their cell entry, or (iii) be virucidal (i.e. permanently in-activate them outside their host). Each of these interactions can be leveraged to address a key biomedical challenge that viruses pose. A series of systematic studies on virus interactions with nanomaterials will be presented to identify the mechanisms that maximize thermal stabilization or virucidal action. The former will be used to produce additives for vaccines capable of keeping viral vectors stable for more than two months at 37°C, thus directly addressing the 'cold chain problem'. Virucidal efficacy is used to create drugs able to reduce the mortality of infections due to Dengue or Hepes. In all cases the focus used in this research is to find nanoparticles, macro- or small molecules that are safe and inexpensive so that the translation of this research in drugs for low-income countries could be deemed as feasible in the near future.

COLL 604

Nanoscale metal-organic frameworks: Emerging materials for catalysis

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Distinct from classic inorganic nanoparticles of solid cores, nanoscale metal-organic frameworks (NMOFs) are of ordered crystalline pores with tunable composite, size and volume, which provide an ideal platform not only to manipulate the reaction active sites but also to understand the structure-functionality relationship. In this presentation, we will introduce two recent works involving catalytic application of NMOFs.

COLL 605

Molecular mechanisms in formation of metal oxide colloids in sol-gel processes

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Metal oxide nanoparticles emerge via nucleation in sol-gel processes in organic media. Both hydrolytic and non-hydrolytic reactions produce in one step nano-size molecular species, with apparent core-shell structure, resembling oxometallates formed on partial hydrolysis in both aqueous and organic media. The core is always well-ordered and often can be identified as crystalline even by X-ray studies, and more securely by electron diffraction in TEM. It bears generally an imprint of the corresponding solid phase resulting from dense packing of metal cations and oxygen anions. The shell contains residual organic ligands inherited from the precursor molecules and is amorphous. This insight into reaction mechanisms permits to control the size and shape of resulting particles, their hydrophilicity/hydrophobicity and surface reactivity. Hydrolytic approach leaves most often residual hydroxide groups and solvating water molecules on the surface of the particles contributing to the amorphous shell. Higher temperature solvothermal reaction offers generally much better crystallinity than the room temperature hydrolytic one. Elevated temperature helps to improve the diffusion of metal ions and removes the hydroxide and organic residues from the surface. The control of crystallinity and composition and structure of the shell define surface interactions of the produced particles and their both solution and chemical stability in biological systems and in the environment.

Application of these insights open for such new applications as generation of biocompatible colloids for bioencapsulation and drug delivery via both hydrolytic and solvothermal approaches. Exploiting the surface reactivity for grafting of metal oxide colloid particles on carbohydrate and protein structures permit to build up new types of biocompatible nanocomposites for drug delivery and wound healing.

COLL 606

Toward the self-assembly of layered multi-nano-composite films with complex anisotropies

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A longstanding roadblock in materials science lies in the controlled preparation of composite materials composed of more than two components and this holds especially true for nanoscale multi-composites. This is due to the fact that phase separation phenomena at the micro- and nanoscale frequently prevent to organize the individual components in a composite with precise distances between them. Over the last 25 years our team has focused on the development of one-dimensional multicomposites, so-called Layer-by-Layer (LbL) assembled films, in which the sequence of different materials and the distances between them are precisely controlled along the layer normal.

An even greater challenge in materials science lies in the preparation of anisotropic materials which possess physical properties, for example optical, electronic or

mechanical properties that differ in different directions of space. Particularly interesting components for the preparation of anisotropic multi-component materials are anisotropic nanoparticles, such as nanofibrils, nanowires or nanorods whose physical properties can often be tuned by varying their aspect ratio. While the physical properties of such nano-objects are usually highly anisotropic at the single particle level, their controlled integration into composites or multicomposites is even more difficult than the integration of their spherical counterparts.

Macroscopic anisotropies are commonly induced by external electrical or magnetic fields, by surface templating or mechanical stretching, but all of these techniques impose severe restrictions with respect to the requirements for the size and the chemical nature of the materials onto which the composite films can be deposited. For keeping the alignment method as general as possible we have therefore recently developed grazing incidence spraying as a LbL-compatible technique for aligning anisotropic nanoparticles essentially by liquid shear with moderate to high aspect ratios in the form of LbL-films.

Here we discuss the preparation and the anisotropic properties of thin films composed of cellulosic nanofibrils and of silver nanowires. The first materials we made have already shown highly interesting properties. Cellulose nanofibrils allow to prepare biodegradable transparent objects with the tensile strength of steel and silver nanowires allow to challenge some of the plasmonic properties of metallic nanostructures that could previously only be prepared by nanolithography.

COLL 607

Surface enhanced Raman scattering on cuprous oxide nanomaterials

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There are increasing interests on using semiconductor nanomaterials as active substrates for surface-enhanced Raman scattering (SERS). In this talk, I will present our recent work on the syntheses and manipulation of nanoscale cuprous oxide nanomaterials, as well as their application as SERS active substrates. Cuprous oxide nanomaterials with various structures, porosity, and crystallinity will be explored and their SERS activities are evaluated. Together with the results of FDTD simulation, we believe that the SERS activity of cuprous oxide nanomaterials can be interpreted as a synergistic effect of strong chemical interactions, localized electromagnetic field enhancement, and hierarchical porosity of the nanostructures. We also find that micro-size cuprous oxide microcrystals can possess SERS activity after a process of chemical etching. An even interesting result is SERS-active supercrystals of assembled cuprous oxide nanocubes. Overall, our work introduced a possible application of cuprous oxide nanomaterials in the field of SERS detection. Considering the photocatalytic activity of the cuprous oxide, these SERS active nanomaterials might be very helpful in studying certain energy storage materials.

COLL 608

Seeded growth and chemical transformations in metal nanoparticles

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Metal nanoparticles display very interesting optical properties, related to the interaction of light with conduction electrons, resulting in coherent oscillations in resonance with certain frequencies, which are called localized surface plasmon resonances (LSPRs). Such LSPRs can be readily modulated through the size and morphology of the nanoparticles, so that the whole visible and near-IR ranges can be covered. Thus, it is extremely relevant to devise methods for the synthesis of particles with different non-spherical geometries. Additionally, geometrical anisotropy can lead to anisotropy of the optical response, which adds to the potential for light manipulation. Many different metal nanoparticles can be prepared by means of colloid chemistry methods, including nanorods and nanopolyhedra. Further tuning of optical properties can be achieved by post-synthesis chemical transformations, including the growth of sharp branches or the creation of internal holes and gaps, which offer advantageous application, e.g. in surface enhanced spectroscopies.

In this talk we shall present some ideas for the combination of anisotropic seeded growth and chemical transformations in metal nanoparticles. Growth mechanisms and thorough characterization will be presented for several recently developed systems.

COLL 609

Award Address (ACS Award in Colloid Chemistry sponsored by Colgate-Palmolive Company). Self-Assembly of nanoparticles

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Inorganic nanoparticles (NPs) have the ability to self-organize into variety of extended and terminal structures, as do many molecular and nanoscale compounds, given a sufficient number of translational and rotational degrees of freedom. Analysis of experimental data for all NPs indicate a general trend of self-assembly under a much wider range of conditions and having much broader structural variability than “building blocks” from organic matter. Remarkably, the internal organization of self-assembled structures spontaneously produced by NPs rival in complexity and functional sophistication to those found in biology. Multiscale collective effects make NP-NP interactions no less fascinating than those of naturally occurring proteins. In this talk, I will address the following questions:

- (a) What are the differences/similarities of NP self-organization compared with similar phenomena involving organic/biological building blocks?
- (b) What are the forces and related theoretical assumptions essential for NP interactions?

(c) What is the fundamental and technological significance of NP self-assembly? Attention will be given to the apparent parallels between self-organization of globular proteins and NPs that lead to the conclusion of biomimetic properties of inorganic nanostructures. The possibility of creating nanoscale bionic architectures stemming from these properties will be argued on the basis of early experimental results. Self-organization of chiral nanostructures will illustrate the importance of subtle anisotropic effects stemming from collective behavior of NPs and non-additivity of their interactions. Chirality transfer from circularly-polarized photons to NPs and its relationship to the origin of homochirality on Earth and origin of life will be discussed. LBL deposition provides the path for technological translation of NP self-organization which will be exemplified by self-assembly of anode/cathode for lithium batteries, highly conductive high strain composites, and chiroplasmonic composites for polarization optics.

COLL 610

Award Address (ACS Award in Surface Chemistry sponsored by the ACS Division of Colloid & Surface Chemistry). Understanding of selective oxidation catalysis through surface science

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The design of efficient catalytic processes increasingly calls for design principles. The tools of modern surface chemistry provide the basis for such design. The case study of selective oxidation of alcohols using gold catalysis is used to illustrate the predictive value of fundamental surface science studies. The work described will demonstrate the high value added of model studies on Au single crystals that integrate reactivity studies with imaging, spectroscopy, and density functional theory for predicting catalytic behavior of nanoporous Au, an alloy with 1-3% Ag, under continuous flow at atmospheric pressure. The author will also discuss the broad application of fundamental surface chemistry as reflected in the work of former students, postdoctoral fellows and collaborators.

COLL 611

Award Address (ACS Award for Research at an Undergraduate Institution sponsored by Research Corporation for Science Advancement). From nanogravimetry, photovoltaics, and plasmonics to elastic light scattering and Raman spectroscopy for theranostics and environmental remediation

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The exciting developments in nanoscience and nanotechnology offer promising perspectives in many fields of life and scientific endeavor. In our studies, the

nanoparticles, nanorods, molecular markers, beacons, and other nano building blocks have always played a key role. Our involvement in nanoparticle syntheses and investigations of interparticle interactions using resonance elastic light scattering (RELS), surface-enhanced Raman scattering (SERS), quartz crystal nanogravimetry (QCN), fluorescence, and colorimetric techniques have resulted in new insights concerning the mechanisms of ligand exchange at nanoparticle surfaces, induced assembly, and nanomaterial surface energy transfer (NSE). As the nanoparticles on solid surfaces considerably enrich the interfacial phenomena, we have incorporated them into the designs of biosensing devices, together with antibodies or DNA probes for recognition of biomarkers of oxidative stress, cancer, and other diseases. We have also developed nanoparticle-based SERS/electrochemical biosensors for studies of DNA damage. Moreover, the functionalized nanoparticles have been utilized for theranostic applications to combine the disease diagnostics with therapy. We have carried out extensive investigations of gold nanoparticle (AuNP) nanocarriers for targeted drug delivery where the targeting ligands attached to nanocarriers were able to recognize cancer cells, enabling the delivery of chemotherapeutic drugs directly to the cancer tissue, thus reducing the damage to healthy cells. Drugs, such as doxorubicin, methotrexate, azacitidine, gemcitabine, dabrafenib, leucovorin, etc. could be covalently bound to nanocarriers and subsequently released in a cancer tissue. Furthermore, our studies have also included prevention. Hence, a considerable attention has been paid to the investigations of the mechanisms of reactive oxygen species (ROS) generation and to counter their damaging activity, as well as to the environmental pollution remediation by photodegradation of pollutants using transition metal oxide semiconductor electrodes. We have also developed field testing methods for the detection of pesticide and herbicide pollutants. In addition to the health- and environment-related fields, we have also investigated other phenomena of the nano world and their applications to design devices, such as graphene@WO₃ hybrid supercapacitors, fast electrochromic devices, quantum conductance nanobridges, photovoltaics, and others.

COLL 612

Nano Letters Award Lecture: Cool chemical transformations and hot carrier upconversion: Emerging plasmonic methods to improve renewable energy technologies

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It is predicted that average temperatures will increase by more than 2°C unless 90% of our energy is from renewable sources by 2050. And yet, in 2015, renewable energy sources only accounted for approximately 15% of world energy consumption. Plasmonic materials offer a promising avenue to help bridge this gap – both improving solar energy conversion efficiencies and enabling new insights into energy storage device operation. This presentation will describe two new plasmonic methods to both understand and improve renewable energy conversion and storage. First, I will describe a technique based on plasmon- and electron-spectroscopy to investigate intercalation-driven phase

transitions, such as those that occur in batteries and fuel cells, *in-situ* and with nanometer-scale spatial resolution and millisecond time resolution. As a model system, we focus on the hydrogenation of palladium nanoparticles. We find that single-crystalline nanoparticles do not exhibit phase coexistence, in contrast to polycrystalline particles. Additionally, we find that certain nanoparticles can self-heal during charging, morphing from a single-crystalline particle to a disordered one and back to a single crystal. This work points towards champion nanostructures for energy storage devices with the longest lifetimes and highest storage capacity. Then, I will describe a new solar upconverting scheme to exceed the Shockley-Queisser limit in solar technologies. This scheme is based on hot-carrier injection from a plasmonic absorber to an adjacent semiconductor. The plasmonic system both induces upconversion based on injection of hot-electrons and hot-holes and also enhances light-matter interactions. This scheme does not require coherent illumination, is a linear process, and can be broadband, paving the way towards high-efficiency upconversion that could enable record single-junction solar cell efficiencies.

COLL 613

Cage molecule self-assembly

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We have shown that upright, symmetric cage molecules self-assembled on surfaces have simple domain and defect structures. Unlike linear molecules, such as alkanethiols on Au{111}, these cage molecules do not tilt and do not conformationally relax. The lattices of the cage molecules are determined by the projections of the cages on the surface. Thus, different isomers, such as carboranethiols on Au{111}, form identical lattice structures. These monolayers enable key tests of simple phenomena, such as the effects of dipole moment direction and amplitude. For example, molecules with dipoles parallel to the surface form nonpolar monolayers and outcompete molecules with dipoles normal the surface, which form polar monolayers. These properties can be measured both at the macroscopic and nanoscopic scales. We understand the enhanced stability of the nonpolar surfaces to aligned dipoles in the monolayers and set out to measure such effects. Using combinations of spectroscopic imaging and novel image analyses, we find that dipoles do align, even across domain boundaries. We use mixed self-assembled monolayers of carboranes to tune and to optimize the band alignment of organic electronic devices without changing the morphology of the active layer. We also assemble multifunctionalized cage molecules and show that we can protonate and deprotonate thiol(ate)s to change the valency of attachment to the surface through simple reactions.

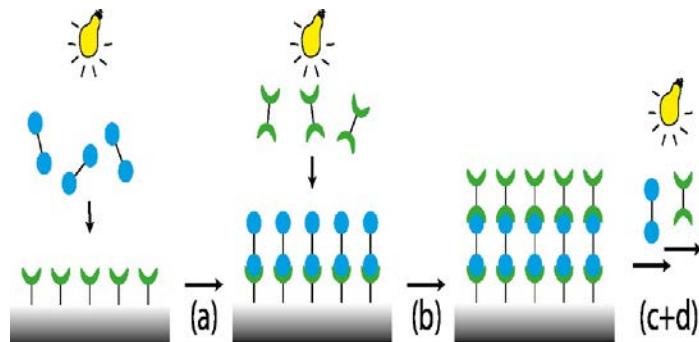
COLL 614

Development of photo-activated iodo-ene reaction for molecular layer deposition

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Molecular layer deposition (MLD) is an emerging technique, which enables molecular precision in the formation of high quality, nanometer-thick polymer films. This green, vapor-phase process to create conformal coatings is appealing for industrial implementation compared to common solution-based techniques. Its unprecedented molecular control, achieved by sequential deposition of bifunctional organic precursors in a self-limiting layer-by-layer fashion, surpasses what is currently achieved by solution and other vapor-phase techniques. Combined, these attributes make MLD increasingly important for several nanoscale applications, such as microelectronics, sensors, and energy technologies.

Our research focuses on the development of new reaction types compatible with MLD with the aim of creating new capabilities. The selection of coupling chemistries currently applicable to MLD is strongly limited, because MLD proceeds from the gas-phase in the absence of catalysts and solvent, and pH cannot easily be changed. We will present the use of light as a direct energy input to facilitate otherwise infeasible reactions, and most importantly how photo-activation opens a novel direction for MLD to create a much broader class of nanoscale polymer films. Here, the photo-activated iodo-ene reaction is implemented in MLD to create new carbon-carbon bonds without the need for a catalyst. We demonstrate how a controlled, surface radical step-growth polymerization with a growth rate of 3 Å/cycle is obtained. This new MLD thin film material exhibits excellent stability. Ellipsometry, XPS, and IR analysis are used to examine the nanoscale polymer films, and to elucidate the mechanism of this new type of photo-activated MLD. Finally, the versatility of the photo-activated iodo-ene MLD process will be discussed. We demonstrate the use of different ene precursors and examine how electron donating versus electron withdrawing substituents affects the polymerization.



Schematic illustration photo-activated MLD. One MLD cycle includes pulses of two different bifunctional precursors, (a) and (b). This cycle is repeated (c+d) in the controlled growth of nanoscale polymer film.

COLL 615

Perfluoropentacene films on gold surfaces grown by supersonic molecular beam deposition

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Here we will present a study of perfluoropentacene (PFP) films on gold surfaces with different morphologies and coatings. Specifically, we used gold films on mica, template stripped gold surfaces and thiol coated gold surfaces as substrates. We will discuss wetting properties and morphologies of PFP films grown on these substrates by means of supersonic molecular beam deposition. The effect of PFP deposition rate, deposition energy and film thickness will be discussed. Finally, construction of a new helium diffraction setup that will be used for characterizing PFP films will be discussed.

COLL 616

Patterning diverse metallic materials directly from solution using laser thermal voxels

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Materials processing has proved to be a rich area for applications of laser technologies. The ability to deliver large energies with high precision and accuracy has facilitated laser materials processing techniques of cutting, welding, ablating, and curing. Laser-driven additive manufacturing processes such as laser powder sintering, laser forward transfer and other laser direct write (LDW) techniques have demonstrated potential to drastically expand the reach of next generation two and 3D patterning across diverse technologies. However, a major roadblock that faces the wide dissemination of these approaches is the limited range of materials that are compatible, particularly 3D printing processes operating at the finest scales (nano to micro) such as multiphoton lithography (MPL) which has been generally limited to photocurable polymers and resists. Thus, recent studies have begun to explore direct patterning of metals such as silver and gold. We recently showed that nanocrystalline platinum and palladium could be patterned using MPL via a photo-reduction mechanism. Unfortunately, this procedure is not readily translatable to other aqueous metal ion solutions given the wide range of reduction potentials across, for instance, the transition metals and the limited availability of suitable photo-activatable reducing agents. However, we have found that patterns could be extending from an existing metal in a metal ion precursor solution using a continuous wave (CW; as opposed to high-energy pulses required to initiate multiphoton processes) laser beam. Calculating a steady state temperature rise at the ‘hot edge’ (where the laser focus and metal interact) of > 1000K, we reasoned that the precursor could be thermally precipitated or reduced, as these conditions are analogous to

hydro/solvothermal chemistry. We show that translation of these laser thermal voxels (LTVs) provides a general route for surface patterning at ~ 1 micron scale of a wide range of metals and metal oxides, including functional nickel metal, a historically challenging direct write material.

COLL 617

Hybrid Monte Carlo and continuum modeling of electron-beam induced processes using liquid reactants

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Electron-beam induced deposition and etching using bulk liquid reactants yields high-purity metal nanostructures (e.g. Pt, Au, Cu, and Ag), introduces new possibilities for depositing alloys and compounds (e.g. AuPt, AuAg, and CdS), and enables processing of materials for which there are no simple gas-phase precursors (Ag) or volatile etch products (Cu). These processes can be conducted on membranes in sealed liquid cells under high vacuum or on bulk substrates in environmental scanning electron microscopes (SEM). However, there has been little work on modeling liquid-phase processes and the relative importance of potential mechanisms (primarily radiation- and electro- chemical) remains unclear. Here we present a hybrid model in which electron Monte Carlo simulations are coupled with continuum finite-element calculations. The Monte Carlo model tracks electron interactions with the liquid and solids, including secondary electron emission, and provides electron energy loss as a function of position. This becomes the input to a finite element model that accounts for radiolysis in the liquid, subsequent reactions, mass transport, and movement of the liquid-solid interface. Here we examine the specific case of radiation-chemical etching of copper films on silicon substrates in aqueous sulfuric acid solutions. We calculate etch rates based on the radiolytic generation of sulfate radicals, the subsequent formation of peroxydisulfate ions, and the oxidation of copper by both species. Calculated rates are compared with experimental results obtained from etching electroplated copper films in an environmental SEM.

COLL 618

Examining cell migration and cell junction dynamics using polymer gel-supported lipid bilayers

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Fate and function of anchorage-dependent cells are known to depend on multiple environmental cues, including those of mechanical origin. Cells probe external mechanical cues through cellular adhesions, such as focal adhesions and adherens junctions, which act as sensitive mechanosensors. Previous progress in the understanding of cellular mechanosensitivity can largely be attributed to the availability of linker-functionalized polymeric gels of adjustable stiffness, which mimic extracellular matrix (ECM) conditions. However, such ECM mimetics are limited in their ability to replicate the remarkable plasticity and dynamics found at cell-cell junctions. To overcome this shortcoming, here we introduce the cadherin functionalized polymer gel-supported lipid bilayer (PGSB) as an improved cell-cell interface mimetic. Its key features include: (i) the dynamic assembly of linker molecules into linker clusters at cell adhesions, enabling cell spreading and migration, and (ii) the ability to alter substrate stiffness by changing the composition of the underlying polymer gel. Experimental findings are presented which show that adherent cells on PGSB substrates of varying gel stiffness exhibit markedly different global properties of cellular mechanosensitivity (i.e., cell area, migration speed, and cytoskeleton organization). Furthermore, cadherin clusters underneath plated cells show long-range lateral mobility with remarkable similarity to the dynamics of cell-cell junctions in cell clusters. These results illustrate that the linker functionalized PGSB is a promising cell surface-mimicking substrate for the analysis of cellular mechanosensitivity.

COLL 619

Artificial biomembrane microsystems for highly sensitive analysis of membrane proteins

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The maintenance of an appropriate intracellular environment is a constant challenge for all living organisms, from prokaryotes to multicellular eukaryotes. Intracellular homeostasis is maintained by membrane proteins, e.g., membrane transporter, transporting various compounds such as ions, sugars, amino acids, and drugs across the biomembrane. Therefore, the analysis of transmembrane transport is crucial to understanding cell physiology as well as for exploring the bioavailability of drugs. Although extensive studies have performed to elucidate the mechanism of membrane transport, quantitatively and reproducibly measuring the transport in a high throughput format has remained difficult due to the complexity of processes involved in membrane formation. Here, we address this issue by developing a novel artificial biomembrane microsystem (ALBiC) that forms sub-million femtoliter reaction chambers, each sealed with an artificial biomembrane with an efficiency of over 90 %. Due to the infinitesimal volume of these chambers, ALCBiC can enhance the detection sensitivity by a factor of 10⁶, demonstrating the single-molecule analysis of membrane transport in a high throughput manner. Moreover, we have recently demonstrated some physiological membrane aspects on ALCBiC, such as asymmetric transbilayer phospholipid distribution, and modulation of membrane potential across lipid bilayers. Thus, our new

platform, ALBiC, holds promise for understanding the mechanism of membrane transport under semi-physiologic conditions as well as for further analytical and pharmacological applications.

COLL 620

Synthesis and characterization of supported lipid bilayer membranes from complex lipid mixtures

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One promising HIV-1 vaccine target is the membrane-proximal external region (MPER) of viral gp41. MPER is poorly immunogenic, however, the two rare neutralizing antibodies (NAbs), 2F5 and 4E10, bind to MPER with great neutralizing ability. It is known that 2F5 and 4E10 are required to first associate with HIV-1 lipids before binding to the target MPER antigen, however, little is known about how lipid membranes contribute to NAb-antigen binding. To this end we have developed model membrane systems to study NAb and antigen lipid interactions. We focus on recreating the lipid phase organization (*i.e.*, domain formation) of native membranes by using supported lipid bilayers (SLBs). We show that AH peptide-induced vesicle fusion is a reliable and facile technique to form a SLB that contains a high cholesterol content and multiple lipid types. The utility of this technique to form biomimetic SLBs was exemplified by forming SLBs from vesicles that recapitulate the native HIV-1 envelope. Without the use of AH peptides, model HIV-1 vesicles fail to form a complete SLB. The SLB formation was characterized by QCM-D and NR measurements, and AFM imaging. NR results show that the formation of the SLB using AH peptides is complete and that peptides are completely removed from the SLB surface after washing. AFM imaging provided a topographical map of the SLB and revealed three distinct membrane domains. Furthermore, AFM imaging showed that imaged SLB areas did not have major hole defects, did not contain intact vesicles, and did not show AH peptide aggregates. Our high resolution AFM imaging experiments on SLBs demonstrate that NAbs 2F5/4E10 do not interact with the highly ordered gel and L_o domains in the SLB but exclusively bind to the L_d phase. This suggests that 2F5/4E10 require low membrane order and weak lateral lipid-lipid interactions to insert into the hydrophobic membrane interior. Thus, vaccine liposomes that primarily contain an L_d phase are more likely to elicit the production of lipid reactive, 2F5- and 4E10-like antibodies, compared to liposomes that contain an L_o or gel phase. In the context of liposomal antigen presentation, our results show that the presence of the MPER₆₅₆ antigen can severely limit the L_d area available for antibody interactions. Subsequently, this reduces the amount of MPER₆₅₆ that is accessible for 2F5/4E10 binding, since MPER₆₅₆ preferentially localizes to the L_d area.

COLL 621

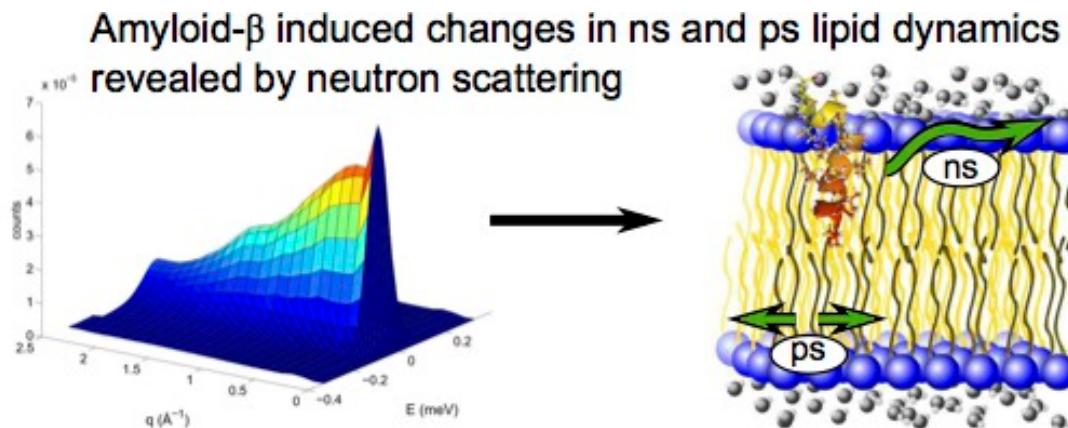
Modulation of lipid membrane structure and dynamics in the presence of amyloid- β peptide

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Hallmarks of Alzheimer's Disease (AD) are extracellular amyloid plaques found in the brain tissue of patients died by suffering AD. These plaques are composed mainly of amyloid- β peptide (Ab), composed of 39-43 residues long. According to the amyloid hypothesis, the predominantly followed concept in AD research, the accumulation of Ab in the brain is the primary influence driving AD pathogenesis. In the recent years, more and more findings point to the fact, that monomeric Ab or small oligomers may be a crucial factor in neurodegeneration typical of AD. The direct interaction of the Ab peptide with the lipid membrane causes membrane disruption as well as may effect signaling and metabolic pathways in the brain. We investigated lipid membranes doped with Ab, and fragments of it with different neutron scattering techniques. In SANS experiments we were able to demonstrate a membrane fusogenic activity of Ab and neutron diffraction revealed detailed structural details on the location of Ab fragments in lipid membranes of various compositions. Quasi-elastic neutron scattering (QENS) was used to study dynamical changes induced by the peptide. To observe the lipid dynamics in a large time window from pico- to nanoseconds, the experiments were performed on neutron spectrometers with different energy resolutions. With this, we could discriminate short range intrinsic lipid dynamics and long range diffusion. The lipid diffusion was altered due to amyloid- β interaction and the observed changes differ in the fluid or gel phase, respectively. For example, in membranes doped with the Ab(22-40) fragment the in-plane Brownian diffusion of lipids near the phase transition temperature was slowed down in comparison to the pure membrane.



Quasi-elastic neutron scattering data (left) allows the determination of lipid dynamics in a membrane (right).

COLL 622

Probing membrane protein organization and dynamics in planar model membranes using single molecule-sensitive confocal detection techniques

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It is now widely accepted that the organization and distribution of membrane proteins in the plasma membrane have a profound influence on membrane protein functionality. However, due to the complexity of the plasma membrane, it remains challenging to decipher the underlying mechanisms that regulate membrane protein organization/distribution and function. To address this important topic, an experimental strategy is discussed, in which mechanisms of membrane protein organization/distribution regulation are explored in planar model membranes of well-defined compositions using single molecule-sensitive confocal detection techniques. This confocal methodology allows the parallel analyses of membrane protein distribution, oligomerization state, and mobility using 2D confocal imaging, photon counting histogram analysis, and fluorescence correlation spectroscopy autocorrelation analysis. By applying this methodology, we demonstrate that changes in membrane cholesterol level have a significant impact on the distribution of integrins without altering integrin oligomerization state. In contrast, changes in the distribution of GPI-anchored urokinase plasminogen activator receptor (uPAR) are mainly caused by ligand-mediated regulation of receptor oligomerization, rather than solely through variations in membrane cholesterol. Moreover, results from dual-color confocal experiments are presented, which provide information about the formation and composition of uPAR-integrin complexes and the role of membrane cholesterol therein. In another example, we discuss the assembly of cadherin chimera into clusters on the surface of a polymer-tethered multi-bilayer substrate to form cell-substrate cadherin linkages underneath migrating cells. Notably, cluster tracking experiments reveal the cytoskeleton-regulated long-range mobility of cadherin linkages, thereby displaying remarkable parallels to the dynamics of cadherin-based cell-cell junctions.

COLL 623

Fusion processes of proteoliposomes into supported planar lipid bilayers

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Lipid bilayers are fundamental structures of cell membranes, at which the transportation of materials and signals in and out of cell membranes take place. These reactions proceed through the actions of membrane proteins, and their proper structures and functions are retained in lipid bilayer membranes. It is necessary to reconstruct membrane proteins into artificial lipid membranes to investigate membrane proteins in

vitro systems. In this study we investigate the fusion processes of proteoliposomes into solid-supported lipid bilayers (SLBs) by using an epi-fluorescence microscope (epi-FM) and an atomic force microscope (AFM).

We prepared the SLB containing phosphatidylcholine (from chicken egg) (PC), phosphatidylethanolamine (from chicken egg) (PE), and cholesterol (Chol) at the ratio of 7:1:2 (w/w) (additionally 0.5 of dye-labeled lipid (BODIPY-H-PC) for fluorescence microscope observation) on a mica substrate by the vesicle fusion method. The lipid component is identical to that for previous ion channel studies using a black membrane [1]. The PC+PE+Chol-SLB had uniform fluorescence intensity in epi-FM images (Fig. 1a), and was continuous and fluid in the measurement of fluorescence recovery after photobleaching (FRAP). On the other hand, AFM observation showed that depressed domains with submicrometer lateral size existed in the SLB. We added the suspension of proteoliposomes, which was extracted from Chinese hamster ovary (CHO) cells, to the SLB. After incubating them at 37 °C for 30 min, the proteoliposomes fused to the SLB and appeared as dark domains (Fig. 1b). The majority the proteoliposome components were isolated from the artificial PC+PE+Chol-SLB. In situ epi-FM observation indicated that the fusion proceeded at specific sites in SLB, and the domains existed stably. AFM observation showed that the depressed domains worked as a specific site for the fusion of the proteoliposome.

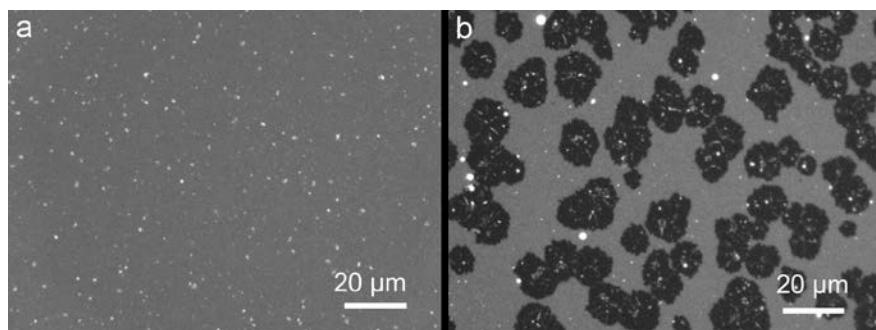


Figure 1. Fluorescence images of the PC+PE+Chol-SLB on a mica substrate (a) before and (b) after the fusion of CHO-extracted proteoliposomes.

COLL 624

Topographic control of membrane functions

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The dynamic deformation of cell membranes is critical to cell functions such as cell division, vesiculation and tubulation. Such transitions between different membrane shapes are usually accompanied by and controlled through a dynamic rearrangement and sorting of phospholipids and membrane proteins. This cooperative rearrangement of lipid and proteins in cell membranes underlies several mechanisms used by the cell to generate, sense, and stabilize local regions of membrane curvature. While such functions are usually attributed to membrane proteins, there is increasing evidence that membrane curvature is not a passive consequence of cellular activity but an active mechanism that is responsible for creating functional domains and facilitating protein binding in dynamic cell membranes. However, understanding the rationale behind the evolution and function of cell-membrane shapes remains to be one of the fundamental questions in current molecular cell biology and biophysics. In this work, we use tunable nanostructured scaffolds as dynamic supports for lipid membranes. The controllable membrane architectures allow us to systematically study the effect of local curvature on membrane structure, function, and dynamics. In this talk, we will discuss how specular and off-specular neutron reflectometry techniques, along with microscopy and fluorescence imaging, can be effectively used to investigate the mechanisms underlying curvature-mediated membrane phenomena, including lateral domain organization and protein sorting. Complementary coarse-grained MD simulations on real-sized membrane systems provide further insights into such phenomena and the atomistic interactions that generate them.

COLL 625

Tubule formation and retraction in the interaction of supported lipid bilayers with SDS

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Sodium dodecyl sulfate is an anionic detergent commonly used to disrupt cell membranes. The interaction of planar supported lipid bilayers with SDS at low concentrations (well below the critical micelle concentration) has been studied by total internal reflection (TIR) Raman scattering and fluorescence microscopy. TIR Raman scattering uses the evanescent wave at the solid-water interface with a sampling depth of ~100 nm. Deuterated SDS is used to distinguish the detergent from the lipids: the C-D stretching vibrations of the detergent are in the vicinity of 2200 cm^{-1} while the C-H stretching bands of the lipid are around 2900 cm^{-1} . Upon exposure of a bilayer of a variety of different lipids to SDS, the detergent is incorporated into the bilayer and the intensity of the lipid peaks decreases, indicating a decrease in the number of lipid molecules within the evanescent wave. Upon rinsing with pure buffer solution, the detergent peaks disappear and the lipid peaks recover. The explanation for these changes can be understood from fluorescence microscopy of the lipid bilayers incorporating a red fluorescent dye. Addition of SDS causes the growth of tubules from

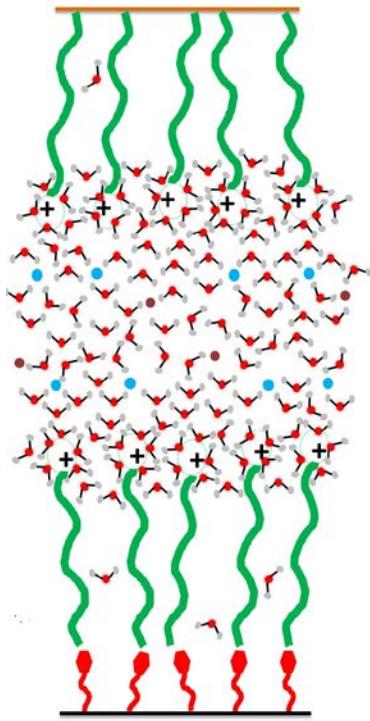
the bilayer, up to several hundred microns long. Given that the penetration depth of the evanescent wave is only ~100 nm, the lipid in these tubules is not sampled by TIR Raman scattering but remains attached to the surface. Upon rinsing with buffer, the tubules retract and the lipid is reincorporated (at least in part) into the bilayer, explaining the recovery in the TIR Raman signal from the lipid. TIR-Raman scattering provides additional information about the phase and composition of the lipid bilayer that is not obtained from the fluorescence images. Fluorescence microscopy is more sensitive to the morphology of the layers.

COLL 626

Interfacial structure of water confined between phospholipid-coated surfaces probed by infrared-visible Sum Frequency Generation (SFG) spectroscopy

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A thin layer of water confined between two phospholipid membranes controls the kinetics of membrane fusion. We will present direct measurements of the structure of this thin confined water layer between two phospholipid-coated surfaces using infrared-visible sum frequency generation spectroscopy (SFG). SFG selectively probes this interface without the need to correct for bulk contributions. Although there is a common consensus on the binding of water to the polar head groups, there is no direct experimental knowledge of the structure of this thin water layer between two phospholipids-coated surfaces. We will present the changes in the structure of this interface upon contact and during sliding. The interaction of zwitterionic and ionic head groups in contact with water will be discussed. Knowledge of this contact interface is important in understanding the crucial role water plays in hydration and fusion of membranes.



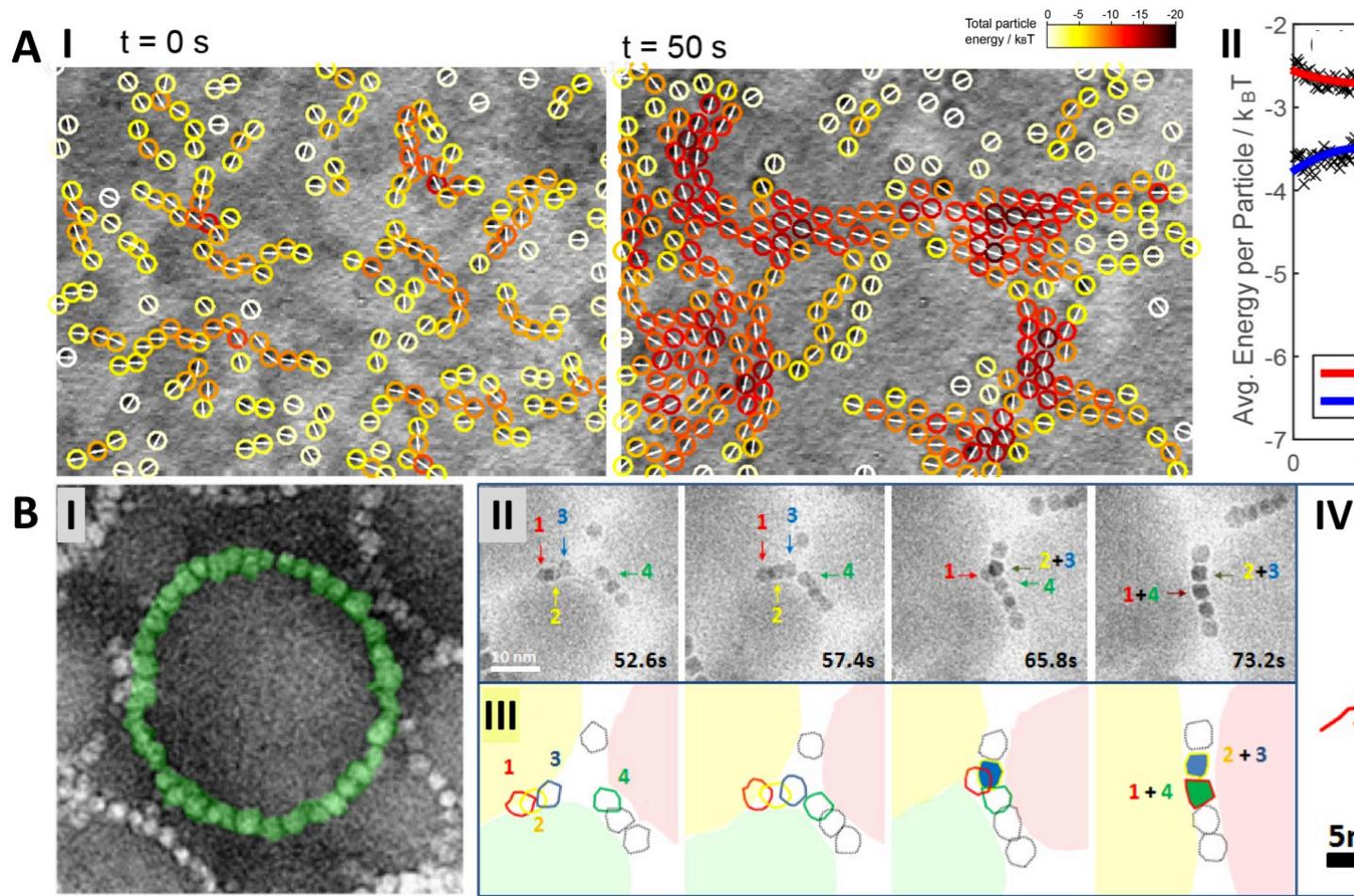
COLL 627

In situ study of colloidal nanoparticle growth and assembly

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We study nanoparticle movement and quantify the interaction between nanoparticles during self-assembly using liquid cell transmission electron microscopy (TEM). A custom image analysis algorithm allows for analysis to be applied to highly effective for noisy and low contrast TEM images with nanoparticles with a large distribution of sizes. By tracing the dynamic processes of random nanoparticles forming chains then a loosely packed configuration, we have estimated the interaction potential, thus the stability and energetic dynamics of assembly. We have also studied CoO nanoparticle ring formation. Nanoparticles nucleate and grow, where liquid nanodroplet perimeter is the attractive site for nanoparticles thus a ring of nanoparticles is obtained.

Nanoparticles are assembled at the edge of liquid droplets. When two nanodroplets meet, it takes an extended period of time for two droplets to merge together, during which nanoparticles can move along the boundary of two droplets. We propose that droplet surface attractive force gradient distribution induced by aspherical nanodroplet morphology contributes to the nanoparticle ring formation. In addition to nanoparticle assembly, we have used liquid cell TEM for the study of nanoparticle growth, on which unique mechanisms of growth have been revealed.



In situ study of Pt-Fe nanoparticle assembly. **(I)** Analysis of energy evolution during nanoparticle assembly. Colored circles indicate location of nanoparticles overlaid on the original image. White arrows indicate dipole orientations. The color corresponds to the total energy of an individual nanoparticle computed from the dipole and Van der Waal interaction with nearby particles. **(II)** The calculated average particle energy evolution over time. **B.** In situ observation of CoO nanoparticle interaction and assembly mediated by liquid nanodroplets. **(I)**. Co nanoparticles assembled in rings around liquid droplets. **(II)**. Sequential images showing nanoparticle interaction at the triple junction of liquid droplets, **(III)** highlights of images in **(II)**, **(IV)** trajectories of particle movements with time.

COLL 628

Polymer-assisted deposition: A simple process for a wider range of electronic materials

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Thin films, coatings, and nanostructured materials have found extensive applications in essentially all technological and scientific areas. Tremendous advances have been made in synthesizing and processing materials with controlled structures at different length scales and desired physical properties using either physical- or chemical-vapor deposition techniques. However, one of the challenges in solution-based processes of complex materials has been the growth of high quality films with desired functionalities. In this talk, I will discuss a polymer-assisted deposition (PAD) technique, an alternative approach to chemical solution deposition, to address this challenge. This technique can be used to deposit a wide range of high performance electronic materials for diverse applications. Different from other conventional solution-based deposition techniques, PAD uses water-soluble polymers to prevent metal ions from unwanted chemical reactions and to keep the precursor solution stable. The unique chemistry and processing design of PAD deliver stable and homogeneous solutions at a molecular level to allow the growth of high quality films. Using metal-oxides, metal-nitrides, and metal-carbides as model systems, I will explain the process, microstructures, and physical properties of these materials grown by PAD.

COLL 629

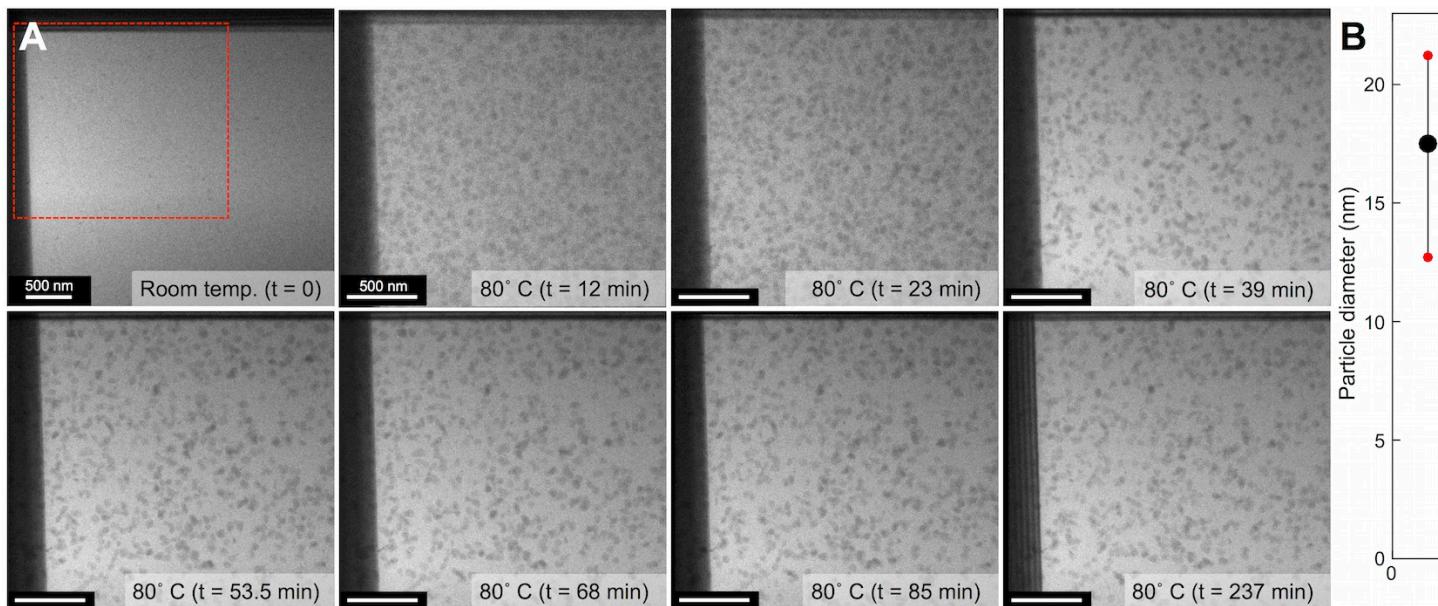
In situ Variable-Temperature Liquid Cell Transmission Electron Microscopy (VT-LCTEM) study of size-stabilized Covalent Organic Framework (COF) nanoparticle nucleation and growth during solvothermal synthesis

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Covalent organic frameworks (COFs) are crystalline, highly nanoporous materials, consisting of extended periodic ligand network nanostructures, which are extremely amenable to synthetic design by appropriately selecting the monomers used in synthesis. Though progress had been made in the development of novel COFs, largely by trial and error approaches, little is understood about the fundamental nucleation/growth mechanisms that lead to formation of the different COF nanostructures and morphologies, greatly limiting our ability to rationally develop next-generation COF materials.

Advances in liquid-cell transmission electron microscopy (LCTEM) instrumentation now enable direct variable-temperature (VT)-LCTEM observations of fully hydrated/solvated systems while uniformly heating the liquid. Here, we study the nanoscale nucleation and growth during the formation of COF-5 nanoparticles (NPs) using VT-LCTEM. The Dichtel lab has developed a new COF-5 synthesis route for producing size-stabilized NPs (diameters 20-200 nm), whereby the diameter of the population of discrete colloidal

COF-5 NPs can be readily modulated by tuning the relative solvent concentrations in the precursor solution. In our VT-LCTEM studies, COF nucleation/growth does not occur at room temperature, even when irradiated by the e- beam at low dose rates. However, when the same COF-5 growth precursor solution is heated to, and held at 80 °C, discrete COF NPs nucleation and growth, seeded on the SiNx window surface, is observed (Figure 1A), which could be consistently reproduced in multiple separate VT-LCTEM experiments. We employ the MOTA-method for particle tracking and quantitative size-measurement image analysis to accurately determine the particle size of the population as the particles grow and size-stabilize over time (Figure 1B). We use these quantitative VT-LCTEM measurements as both a complementary characterization tool to bulk-scattering techniques for accurately determining the true size and morphology of nanomaterials in solution, and more importantly as a window into the underlying mechanisms of solvothermal COF formation, with the aim of applying this knowledge to intelligently modify synthesis conditions to promote the formation of more desirable COFs.



COLL 630

Paramagnetically amplified optical activity of chiral nanoparticles

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Chirality is a property unifying both electromagnetic waves and matter that typically manifests in light-matter interactions as the difference in absorption left- and right circularly polarized light, known as circular dichroism (CD). Although the studies of chiral effects associated with the magnetic component of light have long history and date back to M. Faraday, our sense is that the nexus of magnetism and chirality

represents an underexplored area of science.

Despite importance for fields of multiferroics, skyrmions, spintronics, and homochirality of Earth's life, magneto-optical effects are generally much weaker than their electro-optical analogs. Although the use of these effects in memory, optoelectronics, information processing devices, and catalysis has much technological appeal, the requirements of temperatures around $T=5\text{-}7$ K and magnetic fields of $B = 1.2\text{-}7.5$ T complicates their implementation. Difficulties of molecular design of traditional chiral materials capable of combining chiral and magnetic centers or long-distance coupling of magnetic spins also hinders exploring of the effects.

Emergence of the new field of inorganic chiral nanoparticles (NPs) provides new opportunities for materials design of magneto-optics. Magnetic NPs can enhance both local magnetization of the chiral "centers" and their interaction with photons without externally applied magnetic fields. Here we demonstrated highly enhanced optical activity of NPs by synthesizing them using transition metal components. The chiral paramagnetic NPs exhibited $\sim 10\times$ stronger optical activity compared to conventionally synthesized NPs. The tunable strong optical activity of NPs should contribute to chiral catalysis, chromic filters and display devices.

COLL 631

Photoluminescence blinking and polarization anisotropy of single colloidal semiconductor nanoplatelets

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Colloidal two-dimensional semiconductor nanostructures, also known as nanoplatelets (NPLs), have numerous potential optoelectronic applications due to their unique emission properties, such as narrow linewidth, short lifetime and giant oscillator strength. Herein, we report photoluminescence properties of single CdSe NPLs as a function of shell morphology. Specifically, we show that NPL blinking behavior is strongly affected by the shell quality. In the absence of a shell, CdSe NPLs exhibit large intensity fluctuations that are not accompanied by significant changes in lifetime. Such blinking behavior is mediated by 'hot-carrier trapping' and is referred to as B-type blinking. Addition of a rough CdS shell leads to blinking that is characterized by lifetime fluctuations. This type of blinking follows a charging/discharging mechanism, where emission in the charged state is suppressed by non-radiative Auger recombination processes and is referred to as A-type blinking. In contrast, the growth of a smooth shell results in more B-type blinking than A-type. The variations of blinking behavior with different shell morphology is possibly related to trap states on the surfaces and/or in the shell. In addition, a narrower linewidth in the smooth shell NPLs relative to the rough shell NPLs was observed in low temperature experiments. Furthermore, polarization-resolved spectral investigations revealed certain degree of anisotropic emission in both

core and core/shell NPLs and fine-structure splitting in core/shell NPLs. These spectral observations suggest that fine electronic structures in NPLs are strongly influenced by the shell morphology of NPLs. Overall, our results demonstrate the critical role of shell growth and morphology in controlling the photoluminescence properties of NPLs for various potential optoelectronic applications.

COLL 632

Migration and structural evolution of carbon-encapsulated Fe nanoparticles via *in situ* TEM

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Catalysts are susceptible to deactivation due to poisoning or the loss of desirable structural features; encapsulation of nanoparticles has been used to inhibit poisoning and to limit the amount of inter-particle interaction. Iron and iron-containing nanoparticle catalysts are of interest as cost-effective replacements for expensive noble metal catalysts. Carbon-encapsulated (Fe@C) nanoparticles allow for investigation into the structural dynamics induced by the reaction environment and the effect of carbonaceous growth on catalyst materials. Here we report the preparation of carbon encapsulated Fe NPs catalysts and their subsequent thermal stability – degradation and coarsening. *In situ* transmission electron microscopy (TEM) allowed the dynamic behavior of this material to be studied during reaction, at elevated temperatures (up to 650 °C) and extended durations (minutes to hours). Under these conditions, the particles exhibited liquid-like behavior and a release of the Fe nanoparticles from their carbonaceous shells.

While this behavior was primarily attributed to the increased temperatures, the energy from the electron beam likely also contributed through compression of the carbonaceous shell material, which has been shown to increase the pressure inside the core-shell considerably. Particle coarsening progressed by both Ostwald ripening and particle coalescence as competing mechanisms in parallel. *In situ* TEM enabled the size regimes over which ripening or particle coalescence dominated to be determined. A mechanistic understanding of the morphological evolution of the catalyst structure over the course of the reaction was developed. Because the amount of free surface area is typically correlated with activity of a nanoparticle catalyst, these results provide insight into how the activity of the system changes during reaction.

COLL 633

Two-phase synthesis of metal sulfide nanoparticles

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Metal sulfide nanoparticles have recently attracted significant attention from researchers due to their unique electro-optical and semiconducting properties. These particles are promising candidates for applications in photovoltaics, catalysis, 3D printing, labeling, imaging, and sensing. Successful application of these materials, however, will be largely dependent upon the efficient and tunable synthesis of monodisperse particle samples. Metal sulfide nanoparticles are typically generated via complex synthetic methods that employ either very high temperatures or flow reactors. The products are often of poor quality, where uniform samples can only be produced through time consuming separation processes such as size selective precipitation. The development of a simple, general, tunable, room temperature method for the synthesis of monodisperse samples of these materials is thus highly desirable. Here, a new method for the facile, room temperature synthesis of metal sulfide nanoparticles has been developed and will be presented. In this method, small (1-10 nm) Ag₂S, PdS, and CdS nanoparticles have been synthesized in toluene via the biphasic reaction of tetraoctylammonium metal complexes and sodium sulfide. It is expected that this method can ultimately be extended to the synthesis of a variety of other metal sulfide nanoparticles.

COLL 634

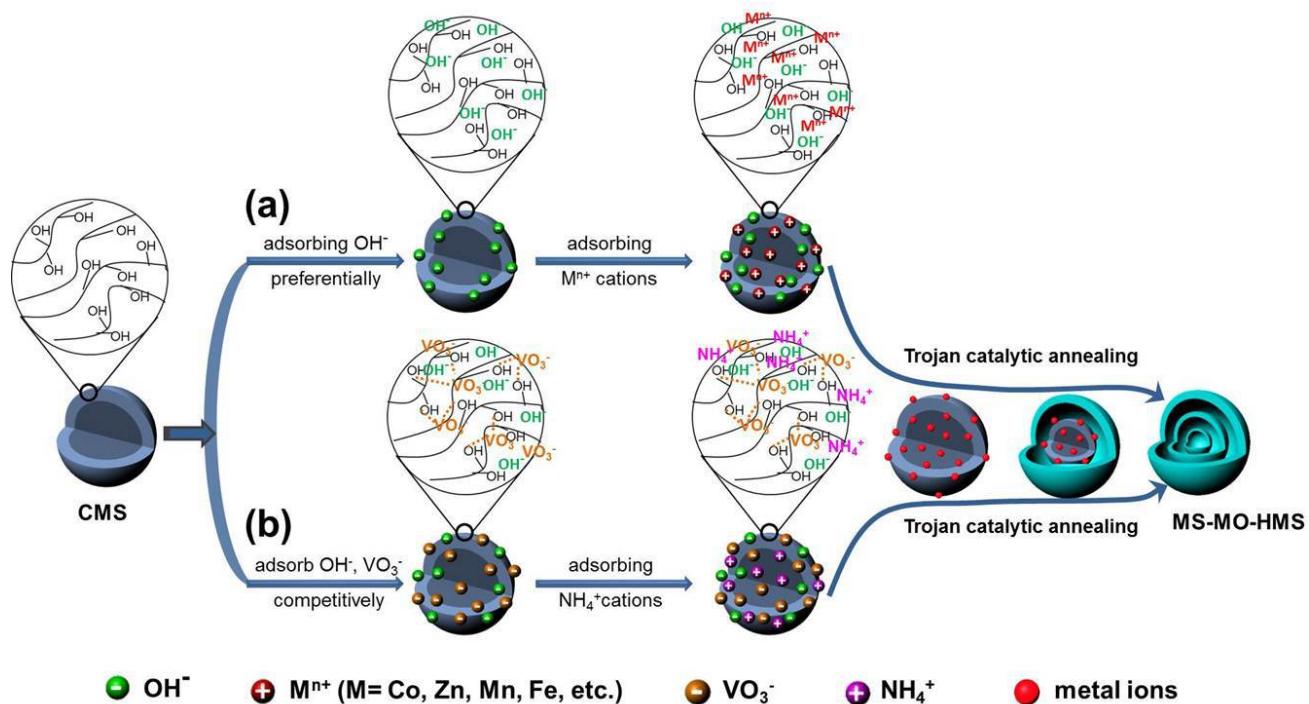
Multi-shelled metal oxides hollow microspheres: Synthesis and applications

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Hollow micro-/nanostructured materials possess attractive properties such as high specific surface area, low density, and high loading capacity, which endow them with potential applications in lithium ion batteries, supercapacitors, solar cells, catalysis, and fuel cells, etc.

Multi-shelled Co₃O₄, α-Fe₂O₃, V₂O₅ hollow microspheres are prepared and tested as anode or cathode materials for LIBs. By controlling the size and diffusion rate of the hydrated metal cations, and ion absorption capability of carbonaceous sphere templates, we can accurately control the number of shells and the interior structures of multi-shelled Co₃O₄ hollow microspheres with a high yield and purity. When tested as anode materials for LIBs, these multi-shelled Co₃O₄ hollow microspheres exhibit excellent rate capacity, good cycling performance and ultrahigh specific capacity. Considering that both the shell thickness and porosity matter greatly in LIBs performances, multi-shelled α-Fe₂O₃ hollow microspheres are prepared with structural aspects including shell thickness, numbers of internal shells, and shell porosity controlled by synthesis parameters. When tested as anode materials for LIBs, thin, porous, triple-shelled α-Fe₂O₃ hollow microspheres showed the best cycling performance, demonstrating excellent stability and reversible capacities up to 1702 mAh g⁻¹ at current density of 50 mA g⁻¹. A new concept of competitive anion-adsorption by

carbonaceous sphere templates followed by a Trojan catalytic combustion process is used to synthesis V_2O_5 hollow microspheres with well-controlled shell number, thickness, porosity and crystallinity. When tested as cathode materials for LIBs, multi-shelled V_2O_5 hollow microspheres exhibit superior high-rate lithium-storage property: record-high specific capacity and excellent cycling stability at a high current density of 1000 mA/g (447.9 and 402.4 mAh/g for the 1st and 100th cycle, respectively) and remarkable rate capability.



Schematic of two synthesis routes of multi-shelled hollow microspheres.

COLL 635

Effect of ligand asymmetry in the properties of nanoparticle membrane

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The self-assembly of nanoparticles at liquid-liquid and liquid-air interfaces has becoming an efficient way to create two-dimensional arrays with tunable electrical, optical, magnetic, and mechanical properties. In these arrays, inorganic nanoparticles are

coated with a shell of ligand molecules that interlock as spacers and provide tensile strength. We have discovered recently that the heterogeneous environment, such as an air-water interface, strongly influences the membrane properties. Highly quantitative surface X-ray scattering shows a difference of ~6Å in average ligand shell thickness between the two sides of the membrane, corresponding to ~30% of the extended ligand length. Experiments and molecular dynamics simulations further elucidate the role and interplay of ligand coverage and mobility in producing and maintaining this asymmetry, even after the water is removed and the membranes become free-standing.

Thermomechanical response of membrane shows hysteretic behavior, which is attributed to reorganization of ligand at high temperature by comparing experimental data with molecular dynamic simulation. Understanding this ligand distribution asymmetry opens up new avenues for designing nanoparticle superstructures.

COLL 636

High-energy-resolution x-ray absorption spectroscopy: A powerful method to push the frontiers of in-situ x-ray absorption spectroscopy of catalysts

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X-ray absorption spectroscopy has proven to be a powerful in-situ technique for characterizing the local electronic and geometric structure of working catalysts, and continues to be the most widely used synchrotron technique by the catalyst characterization community. Here we show how high-energy-resolution x-ray absorption spectroscopy, commonly given the acronym HERFD (high-energy-resolution fluorescence detection) strongly bolsters the arsenal of in-situ catalyst characterization techniques. This advanced spectroscopy is readily applied at synchrotrons, highly sensitive, and suited to dynamic measurements with catalysts in reactive atmospheres. This will be illustrated using results characterizing single-site catalysts, zeolite- and MgO-supported iridium complexes with reactive ethylene and CO ligands, together with other select examples. The talk will also include a look to the future of applying this advanced spectroscopy to the tender x-ray regime in addition to the hard x-ray region, and to prospects of HERFD with the new undulator beamline at SSRL.

COLL 637

Degree of rate control: A tool for analyzing microkinetic models and high-throughput computational screening of catalyst materials

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Applications of the degree of rate control (DRC) in catalysis research will be reviewed. It was initially designed as a tool for sensitivity analysis of microkinetic models to determine which elementary step(s) are the kinetic bottlenecks, i.e., the most rate controlling. It was later generalized such that it quantifies, in a thermodynamically consistent way, the sensitivities of the net reaction rate to a small change in the energy of each species in the reaction mechanism. Thus, the DRC for any elementary step's transition state or for any adsorbed intermediate is defined such that it equals the fractional increase in the net rate that results from a tiny decrease in the energy of that species, keeping all other energies and entropies constant. When there is a single rate-determining step, the DRC for its transition state is unity. The applications of DRC analysis of catalytic reaction mechanisms will be reviewed. These include: (1) determining which species are most critical in affecting the desired rate or selectivity, (2) guiding changes in reaction conditions to achieve higher rates and selectivities, (3) an algorithm based on DRCs, developed by Dumesic's group, which bypasses the need to solve the differential equations in a microkinetic model to calculate its rates, (4) a method for fast computational catalyst screening, which uses the energies of the few species with the highest DRCs for a reference catalyst as descriptors to estimate the rates on related materials, and to predict which are most active or selective. It can also be implemented without a microkinetic model if the degrees of rate control are already known from experiments.

COLL 638

High spatial resolution mapping of catalytic reactions on single nanoparticles

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Uncovering structure-reactivity correlations of catalytically active nanoparticles at the nanoscale is essential for the development of optimized heterogeneous catalysts. In this study we demonstrate that the catalytic reactivity on different sites across the surface of single Pt nanoparticles can be mapped by conducting high spatial resolution vibration spectroscopy measurements. The detection of chemical reactions at the nanoscale was achieved by focusing synchrotron-sourced IR beam onto a metallic AFM tip that acts as an antenna and concentrates the incident light at its apex.

Surface-anchored N heterocyclic carbenes molecules were used as model reactants to overcome the limited temporal resolution of synchrotron infrared nanospectroscopy. These molecules, which were functionalized with a chemically active OH group, were anchored to the surface of Pt nanoparticles. The oxidation of the functional OH group from alcohol to aldehyde and acid and its reversible reduction back into alcohol on different surface sites was mapped under various oxidizing and reducing condition. High spatial resolution measurements determined that the reactivity of molecules which were anchored to the nanoparticle's perimeter was higher than that of their counterparts, which reside on the nanoparticle's center. These results indicate that low-coordinated Pt atoms which are located along the nanoparticle's perimeter are more chemically active than Pt atoms which are located on the flat surface of the nanoparticle. This study

reveals that high spatial resolution vibrational spectroscopy measurements can provide molecular-level understanding of the reaction mechanism of catalytic processes on single nanoparticles, correlating between the surface properties and catalytic reactivity of single nanoparticles.

COLL 639

Monitoring real-time dynamics of nanoparticle formation via trading space with time strategy and synchrotron x-ray absorption spectroscopy technique

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Predicting the formation dynamics of nanomaterials is a long-standing challenge. Generic models are lacking, and existing ones fail to account for chemical or structural properties of particles at the nanoscale. The groundbreaking discoveries of novel nanomaterials are currently achieved via laborious Edisonian trial-error protocols. Bridging this gap between theory and experiment requires tools, techniques and strategies with high spatial, temporal and chemical resolutions. For a successful implementation of predictive tools, it is also essential to probe the real-time dynamics of nanoparticle formation.

Synchrotron X-ray absorption spectroscopy is a technique with chemical sensitivity, and have already achieved X-ray probe sizes in the order of microns and temporal resolution in the order of sub-seconds using Quick XAS mode in which photon energies are scanned rapidly and repetitively. Applying x-ray microprobes in a continuous flow mode renders possible detection of milliseconds time scales by way of trading distance with time.

In this talk, two examples implementing this trading time-space strategy using the microprobe at the Advanced Light Source will be discussed. The first is the in-situ monitoring of reduction, nucleation and growth dynamics of ultra-small bimetallic CoPt nanoparticles. In this case, the time transients in the order of milliseconds are recorded by adjusting liquid flow rates and reactor volume. Mixtures of salt precursors in diethylamine are flowed through a thermally regulated capillary bed while changing the capillary position along its long axis relative to the X-rays. Both near edge and extended edge XAS spectra are obtained at the Pt L₃ and Co K absorption edges.

The second example is the real-time monitoring of the laser-induced formation and self-assembly of Ag nanoparticle gratings in mesostructured titania substrate. A 35-micron spot 532-nm cw laser is lightly focused on a titania substrate impregnated with Ag salt precursor, and a 5-micron X-ray probe is overlapped on the laser spot. Then, the substrate is rastered at a constant speed allowing for laser writing, leading to nucleation and growth of the Ag nanoparticles with subsequent organization along the direction of the laser polarization. By scanning the X-ray microprobe along the laser beam profile, time transients with 50 msec resolution are obtained at the Ag L₃ and Ti K edges affording a window into the dynamics of self-organization in such laser matter interaction.

COLL 640

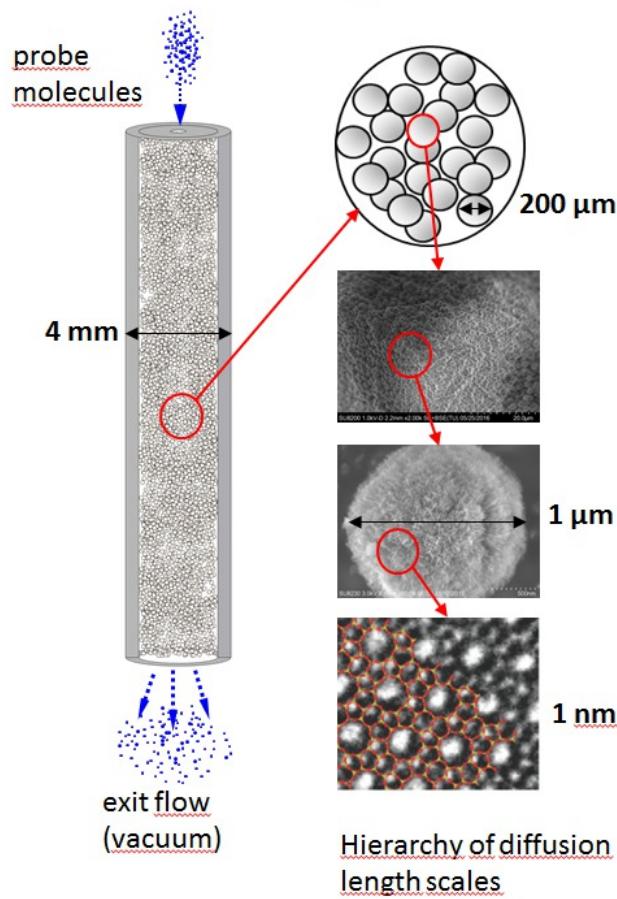
Time-resolved characterization of hierarchical diffusion and reactions in acidic zeolites and zeotypes with Temporal Analysis of Products (TAP) experiments

Evgeniy Redekop¹, Juan Martinez¹, Magnus Morten¹, Bjorn T. Bleken¹, Rebecca Fushimi², Maria Mykland¹, **Unni Olsbye**¹, unni.olsbye@kjemi.uio.no. (1) Univ of Oslo Chemistry Dept, Oslo, Norway (2) the Langmuir Research Institute, Lake Saint Louis, Missouri, United States

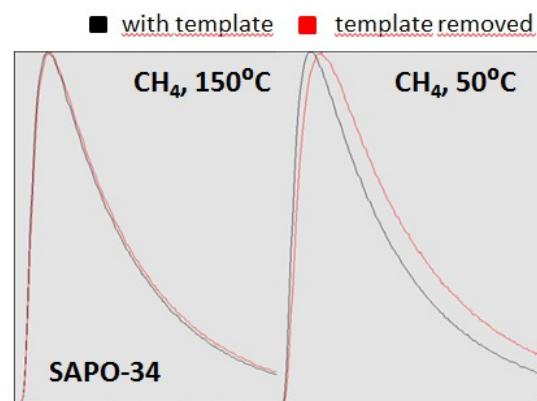
Coupled diffusion and acid-catalyzed reactions in zeolites control a multitude of industrially-important chemistries that exert huge impact on the planetary ecosystem and the society. In this study, macroscopic diffusion in the well-defined Knudsen regime is used as a transport standard to characterize the diffusion within meso- and micropores of zeolites (zeotypes) as well as to measure the intrinsic kinetics of olefin methylation, a key step in the Methanol-To-Olefins (MTO) chemistry. Temporal Analysis of Products (TAP) pulse-response experiments provide time-resolved ($\Delta t=1$ ms) kinetic data which are then interpreted within a 1D reaction-diffusion model to yield the transport and reaction characteristics of investigated materials.

The molecular transport of various low weight guest molecules (4-84 amu range, inert gases and hydrocarbons) was characterized in ALPO-5 (AFI), SAPO-34 (CHA), ZSM-22 (TON), ZSM-5 (MFI), and self-pillared pentasil (MFI) materials. For several materials, novel TAP experiments with *in situ* template removal were performed to characterize, separately, mesoporous and microporous transport. These precise measurements of diffusional properties, in turn, provided means to characterize physico-chemical interactions of various gases with the host frameworks, e.g. Henry constants of molecular uptake by the framework. With the insights gained into the transport properties of microporous frameworks under low-pressure TAP conditions, the intrinsic kinetics of olefin methylation was studied in selected materials and the resulting parameters were compared to theoretical (DFT) estimates. These results contribute to our fundamental understanding of and the practical ability to control shape-selective MTO chemistry occurring in zeolites (and zeotypes) under confinement.

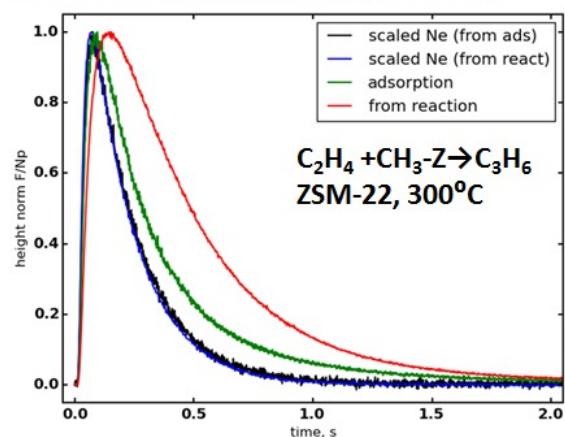
A. Temporal Analysis of Products (TAP)



B. In situ template removal



C. Intrinsic methylation kinetics



COLL 641

Solution calorimetry methods for the study of catalytic solid-liquid interfaces

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The low volatility of biomass-derived compounds and the omnipresence of water in biomass feed streams typically requires that their conversion/upgrading by catalytic routes be conducted at “buried” solid-liquid interfaces. Under these circumstances, the role of solvent becomes critical since it constitutes the majority species in solution and most likely on the catalyst surface. The interactions between solute and solvent in solution (i.e., excess solution thermodynamic properties) and at a solvated interface are complicated but must be accounted for when measuring chemical kinetics (i.e., activities versus concentration) or determining reaction mechanisms. In this tutorial talk, we will review the ability of calorimetry to characterize solid-liquid interfaces. Following an introduction to solution-phase calorimetry, including theory and practical experimental

considerations, I will provide examples from our own research using calorimetry to quantitatively assess water tolerance (or conversely water inhibition) in heterogeneous organocatalysts using a simple esterification reaction. From our participation in collaborative research, I will demonstrate how solvent effects can be accounted for quantitatively for catalytic reactions involving reactions of sugars in zeolites.

COLL 642

Tuning the physical properties of MoS₂ membranes through organophosphonate-based surface functionalization

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Two-dimensional MoS₂ attracts considerable research interest, with substantial prospects for nanoelectronics and -optics. The susceptibility of single layer MoS₂ to charge carrier modulation by the subjacent SiO₂ substrate has been described. Here we report the effect on single layer MoS₂ of functionalization of the SiO₂ support by monolayer self-assembly of aliphatic and aromatic organophosphonates that are terminated with hydroxy-, nitro-, thiol-, phosphonic acid, or maleimido groups. Molecular simulations gave insight into the spatial arrangement of the various organophosphonates on the SiO₂ surface, and functionalization was monitored by static water contact angle analysis, atomic force microscopy, and X-ray photoelectron spectroscopy. Raman spectroscopy further characterized an effect of the various substrates: A shift relative to that for single-layered MoS₂ transferred onto pristine SiO₂ was measured for the Raman-active out-of-plane A_{1g} mode for heterostructures containing a functional interlayer, which indicates a modulation of the intrinsic doping behavior of the MoS₂ nanomembrane, and which illustrates the capabilities of interface engineering in MoS₂-based heterostructures.

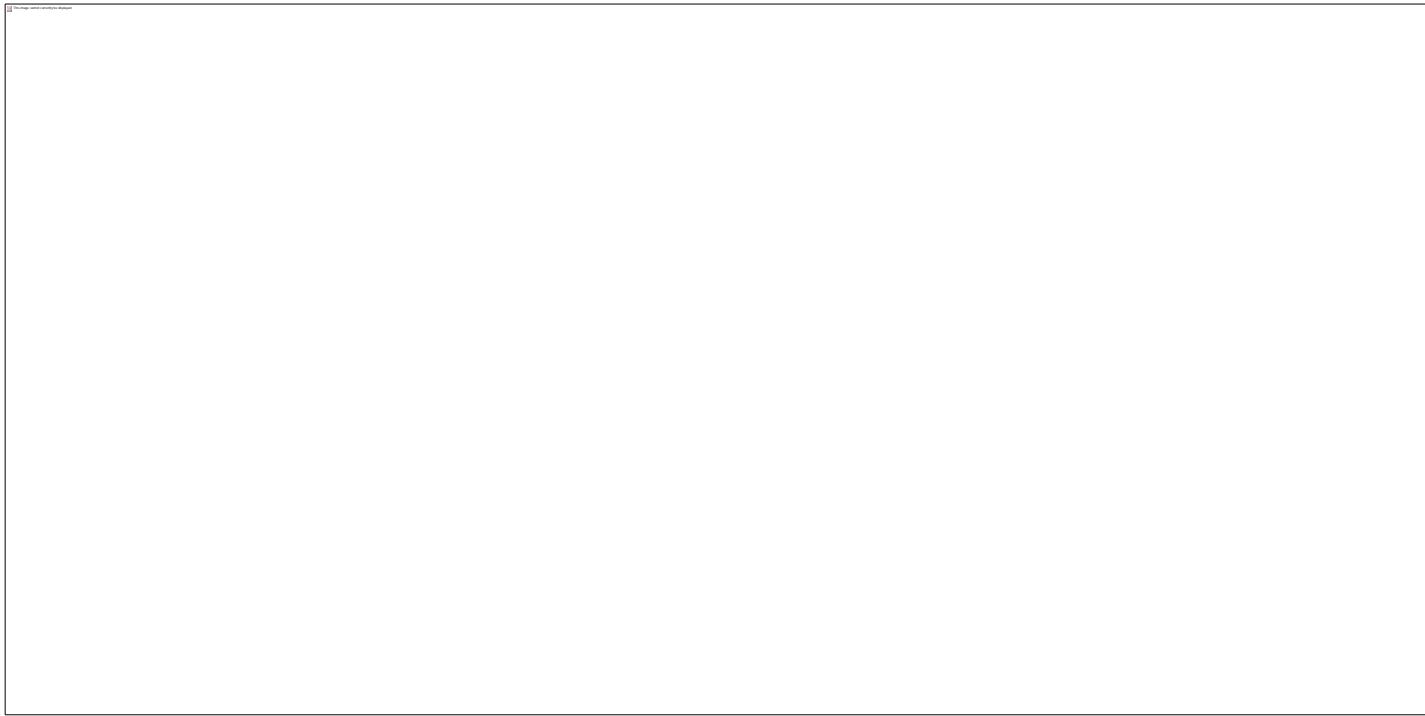
COLL 643

Bottom-up hierarchical self-assembly of zwitterionic dendrimers into stimuli responsive dynamic nanotubes

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Designing well-defined, smart and dynamic nanostructures in solution through hierarchical assembly of materials has always been an exciting goal for many

researchers. These nanoscale objects are very important in different aspects of nanotechnology since they are the key elements for making future advanced materials. Among various fabrication methods, ionic self-assembly has appeared as an important method in designing smart and stimuli responsive nanostructures. Although ionic interactions are important due to their abundance in nature, but incorporating them to design controlled artificial nanostructure has always been challenging. We proposed that through incorporation of zwitterionic functionalities it is possible to control the charged density of ionic building blocks and direct them into desired nanostructures. We showed that with controlling the electrostatic interaction of zwitterionic dendrimers and ionic surfactants by solution pH, we can design smart nanotubes through membrane fusion of bilayer vesicles which found to be responsive to ionic strength. Combination of atomic force microscopy (AFM), transmission and scanning electron microscopy (TEM, SEM) techniques were used to visualize nanotubes while dynamic light scattering (DLS) and isothermal titration calorimetry (ITC) provided information regarding self-assembly process in solution. Zwitterionic materials are important due to their unique behavior compare to typical polyelectrolytes which makes them a potential candidate in designing future novel nanostructures.



COLL 644

2D phase evolution and solvation in dimethyl formamide-lithium ethylene dicarbonate films on Ag(111)

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The interactions of solvent molecules with electrode surfaces impact many interfacial chemical processes. In this talk, we examine the chemical and 2d structure evolution that follows adsorption of the polar solvent dimethylformamide (DMF) on Ag(111). We further reveal the impact of an ionic solute, lithium ethylene dicarbonate, on phase evolution. Complementary STM, XPS and DFT methods characterize DMF dry etching of Ag(111) and Ag(DMF)₂ coordination complex formation. Monolayer phase evolution is tracked from a 2d gas mixture of DMF and Ag(DMF)₂ to ordered and nanophase-separated domains of DMF and Ag(DMF)₂. A surface pressure-composition phase diagram, derived from the data, illustrates how these monolayer phases are tuned by surface pressure. The ionic solute, lithium ethylene dicarbonate, shifts the phase equilibria of the solvent film, seeding the formation of ordered DMF domains at reduced surface pressures. Structural models are given for all ordered phases, and the 2d solvation of LEDC is described.

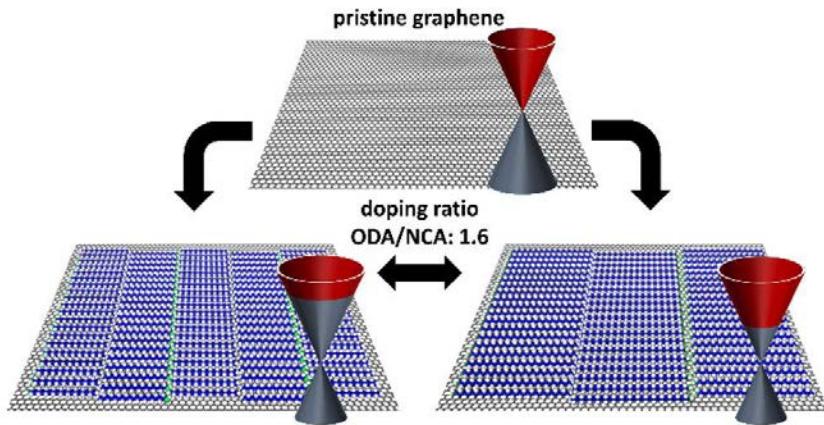
COLL 645

Functionalization of 2D materials: The molecular approach

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Nanostructured monolayers of molecules can be formed at a variety of interfaces. At a liquid-solid interface, such two-dimensional (2D) molecular assemblies can be created by depositing a solution of the compound of interest on top of the substrate (drop casting) or by immersing the substrate into a solution (dip coating). Advanced interface specific methods such as scanning tunneling microscopy (STM) and atomic force microscopy (AFM) provide structural and other types of information at the nanoscopic level.

In this presentation, we focus on several aspects of molecular self-assembly at the interface between a liquid or air, and substrates such as highly oriented pyrolytic graphite and graphene. Highly oriented pyrolytic graphite can be considered as an excellent model surface for adsorption and self-assembly of molecules on graphene. We will reveal concepts of 2D crystal engineering and bring insight into thermodynamic and kinetics aspects of the self-assembly process at the interface between a liquid and graphite or graphene. Based on these insights, we will demonstrate molecular self-assembly based functionalization of 2D materials. Various applications will be presented, including tunable doping of graphene based field effect transistors.



Controlling molecular doping of graphene

COLL 646

Supramolecular arrays and heterostructures on hexagonal boron nitride

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The deposition and organization of monolayers, multilayers and heterostructures of organic molecules on the insulating hexagonal boron nitride (hBN) is studied using ambient atomic force microscopy. It is possible to form extended supramolecular arrays of molecules stabilized by hydrogen bonding between carboxylic groups using molecules such as tetrakis (4-carboxyphenyl) porphyrin (TCPP), terphthalic acid (TPA) and trimesic acid (TMA) which form respectively square, row and honeycomb arrays when deposited from ethanolic solutions. We have also studied bi-component systems such as melamine cyanurate and the combination of perylene tetracarboxylic di-imide (PTCDI) and melamine which form extended highly ordered arrays on hBN. We have also found that sequential deposition of layers is possible and find orientationally controlled epitaxial growth of TPA, TMA, TCPP and PTCDI on melamine cyanurate. This is possible for both monolayers, multilayers and nanocrystals of melamine cyanurate. The energetics controlling the growth of heterostructures has been investigated using molecular dynamics calculations and we find excellent agreement between theory and experiment. The use of the hBN substrate also facilitates the measurement of the fluorescence of adsorbed organic layers and we find shifts in the emission peak position when TCPP is adsorbed on melamine cyanurate which are explained using time-dependent density functional theory. We also discuss interference effects arising from the highly parallel interfaces of the hBN flakes and discuss how

these effects can the optical properties of fluorophores which can be integrated into supramolecular heterostructures.

COLL 647

Self-assembly and post-assembly chemical transformation of reactive compositionally patterned monolayers

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Molecular interactions direct local packing within 2D assemblies. In favorable cases, interaction selectivity drives assembly of crystalline monolayers exhibiting long range order. We have realized designed self-assembly of compositionally patterned, multicomponent monolayers exhibiting long range order using selectivity derived primarily from molecular shape (van der Waals) and in combination with dipolar interactions. Post-assembly chemical transformation is one strategy for using compositionally patterned monolayers to direct further nanoscale assembly. This presentation will describe efforts to utilize patterned multicomponent monolayers to self-assemble patterned arrays of reactive functional groups and to perform post-assembly, spatially controlled reactions at the monolayer-solution interface.

COLL 648

Hierarchy in the self-assembly of novel chiral dyes for photovoltaic applications

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A series of new chiral compounds suitable for solar light harvesting systems have been prepared and endowed with hydrogen bonding moieties to direct their self-assembly. It will be shown how the compounds form hierarchical structures where the symmetry of the molecule and the stereochemistry play defining roles in the chromophore packing. The correlation with solid state structural characterisation in single crystals affords insight as to design features that may favour the formation of polar and chiral arrays of molecules in the thin films that they form.

COLL 649

Structure and function of bilayer organic photovoltaics

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The exciton is a critical part of each of the processes leading to photocurrents in Organic PhotoVoltaics (OPVs), and being able to control the location, lifetime and energy of the exciton is essential to achieving high efficiency. I will discuss our most recent work with both organic dyes, such as squaraines and dipyrromethanes for OPVs. This involves a careful materials design study that leads to both low energy absorption (into the nearIR) and the efficient use of multiple absorbers to efficiently harvest photons through the entire visible spectrum. In particular, I will discuss the structure of bilayer films with these red/NIR absorbers and the role that fullerene diffusion into the donor layers plays on the properties of the photovoltaics. I will also discuss a new approach to designing materials for OPVs that involves symmetry breaking charge transfer. These materials are symmetric molecules that spontaneously form an intramolecular charge transfer complex, with nearly complete one electron transfer from one part of the molecule to another. This intramolecular CT state readily forms a charge separated state at the D/A interface of the OPV. We have explored these materials as both donors and acceptors in OPVs and found that they give good performance and high V_{oc} .

COLL 650

Biophysical properties of salt-induced simple coacervation of interfacial mussel adhesive proteins

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Coacervation of mussel adhesive proteins (MAPs) has been suggested as a formulation that mussels use during secretion due to its high density, no dispersion into seawater, and low interfacial tension. However, absence of anionic partner among MAPs made it difficult to explain how mussels formulate coacervates. Thus, simple coacervation, the liquid-liquid phase separation with only one component, was considered instead of complex coacervation and recent report of simple coacervate formation using fp-3S (slow variant), unique among MAPs with low charge density, supported the possibility of MAP simple coacervation. This intrigues simple coacervation of other MAPs that have high positive charge density. Limited availability of MAPs from extremely difficult extraction has restricted investigation on not only how biophysical properties of MAP simple coacervate can contribute to mussel adhesion but also how MAP simple coacervate can be formed. In this work, we used recombinant MAPs for characterization of MAP simple coacervation with great assistance from mass production. Simple coacervates of interfacial MAPs, fp-3F (fast variant) and fp-5, were successfully demonstrated, which is the first report of MAP simple coacervation other than fp-3S, to the best of our knowledge. Using recombinant fp-3F, we additionally showed salt-induced simple coacervation at low pH corresponding to acidified environment of distal depression during mussel secretion. Rheological analysis confirmed viscous liquid properties and shear-thinning properties. Surface forces apparatus (SFA) analysis confirmed stronger adhesion force compared to surface-deposited protein film. In addition, possible driving forces were suggested based on the investigation of effects from Dopa, His₆ tag, negatively charged amino acids, temperature, and salt.

Collectively, we believe that this study has broadened the scope of understanding for simple coacervation of MAPs.

COLL 651

Effect of additives on the crystal morphology of amino acids: A theoretical and experimental study

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The crystal morphology of amino acids can be altered in a controlled manner through inclusion of tailor-made additives in their structure, in order to widen their scope for applications in drug design and targeted delivery. In this study, the effect of multi-additive combinations of hydrophobic and hydrophilic amino acids on the growth and morphology of L-alanine was investigated. Theoretical calculations were performed using two crystal growth models in Materials Studio software: (1) build-in model; (2) surface docking model. Crystallization experiments were carried out using the metal-assisted and microwave accelerated evaporative crystallization (MA-MAEC) technique with multiple hydrophobic and hydrophilic amino acids added in stoichiometric amounts to L-alanine solution. The crystal morphology was established and compared with predicted crystal morphology. The use of hydrophilic and hydrophobic additives was predicted to have significant changes in the morphology of L-alanine crystals. Multi-additive combinations with hydrophobic amino acids resulted in elongation of L-alanine crystals through the (120) face. Experimental data corroborates with the theoretical predictions in relation to the morphological changes due to additives, indicating the accuracy of theoretical models in predicting the impact of additives in crystal growth.

COLL 652

Adsorption behaviors of mussel proteins on biomaterials with different surface chemistries: A fundamental understanding of mussel inspired adhesive designs

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The goal of this study is to understand wet biological adhesion upon which to develop biologically inspired adhesives. Initial studies have pointed out the definite role of 3,4-dihydroxyphenyl-L-alanine (Dopa) residue during mussel adhesion process and Dopa containing polymers have been the paradigm of mussel inspired adhesives. However, interesting yet unexplored topic is the contribution from residues other than DOPA in mussel adhesion especially on different surface chemistries. Therefore, our objectives were to investigate how protein-surface interaction effects are influenced by surface chemistries and how these effects combine with the protein-protein interactions upon a mussel adhesive protein to influence its structure and corresponding peptide mappings

at adsorbed state. In this study, amino-acid labeling/mass spectrometry (AA/Mass) technique was applied to identify the configurations of a dominantly adsorbed protein from mussel foot proteins (mfps) including mfp-3, 5 and 6 on each self-assembled monolayer (SAM) including SAM-OH, SAM-CH₃ and SAM-polyethylene glycol representing commonly used biomaterial surfaces in buffer solution at pH 8.4. Results in this study were then to provide the molecular-level understandings of mussel adhesions on different surface chemistries, with these findings being able to reveal better developments of mussel inspired adhesive designs.



Source of our MFPs from home raised mussels.

COLL 653

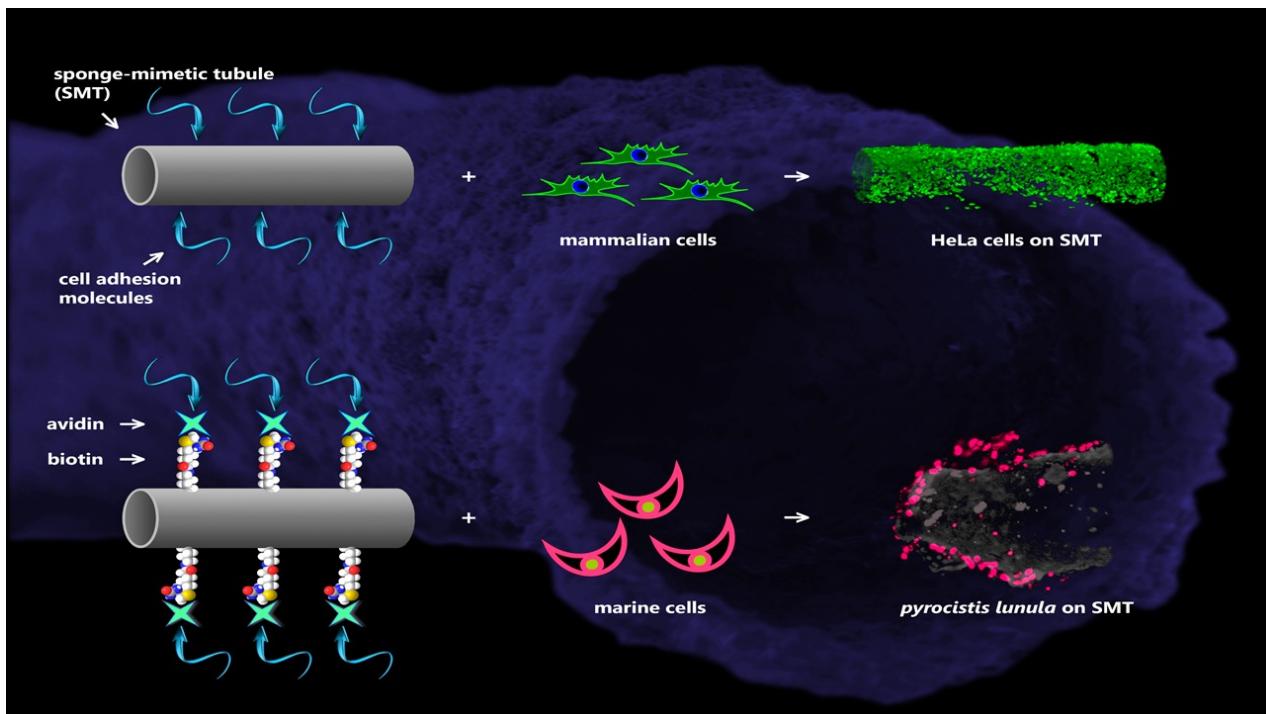
Sponge mimetic tubules: Programmable stigmergy scaffolds for 3D marine, mammalian cell culture and bioelectronics

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The cooperation between multiple copies of individual units from which evolves a collective self is intimately associated with the concept of stigmergy. Sponges are considered the first form of animal life. This work is bio-inspired and evolved after the PI realized that the stigmergy scaffold of a sponge bears a remarkable resemblance to chemical gardens/lost city hydrothermal field constructs, sponges are an intercalating network of the protein spongin associated with silicate or carbonate on which cells are assembled. A robust technology to produce libraries of stigmergy scaffolds consisting of protein intercalated chemical gardens composed of an inorganic component (silicate, phosphate, carbonate with variations in cations and other additives) with proteins or other macromolecules will be presented. The optimized stigmergy scaffolds were further modified with cue molecules that promote cell adhesion and growth. A series of

protocols and analytical methods to characterize this new generation of biomaterials was developed. Marine cells were cultured on surface programmed scaffolds and protocols for attachment and culture of these cell lines on the stigmergy scaffold along with tests for viability of the cells on the constructs were developed. These studies can have a transformative impact on understanding the evolution of animal multicellularity with specific emphasis on the role that scaffolds associated with cell adhesion molecules may have played in promoting unicellular life forms to assemble and cooperatively evolve into a collective

The construction of narrow diameter vascular grafts is very challenging. The technology developed also affords a convenient, inexpensive, green and innovative route to narrow diameter protein tubes and programmable hybrid materials that can potentially serve as ideal scaffolds for the 3D cell culture of mammalian cells to produce vascular grafts.



COLL 654

Dynamic interactions of amelogenin with hydroxyapatite surfaces are dependent on protein phosphorylation and solution pH

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The extra-cellular matrix protein, amelogenin, has been studied for its adsorption to a hydroxyapatite (HAP) surface/solution interface, acting as a surrogate for enamel mineral, using quartz crystal microbalance (QCM). Dynamic flow-based experiments

were conducted to evaluate the effect of solution pH and phosphorylation state of the amelogenin protein. Loading capacities and adsorption affinities (K_{ad}) were calculated when Langmuir isotherm conditions appeared to be met. At pH 8.0, binding was remarkably similar for the two proteins, but at pH 7.4 a higher affinity and lower surface loading for the phosphorylated protein was found. This suggests that phosphorylated amelogenin adopts a more extended conformation than non-phosphorylated full-length amelogenin, occupying a larger footprint on the HAP surface. This surface-induced structural difference may help explain why the phosphorylated protein is a more effective inhibitor of spontaneous mineral formation *in vitro* than the non-phosphorylated version. These collective findings provide new insight into the important role of amelogenin phosphorylation in the mechanism by which amelogenin regulates enamel crystal formation.

COLL 655

Investigation of oligomerization of amyloidogenic peptides at nanoscale gold colloidal interface

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Self-oligomerization of amyloidogenic peptides (i.e., amyloid beta peptide 1-40 (Ab_{1-40}), alpha-synuclein (α syn), and beta-2-microglobulin (b2M)) is regarded as a critical onset step of fibrillogenesis, which is a hallmark mechanism of neurodegenerative diseases. We took an approach of preparing a pre-cursor of oligomer by adsorbing amyloidogenic peptides over nano-gold colloidal particles, providing enough activation energy from the nano-surface charge. Oligomerization was suspected to take place under acidic conditions where the peptides conform unfolded structures. These pH dependent, unfolded structures result in a network with the other peptides situated on the nano-gold colloidal surface. Networking between gold colloids is considered as linked with oligomers. The oligomer units depend on the type of peptide, the colloidal size, and the residual temperature (or thermal energy available from the colloidal surface). The most plausible oligomer unit was concluded to be either dimer or trimer. Recently, we found that formation of a particular oligomer unit is highly associated with the coverage ratio of peptides over the nano-gold colloidal surface, before they cause networking.

COLL 656

Hydrodynamic effects in concentrated protein solutions with repulsive and attractive interactions

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We have measured the self-diffusion, collective diffusion, viscosity and structure factors of highly concentrated ($> 150 \text{ mg/ml}$) antibody solutions. The antibodies in these solutions are subject to both thermodynamic forces mediated by protein-protein interactions and hydrodynamic forces mediated by the solution. Understanding the effect of both forces is essential if one is to be able to predict concentrated solution behaviour from (readily available) dilute solution measurements.

With this in mind we have prepared a range of concentrated solutions in different formulation mixtures, which exhibit both overall repulsive and overall attractive protein-protein interactions. Hydrodynamic forces between antibodies are long-ranged and become difficult to calculate for concentrated solutions. Previous work by Beenakker and Mazur has provided a method, based on an effective medium theory, to calculate hydrodynamic forces for concentrated solutions with repulsive protein-protein interactions. They also provide a scheme to link diffusion measurements with these hydrodynamic forces and the equilibrium structure factor of the antibody solutions. We have extended this approach to include attractive protein-protein interactions within the Baxter adhesive hard sphere model. Our experimental findings are used to test the applicability of the method in predicting concentrated solution properties over the typical range of interaction strengths exhibited by antibodies.

COLL 657

Effects of macromolecular crowding on a coacervation-based model for intracellular organization

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The cellular environment is complex and well organized, utilizing both membrane-bound and non-membrane-bound compartments to localize and modulate biological activity. Recently, a number of non-membrane-bound compartments (e.g. nucleoli, P granules, stress granules) have been shown to exhibit liquid-like behavior, suggesting they were formed through aqueous phase separation. Complex coacervation is an attractive model for polyelectrolyte-rich liquid organelles containing DNA, RNA, and proteins, as it results in the formation of a dense, fluid polyelectrolyte-rich phase. However, coacervate phases are often dispersed in a dilute, supernatant phase, which does not accurately model any cellular compartments. To more closely represent liquid-liquid phase separation within the cellular environment, which is crowded with numerous types of macromolecules, the effects of crowding on complex coacervation were investigated using a variety of polyelectrolyte systems and crowding agents. Initially, the well-characterized coacervate system composed of poly(acrylic acid) and poly(allylamine) was investigated in the presence of both neutral polymer crowders (e.g.

poly(ethylene glycol) and Ficoll) and protein crowders (e.g. albumin). Next, a bio-inspired system composed of a model RNA, polyuridylic acid, and a polycation, spermine, was examined in the presence of the same crowding agents. UV-vis spectroscopy and optical microscopy were utilized to characterize the effect of macromolecular crowding on complex coacervation. The addition of crowding agents to coacervate systems generated an environment that more closely models that of the cytoplasm in which to study liquid-liquid phase separation. This work resulted in a greater understanding of the physicochemical nature of intracellular organization, which can lead to further knowledge of both physical and biological activity through the development of more structurally accurate cell mimics.

COLL 658

Effects of phosphatidylcholine vesicles on adsorption kinetics at an air-water interface

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The surface tension decrease during adsorption of purified dilauroyl or dimyristoyl phosphatidylcholine (DLPC or DMPC) onto a water-air interface was studied via drop profile tensiometry, in order to gain insight into the mechanism of adsorption. These phospholipids are strongly hydrophobic and have low solubility limits in water, above which they separate as lamellar phases which may in turn be dispersed in the form of unilamellar vesicles. Thus, adsorption may involve transport to the interface of dissolved monomer, delivery by vesicles of phospholipid directly to the interface, or a mixed mechanism that depends on molecular exchange between vesicle and monomer. Within each pathway, bulk diffusion or the kinetics of adsorption onto the interface could be rate-controlling. Via dynamic surface tension experiments, we were able to gain insight into this adsorption process, which occurs slowly over timescales of 1000-10,000 seconds for DLPC and longer for DMPC. The adsorption rate for both phospholipids was found to be proportional to the vesicle concentration, indicating a clear mechanistic role for these aggregates: they either directly deliver phospholipid to the interface, or perhaps supply monomer to the solution sublayer next to the interface. Adsorption dynamics was shown to be independent of bulk convection, confirming that monomer diffusion alone is not controlling, and suggesting that the overall process may be limited by interfacial kinetic steps. The mechanistic process that takes place during the kinetically controlled adsorption step, however, remains unresolved. Finally, we have examined the effects of vesicle size, temperature, and chain length on dynamic surface tension as a means of developing an appropriate kinetic model. Success in formulating an accurate kinetic model for phospholipid vesicle adsorption is key for advancement in several areas, including food emulsification and foam formation, spray drying and pharmaceuticals.

COLL 659

New colloidal approaches for human norovirus cleanup and deactivation using surfactants and copper-ion based disinfectants

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We characterize the colloidal interactions of human norovirus reconstituted virus-like particles (VLPs) in aqueous suspension and on surfaces and seek means to control and modify them by using various classes of surfactants. The fundamental understanding of these interactions will aid in practical formulation of novel formulations for virus inactivation and removal from contaminated surfaces. In aqueous solution, we characterize the effects of solution pH and surfactant type and concentration on virus particle aggregation, dispersion, and disassembly using dynamic light scattering (DLS) and electrophoretic light scattering (ELS). We observe that a strong ionic surfactant above its critical micelle concentration (CMC) causes capsid disassembly and breakdown of aggregates. Below CMC, surfactant adsorption onto the virus capsid follows simple adsorption models, depending on the charge of the surfactant and the net charge of the capsid. Micelles formed from strong ionic surfactants can disrupt interactions between capsid protein dimers and cause capsid disassembly. Ionic surfactant adsorption leads to modified apparent surface charge and subsequent aggregation or dispersion, depending on the surfactant charge. We also characterize the effects that copper ions have on virus integrity to explain empirical data indicating virus inactivation by copper alloy surfaces, and to develop novel metal ion-based virucides. High concentrations of Cu(II) ions have little effect on the infectivity of human norovirus surrogates, so we use sodium ascorbate as a reducing agent to generate unstable Cu(I) ions from solutions of copper bromide. Low concentrations of monovalent copper ions (~0.1 mM) cause permanent capsid protein damage that prevents capsid binding to cell receptors and induces a greater than 4log reduction in infectivity of Tulane Virus, a human norovirus surrogate. We reveal the oxidative mechanisms of virus damage, including capsid protein backbone cleavage by SDS-PAGE and RNA degradation by RT-qPCR. The infectivity and colloidal stability data reported here could enable the design of effective and benign virucidal formulations based on copper ions.

COLL 660

Spin selectivity in DNA-mediated charge transport: Base sequence and structure relationships

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Self-assembled monolayers of chiral molecules on metal and semiconducting surfaces have recently demonstrated the capability to filter transmitted electrons depending on spin orientation and the handedness of the molecules. This phenomenon, termed the chiral-induced spin selectivity effect, has renewed interest in probing spin-dependent phenomena in adsorbed chiral molecules, including self-assembled monolayers of double-stranded DNA. While the factors that affect DNA-mediated charge transfer have been extensively studied, the influence of DNA base sequence, GC content, or helical geometry on the spin selectivity in transmitted electrons has not been systematically investigated. We probed the dependence of spin polarization in DNA-mediated charge transfer on nitrogenous base sequence as a means to study spin selectivity in both coherent tunneling and incoherent hopping of charge carriers through helical molecules. Self-assembled monolayers of DNA with varying sequences were formed on multilayer substrates that possess perpendicular magnetic anisotropy, enabling the injection of spin-polarized electrons into the monolayers. The spin-filtering phenomenon was monitored using fluorescence microscopy and photoelectrochemistry by taking advantage of the optical properties of water-soluble perylenedimide derivatives that noncovalently and precisely assemble within double-stranded DNA. Competing charge-transfer pathways that lead to fluorescence or photocurrent generation following photoexcitation of the dye molecules are dependent upon the efficiency of DNA-mediated charge transfer to metal surfaces. This efficiency can be modulated with an external magnetic field used to polarize the spins within the multilayer substrates. Controlling spin transport with light in this manner opens up new opportunities to design device architectures that utilize chiral organic species to generate and to manipulate spin-polarized currents.

COLL 661

Connecting the triangle

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The purpose of this presentation is to put some light in the strategic changes that a small company has done in the last three years passing from distribution business to see the opportunity that represents invest in research and bring that basic science to the market. These strategic changes gives Medcomtech the opportunity to lead innovative fields such as Fast Diagnostic of Infection Diseases or Metabolic Liquid Biopsy. It is not easy though. The company have gone through what we call "Connecting the Triangle". To get together all the parts involved in the project is a major challenge but it is also really exciting.

COLL 662

Optical visualization and quantification of enzyme activity using dynamic droplet lenses

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We describe a new approach to sensing and measuring enzyme activity based on the responsive reconfiguration of complex emulsions. Recently, we reported a method to create complex emulsions in which the droplet morphology is very sensitive to changes in interfacial tension which can be tied to stimuli of interest. We sensitize these droplets to enzymes via the use of enzyme-cleavable surfactants and enzyme-mediated disruption of host-guest interactions. The droplets act as lenses, and so the shape of the droplet affects its transparency; by tracking changes in the optical transmission of droplet films, we demonstrate how simple photodetector measurements may be used to monitor enzyme kinetics. This approach is validated by quantitative measurements of enzyme activity for three different classes of enzymes: amylase, lipase, and sulfatase. We anticipate this materials platform may therefore be useful for low-cost, point of care diagnostics, and the approach to droplet sensitization is highly generalizable and applicable to many other bio-sensing schemes.

COLL 663

Sandwich immunoassays for infectious disease diagnostics using noble metal nanoparticles

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Rapid point-of-care (POC) diagnostic devices are needed for field-forward screening of severe acute systemic febrile illnesses such as Dengue, Zika, Ebola, Chikungunya, and others. Multiplexed rapid lateral flow diagnostics have the potential to distinguish among multiple pathogens, thereby facilitating diagnosis and improving patient care. We present a platform for multiplexed pathogen detection which uses Au or Ag nanoparticles (NPs) conjugated to antibodies to sense the presence of biomarkers for different infectious diseases. We describe results where we exploit the size-dependent optical properties of Ag NPs to construct a multiplexed paperfluidic lateral flow POC

sensor for Dengue, Yellow Fever, and Ebola viruses. Ag NPs of different sizes were conjugated to antibodies that bind to each of the biomarkers. Red Ag NPs were conjugated to antibodies that could recognize the glycoprotein for Ebola virus, green Ag NPs to those that could recognize nonstructural protein 1 for Dengue virus, and orange Ag NPs for non structural protein 1 for Yellow Fever virus. Presence of each of the biomarkers resulted in a different colored band on the test line in the lateral flow test. Thus, we were able to use NP color to distinguish among three pathogens that cause a febrile illness. Because positive test lines can be imaged by eye or a mobile phone camera, the approach is adaptable to low-resource, widely deployable settings. This design requires no external excitation source and permits multiplexed analysis in a single channel, facilitating integration and manufacturing. We will also discuss using star shaped Au NPs for multiplexed biomarker detection by Surface Enhanced Raman Spectroscopy (SERS) as a potential route to increase the sensitivity of the assay.

COLL 664

Measuring heparin activity with a nanoparticle-functionalized catheter

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There are over 500 million doses of heparin given annually, but this drug has a narrow therapeutic window and frequently implicated in overdoses and underdoses. Heparin is currently monitored with the active partial thromboplastin time (aPTT), but the aPTT suffers from long turnaround times, a variable reference range, limited utility with low molecular weight heparin, and poor correlation to dose. Here, we describe a technique that can monitor heparin activity and function using photoacoustic imaging. This approach uses methylene blue and the interactions between this cationic dye and the negatively charged heparin, which results in an increase in photoacoustic signal. We measured clinically relevant heparin concentrations in blood with a detection limit of 0.28 U/mL and validated this approach via the aPTT in six samples (Pearson's $r = 0.86$; $p < 0.05$). We confirmed signal reversibility with the known heparin antagonist protamine sulfate. We then build a catheter using silica nanoparticles—the surface charge of these nanoparticles was critical to ensure methylene blue sequestration as well as good photoacoustic signal (Fig. 1A). Heparin concentrations from 1 – 5 U/mL were detectable with this device, and we envision using this as a wearable tool to monitor heparin dose in subjects (Fig. 1B). To the best of our knowledge, this is the first use of photoacoustics to image anticoagulation therapy with significant potential implications to the cardiovascular and surgical community.

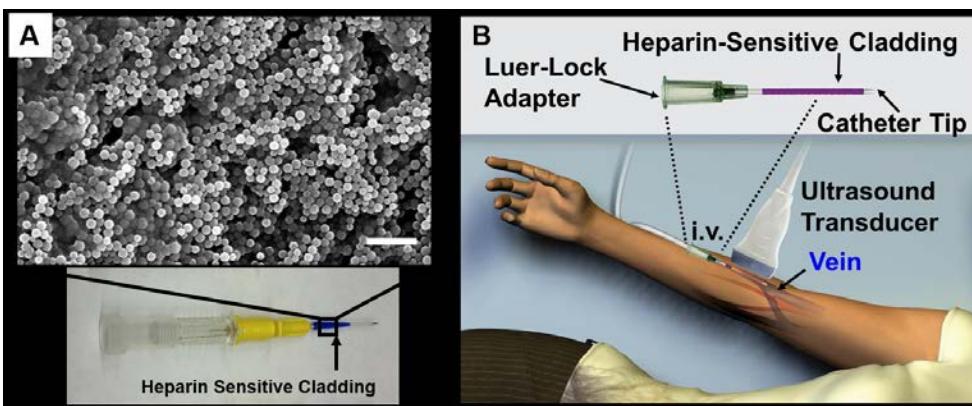


Fig. 1. A) The heparin-sensitive catheter is coated with methylene blue-labeled silica nanoparticles. This is used to measure heparin using photoacoustic imaging. B) Long-term, we envision using this as a wearable tool to titrate drug levels into the therapeutic window.

COLL 665

Highly quenching nickel-gold core-shell magnetic plasmonic nanoparticles for biosensing

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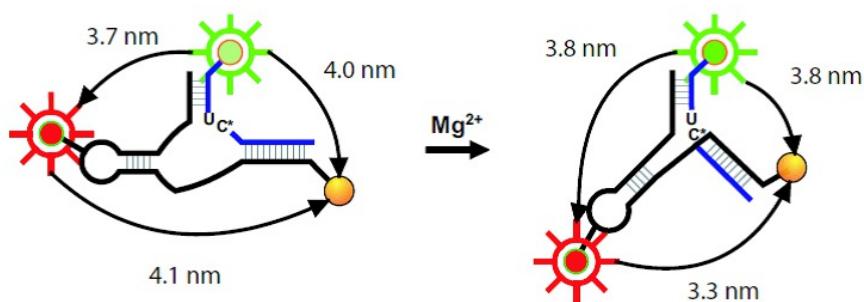
Small (<20nm diameter) plasmonic nanoparticles, gold nanoparticles (AuNPs) in particular, have enabled the development of various biosensor technologies that function on the distance-dependent quenching of fluorescent signals by the nanoparticles. The ability to extend the application of these long-range molecular beacon systems into red and infrared wavelengths while still using a very small nanoparticle size can be achieved through a nickel-gold core-shell nanostructure. These systems show a much higher quenching behavior than pure gold nanoparticles of the same size, and being magnetic in nature allow for easier processing and enable multimodal functionality as well. Here we present the synthesis and characterization of these small core-shell particles and quenching studies on a number of fluorescent dyes. Such particle systems can be used to study the dynamics of biological structures including proteins and DNA without disturbing their native structures.

COLL 666

Enhanced energy coupling within a nanometal plasmon field for molecular ruler and in-vitro event mapping technologies

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There is no doubt that optical probe methods based upon the coupling of nanometals and energy transfer have revolutionized molecular biophysics technique for sensing. As such the development of energy coupling schemes to sense in-cuvette and in-vitro events have rapidly expanded, including, SERS and the manipulation of radiative and non-radiative enhancement of an appended dye at a nanometal surface. In the presentation we will discuss the continued development of surface energy transfer (SET) methods. The application of SET methods to biophysical problems will be explored for 3-D structure analysis by multicolor techniques, enhancing the sensitivity of the SET technique by incorporating a magnetic component, and as a tool to map cell evolution following transfection in in-vitro experiments will be discussed. The description of SET and the development of mathematical models to treat core@shell metal structures will be discussed



COLL 667

Updating the mechanics of cartilage and joint lubrication

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Cartilage contains ~80% water by volume and nearly a century of research suggests that this unique collection of physical attributes requires a biphasic structure. Under compressive loading, the interstitial fluid pushes against the collagenous matrix and pressurizes in response. Pressurized interstitial fluid carries the majority of the contact force hydrostatically (interstitial lubrication), which simultaneously explains unusually low friction coefficients and unusually high stress-carrying capacity. These internal pressures also drive fluid from the tissue, which results in increased friction and strain over time. How fluid re-enters cartilage to restore mechanical function following static loading is not obvious. *In-vivo* x-ray and MRI studies have shown that joint-space thins over time during rest but thickens during activity after rest. The only hypothesis to explain this unexpected recovery phenomenon suggests that ‘wrung-out’ contact areas freely imbibe fluid when exposed to the bath during articulation. This talk discusses and tests an alternate hypothesis. Using *in-situ* measurements, we observed the same fluid recovery process observed in joints without ever exposing the contact to the bath; we call this purely sliding-induced recovery phenomenon ‘tribological rehydration’. Furthermore, we show direct evidence to refute the textbook-suggested dogma that hydrodynamic fluid films primarily lubricate natural joints. The results suggest that

friction is primarily reduced by interstitial lubrication and that boundary films are probably critical for wear prevention. During articulation, hydrodynamic pressures develop and drive fluid into the porous contacting surfaces rather than between them, thus restoring hydration and mechanical function of the tissue. The results indicate that Nature has prioritized tolerance to static loading over fluid film lubrication during sliding. Furthermore, they suggest that a fundamentally different approach is necessary to recapitulate biomimetic function in artificial joints.

COLL 668

Colloid-probe AFM on gels and humidity-dependent AFM on hydrophilic networks: Aqueous tribology and glass-rubber transitions

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This work applies atomic force microscopy (AFM) methods to crosslinked polyacrylamide and polyvinyl pyrrolidone lubricious coatings as well as crosslinked fibrin-based gels for tissue engineering applications. Analytical methodologies are explored under aqueous immersion or versus humidity; in much of the former the sharp AFM tip is replaced with a colloid microprobe.

Beyond rich morphologies, normal and shear force measurements and tip-sample adhesion hysteresis reveals variable material responses as a function of UV crosslinking time and preceding macrotribological measurements. Nanomechanical probing during hydration cycles identifies reversible glass-to-rubber transitions, where the critical transitional humidity also depends on degree of crosslinking. Tip-sample adhesion is also strongly sensitive to humidity-actuated glass-rubber transitions (again dependent on crosslinking), and moreover reveals significant differences between thin (confined) and thick coatings in the case of polyacrylamide.

Shear-force methods further reveal crosslinking-derived differences in coating behavior, especially pertinent to wear on lubricious coatings. Colloid-probe AFM methodologies were developed and utilized to explore both normal and anisotropic shear-modulation response on oriented fibrin gels under aqueous immersion. In all cases mapped measurements, up to several tens of microns in lateral scale, reveal spatial heterogeneities in mechanical or tribological response functions as well as their relationships to morphology. In some cases we find shear response varying by a factor of four across surface regions ~25 microns in extent, underscoring how much more one learns with local measurements. Given the emerging understandings of the importance of nano- to micro-scale structure to interactions between synthetic materials and biological tissue, AFM seems poised to play an increasingly important role in the characterization of intrabody materials.

COLL 669

Nanotribological studies of polymer brushes fabricated by near-field and interferometric lithography

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The tribological properties of polymer brushes with systematically varying grafting densities have been studied by friction force microscopy (FFM). Films formed by the adsorption of aminosilanes on silica have been derivatized in two different ways. First, adsorbates with nitrophenyl protecting groups are deprotected by exposure to a near-field probe. By varying the rate of motion of the near-field probe, the extent of deprotection can be controlled systematically. The deprotected amine groups are derivatized by reaction with bromoisobutyryl bromide. When poly(2-(methacryloyloxy)ethyl phosphorylcholine) (PMPC) was grown from these patterns by atom-transfer radical polymerisation (ATRP), the height of the structures was proportional to the writing rate and hence to the density of initiators created in the lithographic process. The friction coefficient was determined from friction-load measurements and was proportional to the height of the polymer structure. At small writing rates, the brush thickness and coefficient of friction were similar to those measured for unpatterned brush films.

Second, exposure of a brominated surface to UV light in a Lloyd's mirror interferometer leads to debromination in regions exposed to intensity maxima, while in regions exposed to minima, the initiator remains intact. In intervening regions, a gradient of density of Br is formed. Growth of the zwitterionic polymer poly(cysteine methacrylate) (PCysMA) from these surfaces by ATRP yields brush structures with gradients of grafting density, the steepness of which may be controlled by varying the period of the interferogram. At small periods, the polymer structures are narrow and the polymer chains have a comparatively high degree of freedom; consequently the brushes are collapsed. As the period increases, the widths and heights of the polymer structures increase. The height approaches the thickness of an unpatterned brush at a period of ca. 300 nm. In ethanol, a poor solvent for PCysMA, a linear friction-load relationship was observed, consistent with the formation of a collapsed structure in which energy dissipation was largely through molecular plowing. The coefficient of friction was proportional to the heights of the polymer nanostructures. In water, a good solvent for PCysMA, the friction-load relationship was non-linear, and was found to be fitted by Derjaguin-Muller-Toporov contact mechanics. The surface shear strength was found to be proportional to the brush height.

COLL 670

Wear protection without surface modification: Is it possible?

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With the ever-increasing need of more efficient and long lasting machinery and devices, certain issues such as control of wear and fatigue of machine parts have become extremely challenging. The design of lubricating fluids able to protect surfaces against wear and high friction has been one the several tools used by engineers to improve machines' life time. Several design strategies aimed to enhance wear protection have emerged involving polymer brushes either in their molecular form as bottle brush polymers, or grafted on the surface as polymer brush coatings. All these strategies require the lubricating or wear protecting molecules to be strongly anchored to the surfaces in order to avoid close contact between the surfaces. Strong anchoring of molecules on surfaces requires a good knowledge of the chemistry and structure of the surface which complicates dramatically the translation of these technologies towards industrial settings.

We describe the design of lubricating and wear protecting fluids based on synergistic mixtures of bottlebrushes (BB) and linear polymers solutions. To illustrate this concept we used hyaluronic acid (HA) - a naturally occurring linear polyelectrolyte, and water soluble synthetic BB polymers. Individually, these two polymers exhibit poor wear protecting capabilities compared to saline solutions. Mixture of the two polymers in pure water or in saline allows to drastically increase wear protection of surfaces under a wide range of shearing conditions. We demonstrate that this synergy between the BB and HA polymer emerges from a strong, yet transient, cohesion between the two components forming the boundary film due to entanglements between both polymers. We show that this concept can be applied to other types of linear polymers and surfaces and is independent of the chemical and mechanical properties of the surfaces.

COLL 671

Effect of multivalent counterions to the structure and lubrication properties of polystyrene sulfonate brushes

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Surface tethered polyelectrolyte brushes are scientifically interesting and technologically relevant to many applications, ranging from colloidal stabilization to responsive and tunable materials to lubrication. Many applications operate in environments containing

multivalent ions, media in which our scientific understanding is not yet well developed. We synthesized high density polystyrene sulfonate (PSS) brushes via surface initiated atom transfer radical polymerization, and performed neutron reflectivity (NR) and surface forces apparatus (SFA) measurements to investigate and compare the effects of monovalent Na⁺, and trivalent Y3+ counterions to the structure of the densely tethered PSS brushes. SFA friction measurements on PSS brushes show that the presence of trivalent counterions can great alter the lubrication properties of the PSS brushes.

COLL 672

Tactile and hair–hair friction behavior of hair fibers

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There is an increasing interest in finding analytical techniques that could be used to predict various sensory characteristics. Many of the sensorial aspects associated with hair are related to friction. Friction between hair fibers is related to their manageability and volume and friction between a human finger and hair more related to the sensorial touch. The nanotribology of hair was evaluated using the AFM fiber probe technique to measure the friction between two single hair fibers. Tactile friction was measured using a ForceBoard™, on the root, middle and tip part of the hair, both along and against the cuticles. A clear directional effect was observed with higher friction against the cuticles. Hairs treated with a proprietary repairing agent containing ceramides, show a slight trend towards a lower tactile friction coefficient along the cuticles but more evident against the cuticles, compared with the untreated reference and also less difference between the two stroking directions. This indicates that most likely part active is also present at the surface of the hair, where the lower friction against the cuticles may be due to a smoothening of the fiber which could act to reduce the interlocking effect. The AFM fiber-fiber friction results show a higher friction coefficient between treated hair fibers, indicating that the nature of the hair surface is changed upon treatment. In damaged hair, naturally occurring ceramides and fatty acids are missing, resulting in coarse, dry and dull hair. Understanding the bio-tribological effect of ceramides help to optimize the protection and restoration of hair fibers and consequently improve the surface and appearance of the hair. The unique combination of techniques and protocols developed in this work to evaluate the tribological effects of hair treatments is promising. In future studies it would be highly interesting to link the frictional response with quantified sensorial attributes.

COLL 673

Effects of 3D surface patterning on the tribology of human stratum corneum and the topology of a polyurethane skin surface model

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Natural surfaces may exhibit remarkable surface properties due to their structure. In the case of skin, its surface topography (microrelief) may influence many of its perceived sensorial properties (shine, color, touch). In order to explore the effects of superimposed biomimetic surface textures on friction, human stratum corneum samples were prepared with and without an imprinted regular 3D grid pattern. The smaller-scale roughness of the samples measured with Atomic Force Microscopy (AFM) and optical profilometry remained when grid lines with a height of 30-40 µm and separation of about 500 µm were introduced. Surface Forces Apparatus (SFA) friction experiments on rehydrated stratum corneum (SC) were performed at low speed (µm/s, back-and-forth sliding) and at more realistic, high speed (cm/s, rotational sliding). Two stratum corneum surfaces in contact did not adhere to one another and had a friction coefficient of 0.1 or less at low sliding speed. They showed an interesting loading-unloading hysteresis with lower friction on unloading, in particular when the contact was on a grid line of the patterned samples. This suggests that the patterning locally induced different mechanical properties of the stratum corneum and that its recovery was not immediate on unloading. When one SC surface slid against a rigid glass surface, the friction force was always higher than the one recorded when two SC surfaces were in contact. However, because of the differences in size of the real contact area between the smooth glass and the stratum corneum with and without pattern, the friction force in the back-and-forth sliding experiments was lower with the imprinted pattern. To further explore the feasibility of texturing skin-like surfaces, films of self-assembling block- and random copolymers were formed on polyurethane substrates with surface topologies that reproduce human skin microrelief (hand, forearm, face). The resulting randomly patterned or randomly rough coatings were characterized with AFM and optical profilometry. The results will be discussed in the light of their cosmetic implications for the development of future skin-care products that could convey properties similar to those found on natural surfaces, such as superhydrophobicity.

COLL 674

Harnessing shape and bi-specific antibodies for improved cell-targeting efficiency of poly(ethylene glycol) capsules

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Drug carriers that have high targeting efficiency are often required in drug development. It is crucial to understand how the drug carrier properties can be tailored to avoid immune recognition and improve targeting cell association. Polymer based capsules are of particular interest in drug delivery as their physicochemical properties can be tailored. Interaction of spherical polymeric capsules with cells has been studied extensively, however the effects of carrier shape and their potential to enhance systemic targeting have yet to be fully elucidated.

Herein, we report a templating method for the engineering of functional polymer capsules with different aspect ratios through a novel fabrication method, termed continuous assembly of polymers (CAP). Poly(ethylene glycol) (PEG) is known for its immunologically stealth properties and PEG capsules with different aspect ratios of 1, 8, 15, and 20 were fabricated. A bi-specific antibody which binds to both PEG and epidermal growth factor receptor (EGFR) was added to the PEG capsules. The targeting efficiency of these capsules with tuned antibody concentration and shape was studied *in vitro*. EGFR positive human breast cancer cell line MDA-MB-468, EGFR negative hamster ovary cell line CHO-K1 and murine macrophage cell line RAW264.7 were tested against capsule association. It was found that capsules with elongated shapes significantly improved positive cellular association while maintaining negligible negative association. With the same surface area, capsules with aspect ratio 20 had 2 folds increase in cancer cell association compared to the spherical counterparts after 1 hour incubation. All of the PEG capsules regardless of shape could achieve up to 98% of targeting if incubating for 5 hours. PEG capsules were further conjugated with anti-cancer drug doxorubicin to allow pH triggered intracellular release of drug. This study will enable a rational selection of capsule design for future development.

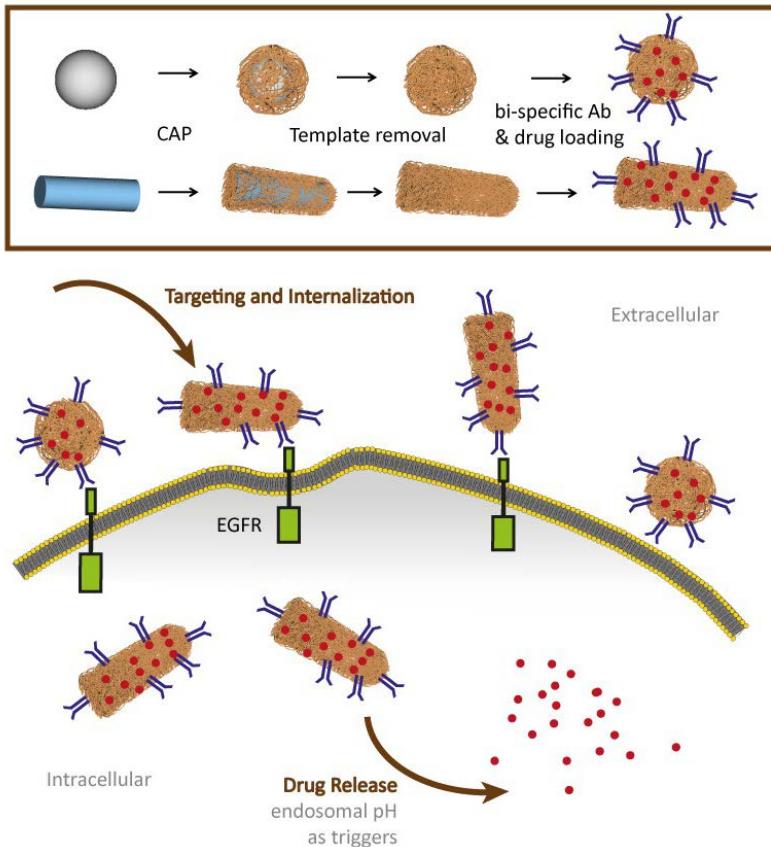


Fig 1. Schematic of poly(ethylene glycol) capsule preparation and cellular association.

COLL 675

Galectin-1-based tumor-targeting for gold nanostructure mediated theranostics

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Anginex (Ax) is an antiangiogenic, synthetic 33mer that binds to galectin-1, which is overexpressed by the tumor endothelium- a critical requirement for effective nanomedicine delivery- as well as tumor cells themselves. In the present study, Ax was used as a targeting agent after conjugation to polydopamine-coated Au nanocages, selected for their photothermal conversion, biocompatibility and functionalization potential. The retention of Ax's biological activity was confirmed through migration assays and tube formation assays, and untargeted Au nanocages did not demonstrate an effect. Targeting was confirmed by darkfield microscopy, photoacoustic microscopy, photoacoustic flow cytometry, which showed that Ax significantly increased the binding with the cell surface. However, as expected from our previous studies demonstrating

that Ax at these levels has negligible effect on cell viability, we observed that conjugated and unconjugated nanocages had an ED₅₀ greater than 100 pM in standard proliferation assays. In contrast, we found that combining 25 pM conjugated nanocages and 10 min near infrared irradiation induced photothermal therapeutic effects resulting in marked cell death for both tumor and endothelial cells *in vitro*. Additionally these targeted Au nanocages were shown to be able to function as a radiosensitizer, reducing clonal survival to one fourth of radiation alone and one half relative to untargeted cages. Ax further enabled these nanocages to specifically target tumor tissue, significantly increasing the accumulation/retention in tumors relative to untargeted cages; accumulation of targeted nanocages was also observed to increase in spleen, and liver. Notably, i.v. injection of a dose of 50 pmol/kg resulted in no observed adverse toxicity over 3 days. Photoacoustic detection of particles was further employed to determine the pharmacokinetic profile, and the particles were found to continue circulating for more than two hours, with gradual increases in tumor accumulation. The *in vivo* photothermal capacity of the construct was characterized. Multiplexing this thermal treatment with additional therapies, particular chemotherapy and radiation, is currently under investigation using *in vivo* models of breast and lung cancer.

COLL 676

Stem cell/nanoparticle conjugates for targeted cancer therapy

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Targeted drug delivery is a long-standing goal for cancer therapy. Nanoparticles have shown promise as platforms for targeted drug delivery, but major challenges remain for controlling the distribution of nanoparticles within tumors. Neural Stem Cells (NSCs) are appealing candidates for use as carriers for nanoparticles in order to overcome these biodistribution challenges. NSCs have demonstrated inherent tumor tropic properties in invasive and metastatic tumor models, migrating selectively to invasive tumor foci, penetrating hypoxic tumor regions, and even traversing through the blood-brain barrier to access intracranial tumor foci following intravenous administration. NSCs do not intrinsically have any anti-tumor efficacy; they must be modified in some way to exploit their tumor targeting abilities. A first-in-human safety/feasibility clinical trial using genetically modified NSCs to treat recurrent gliomas was recently completed. As NSC-based therapy moves into the clinic, there is an opportunity to develop complementary techniques to enable NSCs to destroy tumors. The combination of NSCs and nanoparticles offers the potential of a general drug targeting system. We have demonstrated that NSCs can either be modified to bear nanoparticles on their surface or can internalize them. The nanoparticles can release drugs or used for photothermal ablation. In all cases, the NSCs remained viable and targeted the delivery of the nanoparticles to tumors *in vivo*, enhancing the therapeutic efficacy of the nanoparticles.

COLL 677

Thermo-responsive hybrid peptide nanoparticles in targeting-free cell selection and uptake

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Targeted delivery of imaging agents and therapeutics has been at the forefront of biomedical research. One of the challenges is identification of the unique cell surface targets for cell selection. Here we present the alternative approach, where cell selection does not depend on molecular receptors, but relays on a thermo-responsive peptide-based nanocarrier. The hybrid peptide containing cell-penetrating peptide and collagen domains is designed to undergo coil-to-helix transition (folding) below physiological temperature. Since only helical form undergoes effective internalization by the cells, this approach allows effective temperature-discriminate cellular uptake. The selected cells are cooled down enabling carrier to fold and deliver the cargo. The peptide carrier can deliver fluorescent tags, small molecule drugs and nucleic acid therapeutics. The method is fast (< 15 min) and selective; over 99.6% of cells *in vitro* internalized the peptide carrier at low temperatures (15°C), while less than 0.2% internalized at 37°C. *In vivo* results confirm the high selectivity of the method. This approach is generic as selected cells could differ from the adjacent cells or could belong to the same cell population.

COLL 678

Screening of prostate cancer cells using Zn(II) sensing SERS nanoprobe

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Mobile zinc signatures can be used as a biomarker for prostate cancer prediction, opening the route for the early diagnosis of cancer. Clinicians need a reliable tools which can offer fast, highly sensitive and selective mobile Zn(II) concentration in live cells. Here we will discuss our recent reports on the design of novel and highly efficient surface enhanced Raman spectroscopy (SERS) probe using **p-(imidazole)azo benzenethiol attached gold nanoparticle** as a Raman reporter, which has the capability to identify prostate cancer cells based on Zn(II) sensing. Reported data show that SERS probe can distinguish metastatic cancer cells from normal prostate cells very easily. Designed Raman probe has the capability to be used as chemical toolkit for determining mobile Zn(II) concentrations in the biological sample.

COLL 679

Drug delivery using layered structured nanomaterials

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We are studying new applications of the layered inorganic nanomaterial zirconium phosphate (ZrP). The θ phase of ZrP can be directly ion-exchanged with large metal complexes, producing intercalated phases useful for artificial photosynthesis schemes, water decontamination, amperometric biosensors, and vapochromic materials' applications. Recently, we have demonstrated using X-ray powder diffractometry that the hormone insulin and the anticancer drugs cisplatin and doxorubicin, as well as several metallocenes, can be intercalated in ZrP. The intercalation reaction results in nanoparticles with an expanded interlayer distance. UV-vis spectrophotometry, XPS and ^{31}P -NMR spectroscopies, and molecular modeling studies indicate that for cisplatin the drug's chloride ligands have been substituted by phosphate groups of the ZrP material. Results of in-vitro drug release as well as cytotoxicity studies with breast-cancer cell lines for both anticancer agents indicate that the use of these materials for cancer treatment could prove to represent a new strategy for nanotherapeutics. Nanoparticles of these materials can specifically target tumor cells by the Enhanced Permeability and Retention Effect. We have recently intercalated two neurological agents: carbamazepine and dopamine. Nanoparticle surface derivatization schemes are being developed and studied with extensive ^{31}P -NMR spectroscopy methods.

COLL 680

Probing the stability of liposomal spherical nucleic acids for therapeutic design

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Liposomal nano-bioconjugates are an attractive platform for therapeutic delivery due to their biocompatibility, functionality, and ability to encapsulate or intercalate diverse therapeutic agents. Of these conjugates, liposomal spherical nucleic acids (LSNAs), which feature a lipid core functionalized with a densely packed and highly oriented nucleic acid shell, are being pursued due to their immunostimulatory and gene regulatory potential. LSNAs are synthesized by functionalizing DNA to a hydrophobic intercalator that can spontaneously insert into a lipid bilayer; the use of non-covalent attachments for functionalizing liposomes with nucleic acids makes LSNAs intrinsically dynamic, which potentially reduces their stability and therapeutic efficacy. Here, we examined the dynamic behavior of LSNAs in order to understand how the hydrophobicity of intercalators functionalized to the nucleic acid affects stability of the nucleic acid shell using fluorescence-based reporters. The stability of LSNAs synthesized with either cholesterol or lipids functionalized to DNA was evaluated in the presence of serum proteins, lipidic structures, and cells. LSNAs synthesized with DNA

functionalized to more hydrophobic intercalators (i.e. lipids) exhibited enhanced resistance to degradation compared to cholesterol terminated structures. Moreover, to further increase the stability of the construct, we crosslinked the DNA shell using amine-based linkages. To evaluate the therapeutic effects, we functionalized LSNAAs with unmethylated CpG DNA motifs, which are ligands recognized by toll-like receptors (TLR) involved in immune activation. LSNAAs with enhanced stability resulted in greater activation of TLR9 in reporter cell lines, indicating greater therapeutic activity. This research presents different pathways through which the effective stability of the LSNAAs can be modulated for multiple applications to derive therapeutic benefits.

COLL 681

Development and characterization of free-standing nano films loaded with iron nanoparticles for magnetic drug targeting

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Introduction

Magnetic drug targeting (MDT) using magnetic nanoparticles loaded-liposomes (magnetic liposomes) has become a popular approach because it can provide selective delivery by using an external magnet. However, the effectiveness of using a magnet outside the body to induce magnetic liposomes is limited in situations where the affected area is deeply embedded because the surface layer of skin has maximum magnetic field intensity and its intensity decreases exponentially with the increase in depth. Therefore, we exploited free-standing nano films embedding magnetic nanoparticles. These magnetic films can be magnetized by using an external magnetic field such as magnetic resonance imaging (MRI). Therefore, an affected organ area has maximum magnetic field intensity when these films are affixed there in a homogenous magnetic field (Fig.1). We expect that this system will to accumulate magnetic liposomes on an affected area in higher efficiency than ever.

Results and Discussion

Magnetic nanoparticles with sizes ranging from 5 nm up to 46 nm were synthesized by thermal decomposition of iron (III) acetylacetone in dibenzyl ether. Particle size was controlled by changing the molar ratio of iron (III) acetylacetone and oleic acid. To characterize the magnetic response of nanoparticles, a magnetization hysteresis was evaluated by vibrating sample magnetometer (VSM). Results showed that magnetic parameters were almost size-independent. Meanwhile, dispersibility was strongly size-dependent. A smaller particle has excellent dispersibility.

Free-standing magnetic nano films were fabricated by spin-coated assisted deposition using polyvinyl alcohol (PVA) as a sacrificial layer approach. During the final step, the polymer-coated wafer was soaked in water to remove the PVA layer. We found that thicknesses of the nano films were 180 – 200 nm by atomic force microscope (AFM).

Transmittance electron microscope (TEM) images showed homogeneously dispersed magnetic nanoparticles in polymer matrix. A further investigation of the best conditions for nano films to achieve MDT is currently underway in our laboratory.

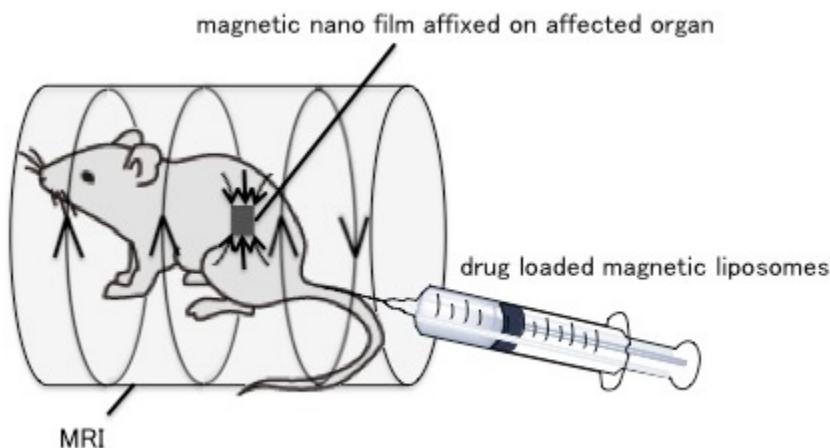


Fig.1 Schematic drawing of this study.

COLL 682

Synthesis and biomedical application of metal and metaloxide nanocrystals

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Metal and metal oxide nanocrystals exhibit many unique properties and these properties make them very useful in a variety of applications. I will talk about the application of magnetic metal oxide nanocrystal in cancel diagnosis and treatment as well as the application of silver nanoparticles as antimicrobial agents. A large library of uniform metal and metal oxide nanoparticles with various shape, size, composition and surface chemistry were generated through solution chemistry method. Using these nanoparticles, we established the relationship between the performance of the nanocrystals and their structure. It was fond that the properties of the nanoparticles are highly dependent on these parameters. The performance of the metal and metal oxide nanoparticles can be greatly enhanced by optimizing their structures.

COLL 683

Nanolipoprotein particles for delivery of therapeutics to the brain

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The blood-brain barrier (BBB) protects the brain from foreign or harmful material, but also blocks access of many potentially therapeutic molecules that could be used to treat conditions of the central nervous system, such as gliomas, infections, and neurotoxin exposure. However, it is known that the vasculature cells comprising the BBB actively transport molecules such as apolipoprotein A1, a component of high-density lipoprotein particles (HDLs), into the brain. With the intention of exploiting these existing transport mechanisms to shuttle therapeutics into the brain, we have developed a synthetic nanoparticle that mimics apo A1 HDLs (referred to as nanolipoprotein particles, or NLPs) that are comprised of lipids and a scaffold protein derived from apo A1. Using small molecules (fluorophore-labeled lipids) as surrogate therapeutic cargo, we have demonstrated that these particles have circulation times *in vivo* on the order of several hours, and that these labels can be seen to be distributed throughout the brain following injection. Importantly, ¹⁴C-labeled lipids may be incorporated into these particles, and quantification of the dose delivered to the brain and cerebrospinal fluid was carried out using accelerator mass spectrometry. This combined data indicate that NLPs prepared with apo A1 derivatives are a promising therapeutic vehicle for CNS delivery.

COLL 684

Formulation and study of highly stable, semifluorinated nanoemulsions with theranostic applications

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Amphiphilic polymers that can form nanoscale assemblies in aqueous solution have found several applications in drug delivery. Nanoemulsions are especially advantageous systems due to their large oil droplet core, perfect for the solubilization of hydrophobic drugs, and their kinetic stability over time. However, drug release from these particles is often too fast resulting in burst release of drug, and as a result, toxicity concerns. The Mecozi group has developed a new class of semifluorinated polymers, consisting of hydrophilic, fluorophilic, and lipophilic blocks, that can form triphilic nanoemulsions. The introduction of the fluorocarbon moiety has allowed for the development of nanoparticles with enhanced kinetic stability over time. The polymer focused on here uniquely demonstrates that hydrophobic drugs, more specifically chemotherapeutics, can be encapsulated with high loading and retention within an oil droplet core. Drug release from the core is modulated by the surrounding fluorous shell of the polymer. Particle solubility and tight packing around the oil droplet core is accomplished by the hydrophilic corona. The incorporation of a fluorous additive provides further particle stability and enhanced drug retention upon the formation of the fluorous phase that seals the lipophilic nanoemulsion core. The additive also plays a

valuable role as an effective ^{19}F MRI contrast agent leading to particles with dual function, a theranostic system. Emphasis will be placed on the formulation of these nanoemulsions, their physicochemical properties, as well as *in vitro* drug release and ^{19}F MRI studies.

COLL 685

Ice adhesion reducing polymers and prepolymers based on siloxanes and F-POSS

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The build-up of ice upon the surfaces of objects has a negative impact on infrastructure. The weight of ice on power lines, buildings, wind turbines, aircraft, refrigeration units, air conditioning and signs can impair these structures. Current techniques to control the build-up and adhesion of ice on aircraft and other structures are often energy and resource intensive and may have environmental implications (such as from the use of chemical de-icers). Durable coatings which can reduce ice adhesion sufficiently to allow passive removal of ice (such as by wind on power lines, or movement for aircraft wings) would allow the design of more robust and energy efficient anti-icing/ deicing systems. Hydrophobic polymers which when applied to surfaces reduce the adhesion of ice have been developed. Two approaches were investigated, siloxane-urethane/ urea copolymer networks, and F-POSS-siloxane containing coatings. These coatings were applied onto aluminium substrates using conventional industrial spray techniques. Ice adhesion of coated substrates was measured via an Instron Universal Testing Machine in an environmental chamber at -10°C. Coated surfaces with reduced ice adhesion compared to commercially available polyurethane and polysiloxane coatings were obtained. The structure-property relationships of siloxane-urethane and siloxane-urea copolymer networks were investigated. Molecular weight (cross-link density), siloxane content, functional group, polyol content and solvent selection was investigated, and the effect on ice adhesion and surface properties (surface energy, hardness, gloss, and roughness) determined. Analysis of the surface with elemental mapping techniques (SEM) and XPS indicated the optimum conditions for efficient migration of low energy components to the surface. The molecular weight of the siloxane and the concentration of siloxane were found to be the most important factors on the final polymer coating properties.

COLL 686

Preparation of pressure-inducible, self-healing bioadhesives by material-independent polymer coating of nanoparticles

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For long-term repair of cartilage damages, tissue engineering-based treatment is a promising strategy. However, the integration of an engineered tissue to the native cartilage lesion is hampered by low interfacial adhesion between them. The anti-adhesive properties and high load-bearing environment greatly hinder the development of efficient adhesives for the cartilage. Herein, we demonstrate a new design principle for an efficient cartilage tissue adhesive in which a cationic polymer-coated nanoparticle (CP-NP) solution glues cartilage and cartilage or a gel together. We hypothesize that CP-NPs would efficiently bind to anionic glycosaminoglycan abundantly present in both native and engineered cartilage via electrostatic interaction. As base materials commercially available silica nanoparticles are used. The surface charge of silica NP is converted to be positive by materials-independent one-step dopamine-assisted coating of poly(ethylene imine)(PEI). 3h-coating results in conversion of the negative NP surface charge (-44 ± 3.04 mV) into the positive one ($+38.2 \pm 0.06$ mV). Adhesion of two bovine knee cartilage pieces is induced by a mechanical press for 30 s after application of the PEI-coated silica NP (PEI-NP) at the interface. The PEI-NP exhibits significantly higher adhesion strength (28.48 ± 5.92 kPa) than unmodified NP (18.9 ± 2.31 kPa), which implies surface-coated PEI contributes to the enhanced adhesion. The adhesion strength by PEI-NP is enhanced when the press force increases from 3N (28.48 ± 5.92 kPa) to 6N (36 ± 5.57 kPa). In addition, the PEI-NP is able to glue native cartilage and engineered tissue composed of anionic biopolymers, namely alginate and gellan gum. Furthermore, adhesion by the PEI-NP exhibits the self-healing property: the detachment stress after 5 repeated attachment-detachment cycles is maintained as strong as 76 % of the one measured at the first. This press-inducible self-healing property makes it an ideal adhesive in high load-bearing cartilage tissue environments. We expect this new class of bioadhesives would lead to a breakthrough in cartilage tissue regeneration and effective cartilage repair.

COLL 687

Rediscovering silicones: Water repellency and water permeability

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Poly(dimethylsiloxane), PDMS, is by far the most important silicone material and is used, as a neat liquid (oil), crosslinked solid (elastomer), or component of a more complex system, in an extremely wide array of applications and technologies. The interactions that PDMS-based materials have with water vary as well - in interesting ways that are not seen with other materials and that are counter-intuitive to most scientists who have been trained in modern materials science and chemistry curricula. PDMS is "hydrophobic" and PDMS-based materials are used to impart water repellency to solids in multiple applications. PDMS oil, however, spreads on water as a molecular layer (Langmuir monolayer) that can be compressed and transferred to solid substrates. Surprising to most is that cross-linked PDMS materials exhibit extremely high water permeability. This high permeability is the basis of moisture-cured RTV silicones, but is also apparently inconsistent with its hydrophobic, water-repellent nature.

Quantitative data on both water repellency and water permeability of model silicone systems will be discussed. In particular, we will discuss the mechanism of water vapor transport in silicone membranes and how the thickness and surface chemistry of the membranes affect permeation. We will also discuss water contact angle hysteresis and how the molecular weight of the silicone can affect water repellency.

COLL 688

Development of new multi-functional polycarbonate platforms

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Polycarbonates are routinely utilized for diverse nanomedical applications owing to their innate biocompatibility and low toxicity. Additionally, functionalized polycarbonate diblock co-polymers are well-known to self-assemble into well-defined nanoparticles, making them excellent materials for therapeutic delivery. In order to provide for robust, dynamic platforms for novel biomedical applications, we have developed new approaches for the incorporation of a diverse array of functional groups into the polycarbonate backbone. In particular, these approaches focus on post-polymerization modification as a critical strategy for the development of functional, multi-block polycarbonate co-polymers, circumventing many of the drawbacks associated with *de novo* monomer synthesis and polymerization. Here we will detail the new routes developed to generate an increasingly diverse array of multi-functional polycarbonate scaffolds for nanoassemblies. Applications of these materials in nanomedicine and therapeutic contexts will also be discussed.

COLL 689

Aqueous channel connectivity in nafion probed by electrostatic force microscopy

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Proton exchange membrane (PEMs) fuel cells have attracted significant interest as a promising power-conversion technology with the potential of a high power zero-emission source. Nafion, the most prominent PEM, has remarkable performance and is chemically stable over a large range of relative humidity and temperatures. Nafion is a perfluorosulfonic acid that consists of a Teflon-like backbone and sulfonic side chain. When cast into thin films, the components phase separate into hydrophilic channels surrounded by a hydrophobic matrix. Understanding proton transport within these channels requires detailed understanding of the membrane morphology on the nanometer length scale. In addition to in-situ conductive probe AFM, we have recently adapted electrostatic force microscopy (EFM) and Kelvin probe force microscopy (KPFM) techniques to investigate the relationship between surface morphology and surface charge distributions of aqueous channels. We have evidence of disconnected

pockets of trapped charge near the surface, which we interpret as isolated channels disconnected from the contiguous network of channels.

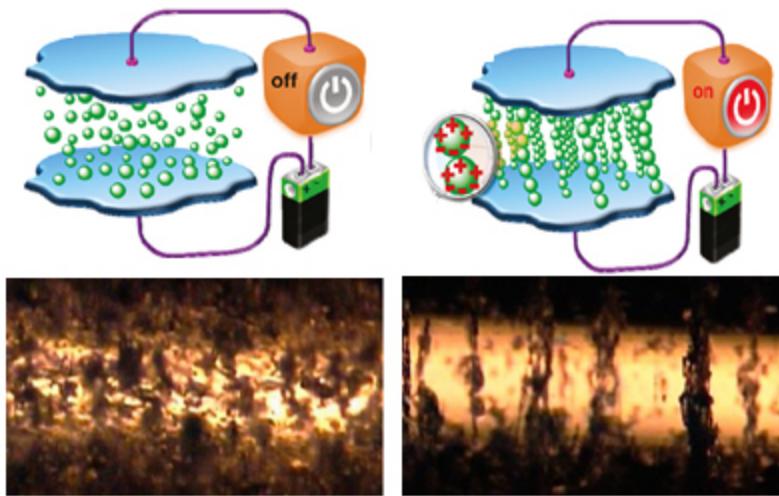
COLL 690

Directly linear alignment as different deacetylation of chitosan under electric field

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For decade, natural polymer, chitosan has been researched as a potential material for bioinspired agent, drug delivery and biosensor, on the basis of properties of biocompatible and biodegradable. We utilized chitosan in suspensions to become linear form under applied electric field, well-aligned linear structures of chitosan with increasing viscosity. The phenomena were caused by applied electric field which polarizes the particles and it changes polymer exterior into induced charge state. This charge produces dipoles of dispersed particles. The charges running on the surface in suspensions are the key role for forming linear type structure in the direction of field. Strengthening polarization of particles has been one of a major study and we figured out effect of deacetylation of chitosan, optimum degree of deacetylation (DD) also. Linearly assembled chitosan was prepared in the process of hydrolysis and T.P.S.-K titration method and then, modified chitosan was obtained in the order of chitosan DD 99.3%, DD 93.4%, DD 87.3%, DD 83.8% and DD 73.2%. FT-IR was used to confirm the synthesis of chitosan DD and amount of organic atoms in deacetylated chitosan was obtained by element analyzer. Morphology and size of materials were detected by FEG-SEM and optical microscopy was carried out to observe the phenomena of alignment of ER fluids. The electro rheological properties of suspensions under DC were investigated by physica couette-type rheometer with a high-voltage generator. Also, it was performed to observe a stable increase in shear stress against impact of heat because solidification or evaporation did not occur during the change of temperature.

Our study focused that phenomenon of the linearly assembled natural polymer which responds to an applied electric field and proposed optimum degree of deacetylation of chitosan. We also showed property of ER fluids in various temperatures. After further work, it will be regarded as a prospective resource for ER application such as human muscle stimulators besides it would be dampers, seismic controlling frame structure and so on.



COLL 691

Stimuli-responsive cyclodextrin-modified microgels: Functional carriers with dynamic crosslinks and binding domains

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Microgels are exiting functional macromolecules and of scientific interest for many years. The controlled integration of chemical functionalities into microgels allows generation of functional polymer systems with unique functions like stimuli-responsiveness, re-shaping, switchability and adaptability.

In this context the integration of cyclodextrin groups into microgels provides functional supramolecular functional tools for the design of new polymer systems. In this paper we describe synthesis of reactive mono and multifunctional cyclodextrins and their controlled incorporation into microgels. Microgels with tunable content and type of cyclodextrins were synthesized and their behavior in aqueous solutions was investigated.

Microgels functionalized with cyclodextrins exhibit interesting complexation properties and can serve as containers for hydrophobic compounds. The accessibility of the cyclodextrins can be regulated by their attachment to the microgel network and crosslinking degree.

Supramolecular cyclodextrin-based crosslinkers were synthesized and integrated into microgels by precipitation polymerisation. Obtained microgels are stable in aqueous solutions and can be easily degraded upon addition of the molecular triggers.

Cyclodextrins in combination with catalytically active gold nanoparticles integrated into microgels play a role of binding domains improving the selectivity of the catalytic processes.

COLL 692

Shape stability and mechanical properties of rhombic dodecahedron multilayer hydrogel capsules at various pH

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Shape and stimuli-responsiveness in addition to size and surface chemistry of micro-engineered delivery carriers play an important role in functional responses of polymeric particulates. We report on the effect of rhombic dodecahedron shape on mechanical properties of poly(methacrylic acid) (PMAA) multilayer hydrogel capsules at various pH values. The $(\text{PMAA})_n$ hydrogel capsules where the subscript denotes the number of PMAA layers in the capsule wall were obtained from chemical cross-linking of PMAA layers within the hydrogen-bonded $(\text{PMAA}/\text{polyN-vinylpyrrolidone})_n$ (PV Pon) multilayer capsules with ethylenediamine. We explore the effect of the PMAA hydrogel capsule wall thickness and hydrogel cross-link density on the ability of these rhombic dodecahedron capsules to retain their non-spherical shape in the pH range from 3 to 7.5 after dissolution of a sacrificial metal-organic-framework core. Also, we investigate mechanical stability of rhombic dodecahedron and spherical $(\text{PMAA})_n$ capsules against deformation in solution under various osmotic pressures induced by increased concentrations of polystyrene sulfonate chains in exterior solution. We have found that increasing the number of faces of the $(\text{PMAA})_{10}$ multilayer hydrogel capsules from 0 (spherical) to 12 (dodecahedron) can improve their mechanical stability against pressure-induced deformations up to 6.7-fold. Also, the dodecahedron capsule shape results in capsule ‘reinforcement’ against deformation upon capsule swelling by 1.3-fold when the solution pH is increased from 5 to 7. We believe this study on shape- and pH-regulated mechanical stability of rhombic dodecahedral multilayer hydrogel capsules can give new insights for developing advanced hydrogel materials with the controllable shape.

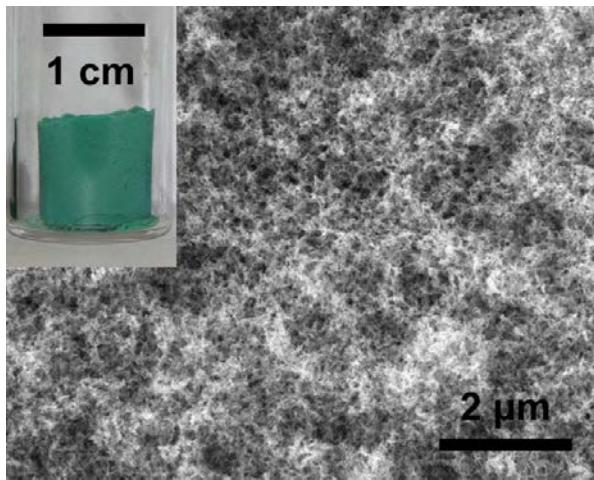
COLL 693

Synthesis of monolithic $\text{Cu}_2(\text{OH})_3\text{Br}$ aerogels

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Copper oxide and hydroxide based aerogels have been among the most difficult to obtain metal oxide aerogels, attributed in part to the tendency of copper alkoxides to form insoluble polymeric species that precipitate prior to gelation. The epoxide-assisted gelation of CuX_2 salts ($X = \text{Cl}, \text{Br}$) has previously provided mixed results, ranging from no gelation to fragile monoliths, even under similar synthetic conditions. In addition, these gels typically contain high levels of residual halide, due to the stability of hydroxy-

halides of the form $\text{Cu}_2(\text{OH})_3\text{X}$. A method for the fabrication of robust monolithic $\text{Cu}_2(\text{OH})_3\text{Br}$ aerogels will be discussed. A typical aerogel is robust, nanocrystalline, and has a density of 120 mg/cm^3 , a specific surface area of $260 \text{ m}^2/\text{g}$, and 97% hierarchical porosity. These aerogels can be thermally converted to nanoporous CuO and Cu^0 monoliths.



COLL 694

Synthesis of poly (2-methoxyethyl acrylate)-based hydrogel particles for bio-coatings and carriers

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Polymer particles can be used for many purposes, including bio- separation, sensing, coating, and so on. For these applications, it is necessary for the particles to have properties, such as bioinert interface and selective adsorption capacity for target molecules, such as drugs and pollutant. In this study, blood compatibility poly(2-methoxyethyl acrylate), pMEA, was selected for the framework of particles, and they showed the selective adsorption behavior of halide compounds, which were necessary to be delivered as a drug and separated from wastewater. In particular, the oxygen atom of methoxy group in pMEA side chain terminal, which usually bonded the freezing bound water (intermediate water), played an important role for the halogen bonding, resulting in the strongly maintenance and the difficult desorption of halide dyes from the surface of pMEA. Indeed, the pellet of pMEA was stained easily with red color of erythrosine after centrifugation (**Figure**). Moreover, to increase the dispersion stability and release efficiency of target halide molecular for pMEA microspheres, the stimuli-responsive pMEA nanocomposite hydrogel particles were synthesized by precipitation copolymerization of pMEA and the poly(oligoethylene glycol methacrylate) as the microgel backbone, which display a lower critical solution temperature in water. The pMEA composite hydrogel particles also showed the specific adsorption behavior of

halide compounds, and the release efficiency of the halide compounds was able to be controlled by changing temperature. These detailed results will be discussed at the session.

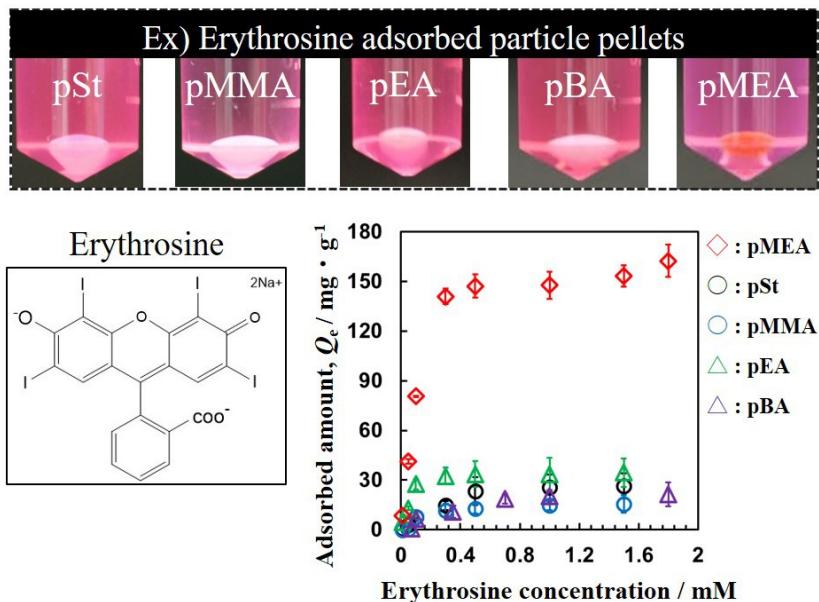


Figure. Erythrosine adsorbed pellets of polymer particles (top), and the adsorbed amounts of halogen dye (erythrosine) per unit gram of polystyrene (pSt), poly(methyl methacrylate) (pMMA), poly(butyl acrylate) (pBA), poly(ethyl acrylate) (pEA), and pMEA particles (bottom) as a function of concentration.

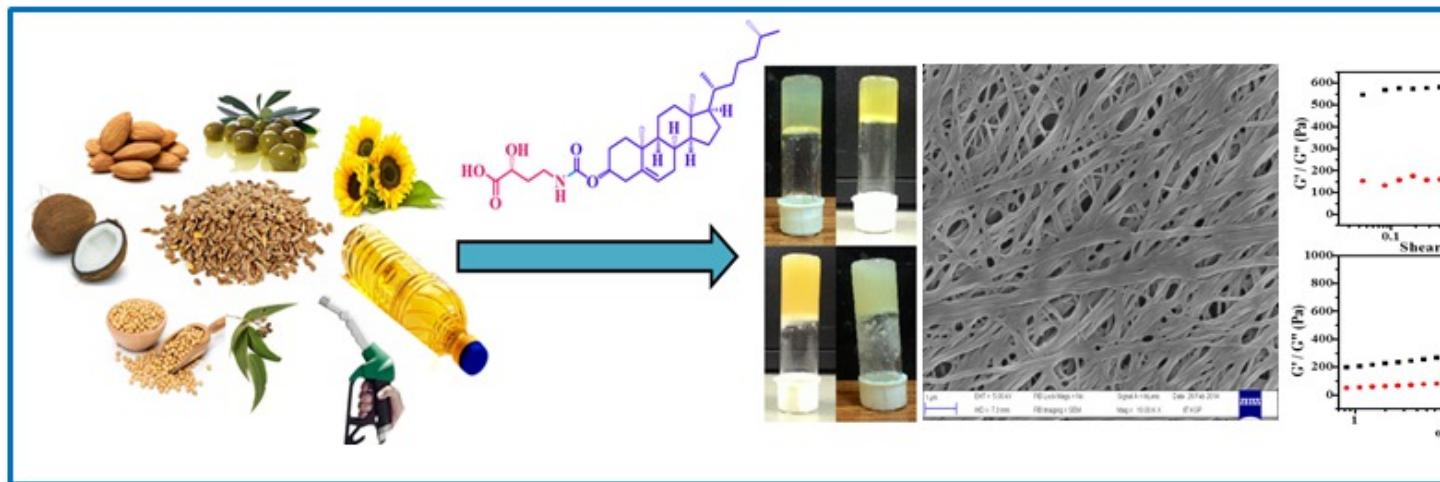
COLL 695

Gelation of vegetable and mineral oils by an efficient and versatile low-molecular-mass gelator

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Gels are a fascinating class of soft matter and have surged tremendous interest for their intriguing properties and potential applications in cosmetics, food processing, drug delivery, and tissue engineering. The present work addresses an amino acid-derived steroidal low-molecular-mass gelator that can efficiently gel a wide spectrum of liquids, including edible oils, mineral oils (as shown in the figure), organic solvents, and aqueous-organic mixtures at reasonably low concentrations (< 2 w/w %). The gelator was found to selectively gel aromatic and chlorinated solvents from their biphasic mixtures with water, thus affording a method for separation and removal of organic pollutants from water beneficial for industries. To the best of our knowledge, no such versatile gelator is known in the prior art that can gel such a large number of liquids. Further, the organogels and in particular, oleogels have shown excellent entrapment efficiency for a number of nonsteroidal anti-inflammatory drugs. The gels were

characterized by use of optical and electron microscopy, and rheological measurements.



Oleogels

COLL 696

Preparation, characterization, and application of nanopore-supported phospholipid bilayers

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Molecular interactions that occur at phospholipid membranes play major roles in a variety of biologically relevant processes ranging from drug and toxin accumulation to cell signaling and the immune response. Typical methods for investigating molecular interactions with phospholipid bilayers fail to provide insight into structural changes that occur upon binding with the bilayer. Raman scattering is a well-established technique that is compatible with aqueous dispersions and can provide both quantitative information, as well as insight into structural changes. Raman scattering is, however, a weak phenomenon, making detection from single planar supported bilayers or individual phospholipid vesicle bilayers challenging. In this work we address the sensitivity challenge by forming supported DMPC (1,2-dimyristoyl-sn-glycero-3-phosphocholine) phospholipid bilayers by vesicle fusion to the silica surfaces of porous chromatographic silica particles. The large specific surface area of the porous substrate provides DMPC concentrations within the particle on the order of 0.5 M, easily detectable by Raman spectroscopy. The small pore size (30 nm) and nearly-matching refractive indices of silica and water allows detection of scattering within the particle by confocal Raman microscopy. To evaluate the structure of nanopore-supported lipid bilayers (NPSLBs), temperature-dependent Raman spectra revealed a broadened (~9 °C) melting transition spanning 15.5–24.5 °C. Spectra of the NPSLB above and below the melting transition compare well with spectra of DMPC vesicles. The bilayer thicknesses of the fluid-

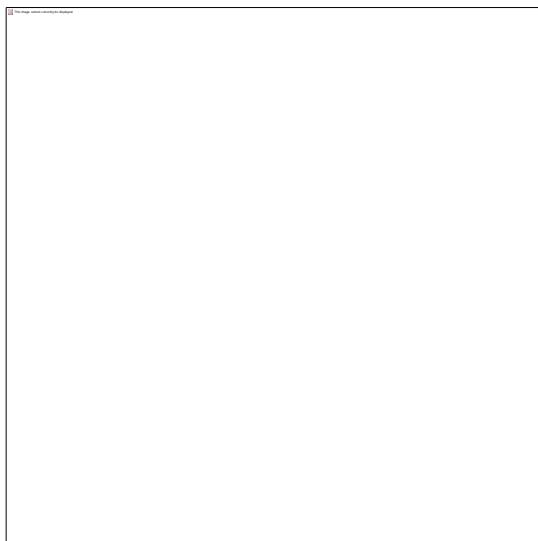
phase NPSLB was determined by Raman measurement of D₂O displacement and found to be consistent with the thickness bilayer thickness measured for fluid phase DMPC vesicles. Additionally, headgroup spacing as computed from carbon analysis and nitrogen BET surface area is also comparable to that measured in fluid phase DMPC vesicle bilayers. Given the structural similarity of the NPSLB supported bilayer, these materials are promising candidates for investigation of biologically relevant processes. Initial experiments highlighting potential uses such as protein-ligand binding and measurement of small molecule partitioning will also be presented.

COLL 697

Biomimetic construction of phospholipid membranes

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Synthetic membranes have the potential to shed light on biological processes such as gene expression and energy transduction, as well as organize chemical reactions in nanoscale compartments. Therefore, there has been an increasing interest to develop novel strategies for the formation of artificial membranes to facilitate signaling responses, drug delivery, encapsulation and extended expression of biomolecules. Here we describe the use of biomimetic approaches to spontaneously generate and remodel phospholipid membranes from water-soluble starting materials. Additionally, we explore the suitability of such bioorthogonal coupling reactions for driving the *in situ* formation of phospholipid membranes and concomitant spontaneous reconstitution of a variety of membrane proteins, with retention of functionality. These studies give us a deeper understanding of the nature of living systems that could bring new insights into the origin of cellular life, and provide novel synthetic chassis for advancing synthetic biology.



COLL 698

Interplay of structure and dynamics in mixed lipid bilayers

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The implication of lipids in tuning protein and cell functions has motivated significant theoretical and experimental research into understanding the role of lipid diversity in determining the structure and dynamics of biomembranes. In particular, hydrophobic mismatch between lipids with different acyl chain lengths is expected to play an important role in determining the local membrane structure and collective membrane dynamics. Here we investigated these phenomena in binary lipid mixtures with a tail length mismatch of 4 carbons, dimyristoylphosphatidylcholine (DMPC, 14:0 C) and distearoylphosphatidylcholine (DSPC, 18:0 C), using neutron scattering techniques. Neutron spin echo spectroscopy (NSE) experiments revealed that the dynamics of the mixed lipid bilayers were highly sensitive not only to lipid composition, but also the phase state of the lipids. In the fluid phase, the mixed lipid bilayers were more dynamic than their single component analogs, with the mixed bilayers having a lower bending modulus and increased thickness fluctuation amplitude compared to the pure DMPC or DSPC bilayers. Meanwhile, the effective elasticities of membranes with coexisting gel and fluid domains were directly determined by the area fractions and bending moduli of the respective phases. Together our results demonstrate the influence of lipid composition on the bilayer biophysical properties and highlight the complex interplay between structure and dynamics in lipid membranes.

COLL 699

Neutron scattering to study membrane systems: From lipid vesicles to living cells

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The existence and role of lateral lipid organization in biological membranes has been studied and contested for more than 30 years. Lipid domains, or rafts, are hypothesized as scalable compartments in biological membranes, providing appropriate physical environments to their resident membrane proteins. This implies that lateral lipid organization is associated with a range of biological functions, such as protein co-

localization, membrane trafficking, and cell signaling, to name just a few. Neutron scattering techniques have proven to be an excellent tool to investigate these structural features in model lipids, and more recently, in living cells. I will discuss our recent work using neutrons to probe the structure and mechanical properties in model lipid systems and our current efforts in using neutrons to probe the structure and organization of the bilayer in a living cell. These efforts in living cells have used genetic and biochemical strategies to generate a large neutron scattering contrast, making the membrane ‘visible’ to neutrons. I will present our results showing *in vivo* bilayer structure and discuss the outlook for this approach.

COLL 700

Human lipoproteins at model cell membranes: Role of the lipoprotein class on lipid dynamics

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High (HDL) and low (LDL) density lipoproteins are thought to play vital roles in the onset and development of atherosclerotic plaques. Atherosclerosis is a major contributor to global morbidity and mortality, deaths from cardiovascular disease were responsible for 17.5 million deaths in 2012. We present a new method to monitor *in situ* kinetics of lipoprotein deposition, lipid exchange and lipid removal at cellular membranes using neutron reflection. Lipid exchange and removal could be unraveled thanks to the use of hydrogenated and tail-deuterated supported lipid bilayers. Both lipoproteins were found to remove lipids from the bilayer, but also to deposit hydrogenated material from the lipoprotein to the bilayer. HDL removed more lipids whereas LDL deposited more hydrogenated material supporting the idea that HDL acts as ‘good’ cholesterol, removing lipid material from endothelial cell walls, whereas LDL acts as ‘bad’ cholesterol, depositing lipids, such as cholesterol esters and triglycerides, into the blood vessel wall.

COLL 701

Lipoprotein structure dependency on lipid cargo and exchange dynamics: Implications for atherosclerosis development

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Atherosclerosis and related cardiovascular disease constitute the leading cause of death in westernized societies. In atherosclerosis, plaques of fat and fibrous elements accumulate in the arteries leading to heart disease and stroke. The levels of different plasma lipoprotein particles, low density lipoprotein (LDL), oxidized LDL (oxLDL), high density lipoprotein (HDL), lipids and cholesterol have been associated with the disease and are therefore currently being used as key clinical markers. However, the impact that the apolipoprotein isoform, the apolipoprotein oxidation state, the lipid cargo and the presence of divalent ions have on the structure and stability of the lipoprotein particles is still not fully known. Together with their subsequent effects on lipoprotein interactions with blood vessel components these parameters need to be thoroughly investigated in order to understand the molecular mechanisms behind the initial events of plaque-build up. This can in turn allow for the development of novel strategies for the diagnostics and treatment of cardio-vascular disease. Here we use small-angle x-ray scattering and small-angle neutron scattering in combination with selective deuteration to provide novel information on both structure of the lipoproteins and the molecular exchange which occurs between lipoprotein particles and cell-membrane mimics. Focusing on the lipid exchange kinetics between both native HDL and LDL and liposomes made of "invisible" PC lipids we show that the apolipoprotein plays a key role in enhancing lipid exchange. Furthermore, we present a novel structural model for LDL and HDL and the effects that temperature and oxidation have on the particles overall structure as well as on the organization of their hydrophobic core and which now allows us to start relating the specific structural changes with the observed lipid exchange.

COLL 702

Probing the structure and dynamics of proteins using neutron scattering

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To fully understand the function of proteins it is necessary to consider both their structure and dynamics. Neutron spin-echo spectroscopy (NSE) has been shown to be ideally suited to probe the slow dynamics of materials, since it gives access to the dynamics on the nanosecond-timescale, making it a very powerful tool when combined with other techniques.

In this talk I will show how we have used NSE and backscattering spectroscopy to probe the dynamics of biologically relevant systems, such as human serum albumin, a protein abundant in blood, which plays a key role in the transport of compounds such as nutrients, hormones and drugs. We are able to detect small changes in the internal dynamics of the protein upon binding of small molecules such as heme and myristic acid under physiologically realistic conditions.

Another example is the use of NSE combined with computer simulations to study of the

internal dynamics of the mercuric ion reductase MerA, an enzyme responsible for catalysing the NADPH-dependent reduction of Hg(II) to the uncharged, and much less harmful, Hg(0).

COLL 703

Effect of cholesterol on the elastic and viscous properties of dimyristoylphosphatidylcholine bilayers

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The dynamics of biological membranes have attracted significant experimental, computational and theoretical attention as they are critical to a large number of biological functions. Cholesterol is an essential component of animal cell membranes, helping to maintain membrane structural integrity and fluidity, as well as being considered to be a main component of raft domains, where saturated lipid and cholesterol segregate from unsaturated lipids. The raft domain hypothesis is still under great debate in biophysics, and the key feature in understanding the formation of these raft domains is characterizing the dynamics of the bilayers and domains. We have used neutron spin echo spectroscopy (NSE) to measure the internal membrane dynamics of a saturated lipid, dimyristoylphosphatidylcholine (DMPC) as a function of temperature at a fixed lipid - cholesterol ratio (20 mol % cholesterol). NSE measures collective membrane dynamics such as undulation and thickness fluctuations on both a nanometre and nanosecond scale. Cholesterol-rich raft domains are considered as liquid ordered phase, which is less mobile than the liquid disordered phase, but more mobile than solid gel or crystalline phases. We observed values for the undulation fluctuations - characterized by the bending modulus - for cholesterol incorporated DMPC bilayers that are in between those of the pure gel and fluid phase DMPC bilayers, suggesting that at 20 mol % cholesterol there exists a liquid ordered phase. However, the temperature dependence is much greater when cholesterol is incorporated to DMPC bilayers. Also, the thickness fluctuations, characterized by the membrane bending modulus and viscosity, produced larger membrane viscosity values for the mixed DMPC cholesterol bilayers.

COLL 704

Observation of nucleation and growth during the formation of cadmium selenide and iron oxide nanoparticles and their use for biomedical imaging

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Although nanocrystals are used already in many applications, the knowledge on their formation is still in its infancy. We will present results on nucleation and growth of quantum dots obtained from uv-vis spectroscopy and x-ray scattering data obtained in a rapid continuous flow apparatus. A second part of the talk deals with the formation of iron oxide nanocrystals by thermal decomposition of iron oleate. We have identified a set of clusters being formed before particle formation starts. We will discuss parameters determining the final size and shape of the nanocrystals.

The key idea for using nanocrystals for biomedical diagnostics is to benefit from their outstanding physical properties in the visualization of biological events or malignant cells or tissues. This requires a special design of the ligand shell, which preserves the fluorescent, magnetic and plasmonic properties of the particles in the biological environment on one side and allows a specific targeting on the other. The lecture reports on different chemical approaches and describes factors determining the biological response on fully synthetic nanocrystals. We will highlight concepts based on PEGylation and show how small deviations in the ligand shell alters the behavior in biological environment substantially.

COLL 705

Suppressed-blinking green-emitting giant quantum dots: From synthesis to structure to function

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Colloidal synthesis techniques can be used to obtain atomic-scale control over the internal structure of semiconductor nanocrystals. It is becoming increasingly clear that this level of control is required for the establishment and optimization of a range of important photophysical properties. A specific example from our group is the ability to eliminate detrimental processes of fluorescence intermittency (blinking), photobleaching, non-radiative recombination channels and self-reabsorption in semiconductor quantum dots (QDs) by precise “nanoengineering” of core/shell structure. This includes nanoscale composition, size and interface effects, and where successful has important implications for light-emission technologies from solid-state lighting to single-photon sources. Our approach has involved the growth of thick epitaxial shells of a higher bandgap material onto a QD core, where the band alignments often entail offset or type II character. The resulting thick-shell or giant QDs (g-QDs) have to date been most successful at red and near-infrared wavelengths. It has remained an outstanding challenge to synthesize green-emitting non-blinking, ultra-stable g-QDs. Here, we report the single-dot photophysical properties of new “green giants” comprising CdSe, ZnS and their alloys. By correlating internal nanocrystal structure and composition (defect density, extent of alloying, shell thickness, etc.) with blinking and photobleaching properties, we draw clear lines between synthesis

conditions and resulting structure and function. Finally, we show how further development of this system and discovery of new functional QDs can be promoted by automating the process of precision hetero-nanostructure growth.

COLL 706

Tunable quasi-amorphous photonic materials with pigmentary colloidal nanostructures

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Quasi-amorphous photonic structures exhibit interesting optical properties such as non-iridescent angle-independent structural colors and isotropic photonic band gaps. Here, we demonstrate colloidal assemblies of engineered quasi-amorphous photonic materials, using pigmentary $\alpha\text{-Fe}_2\text{O}_3/\text{SiO}_2$ core/shell nanoparticles, exhibiting non-iridescent and tunable colors. $\alpha\text{-Fe}_2\text{O}_3/\text{SiO}_2$ nanoparticles based quasi-amorphous photonic structures exhibit short-range order and are weakly correlated to each other, as confirmed by ultra-small-angle X-ray scattering measurements. The observed colors result from combination of colloidal particle arrangements, giving arises to the structural colors, along with the inherent pigmentary color of the $\alpha\text{-Fe}_2\text{O}_3/\text{SiO}_2$ nanoparticles. Dynamic color tunability of $\alpha\text{-Fe}_2\text{O}_3/\text{SiO}_2$ nanomaterials is demonstrated using electrophoretic deposition process with a noticeable difference between transmitted and reflected colors and the resulting colors can be manipulated by shell thickness, particle concentration and external electrical stimuli.

COLL 707

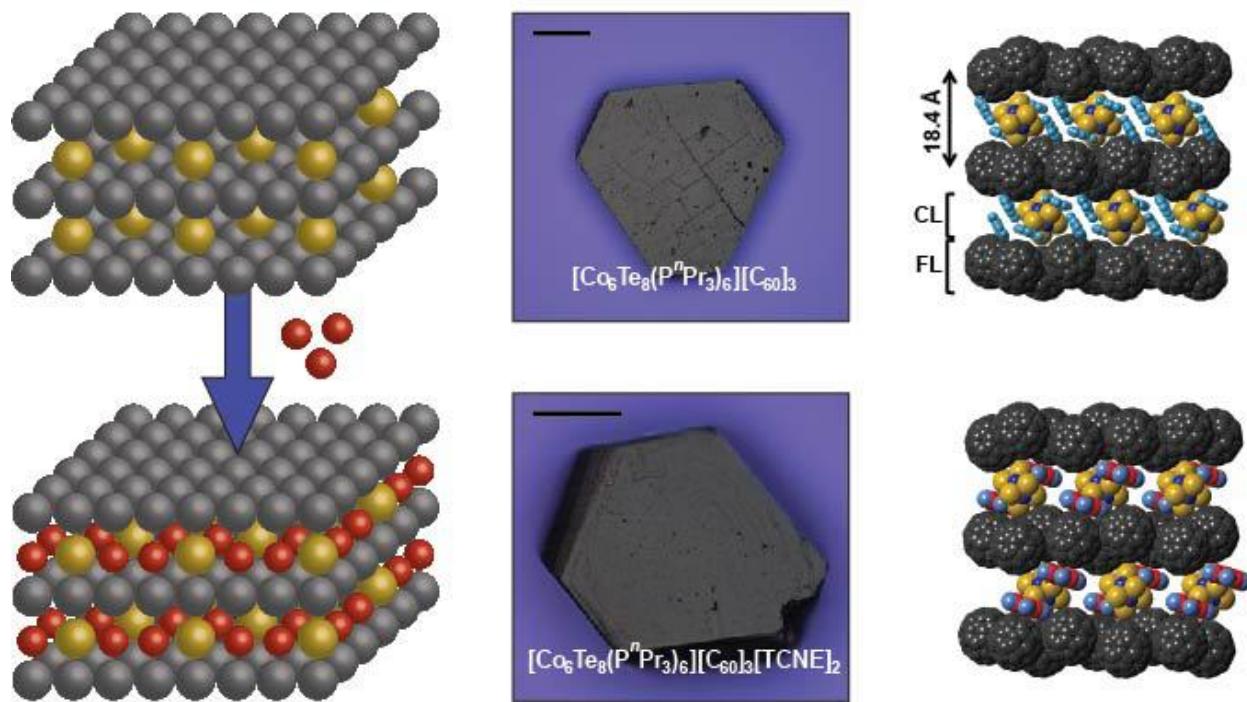
Chemical intercalation of superatomic solids

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The introduction of impurities into the crystal lattice of atomic solids is a cornerstone of materials science. The extension of this concept to self-assembled nanomaterials is an important goal of nanoscience as evidenced by recent work on substitutional doping in nanocrystal arrays. I present the first study of chemical intercalation into materials assembled from atomically-precise molecular cluster building blocks. These materials, which we label superatomic crystals, spontaneously crystallize from tunable building blocks into structurally precise morphologies, combining the most attractive features of both nanocrystal arrays and “atomic” semiconductors.

Our superatomic host crystallizes as an ionic layered structure in which the superatoms $\text{Co}_6\text{Te}_8(\text{P}^n\text{Pr}_3)_6$ are sandwiched between monolayers of C_{60} fullerene. The topochemical

intercalation occurs as a single-crystal-to-single-crystal transformation, leaving the desirable layered morphology completely intact. When the intercalant, tetracyanoethylene (TCNE), is inserted between the C₆₀ monolayers, it removes electrons from the conducting C₆₀ sheets, leading to drastic changes in the electrical and optical bandgap properties of the material. These results chart a clear path towards new semiconducting, metallic, magnetic and even superconducting materials through insertion of electron-acceptors, electron-donors and magnetic guests into superatomic crystals.



Schematic of the intercalation of the superatomic host: [Co₆Te₈(PⁿPr₃)₆][C₆₀]₃. Micrograph and crystal structures of the host and intercalation product are shown alongside their representative schematics.

COLL 708

Self-assembly of nanoparticles via co-crystallization with proteins

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Facile and versatile method to achieve 3D arrangement of nanoparticles remain as a challenge for nanoscientists. On the other hand, self-assembly process is widely found in nature. Here, we present 3D self-assembled structure of nanoparticles using protein crystals as a template. Controlling directed self-assembly of nanoparticles requires understanding interactions between nanoscale building blocks. In this study, we controlled interaction between gold nanoparticles (AuNPs) and hen egg white lysozyme

(HEWL) and achieved 3D assembly of AuNPs incorporated in protein crystals. When gold nanoparticles are functionalized with large poly (ethylene glycol) (PEG), weak attractive interaction between AuNPs and HEWL arises. This weak interaction leads to facilitate nucleation of HEWL crystals and incorporation of gold nanoparticles into HEWL crystals. SAXS and TEM data shows that AuNPs were incorporated into lysozyme crystals and AuNPs inside the crystals have some ordered arrangement within crystal structure. The kinetics of nucleation and distribution coefficient of AuNPs in protein crystals were studied. The phenomenon was independent of nanoparticle type and we found other nanoparticles, such as iron oxide, quantum dots and gold nanorods also occurred if the surface grafting density of PEG was low. This confirms that the surface properties of NP-PEG conjugates, rather than the nanoparticle itself, dictates the protein-nanoparticle solution interactions and the subsequent incorporation of nanoparticles into biomolecular crystals.

COLL 709

Reversible and precise self-assembly of Janus metal-organosilica nanoparticles through a linker-free approach

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Self-assembly of nanoparticles into functional structures has been regarded as a powerful bottom-up approach that can produce new materials, especially metamaterials, with fascinating properties for sensing, optoelectronic devices, catalysis, color printing, surface-enhanced Raman spectroscopy (SERS), and so on. Although extensive approaches of self-assembly have been reported, there are still several challenges. For example, linkers, such as polypeptide, polyrotaxane, spiropyran and DNA are required in most of the reported approaches to connect nanoparticles. They usually suffer from high cost, tedious preparation process, and low stability and adaptability under intricate chemical and biological environments. Here we propose a new method on self-assembly of nanoparticles through a linker-free and fast approach by manipulating the interparticle forces. By taking advantage of the weak interaction between the capping ligand and metal surface, Janus Au-organosilica nanoparticles can be assembled when the nanoparticles are dispersed in ethanol. Meanwhile, since CTAB molecules on the surface of Au nanoparticle are not completely removed, the remaining CTAB surfactants exert short-range steric repulsion which counteracts the attractive force between Au nanoparticles and thus enables reversible disassembly of Au nanoparticles under ultrasonication in CTAB aqueous solution. This reversible self-assembly process can be demonstrated by TEM images and UV-Vis spectra. More importantly, different from reported only random aggregation of Au nanoparticles in self-assembly process, we make this self-assembly process controllable by manipulating the steric hindrance provided by organosilica. High-yield dimers can be formed when the size ratio between Au nanoparticle and organosilica is appropriate. With the size ratio increasing to expose more surface area, each Au nanoparticle can contact with more nanoparticles, leading to the formation of trimers or even quaterners.

Since the VDW attraction force is universal, this linker-free may be applied to various metal materials. Silver (Ag) and palladium (Pd) are demonstrated and same results can be obtained which prove the versatility of this approach. The ability to precisely organize Au nanoparticle into dimers or trimers allows us to take full advantage of the near-field coupling for application in SERS. The enhancement factor (EF) of dimers and trimers are ~13 times and ~31 times, respectively, as strong as monomer.

COLL 710

New class of branched and nanofibrous dendrimeric polymer particles with extraordinary adhesive and structure-building capabilities

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We will discuss the formation and unique properties of a new class of dendrimeric polymer particles (DPPs). The DPPs are fabricated by an efficient and scalable process for massive liquid-based synthesis of nanomaterials. A variety of polymers can be readily made into nanofibrillated particles. The DPPs are hierarchically self-similar, with branched nanofiber corona spreading out all directions. The biomimetic similarity of their structure to the gecko lizards' setae endows DPPs with excellent adhesion on almost any substrate. Our results demonstrate that this strong adhesion are attributed to the contact splitting and van der Waals interactions of their nanofibrous structures. This new class of polymeric particles opens new ways to make strong non-covalent binding coatings and new types of dry adhesives. In addition, the DPPs exhibit high excluded volume induced from their hierarchical structure. They build a stable three dimensional network leading to a gel-like behavior at as low as 1-2 vol.% of DPPs in various liquids. These particles can find a broad range of industrial applications such as components of gelation agents and coating formulations.

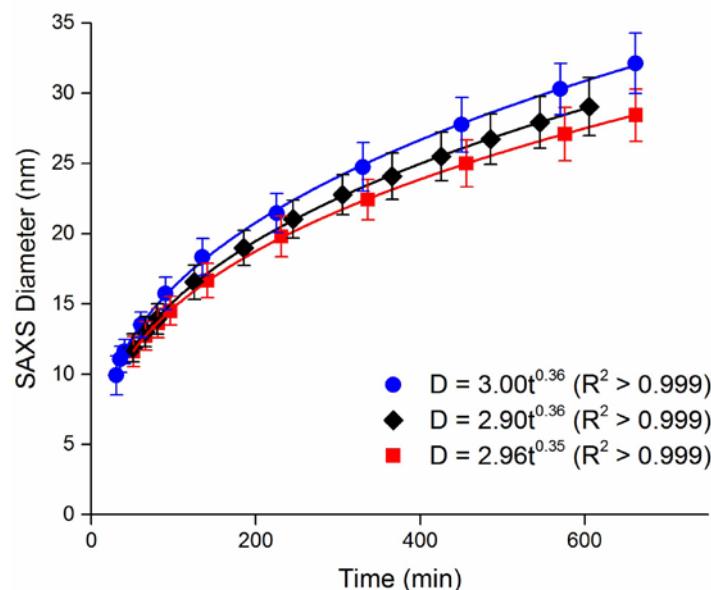
COLL 711

Controlling size in nanoparticle syntheses using the extended LaMer mechanism

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The properties of nanoparticles vary dramatically with size, and reproducibly controlling size is critical for practical applications. This is particularly true when moving into commercial settings, where efficient production requires demonstrated reproducibility that can only be achieved with excellent size control. The Extended LaMer Mechanism is a general method for size control in the synthesis of nanoparticles by establishing steady state growth through the continuous, controlled addition of precursor. The steady

state growth regime is characterized by a constant concentration of unreacted precursor as well as a uniform rate of growth in particle volume. This approach allows reproducibility in particle size from batch to batch, as well as prediction of size produced later in a reaction by monitoring early stages of growth. This method has been demonstrated using important synthetic systems including magnetite, iron, and gold nanoparticles. Pictured is the near real time monitoring of the diameter of magnetite nanoparticles by small angle X-ray scattering (SAXS). The nanoparticle diameter increases at a uniform rate that is dependant upon $t^{1/3}$. Three independent reactions are plotted to demonstrate the degree of reproducibility, with sizes reproduced with a coefficient of variation of less than 2%.



COLL 712

Colloidal superparticles from colloidal crystallization in closed systems

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Colloidal superparticles are nanoparticle assemblies in the form of colloidal particles. Assembling nanoscopic objects into meso/macrosopic complex architectures allows bottom-up fabrication of functional materials, which is essential for many nanomaterial-based technological applications. In this talk, we will discuss the formation of superparticles with supercrystalline structures made from the self-assembly of nanoparticles in closed thermodynamic systems. We shall show that the self-assembly of nanospheres, nanorods, and nanocubes, mediated by shape and structural anisotropy, produces mesoscopic colloidal superparticles having multiple well-defined supercrystalline domains and binary superlattice structures. Further, functionality-based anisotropic interactions between these CdSe/CdS core/shell semiconductor nanorods can be kinetically introduced during the self-assembly and in turn yield single-domain,

needle-like superparticles having parallel alignment of constituent nanorods. Unidirectional patterning of these mesoscopic needle-like superparticles gives rise to the lateral alignment of CdSe/CdS nanorods into macroscopic, uniform, freestanding polymer films that exhibit strong photoluminescence with a striking anisotropy, enabling their use as down-conversion phosphors to create polarized light-emitting diodes.

COLL 713

Surface bonding and chemistry for pyridine-catalyzed CO₂ reduction on GaP

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Experimental studies to aid in establishing the role of the GaP electrode surface in pyridine-catalyzed CO₂ reduction, reported to give high yields for methanol and formic acid, will be discussed. Ambient pressure photoelectron spectroscopy (APPES) was used to spectroscopically identify *in situ* surface-bound species on GaP(110), the most stable surface of GaP, at pressures up to 1 Torr. The data show that the interaction with water is characterized by the presence of a partially dissociated adlayer, with Ga-OH, P-H, and adsorbed molecular H₂O species detected on the surface, consistent with theoretical calculations. Isobaric APPES measurements at elevated pressures were used to probe the thermal stabilities of the P-hydride species as well as the oxidation of surface Ga and P. We observe the surface hydride to be remarkably stable in the presence of water, which is notable given the critical role of hydride transfer to catalysts and CO₂ during chemical fuel synthesis reactions in aqueous environments. This high stability may contribute to the remarkable near-100% faradaic efficiency for methanol generation by solar-driven CO₂ reduction by this system. We have also reported the orbital-resolved adsorption state of pyridine on GaP(110) using scanning tunneling microscopy (STM). By examining the distribution of unoccupied molecular orbitals with high spatial and energetic resolution, we showed that scanning probe techniques could be used to positively identify the sites on pyridine susceptible to nucleophilic attack, consistent with frontier orbital theory. This technique can be used to explore the local reaction centers of adsorbed catalysts relevant to artificial photosynthesis. Our observations of the stable adsorption of both H and pyridine on this surface is notable, because it characterizes the proposed precursor state for the formation of adsorbed dihydropyridine, which could be a key hydride-shuttling catalyst for heterogeneous CO₂ reduction.

COLL 714

Intercalation of metal ions into the interlayer region of layered manganese oxide for improved water oxidation electrocatalysis

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Research shows that the intercalation of metal ions (i.e., Cu²⁺ and Ni²⁺) into the interlayer region of the layered manganese oxide, birnessite, results in an active electrocatalyst for the oxygen evolution reaction (OER) in both a neutral and alkaline medium. Unmodified birnessite displays a relatively high overpotential for water oxidation (700 mV at 10 mA/cm²) and large Tafel slope of 240 mV/decade. It is shown that through metal intercalation the overpotential can be significantly lowered. Copper intercalation results in a lowering of the overpotential to 600 mV, while the intercalation of Ni²⁺ lowers the overpotential to 400 mV (lower than pure Ni hydroxide). In the Ni²⁺/birnessite circumstance the Tafel slope decreases to 65 mV/decade. In the Cu²⁺/birnessite case, density functional theory calculations show that the intercalation of copper into a layered MnO₂ model structure leads to a change of the electronic properties of the material from a semiconductor to a more metallic like structure. Molecular Dynamic Simulation studies suggest that the intercalation of Ni²⁺ into the water-containing interlayer region of birnessite results in enhanced electron transfer rates leading to an improvement in OER catalysis.

COLL 715

Understanding the surface reactions of the lithium-air battery and its consideration for usage in an automotive application

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Vehicle drivetrain electrification is one of the many future challenges that automakers face. While there are many different EV system configurations, the one constant is the need for better electrochemical storage. Initially, this paper will discuss existing electrochemical systems and their potential to meet future vehicle requirements. We will then examine beyond Li-ion systems and their potential to replace current technology. Lithium-O₂ batteries form lithium peroxide (Li₂O₂). This product formed on the electrocatalyst happens to be a wide band-gap semiconductor/insulator. This has ramifications for discharge, charge, and battery design. During discharge, the poor electronic conductivity of Li₂O₂ limits the amount and rate at which product can be formed. Under a constant discharge, the resistance of the electrode increases, causing a voltage drop that becomes sufficiently large and stops any further reaction. On charge, the decomposition of the product is inhibited by the resistance of the product; higher resistances require higher voltages. The implication for battery design is that electrocatalyst surface area becomes the controlling factor to achieve reversibility which increases battery volume. Product conductivity is fundamental to this system and can be marginally controlled by electrocatalyst selection. For an air battery's maximum

capacity, it requires a maximum amount of an insoluble non-conductive product. These are counterproductive. We show many variables such as the chemical composition, electrocatalyst surface structure, rate of electrochemical discharge, and depth of that discharge affect the morphology, shape and type of product. We also show that the nature of the solvent in the electrolyte solution also plays a role. We show this through multi-scan cyclic voltammetry in combination with in-situ electrochemical scanning probe microscopy. With this analysis, it will be shown that the while the product conductivity may be variable, it is not the controlling mechanism, especially in the high power applications required for an automotive application.

COLL 716

Experimental and computation studies of the reaction of hydrogen and organic peroxide on molybdenum hydrogen bronze surfaces

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Molybdenum hydrogen bronze is a unique material that can react with organic peroxides and render them harmless. During the course of the reaction, color and electrical conductivity of this material change dramatically. Using the color change, the reaction rate of molybdenum hydrogen bronze with hydrogen peroxide have been measured colorimetrically. The reaction rate was found to be first order both with respect to time and with respect to the concentration of hydrogen peroxide. Time-resolved reflection UV-spectroscopy shows that the concentration of hydrogen within the material also decreases in a first order fashion. Measurements with organic peroxides are ongoing. The adsorption and dissociation mechanisms were also studied on molybdenum oxide and hydrogen bronze surfaces by means of density-functional computations. On molybdenum oxide clusters, both hydrogen and dimethyl peroxide adsorb molecularly and do not dissociate. However, on the hydrogen bronze surfaces, both compounds can dissociate through a pathway involving either H-O (CH₄-O for the organic peroxide), or O-O bond cleavage. For hydrogen peroxide, hydrogen cleavage is kinetically favored with a barrier for direct H-OOH dissociation of 39.9 kJ/mol. However, the dissociation of the O-O bond leads to the most energetically stable products, two OH species bound to the surface molybdenum atoms with the relative adsorption energy - 430.4 kJ/mol. Computations show that the chemical reaction on the molybdenum hydrogen bronze surface is made possible by the increased electron density at the surface with respect to the oxide due to the contribution from the HOMO orbital.

COLL 717

Systematic approaches to modify the surface and electronic structure of TiO₂ nanocrystals

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Rod shape anatase TiO_2 nanocrystals can be prepared easily in multi-gram quantities according to the procedure reported by the Hyeon group. The nanocrystals are an ideal platform for the design of photoelectrochemical catalysts if the issues of visible light absorption and bottle-necks in electron transfer catalysis can be addressed. We demonstrate three routes to modify the surface and electronic structure of TiO_2 nanocrystals. With the use of inexpensive metal chloride hydrates, quantitative control of the adsorption of transition metal ions (Cr^{3+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+}) onto the surface of TiO_2 nanocrystals was demonstrated. The adsorption is self-limiting up to one monolayer. It is even possible to partially titrate the nanocrystal with one metal ion then fill the remaining surface sites with a second metal, which affords 15 bimetal combinations of the 6 metal ions above. We also show that it is possible to ‘push’ the surface bound metal ions into the nanocrystal to make metal-doped TiO_2 nanocrystals with precise control of the dopant concentration, which is limited by the solubility of the metal in the TiO_2 and the amount of metal ion on the nanocrystal surface. Finally, we demonstrate a straightforward concept for the preparation of a wide range of metal-semiconductor hybrid nanocrystals. So far, we have prepared Ag-TiO_2 , Co-TiO_2 , Ni-TiO_2 , and Cu-TiO_2 hybrid nanocrystals. We find that spontaneous air oxidation occurs with the first-row metals to afford CoO-TiO_2 , NiO-TiO_2 , and $\text{Cu}_2\text{O-TiO}_2$ hybrid nanocrystals. In this way, we could also prepare a ternary-phase hybrid nanocrystal upon formation of a $\text{Ag-TiO}_2\text{-Ni}$ sample that (in air) oxidizes to $\text{Ag-TiO}_2\text{-NiO}$. In particular, this sample may possess key features of a photoelectrochemical catalyst, namely longitudinal separation of the electron/hole pair within the TiO_2 nanorod, electron collection and catalysis at Ag, and hole collection and catalysis at NiO.

COLL 718

Photoelectrical response of mesoporous metal oxides decorated with size controlled platinum nanoparticles under argon and oxygen gas

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The visible light photoelectrical properties of different p-type mesoporous metal oxide (MMO) supports were investigated upon the decoration of size controlled, 1.6 nm, 6.4 nm and 7.9 nm Pt nanoparticles. The near room temperature photoelectrical response of the MMOs was 3-4 times higher after decoration of Pt nanoparticles with a loading of 1 wt%. MMOs decorated with smaller Pt nanoparticles showed the highest photoresponse.

The surrounding atmosphere has striking effect on the photoelectrical behavior, as adsorbed oxygen induced lower photoelectrical response compared to that of argon.

The noble metal nanoparticles show both electronic and chemical sensitization: the first functioning as an electron sink resulting in a new band structure of the photocatalyst, and the second interacting chemically with the oxygen and argon adsorbed from the environment.

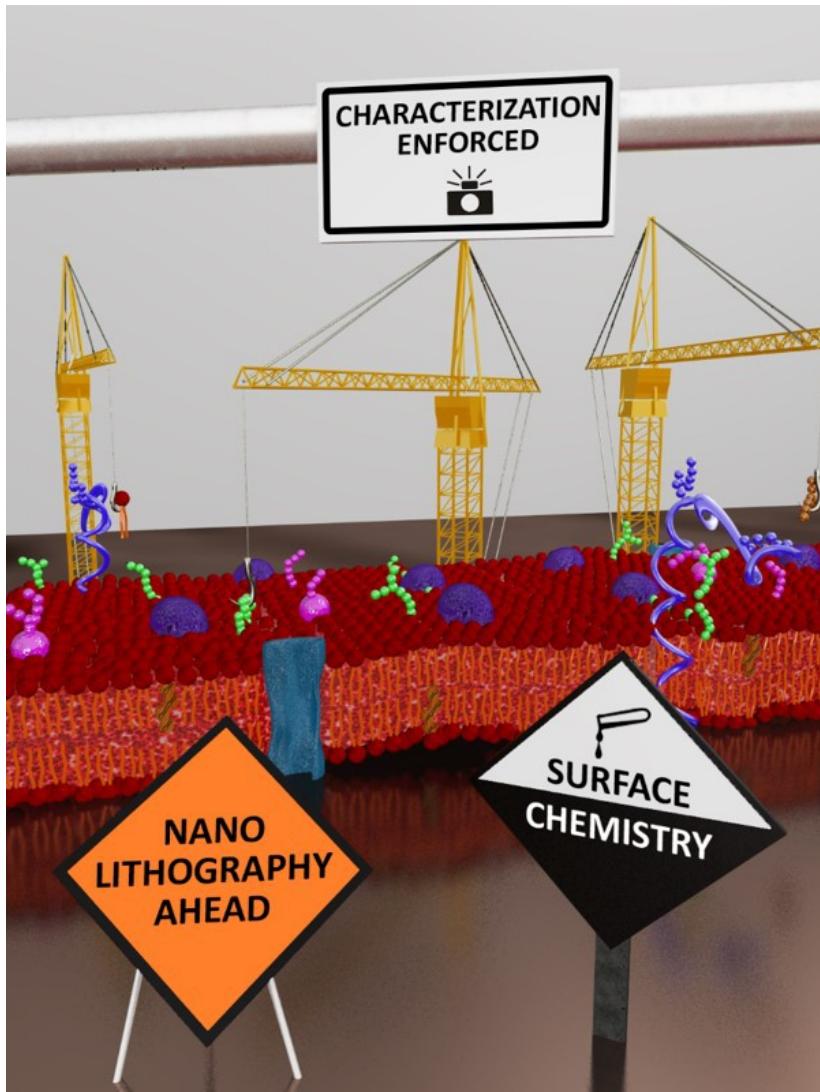
A conceptual model has been proposed in which adsorbed oxygen induces a new potential in the heterojunctions lowering the corresponding potential barrier and as result some electrons can occupy holes (lower in energy) in the interbands of the metal. Upon irradiation, the electrons in the valence band thus require higher energy to reach the free holes resulting in a lower response in the presence of oxygen. The results showed that not only the presence of the noble metal nanoparticles, but also their size had effect on the photoelectrical properties of nanoparticle decorated heterojunction composites.

COLL 719

4D nanolithography using a flow-through polymer printer

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Biointerfaces direct some of the most complex biological events, including cell differentiation, hierarchical organization, and disease progression, or are responsible for the remarkable optical, electronic, and biological behavior of natural materials. Chemical information encoded within the 4D nanostructure of biointerfaces – comprised of the three Cartesian coordinates (x , y , z), and chemical composition of each molecule within a given volume – dominates their interfacial properties (Figure). As such, there is a strong interest in creating printing platforms that can emulate the 4D nanostructure – including both the chemical composition and architectural complexity – of bionterfaces. This presentation will describe how synergistic advances in grafted-from photopolymerizations, tip-based instrumentation development, and surface characterization have been combined to create a 4D printer capable of printing multiple inks in close registration and nanoscopic dimensions.



COLL 720

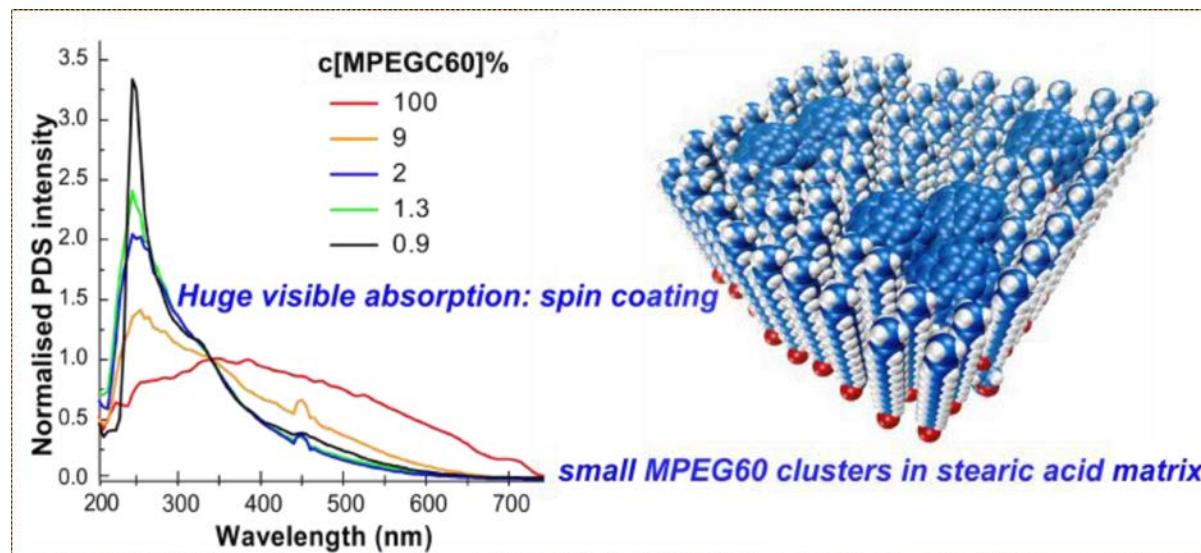
Colored soaps for photonics

Martin Presselt^{1,3}, martin.presselt@gmail.com, Felix Herrmann-Westendorf³, Martin Kaufmann³, Saunak K. Das³, Maximilian L. Hupfer³, Benjamin Dietzek^{2,3}. (1) Functional Interfaces, Leibniz Institute of Photonic Technologies, Jena, Germany (2) Leibniz Institute of Photonic Technologies, Jena, Germany (3) Friedrich Schiller University Jena, Jena, Germany

In organic solar cells (OSCs) and organic light emitting devices molecular order and orientation essentially determines device performances. Particularly, in OSCs the rather random orientation of electron donating and accepting molecules causes a very complex morphology of the active layer which hampers understanding of photo-generation of free charge carriers. Hence, to push basic research forward and to produce photonic layers with well-defined anisotropic properties model systems with

unique molecular orientation are desired. Such systems might be constituted by amphiphilic molecules as inspired by surfactant chemistry.

In this contribution we will show electron donors and electron acceptors as well as exceptional fluorophores, which were functionalized to yield amphiphiles. Thin films of these amphiphiles were produced prevailingly by means of the Langmuir-Blodgett and spin-casting technique. Thus, smooth homogeneous films as well as vesicles and fibers can be produced, which differ markedly in their light absorption and electric properties. Exemplarily, strong changes of the absorption spectra with aggregate growth are shown in the figure. Furthermore, molecularly thin films with a narrow angular distribution of chromophore orientation were produced. Thus, finally the concepts of surfactant chemistry could be successfully transferred to photonics.



Photothermal deflection spectra for spin casted films of MPEGC60 from CHCl_3 solvent for different MPEGC60:stearic acid concentrations. All spectra were normalized to the absorbance at 344 nm.

COLL 721

Metal-organic coordination chains at surfaces: Chemical activity of single-site transition metal centers

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There is a growing need for selective alkane functionalization catalysts to convert small alkanes into value-added products and transportable chemicals. Programming the specific chemistry of single-site transition metal centers at surfaces by organic ligand design is a promising route to improve selectivity in surface catalysts. We work as a

multi-disciplinary research team to design redox-active components for on-surface metal-organic complexation to achieve a high degree of uniformity in single-site transition metal centers on metal and oxide surfaces. We combine ultra-high vacuum surface chemistry studies on model systems with flow reactor and IR spectroscopy experiments in operando conditions on high surface area oxide powder supports to gain two perspectives on the structure and catalytic function of these systems. Our group has recently demonstrated the formation of structurally ordered and chemically uniform platinum, chromium, iron, and vanadium single-site centers with organic ligands on surfaces. The on-surface redox process on model surfaces in UHV relies on straightforward vapor deposition protocols and takes advantage of the catalytic role of the surface to show promise as an approach for the growth of inorganic complexes at surfaces. For the high powder supports, we use a wet-impregnation style synthesis. The ability to tune the reactivity and catalysis of these systems is a central question in this field. We report new results here that probe the extent of metal oxidation state control in these systems using tailored ligands and also probe the chemical activity of these transition metal single sites. The oxidizing power of the tetrazine species is tuned by peripheral functional groups to access two and three electron oxidation processes, as determined by X-ray photoelectron spectroscopy (XPS). Metal-ligand complexes take the form of nearly identical one-dimensional polymeric chains, resolved by molecular-resolution scanning tunneling microscopy (STM). These structures provide highly uniform quasi-square-planar coordination sites for the metal, which contributes to the well-defined chemical state of the metal. The chemical activity of the metal centers is characterized by adsorption studies on the model systems and by operando flow reactor and IR spectroscopy measurements.

COLL 722

Computational design of metal-ligand coordination centers for catalytic applications

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Designing systems that offer stable single atom transition metal sites for reaction may lead to significant advancement in the next-generation catalyst. In this talk, we will discuss our recent effort in understanding and proposing two such systems which have motivated by experimental observation. In the first, our density functional theory (DFT) based calculations provide excellent agreement with the observations of Pt-dipyridyltetrazine complexes on the reconstructed Au(100) surface, in which single Pt atoms are stabilized by dipyridyltetrazine ligands. We find that these complexes form 1-dimensional chains aligned 45° with respect to the Au(100) reconstruction row and with the molecule-molecule distance of 6.93 Å. Bader analysis shows that Pt atoms are cationic with a charge of +0.75, indicating that the oxidation state of the Pt atoms is +2, close to that of Pt atoms in PtO. Furthermore, for Pt-di-pyrimidinyl-tetrazine complexes on the same surface, we find that the complexes form 1D chains that are parallel with the surface reconstruction row and that the distance between molecules are 5.88 Å. In

addition, our computational screening of the propensity of several other metal atoms for assembling similar dipyridyltetrazine molecular chains show sufficiently large formation energies which suggest their stability. More importantly, the coordination centers of the dipyridyltetrazine chains constituted by Mo, Cr, Fe or Co atoms bind CO and O₂ strongly, suggesting that these chains maybe potential candidates for CO oxidation catalyst. The guidelines obtained above will be compared to that gleaned from the coordination networks of 9, 10 dicyano-anthracene and diisocyano-anthracene on Cu(111). The impact of functional groups (N, CN, NC, NH₂, COH, COOH) on the electronic structure of the coordination center, with and without a Cu adatom, will also be presented. Our results show that while the interaction between the naphthalene backbone and the Cu(111) surface is dominated by van der Waals (vdW) forces, in all cases considered the functional group forms a covalent bond with the Cu (ad)atom (on) of the surface. These results provide insights into the different surface coordination behavior of molecules with above-mentioned functional groups.

COLL 723

Two-dimensional organic heterostructures and Co-crystals

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A powerful strategy to design materials properties is to form alloys, mixes or cocrystals of two or more substances. While alloying is widely studied and exploited for metals, organic mixes and cocrystals are much less common. In mixes and cocrystals, the molecules interact via non-covalent interactions, generating physical and chemical properties that differ from the properties of the individual components. This principle will be demonstrated here on the example of the spin-crossover Fe(II) complex of the type [Fe(H₂B(pz)₂)₂(bipy)], wherein the well-known thermally induced spin state transition from a low-spin to a high spin state, which naturally occurs at 150 K, can be suppressed by mixing it with strongly dipolar *p*-benzoquinonemonoimine zwitterion molecules. As a result, a metastable low-spin state can prevail at room temperature, where a spin state transition to the high-spin state can now be triggered optically with soft X-rays. This concept of materials properties design will be discussed further on the example of organic proton-transfer-type ferroelectrics, such as the oxocarbons croconic acid and 3-hydroxyphenalenone, and various benzimidazoles. By exploiting solvent-free self-assembly on crystalline substrate surfaces a large variety of hydrogen-bonded structures and network architectures were stabilized that can't be synthesized by any other solution-based approach. Thus, new 2D structures that exhibit homoconjugated hydrogen bonds of the type –O-H●●O= and –N-H●●N= and the heteroconjugated OH●●N – type hydrogen bonds were formed and investigated with scanning tunneling microscopy, with the goal to design and investigate the shape of the potential energy surface for the proton motion in the hydrogen bonds. This potential is key for the ferroelectric switching behavior of room-temperature proton-transfer ferroelectrics, as will be discussed based on our first-principles simulations. In some of the co-crystals,

such as those of croconic acid and benzimidazole, several different types of H-bonds coexist, which might represent an interesting opportunity to build materials with multiple ferroelectric switching fields. This exploratory solvent-free 2D co-crystallization on surfaces, combined with first-principles calculations, is a departure from existing approaches and could potentially become a blueprint for Materials Genome Initiative-related search strategies for new functional organics.

COLL 724

Axial binding to supported metal porphyrins at the solution-solid interface

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The chemistry of the metal ion contained in porphyrin complexes is of very wide and general interest. Because these complexes play a key role in biology, in catalysis, in sensing, and in organic electronics, their chemical and physical processes have been widely studied in the solid state and in solution. It has only been in very recent times, however, that their single molecule chemistry has been probed at the solution-solid interface. Scanning tunneling microscopy (STM) has allowed us to monitor, at the single molecule level, reactions between surface supported metal porphyrins and molecular species like oxygen, imidazole, and other reactive species that can bind as ligands to the metal. These STM studies have clearly demonstrated that the chemistry of the supported metal porphyrin can be very different than in solution. The application of DFT methods has further allowed us to probe the nature of the substrate-porphyrin-ligand interaction relative to the case where no substrate is present. Whenever the porphyrin is supported on a conducting substrate there is a complex charge exchange process that helps stabilize the molecular binding. In some cases, the interaction is such that even the spin state of the metal ion differs on the surface relative to the same complex in solution or gas phase. We will present some particular examples of STM and DFT studies of this new chemistry.

COLL 725

Development of fragment-based quantum chemical models for understanding supramolecular interactions and self-assembly

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Increasing the accuracy and computational applicability of electronic structure calculations has been a primary objective in computational quantum chemistry for decades. In recent years, we have developed fragment-based methods to compute accurate energies and properties of large molecules. While these methods have been highly successful for molecules that are well described by covalent bonding, the

presence of non-covalent interactions such as π - π stacking can result in significant errors. In this talk, we present fragmentation-based methods developed in our group and their extension to capture weak supramolecular interactions in order to derive accurate interaction energies involving macrocycles and foldamers. The implications of our results for self-assembly of novel organic macrocycles in 2- and 3-dimensions are explored.

COLL 726

Tuning the exchange coupling of transition metal complexes to gold substrates by magnetic fields

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Transition metal complexes in contact with metal surfaces are model systems to study complex magnetic processes and essential building blocks for spintronics. Spin states of the magnetic center are normally controlled by the exchange interaction with a ferromagnetic substrate. Here, we demonstrate that for iron phthalocyanine (FePc) molecules absorbed on a non-magnetic Au(111) surface, the molecule-substrate exchange interaction can also be engineered by varying the external magnetic field. Consequently, the Kondo resonance signature is tuned in a controlled way from a Kondo dip to a Kondo peak. This originates from the transition of the molecular orbitals responsible for the Kondo effect. This work opens up an avenue for molecular spintronics in terms of control and tunability.

COLL 727

Theoretical studies of adsorption and self-assembly of probe organic molecules at metal oxide surfaces

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Titanium dioxide (TiO_2) has been studied and used in very wide range of areas, and in particular, it has been taken as the model system to study adsorption behaviors of probe molecules as well as structure-activity relationship in catalysis. In our recent work, the adsorption behaviors of probe organic molecules at rutile $\text{TiO}_2(110)$ and (011) surfaces were investigated by means of density functional theory (DFT) calculations, corrected by on-site Coulomb corrections and long-range dispersion interactions. Our calculation results show that carboxylic acids prefer to dissociatively adsorb in bridging bidentate configuration, and it induces significant surface relaxation at the adsorption site, which also affects other surface atoms nearby. Interestingly, we have shown that

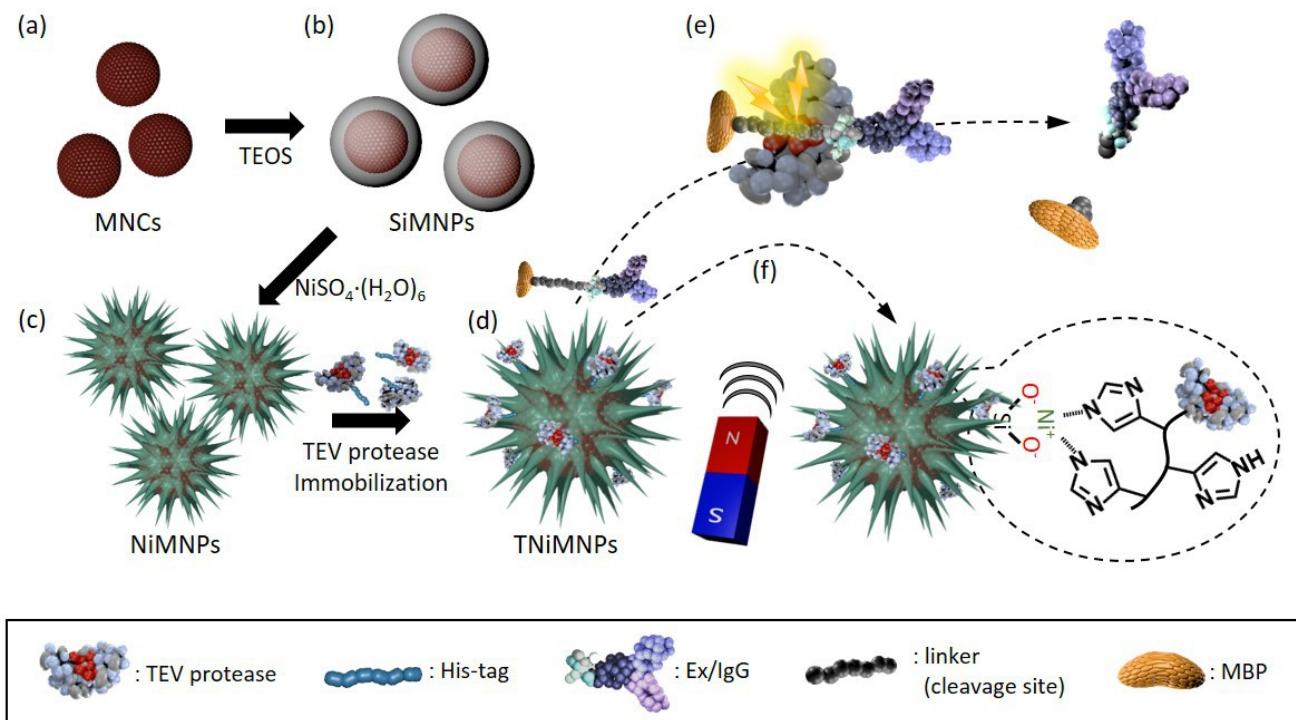
such adsorption induced relaxations still maintain bond symmetries for surface Ti cations within the p(2×1) domain while they are drastically broken within the c(2×2) domain, giving rise to unstable Ti cations at the surface. This work not only explains the long lasting puzzle of the preferable occurrence of p(2×1) domain for the adsorbed carboxylic acids at rutile TiO₂(110), it also proposes a novel scheme that metal oxide surfaces may follow when they are involved in the processes like surface functionalization and self-assembly. For the rutile TiO₂(011) with unique reconstructed conformation, its structures can undergo further restructuring upon interaction with various molecules, which can dramatically affect its activity. In particular, synergic effect of adsorbates causes a strictly directional re-organization of the substrate, which results in one-dimensional adsorbate cluster formation.

COLL 728

Enhanced immobilization of His-tagged enzymes using porous nickel silicate covered magnetic nanoparticles

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Enzyme immobilization techniques using well-tailored supporting materials for easy removal of enzyme from reactants and their efficient reuse have enormously advanced for decades. Specifically in fusion protein technology, Tobacco Etch Virus (TEV) protease is generally used for removal of fusion partners which are conjugated with protein by TEV protease specific cleavable peptide sequences of ENLYFQ. In the case of TEV protease treatment, immobilization system would offer economic benefits by facile removal and reusing of enzyme. Among enzyme binding platforms, using inorganic nanoparticles have been extensively explored because of the advantages of their easy surface modification, large surface area, and high stability in various pH or temperature. Furthermore, to retain enzymatic activity after immobilization, affinity tags such as poly-histidine-tag (His-tag) or polystyrene binding peptide domain-tag were co-expressed with enzyme for site-specific and oriented immobilization on the supporting materials. Herein, we prepared spiky nickel-silicate covered superparamagnetic nanoparticles (NiMNPs) with a facile synthetic route. His-tagged enzymes were rapidly immobilized on the surface of NiMNPs by nickel ion affinity. Porous nickel silicate covered nanoparticles achieved a high immobilization capacity (85 µg/mg) of His-tagged TEV protease. After then, to investigate immobilized TEV protease enzymatic activity, we analyzed the cleaved quantity of MBP-Exendin-fused Immunoglobulin (MBP-Ex/IgG) fusion protein, which conjugated with the TEV protease-specific cleavable peptide sequence. Moreover, easily recollected immobilized TEV protease from the reactant by applying an magnetic field also showed enzymatic activity even after fifth recycled reaction. Consequently, our newly developed nanoplatform for immobilization of His-tagged enzyme would be beneficial for biotechnological industries including fusion protein processing.



Synthesis of (a~c) nickel silicate covered magnetic nanoparticles, (d) His-tagged TEV protease immobilization, and their enzymatic activity; (e) MBP-Ex/IgG cleaved by immobilized TEV protease and (f) their removal using magnetic field

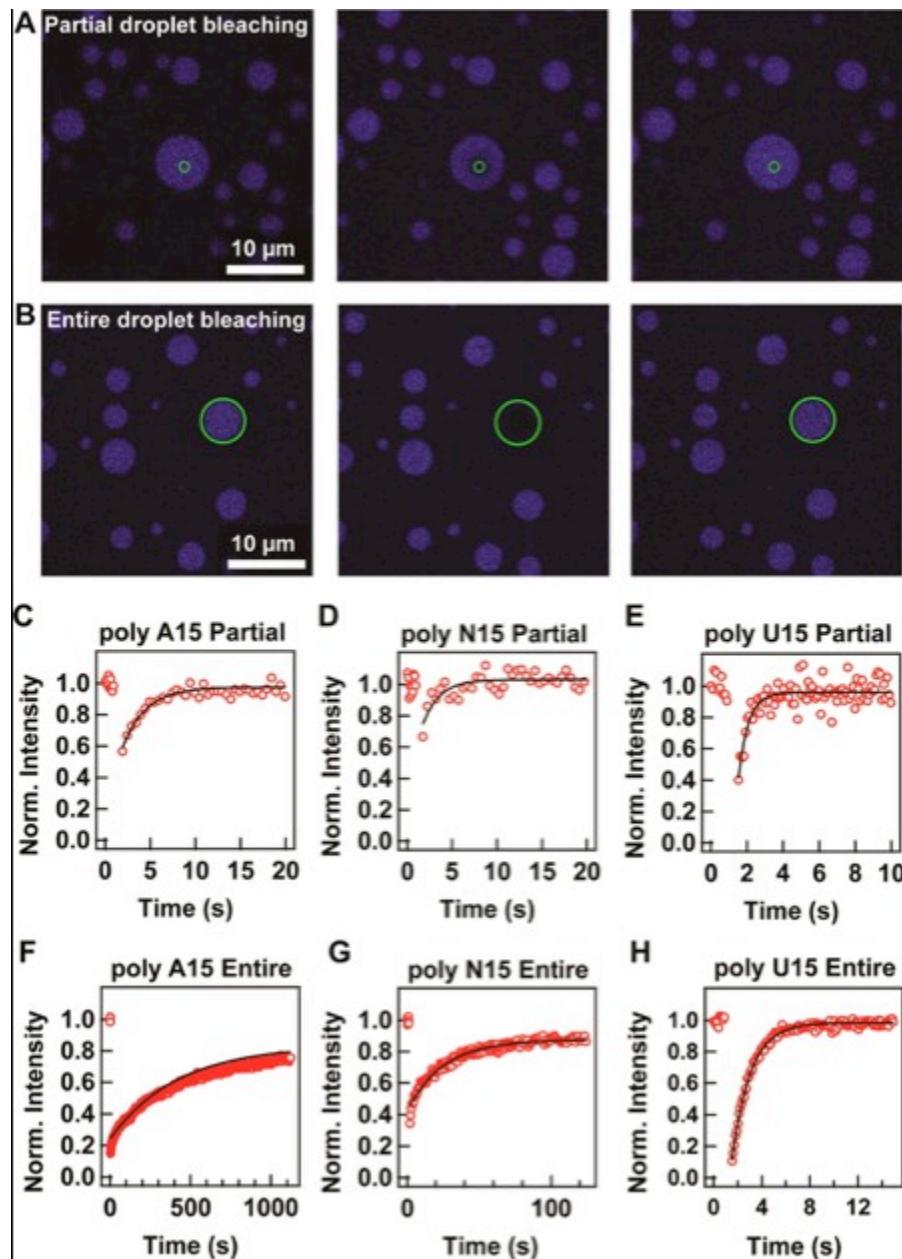
COLL 729

Diffusion of biomolecules in vesicle assembled RNA-based coacervates

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Liquid-liquid phase separation is being investigated for understanding cells in terms of membraneless organelles and protocells. Compartmentalization through introducing aqueous two-phase systems could enable concentration of the genetic and catalytic materials that are presumed to have been present at low concentrations on the early earth. Characterizing and utilizing the physical and chemical nature of the compartmentalization models will allow better understanding and control over these systems. We aimed to investigate intra- and inter-droplet exchange of nucleic acids, that is relevant to their evolution, and explore how partial droplet and whole droplet bleach recovers in coacervates composed of RNA and proteins. Here, we show that complex coacervates composed of low complexity RNA and short polyamines compartmentalize biomolecules (peptides, oligonucleotides) in a sequence- and length- dependent manner. These solutes retain mobility within the coacervate droplets, as demonstrated

by rapid recovery from photobleaching. We further demonstrate that lipid vesicles assemble at the droplet interface without impeding RNA entry/egress. These vesicles remain intact at the interface and can be released upon temperature-induced droplet dissolution.



Fluorescence images of Alexa Fluor 647-labeled poly U15 RNA demonstrating both partial droplet bleaching (A) and entire droplet bleaching (B) and representative FRAP recovery curves for the fluorescent RNAs (C–H). In parts A and B, the first images are the droplet before bleaching. The center images are the fluorescence immediately after bleaching, and the right images are the fluorescence at the end of postbleach recovery. The green circles indicate the

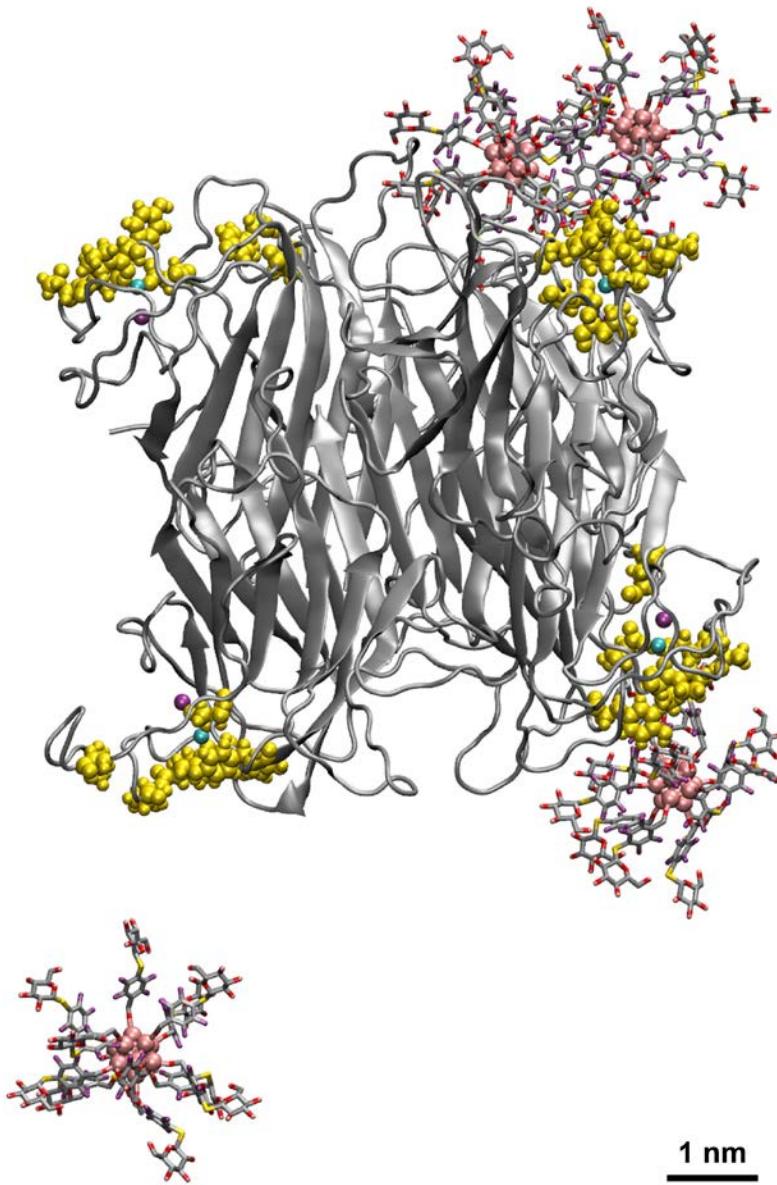
bleaching area. Partial droplet recovery for poly A15 (C), poly N15 (D), and poly U15 (E) and full droplet recovery for poly A15 (F), poly N15 (G), and poly U15 (H) are given.

COLL 730

Atomistic modeling of highly specific bio-active nanoparticles and micelles

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We use molecular dynamics simulations to model nanoparticles and micelles with highly selective biological activities which were tested experimentally by our collaborators. First, we investigate how carefully designed nanoparticles and related molecular complexes inhibit functions of viruses and peptide fibers through a highly specific multivalent binding. Next, we model similarly designed nanoparticles and investigate their binding to sugar-binding proteins. Finally, we discuss the interactions of linear and dendron-based micelles with generic proteins and membrane receptors, with the goal to design suitable nanomedicines.



Multivalent binding of nanoparticles and proteins.

COLL 731

Controlling colloidal drug aggregate stability and protein adsorption

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Many small molecule drug candidates form colloidal aggregates governed by a critical aggregation concentration, below which the compound exists as free drug monomers. A

number of approved drugs form colloidal aggregates at micromolar and sub-micromolar concentrations. Non-specific enzyme inhibition, through protein sequestration to the colloid surface, often leads to false-positives in high-throughput screening. Furthermore, colloids also lead to false-negative results in cell-based assay where the inability of colloids to diffuse across cell membranes leads to an apparent loss in cytotoxic activity of a number of chemotherapeutics.

Though colloids have typically been seen as nuisance compounds, their drug-rich composition and ability to release the monomeric form upon disruption has interesting potential applications. Unfortunately, these aggregates are only transiently stable and often precipitate over the course of a day. In an effort to determine if colloid formation can be exploited, here we investigate the impact of surfactants on colloid stability and interactions with biomolecules. Specifically, we investigate the role of surfactants on the formation and stability of colloid-forming chemotherapeutics. We find that surfactants can stabilize colloids in buffered solutions and biologically relevant media with high protein concentrations, preserving their spherical morphology. Furthermore, the incorporation of surfactants reduces adsorption of proteins to the colloid surface preventing non-specific enzyme inhibition. The results of this work provides further understanding of how the properties of colloidal drug aggregates impact their fate in biological environments.

COLL 732

Investigation of silk fibroin thin films for the improvement of bioactive peptide-based biosensors

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Silk fibroin, while best known in the textile industry for its strength, is an extremely versatile material that has been utilized for an array of applications such as waveguides, diffraction gratings and biocompatible wound dressings. Of particular interest is its ability to enhance the stability and performance of antibody-based biosensors.

Previously, our lab has shown that an array of different covalently immobilized α -helical antimicrobial peptides (AMPs) can detect and discriminate between lipopolysaccharide (LPS) molecules from different strains of Gram negative bacteria. However, the sensitivity and long term viability of the sensor was insufficient. Our objective is to utilize thin silk fibroin and silk fibroin/polymer blend films to augment the surface plasmon resonance (SPR) sensor to improve sensor performance and stability as has been done with antibody-based sensors. Our progress on silk and silk/polymer film characterization, SPR sensor development, optimization, and LPS detection performance will be discussed. The information gained from these studies may be applied in the development of clinically relevant reusable sensor technology.

COLL 733

Oligonucleotide - peptide complexes: Phase control by hybridization

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When oppositely-charged macromolecules are mixed in aqueous solution, counterion release drives formation of polyelectrolyte complexes and phase separation. The resulting condensed phase can either be a hydrated liquid (coacervate) or a solid precipitate. The polymer physics community has devoted substantial effort to understanding the forces underlying phase separation, but a predictive understanding of the relationship between the properties of the macromolecules and those of the resulting complexes is still incomplete. Nucleic acids, in addition to carrying information in their sequences, are highly charged and interact strongly with basic proteins and small cations *in vivo*. Long double-stranded DNA forms toroidal solids when complexed with polyamines and cationic peptides, but the polyelectrolyte behavior of shorter nucleic acids has not been substantially investigated despite the widespread use of cationic polymers for delivery of therapeutic oligonucleotides into cells. Modern synthesis techniques and computer-aided structure prediction allow nucleic acids of nearly-arbitrary length and structure to be designed, allowing exploration of a wide range of polymer combinations. I present results for complexation of single- and double-stranded oligonucleotides (10 – 88 nt) by cationic peptides (10 – 100 aa) and polyamines. We observe several interesting behaviors, the most striking of which is that, while double-stranded oligonucleotides form solid precipitates when mixed with polycations, single-stranded oligonucleotides form coacervate droplets. Complexes are formed over a wide range of charge ratios, polymer lengths, and concentrations, and oligonucleotides in complexes remain competent for sequence-selective hybridization, suggesting the possibility of environmentally-responsive nanoparticles. When salt is added, precipitates formed by longer polymers ‘melt’ into coacervates at a concentration that is largely independent of polymer length, while the complexes’ stabilities vs. dissolution depend strongly on length. Identical phase behavior is observed with RNA oligonucleotides, and substitution of uncharged methylphosphonate linkages suggests that polyelectrolyte charge density, rather than bending rigidity, determines the phase of the complexes. In addition to testing theories of polyelectrolyte complexation, these results also have implications for nucleic acid delivery and membrane-free organelles formed by intracellular phase separation.

COLL 734

Ultra-rapid crystallization of L-alanine using monomode microwaves, indium tin oxide, and metal-assisted and microwave-accelerated evaporative crystallization

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Birol Ozturk¹, **Kadir Aslan**². (1) Department of Physics and Engineering Physics, Morgan
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Monomode microwave heating and the use of indium tin oxide (ITO) was used to crystallize L-alanine (a model amino acid) crystals rapidly. Commercially available ITO dots (<5 mm) were attached to blank poly (methyl) methacrylate (PMMA, 5 cm in diameter with 21-wells silicon isolators: referred to as iCrystal plates) were found to withstand prolonged microwave heating during crystallization experiments.

Crystallization of L-alanine was performed at room temperature (i.e., control experiment), with the use of two microwave sources: 2.45 GHz conventional microwave (900 W, power level 1, control experiment) and 8 GHz (20 W) solid state, monomode microwave source with an applicator tip that focuses the microwave field to a 5 mm cavity. The time for initial L-alanine crystal formation on iCrystal plates with ITO dots took 47 ± 2.9 min, 12 ± 7.6 min and 1.5 ± 0.5 min at room temperature, using a conventional microwave and focused monomode microwave heating, respectively. Complete evaporation of the solvent using the focused microwaves was achieved in 3.2 ± 0.5 min, which is ~52-fold and ~172-fold faster than that observed at room temperature and using conventional microwave heating, respectively. The physical composition and number of L-alanine crystals were dependent on the surface of the 21-well iCrystal plates and the microwave heating method: 33 crystals of 585 ± 137 μm in size at room temperature > 37 crystals of 542 ± 100 μm in size with conventional microwave heating > 331 crystals of 311 ± 190 μm in size with focused monomode microwave. L-alanine crystals were examined to ensure that they were not affected by the microwaves or by the ITO surface by using FTIR, optical microscopy, and powder X-ray diffraction analysis. In addition, the binding of L-alanine molecules to ITO and several different metals were used to show the predicted nature of hydrogen bonds between the solution and the surface by using theoretical simulations.

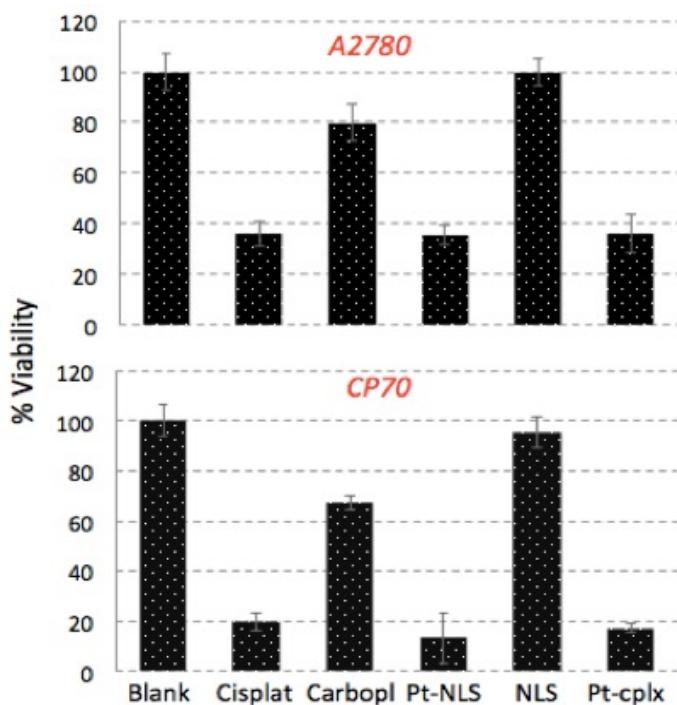
COLL 735

Synthesis of platinum (II) – nuclear localization sequence peptide hybrid for nanoparticle development and anticancer therapy

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Platinum(II) therapy is a well established treatment of many malignancies, including ovarian cancer, and cisplatin is one of the most potent therapeutics. Fast aquation rate of cisplatin results in high systemic toxicity, which led to the development other platinum based agents like carboplatin, with better toxicity profiles but lower effectiveness.

Herein, we report the synthesis of new carboplatin-like Pt(II) complexes $C_{10}H_{21}N_5O_4Pt$ and $C_{10}H_{18}N_2O_4Pt$, with azide and alkyl functionalities, and Pt(II) peptide hybrid with SV40 large T antigen derived PKKKRKV peptide. Our complexes feature carboxylate ligands coordinated to the Pt metal opposite the amine groups analogous to carboplatin. The peptide used belongs to the nuclear localization sequence (NLS) that comprises the intrinsic cellular machinery of nuclear transport and was used to amplify the Pt(II) entry into the nucleus. The Pt(II)-NLS hybrid was formed at the N-terminus of the peptide at the end of solid-phase peptide synthesis. The NLS-Pt hybrid is highly soluble in water (<50 mg/ml), compared to cisplatin (2.5 mg/ml) and carboplatin (10 mg/ml). We found that Pt-NLS is highly efficacious in vitro, lowering the viability 200% better than carboplatin in chemo naïve and in chemo resistant cancer cell lines, with IC_{50} values comparable to that of cisplatin. The NLS-Pt hybrid efficiently accumulates in the cell and inside the cell's nucleus, as confirmed by confocal microscopy. Platinum to DNA base pair ratio within the whole cellular DNA was found to be approximately 1:114 for CP70 and 1:244 for A2780 cell lines, which results in Pt (II) binding to DNA every 20 loops in A2780 and every 40 loops in CP70. The methodology can be extended further to incorporate the Pt(II)-NLS hybrids into the second-generation polymeric nanoparticle of polylactic-co-glycolic acid (PLGA) for sustained release outcomes.



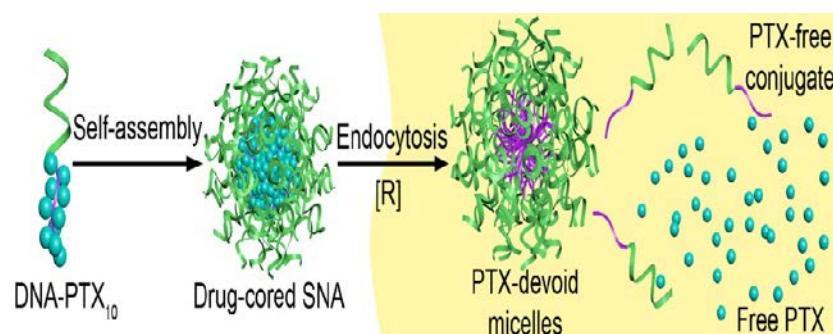
COLL 736

Design and evaluation of trigger-responsive DNA-drug nanostructures

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Herein, we present a DNA-drug conjugate system that we envision can be used to combat drug-resistant cancer. By covalently tethering the two components, which are of opposing hydrophilicities, we are able to form micellar nanostructures. These “spherical nucleic acids” enter cells nearly two orders of magnitude faster than free DNA. Upon cell uptake, the core of the micelle is disintegrated by the reducing intracellular environment, which leads to the release of free drug molecules and DNA. We show that the nanoparticle exhibits similar IC₅₀ to that of the free drug, and that the DNA component can serve as an antisense gene regulation agent. We also demonstrate that the nanoparticles exhibit enhanced stability against nuclease compared with free DNA.



COLL 737

Production of protein nanofibers using new timesaving methodologies for the design of innovative biomedical applications

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Amyloid fibrils are undoubtedly associated to several pathological diseases like Alzheimer's and Parkinson's, and hen egg white lysozyme (HEWL) has been widely used as a model protein to understand the mechanism of amyloid fibrils formation. However, these fibrils have also been gaining a lot of attention as a source of innovative nanomaterials for several technological applications, due to their morphology, functionality and mechanical strength. For example, they have been used in nanofiber-based materials field, as biosensors, bioactive membranes and tissue engineering scaffolds. Nevertheless, most of the methods used so far for the preparation of protein nanofibers can take days, weeks and even months, with the fastest methods reporting 8-15h. Our work presents new and faster fibrillation methods to obtain long and fine nanofibers from HEWL, using imidazolium based ionic liquids and deep eutectic solvents based on cholinium chloride and a range of organic acids, as well as microwave assisted (MW) methodology, reducing the incubation time down to 2h. The influence of experimental variables such as temperature and pH was studied, unveiling

their influence in the fibrillation time and nanofibers morphology. These results open a new scope for nanofibers production enabling their application in a wide variety of fields ranging from medicine to soft matter and nanotechnology.

COLL 738

Carbon nanotube-quantum dot nanohybrids: Coupling with single particle control in aqueous solution

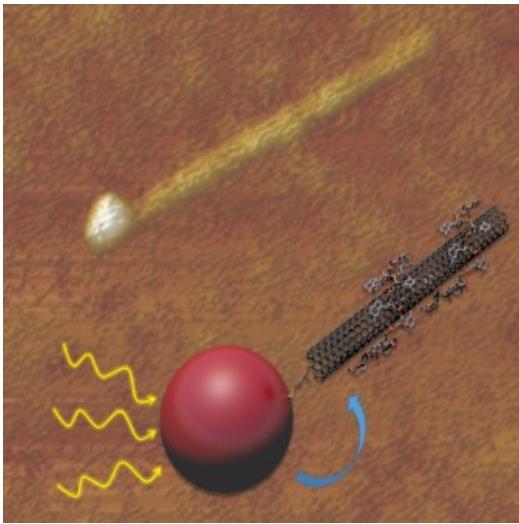
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We present a controlled assembly strategy for the formation of carbon nanotube-quantum dot nanohybrids, where the terminal ends of individual single-walled carbon nanotubes (SWCNT) are selectively functionalised with single quantum dots (QDs), via the formation of covalent bonds. The assembly, in environmentally friendly and biocompatible aqueous solution, was controlled towards the formation of monofunctionalized SWCNT-QD structures.

We use DNA wrapped carbon nanotubes, where the DNA acts as a surfactant for the dispersion of the nanotubes in water. Moreover, the DNA's helical wrapping on the sidewalls of the tubes leaves only the terminal ends of the SWCNTs available for direct functionalization. Atomic force microscopy has been used to image the nanostructures and allowed us to identify the nanodots exclusively at the terminal ends of the tubes. Photoluminescence studies in solution and on surfaces at the single nanohybrid level showed evidence of electronic coupling between the two nanostructures.

Quenching of photoluminescence of the CNT-QD nanohybrids in solution has been observed which indicates an electronic coupling between the two nanostructures as previously observed in QD-SWCNT composites. The photoluminescence blinking dynamics of conjugated and un-conjugated individual quantum dots was investigated showing larger off-state probability densities for QDs attached to the tubes, suggesting an increased photoinduced charging of the nanocrystals.

The strategy presented here provides a general approach for the covalent formation of heterostructure with single particle control which in turn is crucial for novel QD-based optoelectronic and light-energy conversion devices.



Carbon Nanotube-Quantum Dot Nanohybrids: Coupling with Single Particle Control in Aqueous Solution

COLL 739

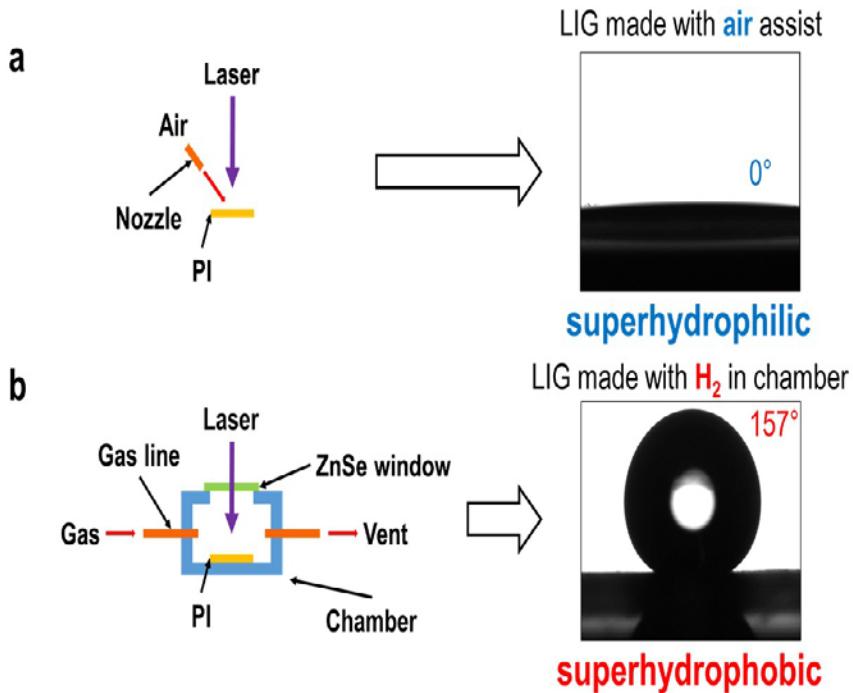
Fabrication of laser-induced graphene under controlled gas atmosphere – from superhydrophilic to superhydrophobic

Yilun Li, lylsilence@gmail.com, Duy Xuan Luong, Jibo Zhang, James M. Tour.
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Graphene has shown promising applications in electronic devices, energy storage, and electrochemical catalysis due to its unique properties. Recently, we reported laser induced graphene (LIG) as a facile and scalable approach to produce 3D graphene structures through a laser scribing process from commercial polyimide films. Various methods have then been developed to tune or improve the physical and chemical properties of the LIG by varying the laser conditions, or by introducing of boron or metal doping in the LIG, and through the electrochemical deposition of active materials on top of the original LIG layer. Yet, all these LIG materials were fabricated in ambient atmosphere, and the yielded surfaces were always hydrophilic.

Aiming to expand the range of properties for LIG, especially to tune the hydrophobicity of the yielded LIG surfaces, and eventually to further extend the field of applications for LIG based on the different properties, we report here a method to fabricate LIG structures under controlled gas atmospheres, where superhydrophilic and superhydrophobic LIG could be directly obtained by switching the gas environment. This change in gas atmosphere permits the enormous change in the water contact angle on the as-prepared LIG, from superhydrophilic when using O₂ or air, to superhydrophobic when using Ar, H₂, or SF₆. SEM, XPS, and Raman spectroscopy showed that the different wetting properties are due to the LIG surface morphology and the edge and surface chemistry of these LIG structures. While superhydrophobicity can be introduced

with Ar, H₂, or SF₆ in the controlled atmosphere chamber, LIG samples fabricated under O₂ flow show an increased number of defects which bring in a significantly improved specific capacitance when applied as the electrode material for microsupercapacitors, showing the versatility of the “controlled atmosphere chamber” fabrication method.



Scheme for the fabrication of LIG with (a) gas assist and (b) gas chamber. The water contact angle for as-prepared LIG is ~0° with gas assist, and 157° with H₂ in gas chamber.

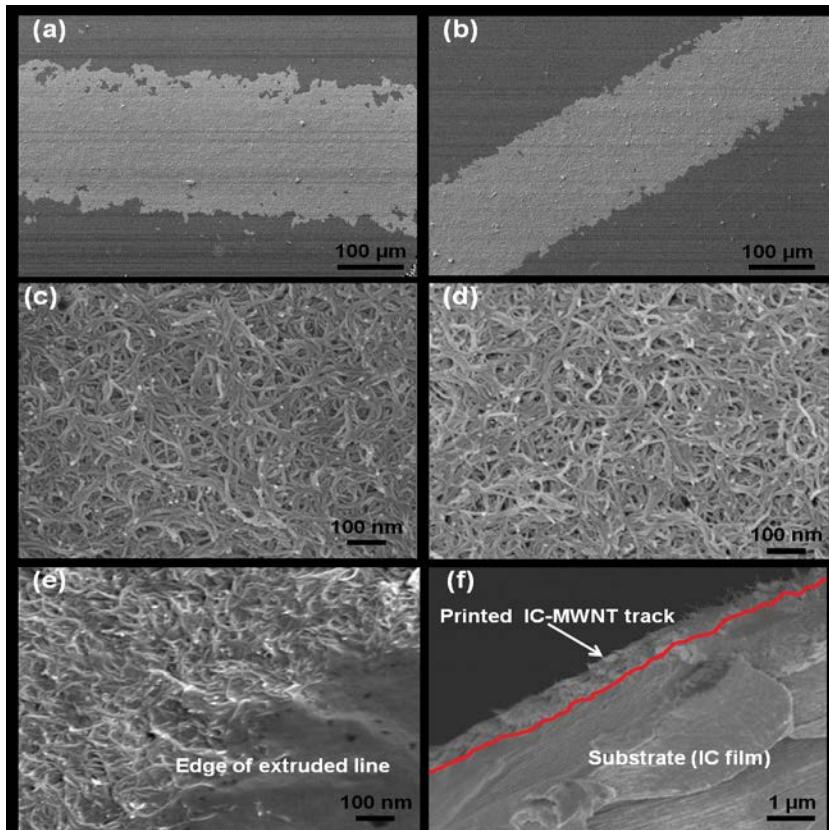
COLL 740

Fabrication of carrageenan/carbon nanotubes conducting patterns by extrusion printing method

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Extrusion printing inks were prepared with multiwall carbon nanotube (MWNT) and iota-carrageenan (IC), a biopolymer thickening agent containing two sulphated groups, extracted from red seaweeds and with glycerin (G), a polyol Newtonian fluid. After adjusting for the proper viscosity of both the inks i.e. IC-MWNT and G-MWNT, they were extruded by a syringe printer on glass slide, IC gel films and PET transparent sheet. Conductive tracks of the deposited printed inks were characterized with microscope, SEM, Profilometry, contact angle measurement and conductivity determination. Conductivity of IC-MWNT track was 9±1S/m and that of G-MWNT was

2942 ± 84 S/m on glass substrate of one layer thick. Profilometry showed that increased numbers of extruded layers gave increased in the cross-sectional area. SEM study showed that printing ink is embedded into surface of IC film, discontinuous on glass slide and smoother on PET sheet



SEM images of G-MWNT extruded patterns onto (a and c) glass, (b and d) PET sheet and (e) IC film substrates. (f) Cross-sectional view of G-MWNT tracks printed onto IC film substrate. The red line indicates interface between track and the substrate.

COLL 741

Multiplexed graphene-based nanomaterials for discriminatory sensing: A combined fundamental and applied experimental approach

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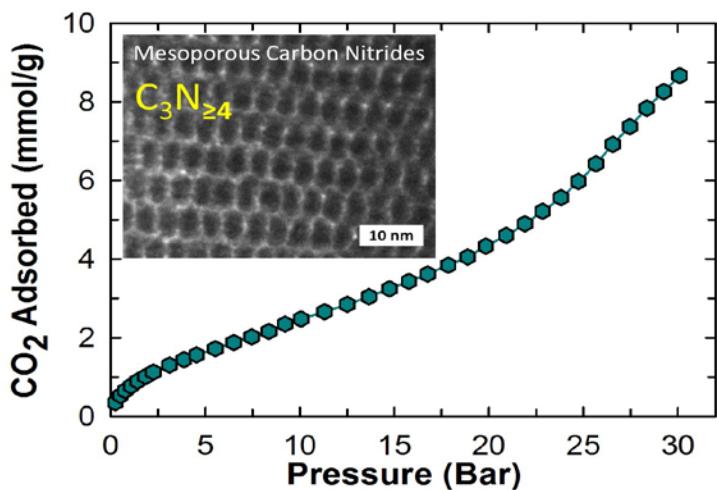
In our research, we are exploring the use of various forms of graphene, including planar graphene substrates and graphene nanoplatelets, as the transductive and functionalizable material for preparing tailored multi-array multiplexed sensors. Using various select polymer coatings and metal oxide nanoparticles as the sensing material, we are simultaneously developing multi-analyte gas sensors towards chemical warfare agent simulants while understanding the fundamental surface chemistry paramount to their performance. So far, using set of just five polymer coatings mixed with graphene nanoplatelets, we've obtained 100% discrimination of seven simulants and nine potential interferents. We aim to combine these technological achievements with a synergistic surface characterization approach, including Raman spectroscopy and imaging, infrared reflection-absorption spectroscopy (IRRAS), to elucidate the potential structure-functional relationships leading to optimal sensor platform design and material coating selection.

COLL 742

Nitrogen-rich mesoporous carbon nitrides for CO₂ capture and conversion

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Mesoporous carbon nitrides (MCN) with perfect stoichiometry C₃N₄ are fascinating materials because the doping of nitrogen in the carbon framework can significantly influence the electronic, electrical, mechanical, conducting and optical properties and are prominent candidates to complement carbon materials in a variety of energy, environmental, and biomedical applications. The definition of CN materials has been changed significantly from the ideal C₃N₄ stoichiometry and now the same has been extended to include compounds such as C₃N, C₃N₂, C₁₀N₃, C₅N, C₃N₅, C₃N₆, C₃N₇ etc., having lower or higher nitrogen content than the ideal C₃N₄ structure. The higher and lower nitrogen content with respect to the ideal C₃N₄ is attributed to the presence of structural defects which are affected by the reaction conditions, degree of condensation and relative reactivity of molecular CN precursors. In this study, highly ordered MCN materials with high nitrogen contents were successfully prepared through the polymerization of different aromatic and/or aliphatic carbon and high nitrogen containing molecular precursors via hard templating approaches. The most important findings here are arrived at: (i) new MCN materials had the large surface areas higher than 300 m²g⁻¹ and tuneable pore diameters from 3 nm and 8 nm with well-ordered 2- and 3-dimensional mesoporous structure; (ii) the MCN materials had a very high nitrogen content with a C/N ratio of less than 0.5, which is lower than theoretical C/N ratio of 0.75 for typical graphitic carbon nitrides; and (iii) the nitrogen-rich MCN materials showed the excellent CO₂ adsorption capacity of more than 8.0 mmol/g at the temperature of 0 °C and pressure of 30 bar. The chemical bonding nature and electronic band structures of these novel MCN materials were also investigated by soft X-ray spectroscopy (NEXFAS data) and UV-DRS spectra. The detailed results of CO₂ conversion using novel MCN materials will be presented during the conference.



COLL 743

Shear thickening behavior of graphene nanoplatelets and carbon nanotubes containing fumed silica suspensions

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Shear thickening fluids are interesting class of fluids in which viscosity increases drastically beyond a critical shear rate. Various parameters can affect the shear thickening behavior such as the size and shape of the dispersed particles. Here, we investigate the shear-thickening behavior of mixture of two different types of nanoparticles: fumed-silica and multi-walled carbon nanotubes (MWCNTs) or graphene nanoplatelets (GNPs). In this work, the mass-fraction of fumed silica was maintained as 0.15, whereas that of MWCNTs and GNPs was changed from 0.01 to 0.025. The concentration of MWCNTs and GNPs affect the critical shear rate and the steepness of shear thickening response beyond the critical shear rate. In addition, with increasing nanotube concentration a transition from viscous liquid to soft-solid has been observed.

COLL 744

Plasma-enhanced graphene and graphene oxide based conducting polymer composites for solar cell and biosensor applications

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Graphene-based materials have been received increasing attention in the last decade due to unique mechanical, optical, electrical and thermal properties of graphene. Among graphene materials, graphene oxide is also very important due to its functional groups located on the basal and edge of its structure.

Graphene-based composites have been prepared by using different physical and chemical methods such as non-covalent mixing followed with adsorption route, in situ polymerization, interfacial polymerization and electrochemical deposition. These methods generally require many chemicals and purification steps. Compared with these methods, plasma method has been also used to prepare polymers and composite materials. By using this method, conducting polymers can be directly coated on graphene surfaces and the obtained composites can be used without further treatment. Based on these properties, plasma method is known as cost-effective, fast and environmentally friendly method.

In this study, the composites of graphene and graphene oxide with three different conducting polymers include polythiophene, polypyrrole and polyaniline were prepared by using RF-rotating plasma method (13.56 MHz, 0.02 torr, 40W, and 3h). The composites were investigated in terms of morphology, chemical structure, chemical compositions, and thermal behaviors with scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS) and thermal gravimetric analysis (TGA). The obtained composites were used in solar cell and biosensor applications and exhibited notable results.

COLL 745

Synthesis and characterization of water-based dispersions of high-purity, thin graphene oxide sheets from different graphitic sources

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Graphene oxide (GO) has a great potential for use in biomedicine, however, understanding how this novel 2D material interacts with biological milieu is fundamental for its development. This work aimed to investigate the role that the starting graphitic material played on the physicochemical properties of graphene oxide (GO) sheets and their impact on mammalian cell viability. Three different GO few-layered sheets were synthesised from three starting graphite material: flakes (GO-f), ground (GO-g) and powder (GO-p) using a modified Hummers' method. The synthetic yield of this methodology was found to differ according to type of starting material, with GO-p resulting in most efficient yields. Structural and morphological comparison of the three GO sheet types were carried out using transmission electron microscopy and atomic

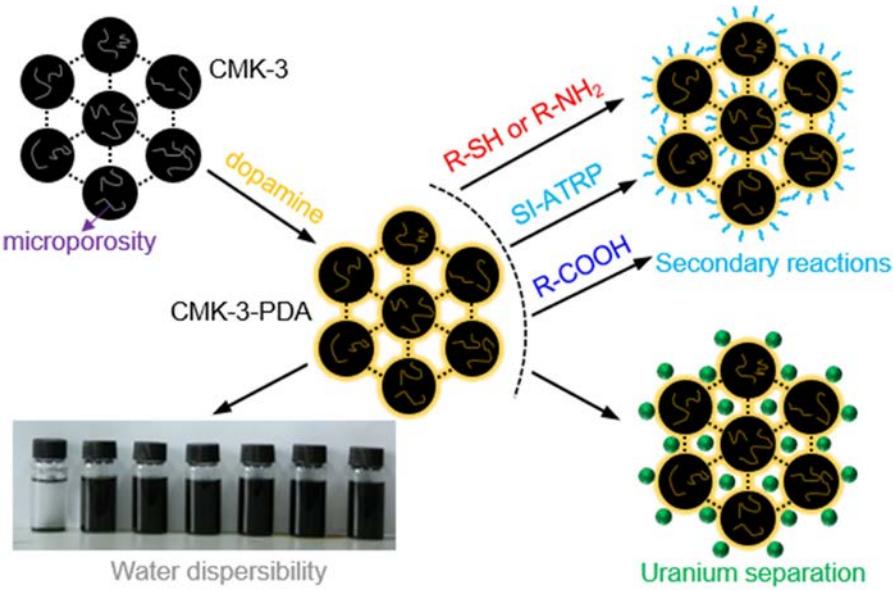
force microscopy. Optical properties were measured using UV/visible and fluorescence spectroscopy. Surface characteristics and chemistry were determined using a variety of techniques. Exposure to human cells was studied using the human A549 lung epithelial cultures. Our results revealed that all three GO samples were composed of few-layer sheets with similar physicochemical and surface characteristics. However, significant differences were observed in terms of their lateral dimensions with GO-p, prepared from graphite powder, being the largest among the GOs. No cytotoxicity was detected for any of the GO samples following exposure onto A549 cells up to 48 h. In conclusion, the form and type of the starting graphite material is shown to be an important factor that can determine the synthetic yield and the structural characteristics of the resulting GO sheets

COLL 746

Bioinspired Polydopamine (PDA) chemistry meets Ordered Mesoporous Carbons (OMCs): A benign surface modification strategy for versatile functionalization

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Mussel-inspired polydopamine (PDA) chemistry was employed for the surface modification of ordered mesoporous carbons (OMCs), improving the hydrophilicity, binding ability toward uranium ions, as well as enriching chemical reactivity for diverse post-functionalization by either surface grafting or surface-initiated polymerization. Uniform PDA coating was deposited on the surface of CMK-3 type OMCs via self-polymerization of dopamine under mild conditions. Surface properties and morphology of the PDA-coated CMK-3 can be tailored by adjusting the dopamine concentration and coating time, without compromising the meso-structural regularity and the accessibility of the mesopores. Due to high density of –NH groups (4.7 mmol/m² or 2.8 group/nm²) and –OH groups (9.3 mmol/m² or 5.6 group/nm²) of the PDA coating, the modified CMK-3 showed improved hydrophilicity and superior adsorption ability toward uranyl ions (93.6 mg/g) in aqueous solution. Moreover, with the introduction of a-bromoisoctyryl bromide (BiBB) initiator to the PDA-coated CMK-3, we demonstrated for the first time that activators regenerated by electron transfer for atom transfer radical polymerization (ARGET ATRP) can be conducted for controlled growth of polymer brushes from the surface of OMCs. Thus, PDA chemistry paves a new way for surface modification of OMCs to create a versatile, multifunctional nano-platform, capable of further modifications towards various applications, such as environmental decontamination, catalysis and other areas.



COLL 747

Aging effects on the transient frictional behavior of MoS₂-based solid lubricants for use in extreme environments

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Solid lubricants are used in high-consequence aerospace applications to insure predictable friction and wear behavior over a wide range of temperatures, with performance that is relatively insensitive to pressure or shear velocity over a large range of contact conditions. Solid lubricants are frequently deposited and stored for years before they are placed in service, and may be stored for years or decades longer prior to actual operation. Molybdenum disulfide based solid lubricants are known to exhibit surface oxidation that results in elevated friction coefficient during initial sliding. The magnitude and duration of this elevated friction coefficient can have significant consequences for device function. Extreme environments in these applications are therefore represented by the requirements of long storage duration, followed by operation with a predictable friction coefficient.

MoS₂ films with various compositions and morphologies have been developed over several decades to improve the environmental robustness of these materials. Various deposition processes for MoS₂ solid lubricants and their resultant frictional performance after aging will be described in this presentation. In particular, sputtered MoS₂ films that were exposed to atomic oxygen in low earth orbit during a space shuttle mission over twenty years ago will be examined, and the frictional performance and surface chemistry compared to the behavior exhibited by these materials today. Insights into the desired structures for MoS₂-based lubricants to resist age-related performance impacts will be discussed.

COLL 748

Understanding friction in MoS₂: Structure, oxidation and run-in

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MoS₂ coatings are used in a wide variety of applications where low friction is needed and performance is required. For parts manufactured in the aerospace sector (such as satellites) this means coatings must withstand a history of testing and storage in humid environments before launch and outside of targeted operating conditions in low earth orbit. This study utilizes MoS₂ coatings deposited via rf-magnetron sputtered (amorphous) and N₂ sprayed (highly ordered basal texture). Effects of oxidation resistance for amorphous and highly ordered MoS₂ were investigated with a high-sensitivity, low energy ion scattering (HS-LEIS) spectrometer. Recent studies have shown that N₂ sprayed MoS₂ coatings possess a preferential surface parallel basal plane texture as deposited due to the kinetic energy imparted during spraying, effectively shearing MoS₂ particles onto the surface. As such, the highly ordered structure of the sprayed coatings both at the surface and throughout the bulk of the film possess large continuous crystallites of MoS₂. It is hypothesized that the large fraction of crystallites on the surface as compared to their sputtered counterparts help to act as safeguards against intrusion of environmental contaminants. Coatings were exposed to molecular oxygen at 250°C and atomic oxygen at 20°C for 30 minutes each and subsequently depth profiled in the HS-LEIS. Results show that N₂ sprayed coatings were successful in limiting the depth of oxidation for both types of exposure. The main contributor, however, to increased initial friction post exposure was the type of coating (amorphous vs highly oriented). Tribological experiments in dry nitrogen and humid air showed the initial friction response to be unaffected for sprayed samples while greatly affected for sputtered. Spiral orbit tribological testing was utilized in dry and humid nitrogen environments to further assess the effect of prolonged sliding on purely amorphous MoS₂ with and without formation of a transfer film. It is hypothesized that water does not poison friction behavior of established films of highly oriented MoS₂, but it does poison the ability to form long range order and sintering of crystallites during run-in.

COLL 749

Lubricant effects in space system performance

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Moving mechanical systems on spacecraft must perform under harsh conditions, typically with a limited supply of lubricant required to endure for a decade or longer without replenishment. We monitor performance with telemetry, typically limited to variables like speed, temperature, and motor current. We have developed methodologies to aid our understanding of the lubricant condition, both amount and physical properties, to aid in our assessments. For example, liquid lubricants age while in use in the vacuum of space, experiencing evaporative loss and chemical breakdown, affecting the physical properties of the fluid. In turn, those changes can affect system performance. In this talk, we will review the application of these methods for liquid lubricated systems such as rate gyroscopes and momentum wheels to demonstrate how the science of tribology aids in the management of critical space assets.

COLL 750

Interactions between oil-soluble phosphonium-phosphate ionic liquids and steel in the mixed and boundary lubrication regime

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Organophosphates remain the dominant additives for extreme pressure in high-end aerospace lubricants with little change for over half a century. Phosphonium-phosphate ionic liquids (IL) with oil-soluble alkane moieties have recently shown promise as effective antiwear additives. In this contribution, we demonstrate that trihexyltetradecylphosphonium bis(2-ethylhexyl) phosphate [THTDP][DEHP] can function as an effective extreme pressure additive and discuss some of its tribofilm formation characteristics. [THTDP][DEHP] will be shown to delay the onset of scuffing in high-speed sliding-rolling steel contacts (approx. 15 m/s) during starved lubrication when used in a fully-formulated lubricant. In Fig. 1, the oil supply was ended at time 0 s for a lubricant with and without IL in a ball-on-disc tribometer. The onset of scuffing (when the coefficient of friction rapidly increases) occurs around 200 s for the lubricant with IL, significantly later than without at 50 s. To isolate the mechanisms of mixed and boundary lubrication from those of the full additive package, further characterization of the lubrication properties of both neat and dilute [THTDP][DEHP] (in a polyol ester basestock) will be presented from pin-on-flat and ball-on-disc tribometry as a function of sliding speed and lubricant film thickness. The surface chemistry and tribofilm formation leading to the extreme pressure behavior will be discussed with the support of microscopic and spectroscopic post-analysis from the contact zones of the various tribological measurements.

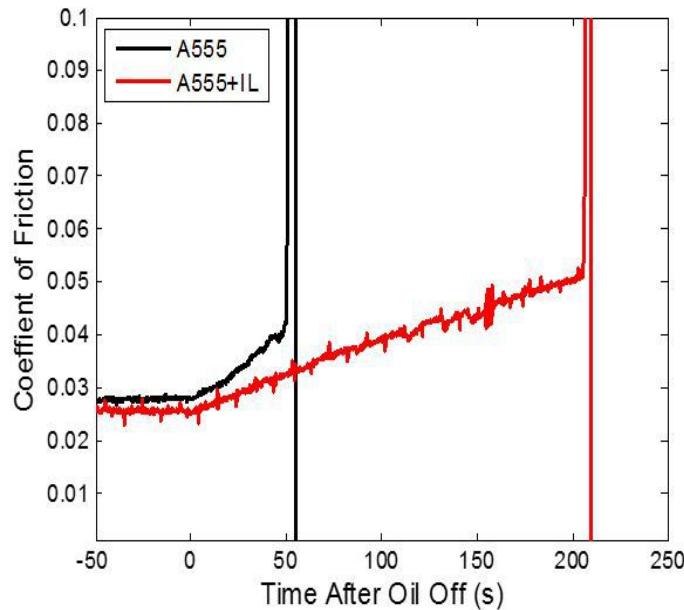


Fig. 1 Coefficient of friction after oil supply is turned off at 0 s.

COLL 751

Linking microstructure to wear-induced pitting corrosion in aged 2507 super duplex stainless steel

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Grade 2507 super duplex stainless steel ordinarily achieves a balance of corrosion resistance and mechanical properties through its dual phase ferrite-austenite microstructure. However, heat treatment in the 600-900°C temperature range causes phase transformations to occur, developing complex microstructures with secondary phases including sigma phase, secondary austenite, chi phase, and chromium nitrides. It has been shown that in tribocorrosion experiments in 0.6 M NaCl in anodic conditions, the passivity of aged 2507 can be eliminated due to mechanical wear, causing pitting to occur in and near the wear track. However, the precise mechanism of this loss of passivity is not yet understood. In the present study, we explore the tribocorrosion behavior at selected phases and grain boundaries. Correlating the microstructural features to local surface topography changes and the current transient response promises to reveal precise details of the wear-induced corrosion behavior.

COLL 752

Amazing friction properties of graphene and water

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Graphene has not only unique electronic properties that arise from its peculiar electronic structure, but also unique mechanical and chemical properties. I will present and discuss some of these, including:

- a) Formation of friction domains on exfoliated monolayer graphene deposited on SiO₂-Si wafers, due to ripple distortions along preferential crystallographic directions. Within each domain the friction is anisotropic;
- b) Graphene layers grown on reactive substrates like Ru(0001) can be split along grain boundaries by reaction with water. Subsequently the water intercalates between graphene and the Ru metal and changes the friction of graphene;
- c) Graphene flakes exhibit superlubric properties when sliding over large graphene layers, even at temperatures of 5 K.
- d) Water intercalated between graphene and mica or SiO₂/Si increases friction. With the help of DFT phonon spectra calculations we can explain the role of water in increasing friction energy dissipation.

COLL 753

Effect of thickness and chemical reduction of graphene oxide on nanoscale friction

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Tribological properties of two dimensional (2D) atomic layers are quite different from the three-dimensional (3D) continuum materials, due to the unique mechanical responses of 2D layers. Friction in 2D layered materials is highly dependent on thickness, substrate, chemical composition, and microstructure such as ripple. It has been found that friction of 2D layered materials increases when the thickness decreases. It was also found that friction in 2D materials is drastically increased after chemical modification, such as fluorination, oxidation and hydrogenation.

In this study, we show the nanotribological properties of graphene oxide (GO) investigated with friction force microscopy in ultrahigh vacuum. By using the combination of friction force microscopy and conductive atomic force microscopy, we investigated the subdomain structures of single-layer GO. Friction and conductance mapping showed that a single-layer GO flake has subdomains several tens to a few

hundreds of nanometers in lateral size. The GO subdomains exhibited low friction (high conductance) in the sp₂-rich phase and high friction (low conductance) in the sp₃-rich phase. The friction of GO and reduced graphene oxide (rGO) were studied as changing the number of layers. We show that friction on GO does not exhibit the thickness dependence, while that on rGO shows the clear thickness dependence. We provide the relevant theoretical interpretation to explain the influence of thickness and chemical reduction of GO on the nanoscale friction.

COLL 754

Studies of the dynamic frictional properties of 2D nanomaterials

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Control of friction and wear is a ubiquitous challenge in numerous machined interfaces ranging from biomedical implants, to engines, to nano- and micro-scaled devices. A key challenge in developing boundary lubrication schemes for such systems is how to reduce wear at the rough surfaces of such devices, where nanoscaled asperities dominate the interfacial contacts. The robust mechanical properties of two-dimensional (2D) nanomaterials has made them of significant interest for modifying surface frictional properties. While it has been found that many 2D materials can readily adapt to surface structure on the atomic scale, when deposited on substrates with nanoscopic roughness (~ 10 – 20 nm rms, as is common in many machined interfaces) a conformal coating cannot be fully formed due to competition between adhesion to the nanoscopic asperities of the substrate and the corresponding bending strain of the material. This often leaves a mixture of supported and unsupported regions which respond differently to applied load. Here we describe a combination of AFM nanomechanical and confocal Raman microspectroscopy studies of graphene, MoS₂ and MXenes on silica surfaces with controlled nanoscopic roughness to examine how substrate topology impacts the frictional properties of these materials, and their corresponding tribochemical properties.

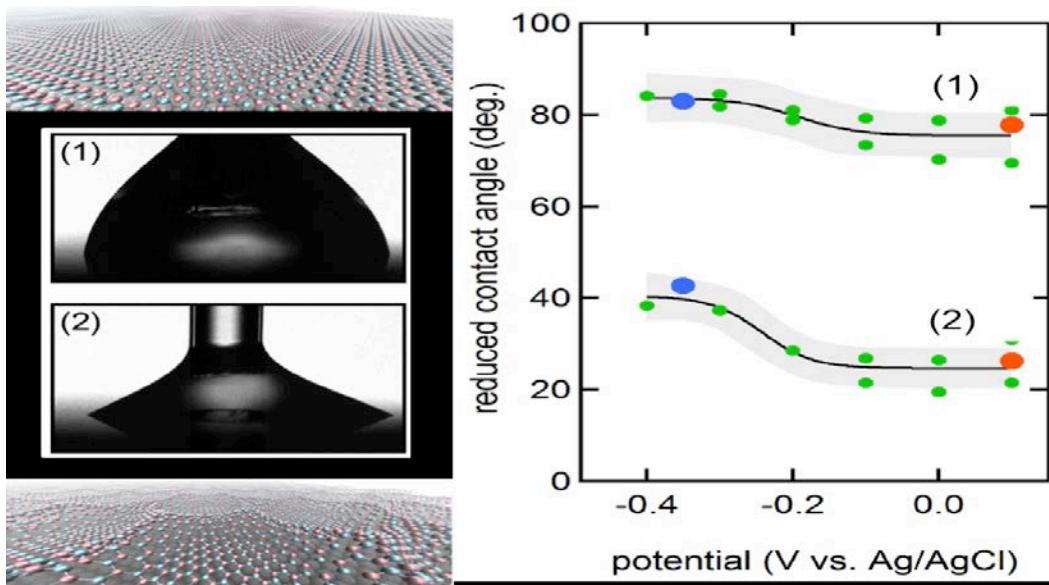
COLL 755

Boron nitride nanomesh model system for stiction and adhesion

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The boron nitride nanomesh is a corrugated monolayer of hexagonal boron nitride (h-BN) on Rh(111), and forms because of the lattice mismatch between the two materials. Here, we demonstrate how the nanomesh can be used as a model system in the study

of stiction and adhesion of a sessile drop of liquid, six orders of magnitude larger than the lattice constant of the corrugation. Electrochemical intercalation of atomic hydrogen between the h-BN monolayer and the rhodium substrate weakens the Rh–N bond and reversibly switches off its corrugation, and with it in-plane electrostatic dipole rings that are responsible for its adsorptive properties. The intercalation is proven directly by electrochemistry-to-vacuum transfer of a deuterium-loaded sample followed by thermal desorption spectroscopy. By performing dynamic contact angle measurements under electrochemical potential control within the sessile drop, we are able to link the change in surface morphology to a 10% change in adhesion forces between the substrate and the liquid drop. Quantitative agreement is found with experiments of water adsorption on the nanomesh, if the flat state is taken equivalent with unfavourable adsorption on the wire regions. The relatively simple structure of the boron nitride nanomesh allows accurate descriptions down to the atomic level, and makes the nanomesh an attractive model system for full-scale theoretical analyses of switchable surfaces, wetting, friction and lubrication.



Electrochemical hydrogen intercalation flattens the nanomesh and changes advancing (1) and receding (2) contact angles

COLL 756

Understanding the influence of environment and surface patterning on the tribological behaviour of silicon-oxide containing diamond-like carbon (a-C:H:Si:O) films

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a-C:H:Si:O film are generally described as fully amorphous films consisting of two interpenetrating and interbonded networks, one being a silica glass (SiO_x) network and the second one an amorphous hydrogenated carbon network (a-C:H). Their friction behaviour has been found to be dependent on the sliding environment and in particular, on the relative humidity. As demonstrated by Scharf et al., humidity plays a major role in the composition and the mechanical behaviour of the interfacial film generated while sliding: in dry environment, a carbon-rich tribofilm with low shear strength is found, while under humid conditions it consists of silica fragments and exhibits a higher shear strength.

In this work, we investigated the effect of environment on the tribological performance of a-C:H:Si:O films by using a linear reciprocating pin-on-flat tribometer under controlled environment. Inert gases (N_2 , Ar, dry air) were successively blown in the contact, leading to a decrease in the friction independently of the gas for non-patterned a-C:H:Si:O. We were thus able to show that while the frictional response strongly depends on the mechanics of the interface, water vapour protects the surface against wear while oxygen promotes it. Furthermore, the effect of surface patterning on environment-dependent tribological performance of a-C:H:Si:O was also investigated.

The tribochemical reactions occurring while sliding patterned and non-patterned (as grown) a-C:H:Si:O against a 52100 steel were also studied by different analytical techniques.

COLL 757

Antioxidant carbon nanomaterials for treating autoimmune disorders

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There is a distinct need for an alternative to broad spectrum immunosuppressants for the treatment of autoimmune disorders. Antioxidants represent one possible alternative; however, naturally occurring antioxidants have proven unsuccessful in treating these diseases. This work reports a new potential treatment for T Cell-mediated autoimmune diseases using incredibly potent antioxidant carbon nanomaterials that scavenge reactive oxygen species (ROS) with much greater efficacy than endogenous antioxidants. Additionally, these carbon nanomaterials show affinity exclusively towards T Cells, demonstrating that they are not broad spectrum immunosuppressants and making them ideal vectors for targeted therapy. This work reports that the nontoxic PEGylated hydrophilic carbon clusters (PEG-HCCs) and PEGylated graphene quantum dots (PEG-GQDs) quench superoxide and hydroxyl radicals and are preferentially internalized by T Cells over other immune cells. This selectivity allows inhibition of T Cell activation and proliferation *in vitro* and *in vivo* without suppressing the rest of the immune system. This work also presents the promising *in vivo* effectiveness of PEG-HCCs to treat rat models of multiple sclerosis and rheumatoid arthritis. In addition to

those studies, this presentation will also cover the antioxidant mechanism of these nanomaterials as well as the future plans in treating other ROS-related disorders.

COLL 758

Characterization of amphiphilic copolymer micelles for drug delivery

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Amphiphilic copolymers with a polyethylene glycol (PEG) backbone and side chains of different molecular weight and hydrophobicity form spherical aggregates (micelles) in aqueous solution. These copolymer aggregates can be used as carriers of hydrophobic drugs and for imaging purposes. Certain types of aggregates are expected to be more suitable for incorporation of small hydrophobic molecules in their core and subsequent release. The aggregates adsorb very sparingly to hydrophilic, negatively charged surfaces because of their outer, PEG-containing region. Atomic force microscopy (AFM) in tapping mode in liquid was used to characterize the adsorbed aggregates to detect the presence of a hydrophobic core and monitor possible size changes with other molecules incorporated. A good correlation was found between the volume of individual adsorbed aggregates of different copolymers as determined with AFM and light scattering data on the corresponding aggregates in solution.

COLL 759

Tuning the drug uptake and release from silica nanostructures as a function of etching medium

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Silica nanoparticles have traditionally been used in drug delivery owing to their easy synthesis, nearly inert behaviour and ability to tune its surfaces for attaching targeting moieties. Recently etching silica nanoparticles with selected etching agents have also been explored as means of increasing the drug adsorption capacity as etching increases the active surface area available for adsorption of drugs. It is generally assumed that increase in surface area results in increase in drug adsorption as well as its release in the suitable medium. In the present study, solid silica nanoparticles (SNPs) were synthesized by Stober method and etched using a combination of HF/Water, HF/Ethanol and their mixtures. Loading and release of Docetaxel, a hydrophobic drug, on as-synthesized and etched SNPs was studied at pH 7.4 and pH 4 in phosphate buffer saline. It was found that increasing the surface area of SNPs, by etching its surfaces, increased the surface area normalized drug loading and that the

drug adsorption was also influenced by the polarity of the resulting etched surfaces. Etching in HF/Ethanol created nonpolar surfaces resulting in stronger bonding of the drug on silica surfaces. Consequently the drug was released slower from etched surfaces as compared to unetched surfaces. Physico-chemical properties of SNPs before and after etching were characterized using DLS, TEM and FTIR and the surface chemistry after etching was probed using X-ray Photoelectron Spectroscopy. A comparative study of loading and release of docetaxel from as-synthesized and etched-SNPs and the role of different surfaces in tuning the uptake and drug release will be presented.

COLL 760

Filomicelles deliver retinoids and chemotherapeutics to durably control carcinoma cell fate

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Flexible ‘filomicelles’ self-assembled from amphiphilic block copolymer (PEG-PCL) and demonstrate effective delivery of two very different hydrophobic compounds. Retinoic acid (RA) and other retinoids regulate RA receptor transcription factors that induce differentiation and arrest proliferation of many cell types, including cancer cells. Paclitaxel, on the other hand, stabilizes microtubules and induces aneuploidy by blocking mitosis, which greatly increases cell death. When cancer cells are treated with either of the drugs alone, over several periods of the normal cell cycle, they revert back to the original proliferative state, consistent with relapse commonly seen after conventional chemotherapy. On the other hand, combining RA with select chemotherapeutics has for several decades produced durable cures of select cancers, notably pro-myeloblastic leukemia (PML) where RA differentiates cells while chemotherapeutic kills the cancer stem cell. With carcinoma lines, we find dual drug treatment with RA plus Paclitaxel increases aneuploidy and cell death beyond those achieved by either drug single-handedly, with effects being durable. A month after treatment, relapse rates are low for RA-Paclitaxel treated cells (15%), compared to almost all (92%) for cells treated with Paclitaxel alone. Reduction in levels of key cell cycle factor Cyclin-D1 and proliferation marker Ki-67 help clarify the basis for this synergy. These effects are greatly enhanced by loading the drugs into filomicelles. Co-loading the drugs into filomicelles lead to a more potent system compared to separate loading, with no loss in the integration efficiency of drugs. Notably, relapse rates were ~2% three months after treatment, highlighting the improvement offered by filomicelles. The combination retains its potency across multiple cancer cell lines (liver, lung and bone) despite varying responsiveness to RA alone. Preliminary tests *in vivo* demonstrate sustained delivery for days as well as efficacy in shrinking tumors. Injections of free RA-Paclitaxel combination are able to arrest growth of subcutaneous lung tumors for over 15 days, a feat not achieved by Paclitaxel alone. Drug loaded filomicelles are able to control the growth of subcutaneous lung and liver tumors. These

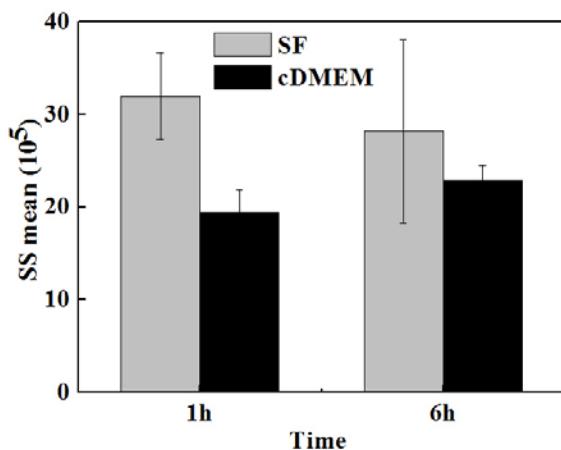
results highlight the irreversible synergy of killing cancerous cells while driving differentiation.

COLL 761

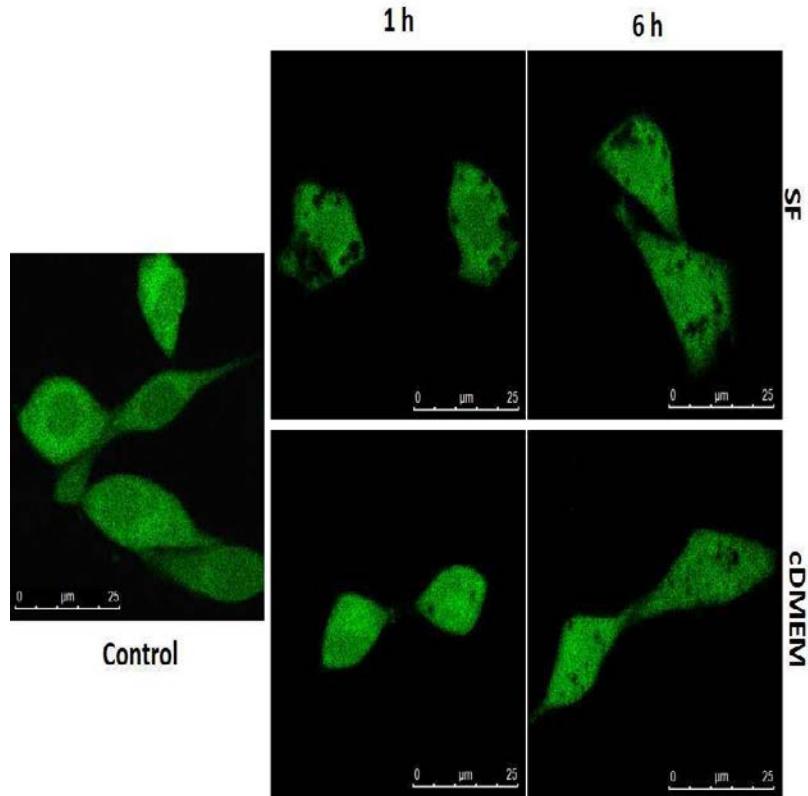
Influences of serum proteins on the uptake of Fe_3O_4 nanoparticles by human breast cancer cells

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Fe_3O_4 nanoparticles (NPs) are attractive for biomedical applications due to their unique magnetic properties and good biocompatibility. In this study, human breast cancer cells MDA-MB-231 were exposed to Fe_3O_4 NPs in serum free medium (SF) and 10% fetal bovine serum containing medium (cDMEM) to evaluate the influences of serum proteins on the cellular uptake of Fe_3O_4 NPs. Flow cytometry and confocal microscopy were applied to detection and observation the uptake of NPs by cells. Results shown that the serum proteins significantly reduced the uptake of Fe_3O_4 NPs by MDA-MB-231 cells. It is now well accepted that NPs will be coated with proteins to form protein coronas in a serum containing medium, and their influences on the non-specific interactions between particles and cells should not be disregarded. According to above results we made the conclusion that the serum proteins decreased the uptake of Fe_3O_4 NPs by MD-MB-231 cells through formation of protein coronas which lowered the surface free energy of Fe_3O_4 NPs and lead to weakened non-specific attractive forces at cell-particle interface, and ultimately reduced the cellular uptake of Fe_3O_4 NPs.



Uptake level of Fe_3O_4 NPs (average values of SS) by cells. Cells were exposed to Fe_3O_4 NPs in serum containing medium (cDMEM) and Fe_3O_4 NPs in serum free medium (SF) for 1 hour and 6 hour.



Images of Fe₃O₄ NPs in cells, and cells were exposed to NPs for 1 hour. Fe₃O₄ NPs were shown as black spots.

COLL 762

Hyperthermia properties of superparamagnetic ferrite (MFe₂O₄) nanoparticles synthesized via the thermal decomposition method

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Advances in the atomic scale investigations propelled developments and innovations in the nanotechnology and generated a new discipline called nanomedicine, an interdisciplinary field. It has seen rapidly development in therapeutic and diagnostic concepts especially in cancer treatment. In the present work, we have investigated the magnetic hyperthermia properties of superparamagnetic (MFe₂O₄) water dispersible ferrite nanoparticles. These particles were synthesized by the thermal decomposition approach in diethylene glycol and ethylene glycol solvents with a volume ratio of 1:1. These superparamagnetic nanoparticles have been thoroughly characterized for structural, morphological, magnetic and induction heating properties. The obtained values of temperature rise and specific absorption rate (SAR) were discussed in

correlation with the magnetic nanoparticle (MNPs) concentration for potential applications in cancer hyperthermia as well as an adjuvant to conventional chemotherapy and radiation therapy.

COLL 763

Microwave heating of synthetic skin for potential treatment of gout using the metal-assisted and microwave-accelerated decrystallization technique

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Physical stability of synthetic skin samples during their exposure to microwave heating was investigated to demonstrate the use of the Metal-Assisted and Microwave-Accelerated Decrystallization (MAMAD) technique for potential biomedical applications. In this regard, optical microscopy and temperature measurements were employed for the qualitative and quantitative assessment of damage to synthetic skin samples during 20 s intermittent microwave heating using a monomode microwave source (at 8 GHz, 2 W- 20 W) up to 120 s. The extent of damage to synthetic skin samples, assessed by change in surface area of skin samples, was negligible for microwave power of < 7 W and more extensive damage (>50%) to skin samples occurred when exposed to >7 W for skin at initial temperature range of 20 °C to 39 °C. Initial temperature of synthetic skin samples significantly affected the extent of change in temperature of synthetic skin samples during their exposure to microwave heating. The proof-of-principle of the MAMAD technique was demonstrated for the decrystallization of a model crystal (L-alanine) placed under synthetic skin samples in the presence of gold nanoparticles. Our results showed that the size (initial size ~850 nm) of L-alanine crystals can be reduced up to 60% in 120 s without damage to synthetic skin samples using the MAMAD technique. Finite Difference Time Domain (FDTD) based simulations of the electric field distribution of an 8 GHz monomode microwave radiation showed that synthetic skin samples are predicted absorb ~92.2% of the microwave radiation.

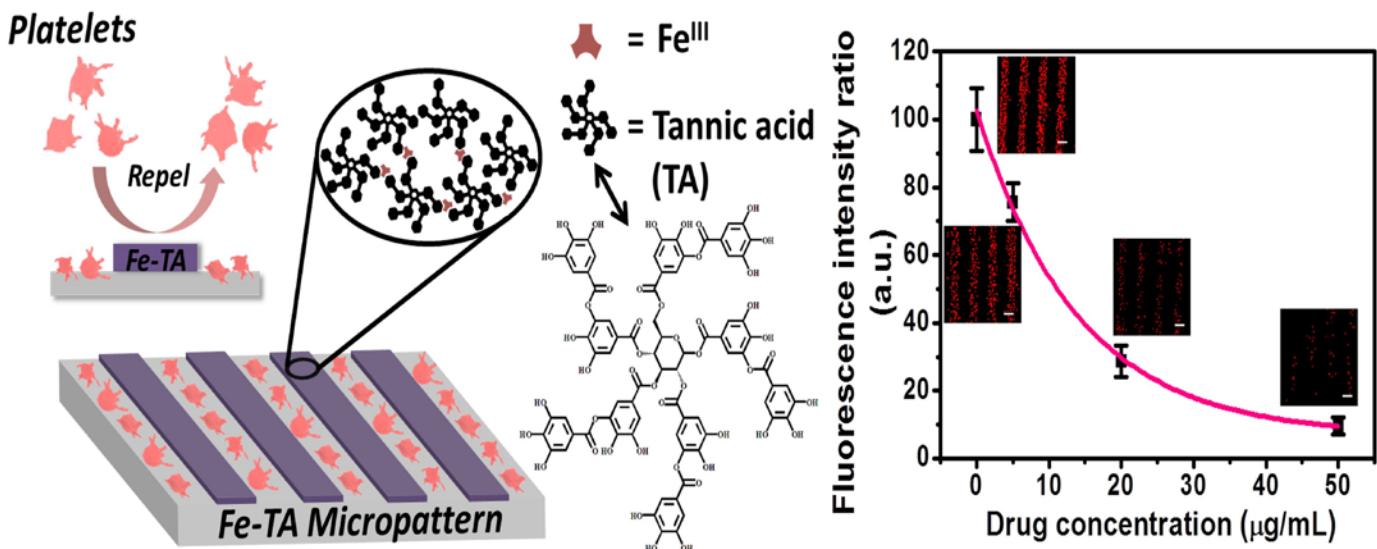
COLL 764

Novel platelet-repellent polyphenolic surfaces and their micropattern for platelet adhesion detection

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Surface patterning provides a powerful tool to the diagnosis of platelet adhesion. However, the current methodologies of constructing platelet-patterned surfaces require laborious and complicated steps. Herein, a novel and simple platelet-repellent surface was reported by metal (Fe³⁺ ions)-polyphenol (tannic acid, TA) coordination

interaction. The platelet-repellent effect was significantly better than that of poly(ethylene glycol) (PEG) in a long-term. Moreover, the platelet-repellent behavior could extend to other polyphenols-functionalized surfaces. On the basis of these observations, a TA-based micropattern was fabricated *in situ* by one-step microcontact printing for well-defined platelet adhesion, which can effectively avoid the traditional introduction of inert hydrophilic polymers and bioactive ligands. Afterward, the TA-based micropattern was applied to monitor the adhesion of defective platelets treated with an antiplatelet drug (tirofiban). This work provided a facile, versatile, and environmentally friendly strategy to construct platelet-repellent polyphenolic surfaces and their micropattern. We expect that this simple micropattern could act as a low-cost and label-free platform for biomaterials and biosensors, and could be widely used in the clinical diagnoses of platelet adhesive functions and the evaluation of antiplatelet therapies.



A novel platelet-repellent surface containing polyphenols was introduced. Utilizing this surface, a polyphenol-based micropattern was fabricated by one-step microcontact printing to effectively evaluate platelet adhesion. Moreover, this selective platelet adhesion surface is also a simple, rapid, and low-cost platform for antiplatelet drugs screening assays and evaluation of antiplatelet therapies.

COLL 765

Modeling of polymer based micelles and DNA delivery medicines

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Molecular dynamics simulations were used to test the stability of Dendron (DM) and linear micelles (LM) (synthesized by our collaborators) in the presence of Bovine serum

albumin (BSA). The simulations show that the relaxed PEG chains in DM₆₀₀ give a rather smooth micelle surface, providing a little room for strong BSAs coupling. On the other hand, the BSAs easily submerge into the relaxed PEG chains of LM_{5k}. The total coupling energy of BSAs with LM_{5k} is about 3 times larger, which explained the destabilization of LM_{5k} by BSA in the experiment. Considering the highly stability of DM₆₀₀, it shows promising drug delivery properties. In a separate study, we tested the DNA delivery ability of TAT-like polymer (synthesized by our collaborators). 30 TAT-likes with a double stride DNA (dsDNA) were immersed in a 150 mM NaCl solution, but only 20 TAT-likes were attached to the dsDNA. Therefore, at least 20 TAT-likes were needed to delivery dsDNA, which is consistent with the experimental result. The binding energy inside the dsDNA is 1.5 times larger than that between dsDNA and TAT-likes, which shows TAT-likes is a promising DNA delivery medicine which can't destroy dsDNA during delivery.

COLL 766

Surface modification of nanoscale diamond for biolabelling with the nitrogen vacancy center

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Development of highly sensitive techniques for cancer detection can increase survival rates due to early detection. Fluorescent high pressure, high temperature (HPHT) nanodiamonds with nitrogen vacancy centers (NVC) represents an emerging fluorophore that has the potential to lead to new oncological advancements. NDs are attractive for biolabelling due to their chemical inertness and lack of cytotoxicity, as well as the magnetic and electric field sensing properties of the nitrogen vacancy center. Here we use gas phase and wet chemical techniques to modify the surface with amines and thin shells of SiO₂ for biolabelling purposes. Our goal is to increase the chemical reactivity of the inert diamond surface and probe new routes for functionalization. We confirm the ND surface moieties using overlapping spectroscopies based on laboratory (FTIR) and synchrotron based techniques (NEXAFS and XPS). Polyethylene glycol and amine moieties were grafted onto the ND surface for stabilization and bioconjugation in cell media, respectively. The amine moieties were then used as a molecular anchor for conjugation of a small molecule library that has been previously shown to differentiate cancer cell types and cellular metabolic states. Cellular uptake of the ND probe was confirmed via fluorescence confocal microscopy and is understood to take place due to multivalent interactions at the cell surface. Our work is promising for both the fundamental surface science of diamond surfaces and their applied use in biolabelling modalities based on the nitrogen vacancy center.

COLL 767

Classification of bacteria by surface enhanced Raman spectroscopy and principal component analysis

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Food contamination by pathogens provides a significant health concern in the United States. 48 million Americans become ill by eating contaminated food each year, resulting in more than 3,000 deaths and more than 100,000 hospitalizations. Currently, the USDA recommends conventional bacteria culturing for detection and identification of foodborne pathogens. This involves enrichment, colony isolation, and confirmation. Other potential methods including DNA amplification using polymerase chain reaction (PCR), antibody-based assays, and mass spectroscopic techniques. Unfortunately, due to instrumentation and aseptic requirements, these techniques are significantly limited. In addition, false identifications, numerous reagents, and multiple-steps make these alternative inconvenient. Consequently, the development of a portable, rapid and sensitive biosensors with on-the-spot interpretation of results is beneficial for testing. Surface enhanced Raman spectroscopy is an alternative approach that satisfies most of the requirements for on-site testing; it is specific, noninvasive, nondestructive, and can be rapidly performed. In this research, foodborne bacteria are quickly detected and identified using ferritin-silver nanoparticle assemblies. Surface-enhanced Raman scattering (SERS) provides rapid fingerprinting of biomaterial in a non-destructive manner and principal component analysis (PCA) is used to discriminate between several types of bacteria, including *E. coli* and *Salmonella*.

COLL 768

Light driven diffusioosmosis: Manipulation of particle assembly

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Recently, we have discovered a peculiar phenomenon related to colloids adsorbed at a solid- liquid interface, and immersed into aqueous solution of photosensitive surfactant (photosoap). Upon illumination with UV light, the colloids are driven out of the irradiated area. Without the presence of the surfactant, the particle assembly does not change, ruling out heating effects or gradients in the intensity of the electromagnetic field as a source of driving. The presence of the surfactant leads to two simultaneous effects. The first involves the local modification of surfaces even without illumination. The most important and novel aspect to be discussed in the talk is, however, that the *trans-cis* photo-isomerization is also the basis for initiation of local hydrodynamic flows and corresponding forces on the colloids. The photosoap consists of a charged ammonium

bromide head bound to a hydrophobic tail incorporating an azobenzene group. Azobenzene molecules undergo reversible *trans*-*cis* photo- isomerization when illuminated with either UV or visible light leading to substantial changes in physico-chemical properties e.g. *trans*-to-*cis*-isomerization decreases the hydrophobicity of our *photosoap*.

We will provide a theoretical account of how the local liquid flows emerge. It will turn out that the phenomenon is best understood as light-driven diffusioosmosis. In this way, the surfactant becomes a *photo-soap* in a new sense: not only particle-surface interaction is reduced, but also control over the “rinsing” of contaminants (particles) can be gained.

COLL 769

Block copolymer morphology switch *via* colloidal assembly and local reorganization

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As with small molecule synthesis routes, self-assembly strategies for materials aim to achieve rationally designed structure and function from simple molecular structure and conditions. To realize this goal, an understanding of the self-assembly pathways is needed. For block copolymer self-assembly, despite the fact that many systems are known to be kinetically trapped, structures are nevertheless designed based on considerations of minimum energy organization and hence the packing parameter for both static and responsive systems. Here, we show through rational design of different block copolymers that both the thermodynamic and kinetic pathways of reorganization from stimulus can be explored. Moreover, we propose a vesicle assembly pathway, which was induced from an enzyme stimulus that was inaccessible via typical assembly methods.

COLL 770

Tailored nanoparticles by wet chemical particle technology: From lab to pilot scale

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The merits of tailored nanoparticles synthesised bottom-up in dispersions will be presented and underlined with examples. This is followed by a discussion on the challenges to upscale and process small (nano) particle suspensions.

Bottom-up chemical syntheses of small particles (nanoparticles) come with many advantages: Firstly, particles can be tailored during synthesis as multi-functional objects by adding various attributes via molecular building-blocks. As a result, particles of desired chemical composition, size, shape and physical and chemical effects (magnetic,

optical, catalytic and adsorbing properties, etc.) can be obtained. Secondly and most importantly, stable dispersions of individual nanoparticles (so called sols) can be obtained. Unlike most other particle synthesis methods nano-building-blocks and not only nanostructured aggregates are available in these dispersions. These individual particles may be used as value-adding ingredients in composites or coatings to ultimately exploit the advantages of “nano” and create superior, novel materials.

The challenge of preparing nanoparticles by means of wet-chemistry is, however, that the dispersions are highly diluted and unwanted by-products may still be present in the reaction solution after synthesis. Therefore, to obtain clean particle products, innovative processing methods need to be established.

Wet-chemical bottom-up nanoparticle syntheses methods need to be scalable to yield an industrially relevant output of particles. However, large chemical reactors pose challenges to the close in-situ control of the particle formation in large volumes of liquids.

In this talk, the current research focussing on these challenges, aiming at pilot scale synthesis of tailored nanoparticles in dispersion is presented. It will be shown that upscaling of nanoparticle syntheses, although scientifically not sounding very exciting, comes with new discoveries and scientific insights once the hurdles of scaling syntheses are overcome. The talk also demonstrates how in-situ analysis and downstream processing, to tailor nano building-blocks in sufficient quantities for advanced composite materials, can be integrated during upscaling.

COLL 771

Multipole re-expansion model for assembly of dielectric particles in external electric field

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We have investigated assembly of dielectric latex particles in an external alternating current (AC) electric field using a combination of electrostatics theory and experiments. For a given voltage and particle size, latex particles co-assembled between coplanar electrodes into chains (1D) of varying length as well as into 2D architectures. The average chain length and onset of 2D assembly was found to be dependent on electric field frequency and particle concentration. We have used a multipole re-expansion model for dielectric particle chains in an external electric field¹ to determine chain length and onset of 2D assemblies as a function of electric field frequency, particle size and voltage. The model was used to determine the contact point force experienced by a particle at the chain-end. We predict saturation in contact point force with an increase in chain length. In further agreement with experiments, we were able to predict a decrease in chain length with field frequency. The multipole re-expansion model was then extended to determine potential energy associated with two particle chains assembling perpendicular to the applied electric field (2D assembly) versus parallel to the electric field (1D assembly into a longer chain). We are able to predict experimentally observed

cross-over from 1D particle chains to 2D coarsening of chains at different frequencies and particle chain lengths. Finally we have also investigated the effect of an external shear field on these electric field driven particle assemblies using Brownian dynamics simulations.

COLL 772

Patchy particles via cluster fusion

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Directional self-assembly is the key to 3D hierarchical colloidal structures, which find their applications in photonics, electronics, biomaterials, and catalysis. Here, we introduce a novel method fabricating patchy particles via cluster fusion, which generates well-defined patchy motifs. In our work, high yields of colloidal tetrahedral clusters are achieved via heteroaggregation of solid shell and liquid core particles. The resulting hybrid cluster is then plasticized and fused into a spherical particle. During fusion, surface tension extrudes the inside liquid core to surface through the interstices, resulting in patchy particles with a well-defined geometry. The patches have tunable curvatures and functionalities. For example, they can be modified with DNA to realize high-ordered structures. This evolution of patchy particles with reactive patches in a tetrahedral symmetry from core-shell clusters offers a long-awaited building block in the field of colloidal self-assembly, making the realization of open 3D architectures possible.

COLL 773

Modeling of magnetization in self-assembled magnetic nanocubes

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We use Monte Carlo simulations to study magnetic properties of self-assembled superparamagnetic and ferromagnetic nanocubes prepared and investigated by our collaborators. First, magnetic properties of superparamagnetic (13 nm) iron oxides nanocubes are studied at low temperatures. The experiments reveal large magnetic hysteresis, depending on the cube density and self-assembly structure. Our simulations explain the origin of this hysteresis in dependence on the dipole-dipole coupling of nanocubes. We also model at room temperature the magnetic behavior of self-assembled FeCo oxide ferromagnetic nanocubes in the presence and absence of external magnetic field. The experiments and our simulations show that self-assembled magnetic nanocubes can form new types of highly tunable magnetic materials with numerous potential applications.

COLL 774

Reconfigurable colloids via stimulated dewetting

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Many biological processes function via reconfiguration on a molecular level. Implementing the capability of reconfiguration into the synthesis of materials is a challenge in material science and engineering. Here, we demonstrate the bulk synthesis of colloidal particles which contain built-in shape-changing properties. We exploit the dynamic wettability of an oil phase on various solid substrates to engineer shape-shifting colloidal particles whose geometries can change upon exposure to a chemical or optical stimulus. We find the approach to be general and applicable to many materials, including polymers, semiconductors, and magnetic materials. We further demonstrate that the reconfiguration of an entire colloidal crystal, containing particles with built-in shape-shifting properties, can lead to macrostructures that would be inaccessible via direct self-assembly. We expect this synthetic method to aid in the bulk synthesis of functional colloids such as active Janus particles, colloidal surfactants, and self-assembling materials.

COLL 775

Burstable nanostructured micro-raspberries: Toward redispersible, adjustable nanoparticles from dry powders

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For almost any application, nanoparticles can only unravel their attractive properties if uncontrolled agglomeration is avoided. Undefined lumps of nanoparticles rather worsen the properties of the materials they are added to. Therefore, it is highly desired to deal with nanoparticles in dispersion. That, however, means to handle and process liquid nanoparticle suspensions, so called sols. But, these liquid dispersions typically contain very low solids content. Especially when it comes to storage and shipment, this is very impractical. Dry powders would therefore be much more preferred. But unfortunately, typical nanoparticle dispersion systems have to be prevented from drying-out as then, irreversible agglomeration occurs, sometimes called “hard-agglomeration”.

Herein, we report on an easy to handle powder consisting of nanostructured micron sized raspberries. These nanostructured micro-raspberries are composed of individual nano-particles which are equipped with molecules that introduce a separating effect or “spring” functionality. Thereby, a powder system is obtained that allows for an easy and complete redispersibility of the agglomerates down to the level of individual nanoparticles in solvents and polymers. Furthermore we want to create “secondary

nanostructure" which has an important influence on many material properties in elastomer composites. Herein the nanoparticles are arranged with their neighbours to form slightly larger entities which consist of several tens to hundreds of nanoparticles.

Redispersible nanostructured micro-raspberries

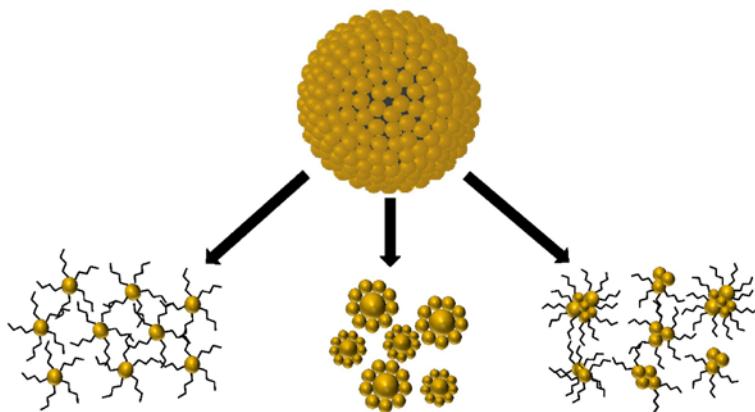


Figure 1: Silica nanostructured micro-raspberries which are easily redispersible into primary nanoparticles or adjustable secondary structures, depending on the modification.

COLL 776

Inducing an order-order morphological transition via chemical degradation of amphiphilic diblock copolymer nano-objects

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The disulfide-based cyclic monomer, 3-methylidene-1,9-dioxa-5,12,13-trithiacyclopentadecane-2,8-dione (MTC), is statistically copolymerized with 2-hydroxypropyl methacrylate (HPMA) to form a range of diblock copolymer nano-objects via reversible addition-fragmentation chain transfer (RAFT) polymerization.

Poly(glycerol monomethacrylate) (PGMA) is employed as the hydrophilic stabilizer block in this aqueous polymerization-induced self-assembly (PISA) formulation, which affords pure spheres, worms or vesicles depending on the target degree of polymerization for the core-forming block. When relatively low levels (< 1 mol %) of MTC are incorporated, high monomer conversions (> 99%) are achieved and high blocking efficiencies are observed, as judged by ¹H NMR spectroscopy and gel permeation chromatography (GPC), respectively. However, the side reactions known to occur when cyclic allylic sulfides such as MTC are statistically copolymerized with methacrylic comonomers lead to relatively broad molecular weight distributions. Nevertheless, the worm-like nanoparticles obtained via PISA can be successfully transformed into spherical

nanoparticles by addition of excess tris(2-carboxyethyl)phosphine (TCEP) at pH 8-9. Surprisingly, DLS and TEM studies indicate that the time scale needed for this order-order transition is significantly longer than that required for cleavage of the disulfide bonds located in the worm cores indicated by GPC analysis. This reductive degradation pathway may enable the use of these chemically-degradable nanoparticles in biomedical applications, such as drug delivery systems and responsive biomaterials.

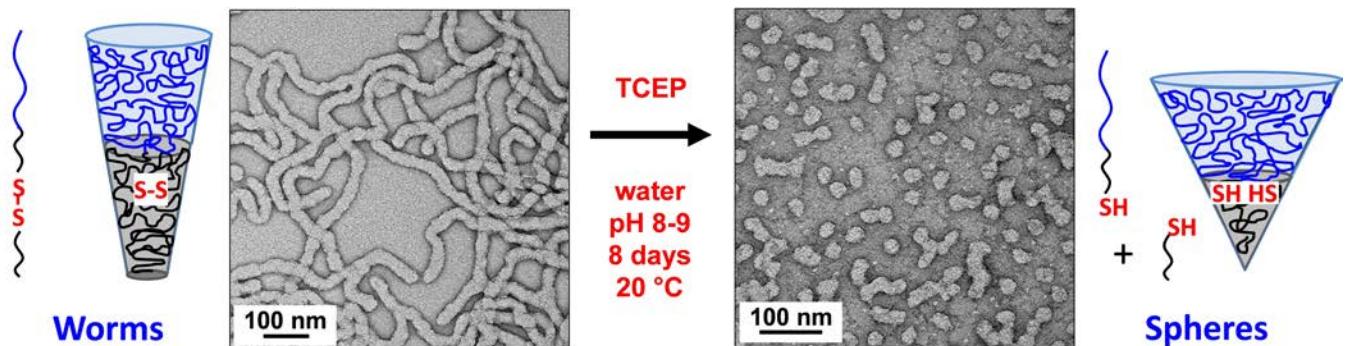


Figure 1 TEM images obtained for an aqueous dispersion of PGMA₅₆-P(HPMA₁₇₀-*stat*-MTC_{0.85}) before and after exposure to TCEP, with a cartoon demonstrating how the worm-to-sphere transition is likely to have affected the copolymer chain packing.

COLL 777

Controlled drug release from magneto-liposomes via ultrasound generation

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Generating ultrasound remotely by means of magnetic fields is an important technological development to circumvent the drawbacks of the traditional means of ultrasound generation techniques. In this report, it is demonstrated that ultrasound is generated from colloidal superparamagnetic nanoparticles when exposed to pulsed and alternating magnetic fields. In strong magnetic fields, the ultrasound generated from the colloidal magnetic nanoparticles shows reasonable agreement with the magnetostriction effect commonly observed for bulk ferromagnetic materials. At low magnetic fields, the colloidal magnetic nanoparticle dispersion produces considerable amount of ultrasound when exposed to ac magnetic fields in the 20–5000 kHz frequency range. From these experiments, the measured force/ magnetic particle is found to be in the range 1×10^{-18} – 1×10^{-21} N for magnetic field gradients from a few T/m to a few hundred mT/m, respectively. It is expected that the ultrasound generated from magnetic nanoparticles will have applications toward the acoustic induction of bioeffects in cells and manipulating the permeability of biological membranes.

COLL 778

Mechanical characterization of self-assembled surfactant micelles at graphite surfaces via atomic force microscopy

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Breakthrough forces are a common means of mechanically characterizing supported lipid bilayers and monolayers using AFM. In this work, we use atomic force microscopy (AFM) to study the mechanical properties of sodium dodecylsulfate (SDS) and dodecylamine hydrochloride (DAH) films at a graphite surface. These surfactants self-assemble into hemicylindrical micelles at the graphite-water interface. The nanoscale structures they form, similar to lipid layers, have a characteristic breakthrough force required for the AFM tip to breach the film and reach the surface beneath. The breakthrough forces for these films were measured using silicon nitride cantilevers, and found to be 1.1 ± 0.1 nN for a 10 mM DAH film and 3.0 ± 0.3 nN for a 10 mM SDS film. Salts and hydrated ions are common contaminants in surfactant systems, and have been shown to increase the strength of supported lipid films. For 10 mM SDS and DAH films, it was found that the addition of 1.5 mM of NaCl, Na₂SO₄, or MgCl₂ produced a 50-70% increase in measured breakthrough force. A model was developed using previous work on lipid monolayers and CMC data gathered via spectrofluorometry measurements to predict the change in normalized breakthrough forces with added salt concentrations. Using this model, it was found that the activation volume required to initiate breakthrough was roughly 0.4 nm³ for SDS and 0.3 nm³ for DAH, roughly the volume of a single molecule. Normalized breakthrough force data for SDS with added MgCl₂ showed an unexpected dip at low added salt concentrations. The original model was adapted to account for changing activation volumes, and a curve of activation volume versus magnesium concentration was obtained, showing a minimum volume of 0.16 nm³. The addition of 0.2 mM SDS to a 10 mM DAH solution was found to double the measured breakthrough force of the film. Images taken of the surface showed a phase change from cylindrical hemimicelles to a planar film that may have produced the observed differences.

COLL 779

Carbon nanotube enhancement of water and ion permeability of diblock copolymer membranes

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Recently developed block copolymer polymer membranes have generated interest due to their robust mechanical properties, namely greater bending resistance (K_b 40–460 vs 10–30 $K_B T$) and lower stretching moduli (K_a 80–100 vs 250–1000 mN/m) over conventional self-assembling lipid bilayer membranes. However, due to enhanced thickness of hydrophobic block length and chemical composition, bilayer permeability is lowered considerably. To this end, we investigated whether polymer bilayers are a suitable substrate for housing synthetic nanoscale membrane channels in the form of carbon nanotubes porins (CNTPs). Briefly, CNTPs were added to diblock copolymer films to generate vesicles such that the CNTPs were properly spanning the membrane. Once formed, water and proton permeability were measured by stopped flow apparatus and sensitive fluorophores, respectively. Our results not only suggest that polymer membranes can incorporate more CNTPs compared to lipids, but also that the transport of water and protons is fast within those CNTPs. Therefore, polymer membranes are capable of enhanced water and ion transport with the addition of a small membrane component (<0.001%) of vesicle area.

COLL 780

Shape morphogenesis in giant lipid vesicles in an osmotic field gradient

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We report experimental observations of morphological transformations of giant unilamellar vesicles (GUVs) subject to a temporally controlled osmotic field gradient. Specifically, we subjected single GUVs consisting of single unsaturated phospholipid, namely 1-palmitoyl 2-oleoyl-sn-1-glycero-3-phosphocholine (POPC) and encapsulating 150 mM sucrose to a temporal gradient of extravesicular, hypertonic osmolyte concentration (from 150 to 1000 mM) using a poly(dimethyl)siloxane (PDMS) based diffusion chamber, and visualized the ensuing shape transformation in *real-time* using wide-field epi- or confocal fluorescence microscopy. We find that single GUVs exhibit a dramatic sequence of well-defined dynamic instabilities, which break symmetry and induce morphological and topological transitions. The sequence of shape transformations is highly deterministic and fully reproducible: It includes (1) the appearance and growth of membrane tubules within the vesicular interior; (2) reabsorption of the internal tubules with the peripheral membrane; (3) a pronounced wrinkling of the membrane boundary producing tubular tentacles, which pearl; followed by (4) a topological transition producing a population of closely interacting spherical

progeny vesicles. This highly deterministic sequence of non-equilibrium shape evolution of deflated vesicles appears to result from a subtle interplay of membrane elasticity and apparent lowering of membrane permeability caused by the temporal osmotic concentration gradient – both of which guide the non-equilibrium response of GUVs because of the gradual increase in the availability of excess membrane area for the encapsulated volume.

COLL 781

Single-molecule detection of biomarker molecules in a nanometric gap structure with fluid lipid membrane

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Single-molecule detection of biomolecules is potentially useful for diagnostic and biosensing applications. However, single-molecule observation in the presence of high concentrations of coexisting molecules poses technological challenges. We developed a nanometric gap structure (nanogap-junction) with a fluid lipid membrane for detecting biological molecules in a solution having high concentrations of coexisting molecules. The nanogap-junction comprised a patterned model membrane having polymerized and fluid lipid bilayers. The polymeric bilayer was bonded to a polydimethylsiloxane (PDMS) sheet with an adhesion layer (lipid vesicles), and a nanogap-junction was generated between the fluid bilayer and PDMS. The thickness of the gap structure was controlled to less than 100 nm by the adhesion layer. From a mixture of proteins (cholera toxin and albumin), cholera toxin (model target molecule) was selectively transported into the gap by the specific binding to a glycolipid (GM1) in the fluid bilayer and detected with an elevated signal-to-noise-ratio, due to the reduced background noise in the nanogap-junction. In the present study, we developed a methodology to observe non-labeled biomarker molecules for realizing single-molecule diagnostics. Prostate specific antigen (PSA), a prominent biomarker of the prostate cancer, was used as a model. By using a combination of membrane-bound anti-PSA antibody (PS1) and fluorescently labeled anti-PSA antibody (PS2), we could observe PSA molecules on the membrane by the sandwich immunoassay method. Single molecules of PSA could be observed to diffuse laterally in the nanogap-junction. Furthermore, we could detect PSA at higher concentrations, where observation by the conventional total internal reflection fluorescence was not possible due to the high background noise. These results demonstrate the feasibility of nanogap-junction for the single-molecule diagnostics. The nanogap-junction offers a versatile platform for broad biomedical applications by realizing highly selective and sensitive detection in samples containing diverse coexisting molecules.

COLL 782

Phase separation and curvature generation in biphasic giant lipid vesicles reconstituting plant plasma membrane lipids

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Giant unilamellar vesicles (GUVs), consisting of ternary mixtures of soy-PC, sitosterol, and Glucosylceramide (GlcCer), spontaneously phase separate producing single large, microscopic monodomains. Imaging the domain texture of these GUVs using phase-sensitive complementary fluorescent probe confirms the fluid-fluid co-existence characterized by the macroscopic separation of the sterol-GlcCer enriched, liquid-ordered (lo) phase from the liquid-disordered (ld) phase consisting primarily of soy-PC. When rendered tense, such as by osmotic swelling, these vesicles produce a remarkable breathing/squeezing pattern characterized by the periodic appearance of transient microscopic pores at the domain boundaries and concomitant sequence of transient budding of the ld-phase domains. The former, transient poration, reflects the reduced activation energy for pore nucleation at the domain boundaries and the latter, periodic budding, emerges as a consequence of the balance of line (or edge) tension at the domain boundaries and the curvature energy of the ld phase domain. Furthermore, when subject to osmotic deflation through exposure to hypertonic solution, the ld phase domains bud and under certain conditions transform the bud into a complete bud, pinching off a single daughter vesicle composed of the ld-phase components. This budding to vesiculation transition indicates that the lateral tension exerted by the budding domain on the surrounding membrane of the mother vesicle can exceed the lysis tension. Taken together, these results illustrate the important roles of membrane compositional heterogeneity and domain texture in enabling fundamental processes of membrane poration, budding, and vesiculation, which enable fundamental biological processes of endocytosis, exocytosis, and barrier functions of bilayer membranes.

COLL 783

Evaluating the interactions of lipid raft and proteins involved in phototransduction by using a micropatterned model membrane

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Disk membranes in the rod photoreceptor cell are loaded with a series of proteins for phototransduction cascade, including rhodopsin (Rh), G-protein transducin (Gt), phosphodiesterase6 (PDE6), rhodopsin kinase (GRK1), and S-modulin (frog of recoverin). Membrane micro-domains, lipid rafts, are believed to regulate the phototransduction by modulating the local accumulation and interactions these proteins. However, the regulation mechanism are poorly understood, partially because the affinities of the proteins to lipid rafts (raftophilicity) are not known.

In this study, we evaluate the raftophilicities of the proteins involved in phototransduction by using a patterned lipid membrane having liquid ordered (Lo) (raft

model) and liquid disordered (Ld) (non-raft model) bilayer domains. We microscopically determined the densities of molecules in the Lo and Ld regions, and quantified the raftophilicities of the proteins, including Rh monomer, Rh dimer, Rh-Gt complex, Gt trimer, Gt a-subunit (Gat), PDE6, and S-modulin. The raftophilicity of Rh increased upon forming a Rh-Gt complex or a dimer, suggesting that Rh accumulate in lipid raft upon photo-activation. On the other hand, raftophilicity of Gat was lower than that of Gt trimer, indicating that Gat dissociates from lipid rafts after photo-activation and migrates toward PDE6, which has a very low raftophilicity. The obtained raftophilicities were generally consistent with the localization of proteins observed in disk membranes. These results should help to evaluate the localization of proteins in the membrane and its influences in modulating the phototransduction rates. We discuss on the implications of varied raftophilicities and the functional roles of lipid rafts.

COLL 784

Morphological consequences of surface-mediated spinodal decomposition inside giant vesicles

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Systems far from equilibrium can exhibit complex transitory structures, even when equilibrium fluctuations are mundane. The interior of a living cell is packed with large macromolecules (e.g., nucleic acids, proteins and polysaccharides), cytoskeletal filaments, and organelles. Furthermore, this physical crowding in the cellular cytoplasm is highly dynamic continually changing the diffusional properties of embedded solutes, molecular (and ionic) concentration gradients, and phase separation or dynamic microcompartmentalization of the cytosolic fluid. But how this cytoplasmic macromolecular crowding and accompanying dynamic microcompartmentation affects membrane shapes and molecular organization is largely unknown. Building on the experimental model system developed by Keating, Dimova, and Lipowsky, we reconstitute minimal crowding and conditions for dynamic microcompartmentation inside cell-sized giant vesicles. Specifically, we encapsulate a uniform aqueous phase mixture of two water soluble polymers (namely, dextran and poly(ethylene)glycol), which when subject to osmotic deflation, assumes relative concentrations that produce aqueous two-phase separation (ATPS) in real-time. We find that the onset of vesicular microcompartmentation in the encapsulated aqueous phase is accompanied by an active membrane remodeling inducing vesicle morphogenesis. Unlike equilibrium configurations characterized by a single bud, we find that multiple buds of essentially uniform size decorate the membrane boundary reflecting a complex interplay between

the phase coarsening dynamics during the spinodal decomposition of the ATPS and preferential wetting of the membrane surface by the dextran-rich phase.

COLL 785

Small molecule induced fusion of a model protocell membrane composed of fatty acids: A new insight into the membrane fusion monitored through fluorescence lifetime imaging microscopy

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The development of stable vesicular assemblies and understanding their interaction and dynamics in aqueous solution is a long standing topic in the research of chemistry and biology. Fatty acids are known to form vesicle structure in aqueous solution depending on the pH of the medium. Protic ionic liquid of fatty acid with ethyl amine (Oleate ethyl amine, OEA) as a component spontaneously form vesicle in aqueous solution. FLIM images of vesicles suggest that the membrane of the OEA vesicle is more dehydrated compared to that of fatty acid vesicles and it facilitates OEA vesicles to fuse themselves in presence of electrolyte, sodium chloride (NaCl). Besides, the fusion of the vesicles is also possible in presence of different imidazolium based ionic liquid (IL). The fusion of OEA vesicles in all the cases are successfully demonstrated by the Time Scan FLIM measurements. The distinct mechanism of the interaction between the ionic liquid and membrane could be correlated with the biological activities of ILs. Thus, tuning the membrane interaction of ILs can be an important factor for designigning the future environemnt friendly compounds.

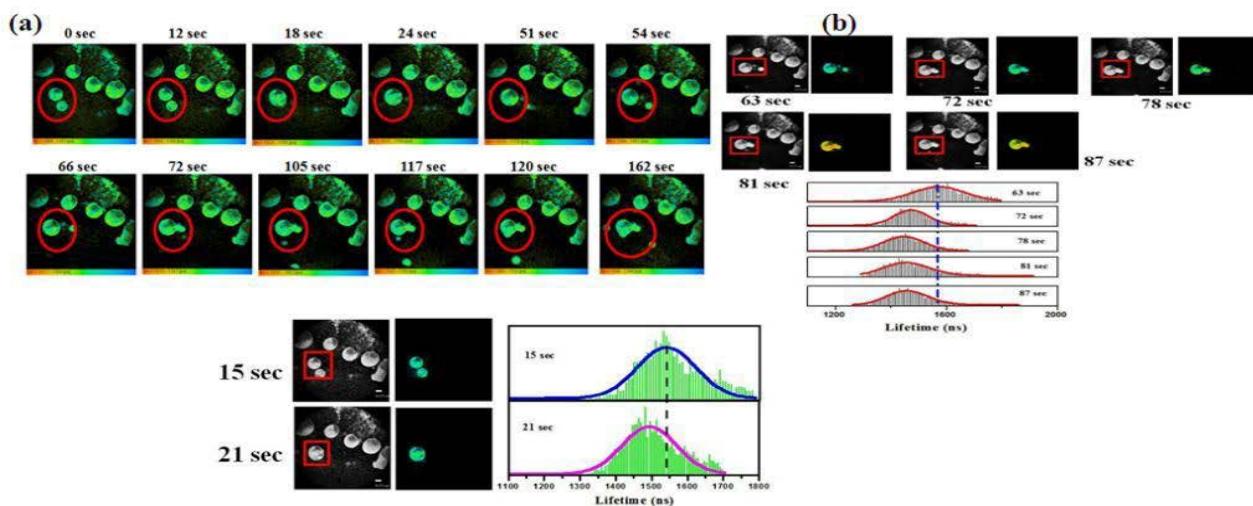


Figure 1. (a) FLIM images of OEA vesicle in presence of 60 mM NaCl collected in different time scale. (time zero indicates the time when the image of the sample is started to record; it does not imply the starting time of the reaction after addition of NaCl into the medium.) (b) Intensity images and FLIM images of OEA vesicles in presence of 60 mM NaCl collected in different times. Lifetime distribution in each image is calculated in a particular area of the intensity image and the area in the intensity images are shown by the red box. (scale bar represents 8 μ m)

Fusion in presence of electrolyte

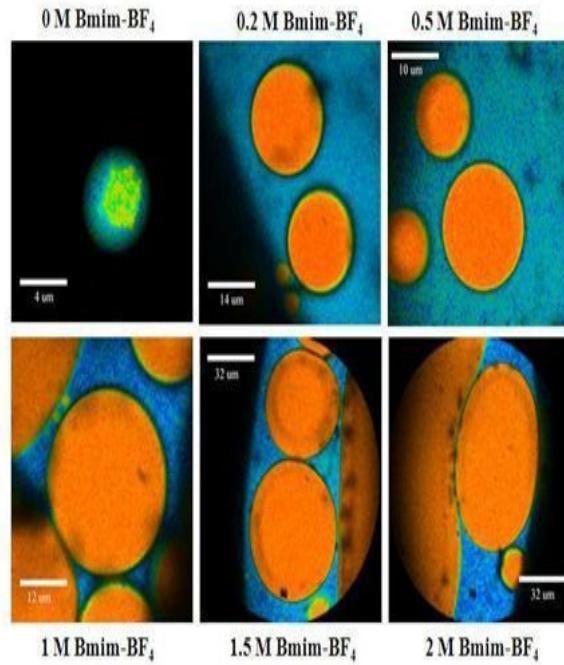


Figure 2. FLIM images of formation of different sized vesicles of 0.1 (M) OEA in presence of Bmim-BF₄

Formation of vesicle in presence of ionic liquid

COLL 786

Modeling nanoparticle assembly: Using polymer coatings, interfaces, and pressure to build 1D, 2D, and 3D nanostructures

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Nanoparticles and nanoparticle assemblies are important components of future energy and technology applications. We use fully atomistic simulations of simple polymer-coated nanocrystals to understand the role of coatings in the assembly of larger nanostructures. We show that ligand-coated nanoparticles respond to anisotropic environments, at ambient or high pressure, to produce 1D, 2D and 3D nanostructures.

First, we show how spontaneously asymmetry in coatings on very small (2-6 nm) diameter nanoparticles can be amplified using liquid-vapor interfaces to assemble nanorods, and membrane structures. Second, we elucidate the processes under which pressure-driven assembly, using extreme pressures, can sinter metal nano cores into

permanent nanowires, nanosheets and 3D structures. We compare to recent experiments where such structures were successfully produced using ultrafast dynamic compression technology at pressures up to 15 GPa over nanosecond times.

COLL 787

Constructing theranostics based on fluorescent carbon nanodots

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Carbon dots, as new fluorescent agent have attracted continuously attention for potential applications in LED, solar cells, sensor, bioimaging and photocatalyst. However, its photo luminescent quantum yield (PL QY) is still quite low, especially emission in long wavelength region like red light. Herein, we proposed increasing the PL QY by doped carbon dots with N or S, N. The PL QY of carbon dots dramatically rises up after doping with N. It can reach over 90%. The carbon dots prepared via bottom-up route show excitation independent emission. In order to extend the absorption in the visible light region, S element is further introduced into the carbon dots to form S, N co-doped carbon dots. Due to the introduction of S and N, there is another S state was introduced into the band gap. That results in the new emission at red light region. Blue, green and red light emissions were obtained from carbon dots. Due to the excellent biocompatibility and low cytotoxicity, we further conjugated the cisplatin with carbon dots to obtain the theranostic agent. We explored to adding more function onto the carbon dots, like self-targeting and therapeutic function to construct the nanomedicine integrating with targeting, bio-imaging and therapy function together.

COLL 788

Engineering bimetallic nanocrystals as artificial enzymes for colorimetric detection of disease biomarkers

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Enzyme-based colorimetric assays (e.g., enzyme-linked immunosorbent assay (ELISA), immunohistochemistry, and western blot) have been extensively used in research labs and clinical diagnostics for decades because of their simplicity and reliability. Nevertheless, their detection sensitivities have not been substantially improved in recent years, which inhibits many critical applications such as early detection of cancers. In these assays, the detection sensitivity is inherently limited by the catalytic efficiencies of enzymes that are responsible for the generation of detectable color signal. In this talk, I will introduce our recent research on development of bimetallic nanocrystals as artificial enzymes with significantly enhanced catalytic efficiencies relative to their natural counterparts. Chemical synthesis, structural characterizations at the atomic level using high-performance electron microscope, and mechanistic understanding with

computational modeling for the artificial enzymes will be illustrated. Applications of these artificial enzymes as alternatives to natural enzymes in in-vitro diagnostics of cancer biomarkers will be highlighted.

COLL 789

Tuning functional nanoparticulate and nanoporous structures using atomic layer deposition

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Properties of nanostructured materials are strongly dependent on their dimensions and surface chemistries. Atomic layer deposition (ALD) is a burgeoning thin film deposition technique that builds up a surface modification coating layer by layer with each layer in atomic thickness, making it a perfect means of gradually tuning the dimension and surface chemistry of nanostructures, thereby achieving precisely engineered materials with designed properties. In this talk, the application of ALD in tuning functional nanoparticulate materials and their reverse structures, the nanoporous structures, will be addressed. To ensure uniform coating on a large quantity of nanoparticles and to prevent the loss of nanoparticles during ALD's purge steps, an agitated powder ALD system will be introduced, and examples of ALD of catalytic nanoparticles, ALD of core-shell structures, and ALD modification of battery electrode materials will be laid out. Also, the approach of ensuring the small size of as-deposited ALD catalytic noble metal nanoparticles will be discussed. Moving onto the ALD of nanoporous structures, the behavior of ALD on a nanoporous matrix will be presented. Two extreme cases: how to ensure uniform ALD all over the internal pores of a nanoporous matrix, and how to eliminate ALD on the internal pores of a nanoporous matrix thereby confine the ALD only on the external top surface of a porous substrate, will be illustrated. For the second case, we introduce the ultra-thin membrane fabrication by using a "plasma-defined" ALD process where the location of ALD deposition is defined by the location of plasma irradiation, and the example of sub-10nm ultra-thin membranes formed on porous supports with excellent performances in water desalination, CO₂ capture as well as selective ion transports, will be elaborated.

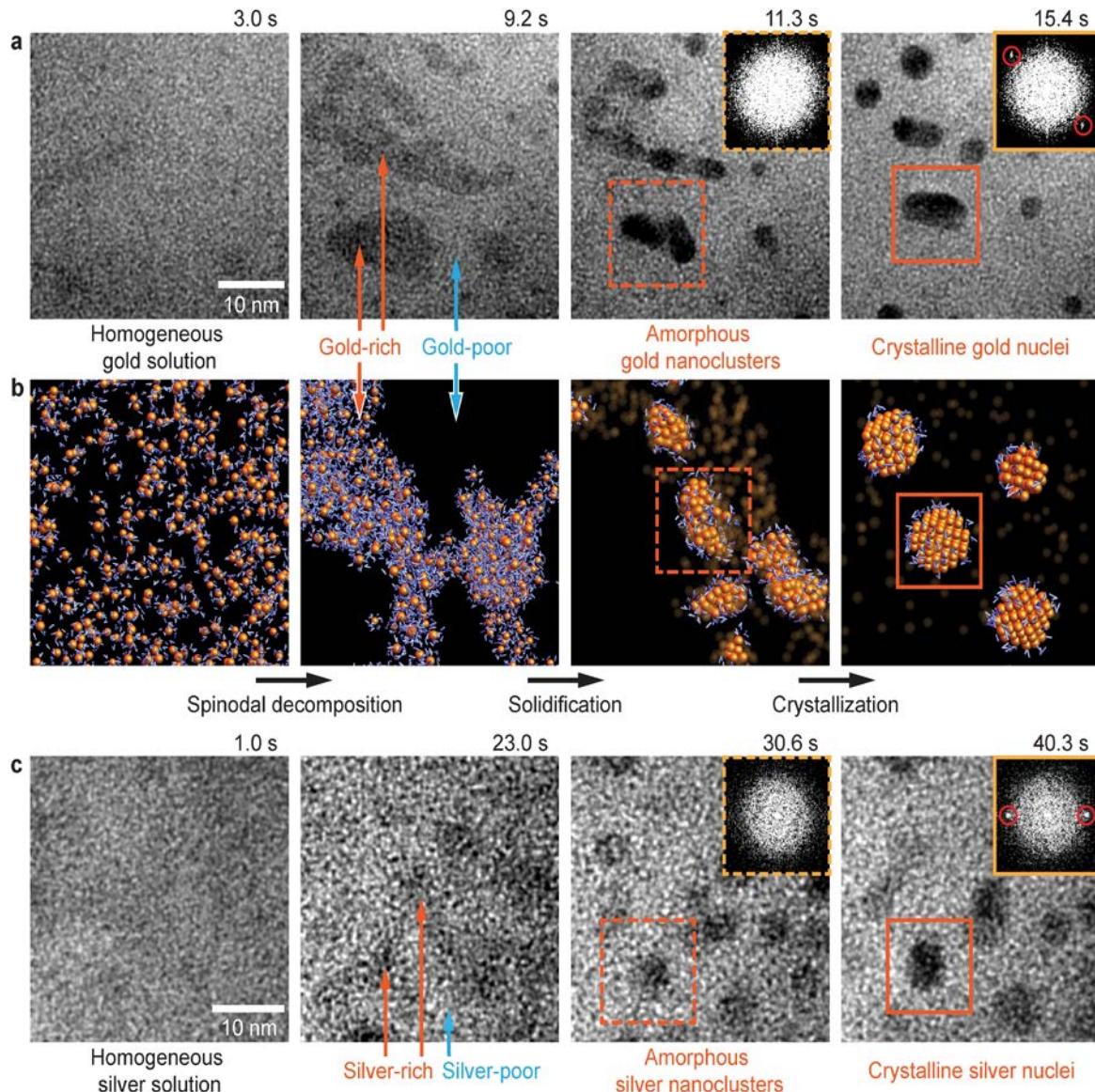
COLL 790

Atomistic modeling of nanoparticle formation, modification and self-assembly in liquid cells

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In recent years, we have used both mean-field and atomistic simulations to model complex interactions acting between nanoparticles during their self-assembly. To shed more light on some of these processes, *in situ* transmission electron microscopy was

used to visualize their dynamics in liquid cell experiments. Here, we present our atomistic modeling of these dynamical self-assembly processes. First, we describe multistep nucleation and growth of gold nanoparticles, where a spinodal separation, amorphous cluster formation, and crystallization steps have been observed. Then, we present our modeling of a linker-mediated self-assembly dynamics of charged nanoparticles with different aspect ratios and ligands. Finally, we discuss briefly our modeling of precise etching of nanostructures, performed in liquid cells.



Self-assembly of gold and silver nanoparticles in a liquid cell.

COLL 791

Modeling of self-assembly dynamics of charged nanoparticles in liquid cells

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In collaboration with experimentalists, we model a stepwise self-assembly of surfactant-coated and hydrated gold nanoparticles (NPs) of a diameter 3.8 nm into linear chains or branched networks. Experiments show that the NP form a linear chain when the concentration of linker is low and branched network, when the linker concentration is high. The NP binding is facilitated by linker molecules, ethylenediamonium, which form hydrogen bonds with surfactant molecules of neighboring NPs ~15 Å, which matches with two combined lengths of two surfactants and one linker molecule. We model this behavior using atomistic molecular dynamics simulations and show that for lower concentration of linkers, NPs with charged surfactants cannot be fully neutralized by strongly binding divalent linkers, so NPs carry higher effective charges and tend to form chains, due to poor screening. The highly polar NP surfaces polarize and partly immobilize nearby water molecules also promotes NPs binding. Presently we are studying the stepwise self-assembly of CTAB coated gold nanocubes. Here we are trying to understand what drives CTAB coated gold nanocubes to self-assemble into 2D-close pack arrays.

COLL 792

Modeling the nucleation and growth of palladium nanoparticles in the presence of capping ligands

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The synthesis of metal nanoparticles with good control over size, size distribution, and shape has attracted much attention due to their wide applications in the fields of catalysis, photonics, electronics, and medicine. Tailoring the nanoparticle size requires a thorough understanding of the mechanism and kinetics of nucleation and growth. However, due to the complex interactions of capping ligands with the metal precursor and nanoparticles, developing a robust kinetic model that can explain the chemistry of nucleation and growth has been a challenging task. In this work, we developed a novel kinetic model that captures the in-situ nucleation and growth kinetics of colloidal palladium (Pd) nanoparticles in the presence of trioctylphosphine (TOP) capping ligand. In-situ small angle X-ray scattering (SAXS), was used to measure the diameter and number of particles during the synthesis. Our kinetic model for the first time accounts separately for both the nucleation and growth events obtained from in-situ SAXS. This is achieved by fitting the time evolution of number of nanoparticles (nucleation event) and number of atoms in nanoparticles (both nucleation and growth events) simultaneously as opposed to fitting only the number of atoms in nanoparticles or the nanoparticles size as in previous models. Based on the results we show that nucleation is slow, while growth is fast. Our modeling results show that the capping ligands interaction with both the precursor and nanoparticle's surface are responsible for controlling the rates of nucleation (binding to precursor) and growth (binding to the nanoparticle surface). The

modeling and experimental results demonstrate that the final size of the nanoparticles is governed by the growth/nucleation rate which can be tuned by the ligand type, concentration and/or type of solvent. Finally, our kinetic model was used to predict the final particle size under different ligands and precursor concentrations and we show excellent quantitative agreement between the predicted and experimentally measured nanoparticle sizes. Our new kinetic model takes into account the interactions of capping ligands with both precursor and particle's surface, which can be applied to other synthesis systems (i.e. different metals) and therefore can provide a powerful tool for predictive synthesis of colloidal nanoparticles.

COLL 793

Cellulose nanocrystal-derived stimulus-responsive cholesteric microgels having catalytic properties

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Polymer microgels which have a network structure swollen in a solvent are an important class of soft matter materials with variety of potential applications including drug delivery vehicles, sensors, photonic crystals and etalons, microreactors, cell culture media, and separation and purification technologies. Nanofibrillar hydrogels shows interesting properties such as nonlinear viscoelastic behavior, good transport due to large pore size and thermal stability. Particularly, rod-like cellulose nanocrystals (CNC), one of nature-derived filament-like nanoparticles, are attractive building blocks for hydrogel assembly with their surface functionalities and the ability to form cholesteric (Ch) liquid crystalline phase.

Recently, we reported nanofibrillar, composite stimulus-responsive CNC-derived microgels with a Ch structure. Microgels with a narrow size distribution were prepared by microfluidic emulsification, followed by the photopolymerization of the precursor droplets. The spherical confinement of CNC led to the liquid crystalline morphology altered from the spherical concentric to the bipolar planar Ch structure by reducing the droplet dimensions. The microgels exhibited collective properties of CNCs and polymer hydrogels. The stimulus-responsive nature of the microgels was governed by the polymer component and was evidenced by tuning the microgel size and pitch at varying ionic strength and temperature of the ambient medium. The microgels exhibited catalytic performance in a hydrolysis reaction and were used for the *in situ* synthesis of plasmonic AgNPs. The resulting AgNP-laden microgels exhibited catalytic activity in a reduction reaction. In this presentation, design, synthesis, and performance of the composite microgels for catalytic activities will be discussed.

COLL 794

Controlled self-assembly of porphyrin and applications

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Porphyrin self-assembly nanomaterials, as visible-light harvesting materials in the artificial photosynthetic systems that mimic natural photosynthesis, have been well designed and developed via molecular self-assembly with non-covalent interactions including electrostatic force, metal-ligand coordination, π-π stacking, hydrogen bonding as well as host-guest interactions. And porphyrin self-assembly with well-defined structures have drawn much attention in a wide range of fields including light-energy conversion, photonics as well as photodynamic therapy due to their attractive photophysical, photochemical and electronic properties in the visible-light region. We report a surfactant self-assembly induced micelle encapsulation method to fabricate porphyrin nanocrystals using the optically active precursor zinc porphyrin (ZnTPP). Through confined non-covalent interactions of ZnTPP within surfactant micelles, nanocrystals with a series of morphologies including nanodisk, tetragonal rod, and hexagonal rod, as well as amorphous spherical particle are synthesized with controlled size and dimension. A phase diagram that describes morphology control is achieved via kinetically controlled nucleation and growth as shown in Figure 1. Due to the spatial ordering of ZnTPP, the hierarchical nanocrystals exhibit both collective optical properties resulted from coupling of molecular ZnTPP and shape dependent photocatalytic activities in photo degradation of methyl orange (MO) pollutants.

COLL 795

Probing heterogeneity and bonding at silica surfaces through single-molecule investigation of base-mediated linkage failure

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Many chemical systems, including heterogeneous catalysis and functionalized-silica chromatographies, depend on robust surface linkages to silica surfaces for reliable usability. However, it has been shown that silyl ether-silica linkages are susceptible to detachment under basic conditions. In this work, we use single-molecule spectroscopy to determine the rate and mechanism of surface linkage detachment when exposed to basic conditions. Kinetic analysis was performed to reveal the difference in surface stability between various deposition conditions, including thermal annealing and addition of a steric and electrostatic blocking layer. It was found that improvements in stability from modified deposition conditions were caused by decreasing the rate at which base molecules access the surface as opposed to reducing surface linkage reactivity. Our results also show that the observed heterogeneity in surface linkage disruption kinetics is caused by the inherent structural diversity of the silica surface.

COLL 796

Balancing multiple orthogonal functions simultaneously on a single surface

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Enhancing Warfighter survivability against chemical and biological threats can be achieved via improved protection on the uniform. A uniform comprised of a single multifunctional layer would be optimal because it could perform multiple functions without increasing the burden of the Soldier. Two critical functions to add to a Soldier's uniform would be water repellency and decontamination. Enzymes have been shown to be effective and selective chemical decontamination agents. A multifunctional coating that is predominantly hydrophobic would repel water, keeping the wearer dry and comfortable, and provide passive protection by allowing aqueous liquids to roll-off. However, enzymes often require aqueous environments for proper activity. This situation presents an interesting problem; how can we achieve the highest decontamination activity without negatively affecting the water repellent properties and vice versa? In nature, the skin of the Stenocara desert beetle effectively balances orthogonal hydrophobic and hydrophilic surface properties. No catalytic activity occurs on the beetle's skin, but it does have hydrophilic patches that collect moisture and hydrophobic channels for liquid transport to its mouth for drinking.

In order to create a multifunctional surface for decontamination and water repellency, we have taken a cue from the Stenocara beetle skin and fabricated an amphiphilic surface by using a binary thiol self-assembled monolayer system. In collaboration with UMass-Lowell, we have used photolithography to pattern micron-sized hydrophilic domains amongst a hydrophobic background. Once patterned, we can covalently attach enzymes to the hydrophilic regions for decontamination activity while the hydrophobic background provides the water repellency function. Using photolithography we can control the size and spacing of the hydrophilic domains to determine the effects this has on the two functions of interest. In this study I use contact angle goniometry, fluorescence enzyme assays and surface characterization techniques such as atomic force microscopy and infrared spectroscopy to find the surface composition that maximizes both functions simultaneously.

COLL 797

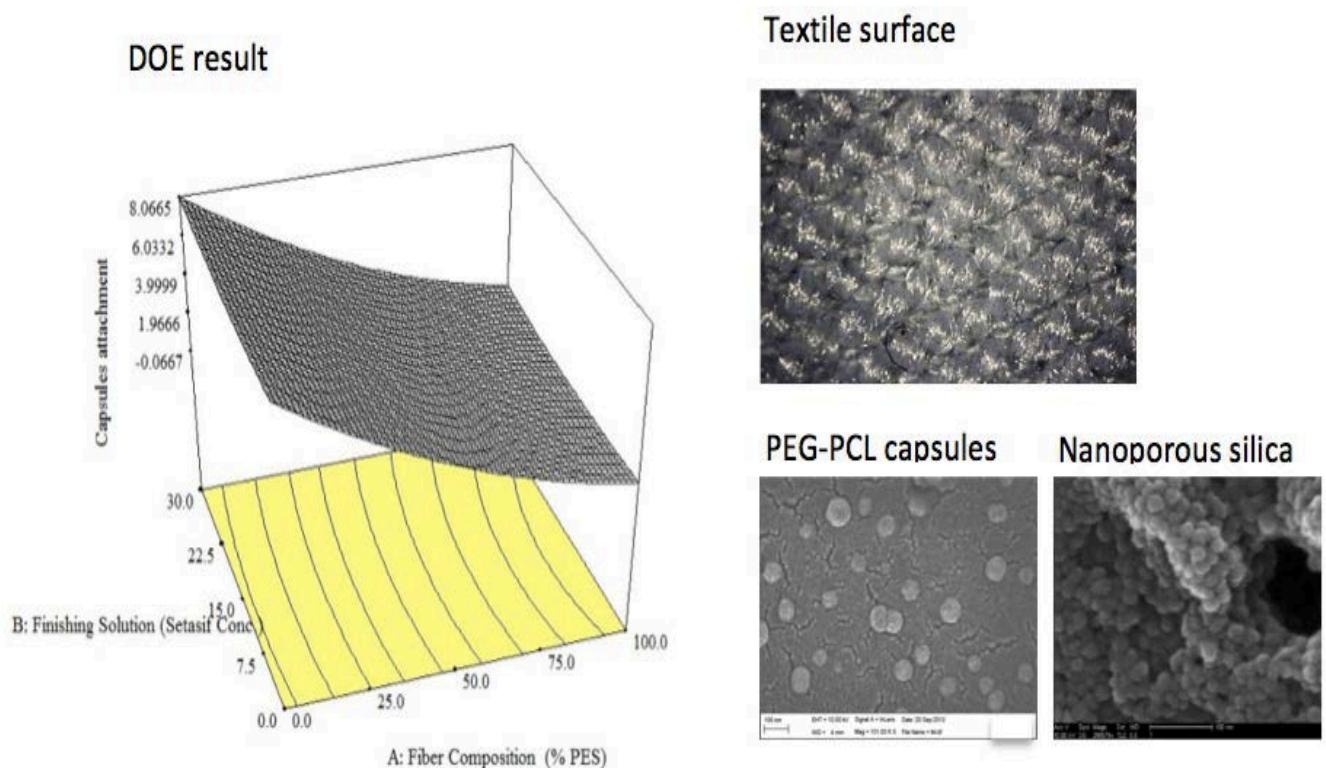
Optimization of micro/nanocapsules attachment by tailoring the surface nature of textiles

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Potential growth of microbes during the use and storage of textiles negatively affects the durability while simultaneously resulting in infections. In this study, surface

characteristics of the textiles have been systematically modified to enhance the attachment of micro/nano-capsules containing active agents to repel insects or ticks or prevent the growth of microbes.

The attachment of capsules to textile surfaces depends on the fabric composition and surface finish. For systematic selection of textile for functionalization through capsules attachment, surface properties of %100 cotton, %100 polyester, %100 viscose and %100 tencel textiles were studied. Cotton and polyester and their blends were chosen for further study due to their wide availability, use in sports outfits and higher contact angles to help stain resistance. For the determination of most suited blend, a design of experiment (DoE) was conducted. The DoE revealed 13 tests to be performed for the design of optimum surface properties to enable maximum micro/nano-capsule adherence to the textile samples. The optimization of the responses in DoE being focused on higher hydrophobicity and less negative surface charge resulted in highest desirability for 100% cotton fabric treated with higher silicon content in the finishing solution to maximize the capsules attachment. The selected textile was treated, sprayed on the cotton side with the prepared nano-micro capsules loaded with eucalyptus oil as an example of tick repellent textiles. Two novel capsule formulations were studied including (i) the biodegradable PEG-PCL co-polymer micelles and (ii) porous silica coated with polymeric shell after impregnation of the eucalyptus oil. While the capsule attachment correlated to the hydrophobic and electrostatic nature of the capsules and the textile surface, the type of capsules affected the controlled release of the active ingredient to make the textile surface functional.



COLL 798

Determining optimum surface preparations to control the selectivity of ethanol chemistry over TiO₂/Au(111)

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Depending on the surface preparation, Au(111) supported TiO₂ nanoparticles catalyze either the reduction or oxidation of small alcohols. The desire to selectively form oxidized or reduced products merits an investigation of alcohol reactivity over differently prepared TiO₂/Au(111) surfaces. In this work, a systematic study of ethanol reactivity over several TiO₂/Au(111) surfaces elucidates the effect of surface conditions on the selectivity of the reaction between ethanol and TiO₂/Au(111). Methods to control the surface conditions of TiO₂/Au(111) include: 1) Altering the monolayer coverage of TiO₂ nanoparticles on Au(111); 2) Controlling the oxidation state of TiO_x ($x < 2$); 3) Annealing the TiO₂/Au(111) surface at different temperatures (600 K vs. 850 K); 4) Introducing co-adsorbates (H₂O) to the surface prior to the reaction with ethanol. Atomic force microscopy (AFM) provides information regarding the structure of the Au(111) supported TiO₂ nanoparticles and ultrahigh vacuum temperature programmed desorption (TPD) monitors the selectivity of the reaction between ethanol and each TiO₂/Au(111) surface. This study investigates the selectivity of the reaction between ethanol and several TiO₂/Au(111) surfaces and determines the optimum surface conditions necessary to selectively form either oxidized or reduced species.

COLL 799

Directing and morphing bouncing water droplets using chemically patterned surfaces

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Droplet impact on solid surfaces has been studied extensively due to its importance in nature and technology. A drop striking a flat surface retains its circular symmetry throughout the impact process. Research on controlling such impact dynamics has focused on optimizing pre-impact parameters, e.g., droplet size and velocity. Here we show that chemically patterned surfaces can affect and control the bouncing dynamics of droplets with distinct asymmetric morphing behavior during and after impact. Substrates were modified using combinations of surface modification chemistry and UV photolithography designed to form surfaces that exhibit extreme superhydrophobicity tailored with hydrophilic domains of precise shape, size and orientation. Droplets impacting such surfaces in precise position relative to the hydrophilic domain can be morphed to complex shapes during restitution and rebound in prescribed directions with

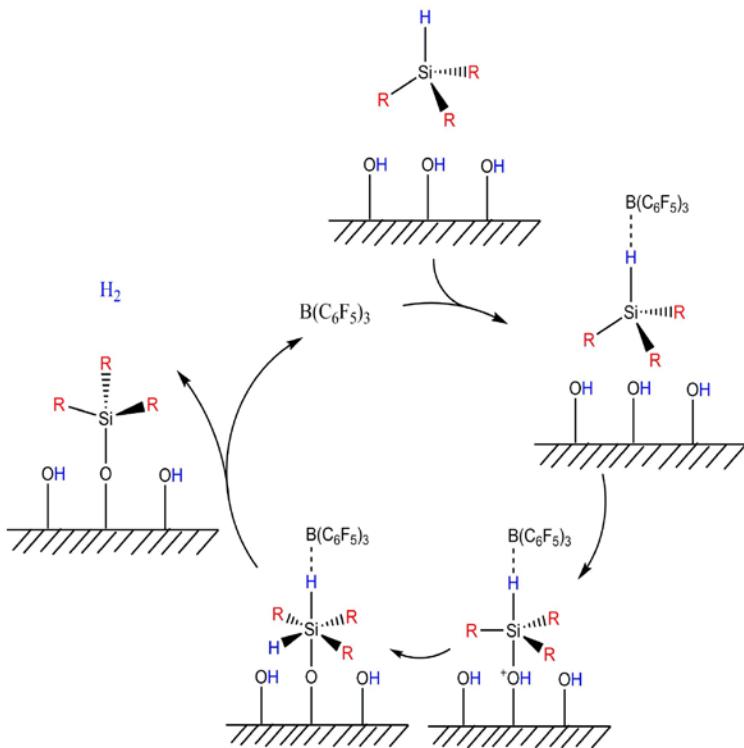
substantial controllable lateral distances. The impact position and size of the hydrophilic domain play important roles in the trends of morphing and directing, while the impact velocity amplifies the asymmetric deformation during the process. The study shows a versatile approach to manipulate bouncing droplets with ramifications for novel microfluidic systems.

COLL 800

Rapid covalent surface modifications using the Piers-Rubinsztajn reaction

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Covalent attachment reactions of alkylsilanes to form monolayers using chloro-, amino-, or alkoxy- silanes can take days at elevated temperatures to reach maximum bonding densities. The rapid activation of hydridosilanes by tris(pentafluorophenyl)borane (BCF) has been used in precision silicone synthesis, organic chemistry and to modify silica particles. We studied the kinetics of formation and structure of BCF-catalyzed trialkylsilane monolayers on smooth surfaces using dynamic contact angle and found that reactions are complete in minutes to hours at room temperature. In comparison to monolayers formed from chlorosilanes, these monolayers exhibit lower contact angles, lower contact angle hysteresis and demonstrate a relationship between contact angle and alkyl chain length that is not observed for chlorosilanes. We attribute the lower bonding density of the monolayers to the steric requirements of the catalyst. Preparation of vinyl group-containing surfaces and subsequent chemistry highlights an additional utility of this modification procedure. Additionally, the modification of silica with hydride-containing polysiloxanes was carried out to create low hysteresis, covalently-attached polymeric monolayers. The wetting properties can be varied by changing the placement and content of hydrides in the polymer. Polymers with greater hydride content are less mobile due to the lower molecular weight between surface attachments. As mobility increases with decreasing hydride content, contact angle increases and contact angle hysteresis decreases. The Piers-Rubinsztajn reaction is an efficient way to covalently modify silica surfaces.



COLL 801

Single-nanogap level characterization of ultra-dense Nanogap-Enhanced Raman Scattering (NERS) array surface

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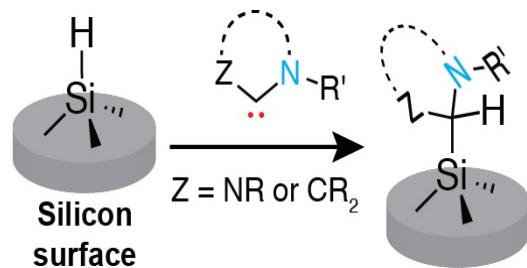
Controlling surface-enhanced Raman scattering (SERS) hotspot toward a narrow distribution of SERS enhancement factor (EF) is of paramount interest for linear response of SERS signal to the analyte concentration. In this talk, a single-nanogap level near-field characterization of ultra-dense nanogap-enhanced Raman scattering (NERS) array surface will be presented. Nanogaps were heavily populated between globular Ag nanoparticles (~ 120 particles/ μm^2) using a nanolithography-free simple process consisting of an Ar plasma treatment on polyethylene terephthalate (PET) wafer and successive Ag sputter deposition. Such compact nanogaps led to an exceptionally narrow SERS enhancement factor (EF) distribution ($\text{EF}_{\max}/\text{EF}_{\min} < 10^1$) measured from 3.1×10^5 confocal spots ($0.1 \mu\text{m}^2$), which is one order of magnitude smaller than the detection areas ($>$ a few μm^2) used in the vast majority of studies. The local near-fields at these nanogaps were visualized using photo-induced force microscopy (PiFM) that directly detected the near-field force under ambient conditions. An unprecedented spatial resolution (3.1 nm) was attained and the resulting photo-induced near-field force signals were quantitatively measured at each nanogap.

COLL 802

Reactions of persistent carbenes with silicon surfaces

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Controlled functionalization of silicon surfaces is foundational to the production of silicon microelectronics, photovoltaics, and the emerging technologies based on silicon nanomaterials. Consequently, new methodology to manipulate the chemical functionality at silicon surfaces has far-reaching potential: it may enable previously inaccessible function to be extracted from silicon devices. In juxtaposition to the plethora of examples of inorganic methods, or radical-based or nucleophilic substitution mechanisms, reports of carbene insertion in this context are scarce: only two precedents were known until recently, both of which dealt with reactive, non-persistent carbenes or carbenoids. The present discussion will detail the first inquiry into the reactivity of *persistent* carbenes with hydrogen-terminated silicon surfaces. This discussion will cover a range of carbene types to demonstrate the impact of carbene stereoelectronic factors on their Si-H bond insertion reactivity; likewise a range of silicon materials will be covered: from molecular silane surface analogues to hydrogen-terminated silicon nanoparticles, and silicon (111) surfaces. A combination of experimental and theoretical evidence will be presented to provide molecular-level detail concerning these silicon surface transformations. Within a broader context, these findings highlight persistent carbenes as promising candidates in the search for universal surface anchors.



COLL 803

On the role of non-bulk interfacial structures in rutile-anatase TiO₂ interfaces

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The interface junction of composites is key to their fundamental properties and enhanced performance in many technologies. However, this is difficult to probe experimentally and is largely ignored in recent theoretical examinations of photocatalysts composed of TiO₂ rutile-anatase composites. Computational advances permit detailed modeling of the structural, electronic and optical properties of composites. In this contribution, we focus on a model system of mixed-phase rutile-anatase TiO₂ and use density functional theory (DFT) to interrogate the key structural feature, namely, the rutile–anatase interface. We discuss its relationship to and effect on photogenerated charge localization, bulk band alignments, and defect formation. The interfacial region is disordered and distinct from rutile and anatase and contains low coordinated Ti sites and oxygen vacancies, both drivers of charge localization. The relaxations of the interface upon formation of excited electrons and holes determine the final location of charges which cannot always be predicted from bulk band alignments. We also investigate rutile modified with varying thickness of anatase and vice versa to explore the influence of the interface region in different realisations of this phase junction. A detailed understanding of the interfacial phase junction between two materials lays the foundation for directed synthesis of highly active and efficient composite photocatalysts.

COLL 804

***In situ* chemical imaging of energy and environmental interfaces**

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The surfaces of the liquid phase and thin films have unique kinetics and thermodynamics, distinct from the bulk. However, major surface analytical techniques are mostly vacuum-based and direct applications for volatile liquid studies are difficult. We developed a vacuum compatible microfluidic interface, System for Analysis at the Liquid Vacuum Interface (SALVI), to enable direct observations of liquid surfaces and liquid-solid interactions using time-of-flight secondary ion mass spectrometry (ToF-SIMS) and scanning electron microscopy (SEM). SALVI was recently applied to investigate dynamic energy and environmental interfaces. In this talk, a few novel applications of interfacial physics and chemistry are presented. Specifically, the solvent structure of switchable ionic liquids has been investigated and spatially mapped using *in situ* molecular imaging mass spectrometry. Morphological changes of boehmite particles suspended in aqueous solutions are studied using *in situ* liquid SEM. The solvation sphere dependence on the solution pH is investigated using liquid SIMS. Collectively, a more holistic view of the dynamic material interface in liquid is provided. Our results demonstrate that interfacial chemistry involving important molecules and evolving interfaces can be studied from the bottom up based on microfluidics and advances in analytical tools. Our transferrable microfluidic reactor sets the foundation

toward chemical imaging of complex phenomena occurring in the mesoscale, underpinning chemical changes at the molecular level in the condensed phase.

COLL 805

CuInS₂-ZnS-based electro optic devices: Surface, surface and surface

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Multinary quantum dots are promising heavy metal free alternatives in energy harvesting and light emitting devices (LEDs). Typical synthesis of multinary compounds requires careful balancing of cations reactivity by selection of proper ligands molecules. Selection of the ligands also determines the process solvent, charge mobility and finally the functionality of the device. Several works have examined effect of ligand type on charge recombination dynamics in nanoparticles composed of heavy metal ions (i.e. Pb, Cd). However this information is missing for multinary nanoparticles. Moreover, although synthesis of water or ethanol soluble nanoparticles is environmentally and economically preferable most of the research focus on nanoparticles that are dissolved in high hydrophobic solvents. In this work, we examine different approaches (with and without ligand exchange) for synthesize of water or ethanol soluble Cu-In-Zn-S (CIZS) alloyed nanoparticles. Subsequently, we utilize transient absorption measurements to examine charge transfer kinetics between the nanoparticles in polar solvents and films. And discuss the correlation between the fundamental optical and charge transfer properties to the performance of the devices.

COLL 806

From standing to sitting: Leveraging iterative phase segregation to create hierarchically nanostructured synthetic materials

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The design of complex hierarchical interface structures at few-nanometer scales is a significant ongoing challenge in the development of nanoscale electronic and optoelectronic materials. Biology routinely addresses a related challenge in the context of the lipid bilayer, using the hydrophilic-hydrophobic orthogonality intrinsic to the bilayer to create hierarchical nanostructures of exquisite precision and functional complexity, using not only peptides but over 100 structurally different lipids. Conventional standing phases of phospholipids do not directly meet many of the interfacial patterning requirements for synthetic materials. However, polymerizable amphiphiles can be ordered into sitting or lying down phases on layered materials, exposing both heads and tails to the environment in patterns useful for controlling nanoscopic wetting and phase

segregation, as well as the adsorption of analytes. Here, we discuss the use of an iterative phase segregation strategy to create hierarchical nanoscale assemblies of multiple functional molecules, and demonstrate the utility of this strategy in controlling local interfacial physical properties.

COLL 807

Effect of the first layer on polyelectrolyte multilayer structure

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Polyelectrolyte multilayers (PEMs) are prepared by layer-by-layer deposition of polycations and polyaions on gold substrate. We have previously observed that surface roughness, as measured by contact mode atomic force microscopy (AFM), is highly dependent on the chemistry as well as the deposition conditions of the first adsorbed layer of a PEM. In this study, QCM-D was used to analyze mass absorption of each single layer during deposition process. When using different polyelectrolytes as the first layer, total mass accumulation of the PEM coating is different, while the mass adsorption of each single layer also changed. Thickness of PEM film also changed after change first layer material. Atomic force microscope was used to measure the surface roughness of PEMs. When using different polyelectrolytes as the first layer, the surface roughness of PEMs is different. These results imply that the first layer has an impact on polyelectrolyte adsorption in long range, while the internal structure of PEM is also affected.

COLL 808

Partitioning of organic solutes into bilayers formed by non-ionic surfactants

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Solute uptake in microstructured soft materials is a reoccurring theme across several fields. For personal care or household cleaning formulations, one may be concerned with controlling uptake of additives in surfactant assemblies and mitigating their effect on the stability of these assemblies. In drug delivery, one may be interested in development of an optimal vehicle to transport a relatively non-polar pharmaceutical compound through an aqueous medium. Regardless of application, however, several questions arise about the challenge of tuning solute uptake: Do solutes distribute

preferentially into certain regions of surfactant assemblies and how does solute uptake affect micellar and mesophase structure? How do these changes vary with the chemical functionality of solutes and how does introduction of additional components influence solute uptake and assembly stability? The present work addresses these questions for nonpolar and polar additives (n-nonane, ethyl butyrate, and 1-hexanol) in a bilayer system containing nonionic oligo(ethylene glycol) alkyl ether surfactants. These systems are studied through the use of configurational-bias Monte Carlo simulations in the constant-stress, osmotic Gibbs ensemble that allows for prediction of solute uptake at a given bulk concentration and concomitant change of the bilayer structure (interfacial area and thickness).

COLL 809

Beyond self-assembly: 2D chemical interactions and patterns, a computational approach to complex systems

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Nanoscale interactions range from van der Waals contacts, to hydrogen bonding, to Coulombic. They govern ordering and assembly of molecules. The same forces can modify systems that reach up to lengthscales several orders of magnitude greater than the nano and are even able to modify the geometric shape of living cells to make them form of a variety of cusped polygons. The practical applications of variations of the geometrical structure and mechanical dynamics of cells have far reaching consequences. Cell shape influences the differentiation of human mesenchymal stem cells. Cells cultured in rectangles and pentagons display different adipogenesis and osteogenesis profiles. Understanding the response of living cells to patterned chemical cues is intrinsically linked to our comprehension of the interactions that drive hierarchical self-assembly.

I will discuss simulations where chemical objects are coarse grained as parcels of fluid, which interact through forces that combine conservative, dissipative and random components. At the nanometric level, I will examine the interactions of lipid bilayers with variously functionalized graphenes and discuss the results in terms of nanotoxicology. At the micrometric level, I will show that the mechanical response of living cells on a 2D pattern of chemical cues can be modelled. The cells are effectively represented by drops that are endowed with the presence of additional forces that make them active. With the proper choice of these forces, the phenomena that emerge from the dynamics simulations match the experiments. In particular, a combination of hydrophilic and lipophilic forces allows the active drops to respond to geometric shape cues and form squares, pentagons, hexagons and flowers, just as living cells do. The mechano-chemical interactions that orchestrate cell behavior are therefore harnessed and used to beat the surface tension that characterizes an inactive drop.

COLL 810

Understanding polymorphic accessibility and stability in molecular semiconductor thin films

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We investigated the polymorphic stability and reversibility of thin films of a series of naphthalene diimides (NTCDIs) with varying alkyl substitutions. Each derivative adopts its β -phase upon thermal evaporation; post-deposition processing via solvent-vapor annealing converts the β -phase to the α -phase in two of the four derivatives. NTCDIs adopt layered structures driven by strong intralayer π - π interactions and weaker interlayer van der Waals interactions. The presence of interlayer short contacts effectively locks the structure in place, preventing any molecular reorganization. The absence of such short interlayer contacts is instead correlated with reversible access of both polymorphs; judicious selection of post-deposition processing conditions tunes the polymorph accessed. This finding is generalizable across a wide range of molecular semiconductors that adopt layered structures, including derivatives of benzothiophene and functionalized acenes. Beyond organic electronics, this finding has implications on pharmaceuticals and the food industry as polymorphic stability governs bioavailability and solubility.

COLL 811

Principles and applications of grazing incidence small angle and wide angle x-ray scattering

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This talk will briefly review principles of both grazing incidence small angle x-ray scattering (GISAXS) and grazing incidence wide angle x-ray scattering (GIWAXS). These techniques have played a key role in understanding structures of organic thin films. GISAXS is for nanoscale structure determination and GIWAXS, also called grazing incidence x-ray diffraction (GIXD), is for molecular or atomic structure determination. Due to their weak signals, these methods are typically useful with a synchrotron X-ray source such as Advanced Photon Source (APS). Recent experimental results on organic films performed at 12-ID-B beamline at the APS will be presented to demonstrate what types of information can be obtained along with practical information such as how to prepare sample, where else the measurement can be done and how data has been analyzed.

COLL 812

Rational design of block copolymer compatabilizers for ternary blend polymer bulk heterojunction solar cells

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In this talk, we discuss our recent work in the context of the use of block copolymers (BCP) as compatibilizers in ternary blend organic photovoltaic devices. While a number of earlier experimental studies have employed BCPs as a means to improve the long-term stability of the donor-acceptor based devices, in our work we pursued the hypothesis that the physico-electro-chemical properties of BCP compatibilizers may be targeted as a handle to modulate the morphology and device characteristics of such systems. In this regard, we developed coarse-grained computer simulation tools, despite being limited in their ability to capture complex interaction features and crystallization phenomena, to serve as a guide to narrow and/or identify parameteric regions where morphologies desirable for better exciton and charge transport can be achieved. The output of such morphological predictions were combined with coarse-grained device simulation approaches to identify the overall photovoltaic properties of the ternary blends containing such BCP compatibilizers. Together, such computational studies served to connect the molecular structure and electronic properties of the BCP to the overall device properties and, thereby, enabled a rational molecular design of BCP compatibilizers for organic photovoltaic devices.

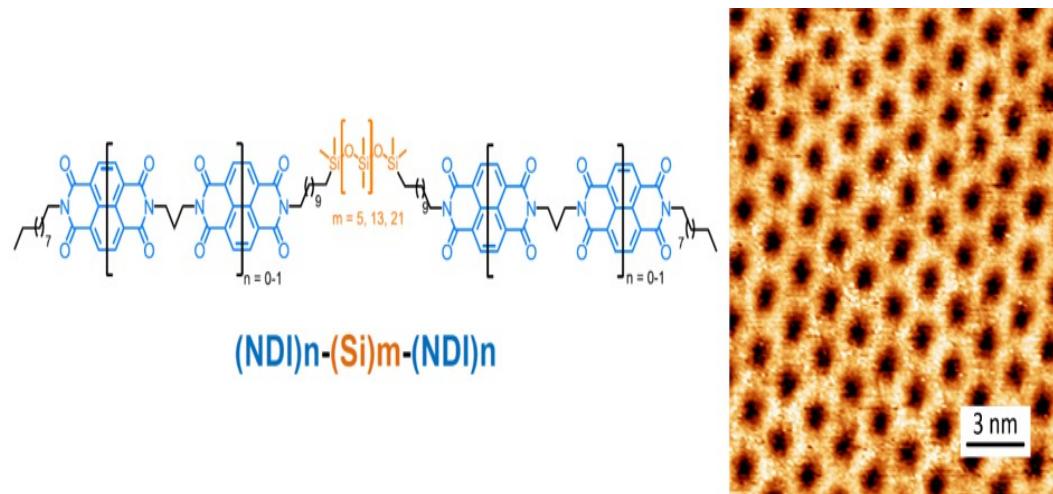
COLL 813

Nano-phase behavior of surface-adsorbed, monodisperse oligodimethylsiloxane-based block molecules

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Block-copolymers (BCPs) represent a class of functional materials with properties that can be readily tuned by modifying the chemical identity and compatibility between the different blocks. This, in turn, strongly affects their structural organization and phase-separation. BCPs with immiscible segments create nanoscopic patterns on solid surfaces with domain sizes proportional to the length of each block. Such self-assembled periodic structures are promising for soft nanolithography, but are limited to domain sizes significantly larger than 10 nm. Sub-10 nm domain sizes may be better achieved with so-called high x-low N structures and block molecules. While the bulk organization of such systems can be studied at sub-10 nm resolution with X-Ray Scattering techniques, the single molecule characterization of the nanophase separation between their incompatible blocks has not been carried out to date. Here we present a novel, rationally designed block molecules composed of highly immiscible blocks composed of naphthalenediimides (NDIs) and oligodimethylsiloxanes (ODMS). The adsorption, nanophase separation and influence of ODMS on the surface-

directed self-assembly were studied on graphite surface using scanning probe microscopy (STM and AFM). A comparison between our results and previous studies on oligomethylene functionalized-NDI provides new insights into the interplay of supramolecular interactions between the different blocks and the surface. The understanding of the nanophase separation at the single molecule level will provide a valuable feedback for tuning the morphology and periodicity via manipulation of the block architecture, which will ultimately extend the applicability of block molecules lithography.



Molecular structure of the investigated NDI-ODMS conjugates and STM image (recorded at the 1-phenyloctane/graphite interface) corresponding to the NDI-Si-NDI compound with $n = 0$ and $m = 5$.

COLL 814

Fast, facile, and scalable fabrication of slippery liquid-infused surfaces using layer-by-layer assembly enabled by in-situ proton transfer

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Slippery liquid-infused surfaces (SLIPS) have attracted tremendous research attention for their excellent hydrophobic, anti-icing, anti-fouling, and anti-thrombogenic properties amongst others. Here we report the simple fabrication of a SLIPS type surface based on sequential deposition of ionizable polymers using scalable methods. The facile fabrication of SLIPS is based on the state of the art layer-by-layer (LBL) assembly using branched polyethylenimine (BPEI) and Nafion in methanol. Driven by electrostatic attraction which is induced by in-situ proton transfer from the sulfonic acid group on Nafion to the amine group on the BPEI, the LBL assembly allows fast deposition of multilayer films onto the PET substrate. The use of organic solvent enables the homogeneous buildup of hydrophobic functional groups on the surface and the fast evaporation rate makes it possible to carry the fabrication process to roll to roll

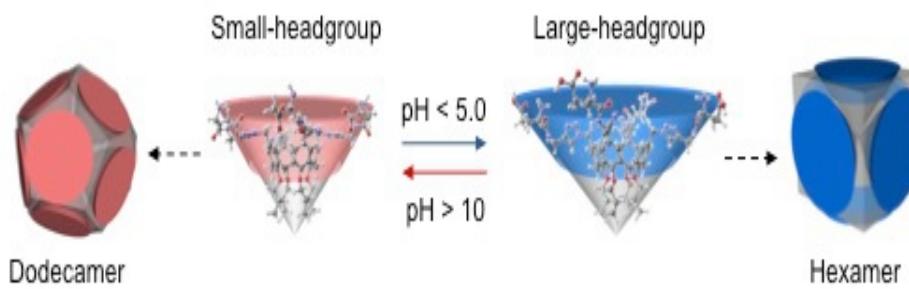
techniques. In addition, this LBL fabrication process can also be carried out via spray coating, another readily scalable technique, on various surfaces including glass, silicon wafer, and metal. The SLIPS fabricated by both techniques show great dewetting properties against water, organic solvents, and biologic fluids. By varying the deposition conditions, however, it is all possible to create water pinning surfaces from the same system showing that geometry rather than chemistry is the predominant effect. The highly transparent optical property and mechanically flexible property afford the potential of the SLIPS to be made into stick-on films which can be applied to various surfaces.

COLL 815

Platonic micelles: Glutamic acids bearing calix[4]arene micelle: pH-controllable aggregation number corresponding to regular polyhedra

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We have prepared a new calix[4]arene-based lipid containing glutamic acid as the hydrophilic group. The α -amine and the γ -carboxylic acid groups of the glutamic acid moiety allowed a continuous change of the state of the head-group from cationic to zwitterionic and then to anionic with increasing pH. Accompanying this head group change, micelles of the lipid underwent a morphological transformation from spherical to cylindrical, and again to spherical. The morphological transition was ascribed to the change of in the lipid conformation corresponding to the pH conditions. Interestingly, at acidic and basic pH, the spherical micelles demonstrated monodispersity based on the aggregation number, which agreed with the face number of Platonic solids, indicating the formation of Platonic micelles. At acidic and basic pH, the lipid conformations were almost identical, but there was a slight difference in the hydrophilic volume, which might affect the packing behavior of the lipid into micelles and account for the difference in the aggregation number. This study clearly demonstrates the precisely pH-controllable aggregation number of micelles, which belong to the Platonic micelle systems.



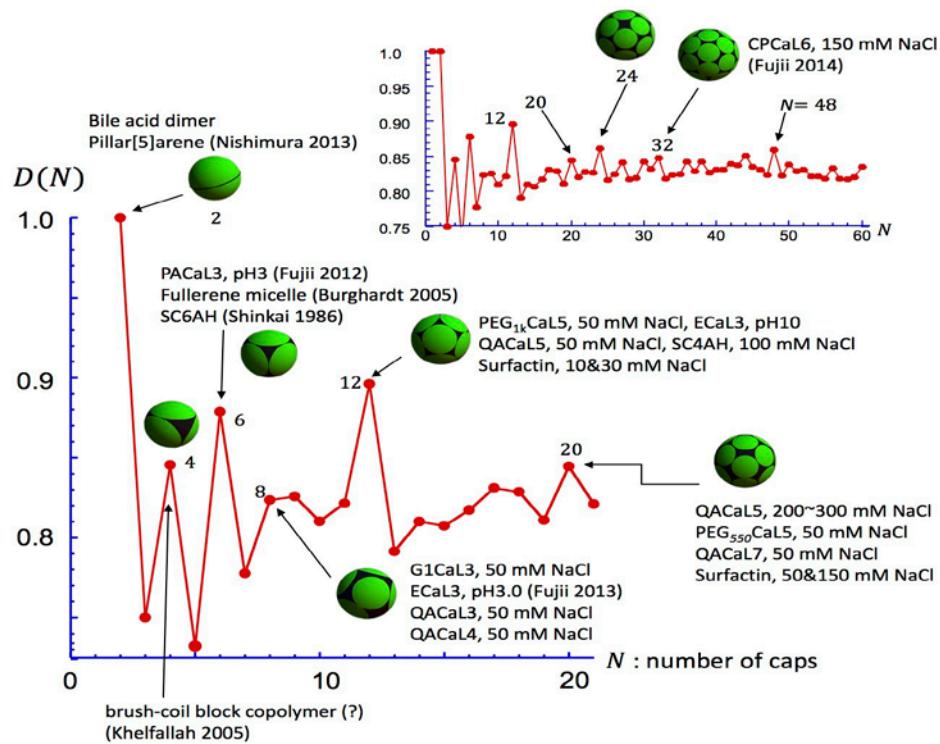
COLL 816

Platonic micelles: Thermodynamic consideration of the micelles with the discrete aggregation numbers and mon-dispersity

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The concept of micelles was first proposed in 1913 by McBain and the packing parameter principle of micellar architecture and its thermodynamic theory have been used to successfully rationalize numerous experimental results in the last century. It is generally agreed that the aggregation number for spherical micelles gradually changes with changes in solvent conditions and that has no exact value but rather a distribution in the value. However, our studies of spherical micelles made from calix[4]arene-based lipids and other systems by use of scattering, fractionation, and ultracentrifugation techniques, showed that they were monodisperse with a defined aggregation number whose values are chosen from 4, 6, 8, 12, 20, and 32. Interestingly, some of these numbers coincide with the face number of Platonic solids (or regular polyhedra). Our results indicate that a suitable combination of tail length, head volume, and sufficiently small is required to achieve such monodispersity and discreteness of; we named these systems "Platonic micelles". The preferred values were explained in relation to a mathematical quiz called the Tammes problem i.e. how to obtain the best coverage ($D(M)$) of a sphere surface with multiple identical circles. This is because better coverage results in lower interface free energy due to reduced interaction between water and hydrophobic tails. For the Tammes problem, the coverage ratio can be calculated and produces maxima at the certain circle numbers, coinciding with the values observed in our systems. We presume that "the platonic nature" may hold for any spherical micelles when is sufficiently small.

Figure 5



COLL 817

Synthesis of epoxy-functional diblock copolymer nano-objects via polymerisation-induced self-assembly and their use as Pickering emulsifiers

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The synthesis of various epoxy-functional diblock copolymer nanoparticles has been investigated *via* polymerisation-induced self-assembly using a reversible addition-fragmentation chain-transfer aqueous emulsion polymerisation formulation. A poly(glycerol monomethacrylate) (PGMA) chain transfer agent was chain-extended using glycidyl methacrylate (GlyMA) at 50 °C (Fig. 1A). The solution pH was maintained at pH 7 to preserve the epoxy functionality of the hydrophobic PGlyMA block. Fast rates of polymerisation and high final monomer conversions (>99%) could be obtained under these relatively mild conditions when targeting 10% solids. Varying the mean degrees of polymerisation (DP) of the PGMA stabiliser block and the PGlyMA core-forming block resulted in well-defined nano-objects with either spherical or worm-like morphologies (see Fig. 1B and 1C, respectively). The average worm width (19 nm) corresponded to

the average sphere diameter (16 nm), and worm lengths were in the range 0.1-2 μ m, determined by TEM. Analysis of the diblock copolymer nanoparticles by GPC revealed low dispersities (<1.25) with lower core forming block lengths (DP GlyMA <100).

Cationic nanogels could be prepared from these epoxy-functional precursor nano-objects via diamine cross-linking in aqueous solution. Addition of DMF, a good solvent for both blocks, caused molecular dissolution of the linear precursor nanoparticles, whereas diamine cross-linked nanoparticles became swollen but retained their morphology, as judged by DLS and TEM. These reactive epoxy-functional nanoparticles have been evaluated for their suitability as Pickering emulsifiers for the preparation of oil-in-water (nano)emulsions. In principle, the reactive epoxy groups can be utilised to produce colloidosomes *via* crosslinking between adjacent nanoparticles adsorbed at the oil/water interface.

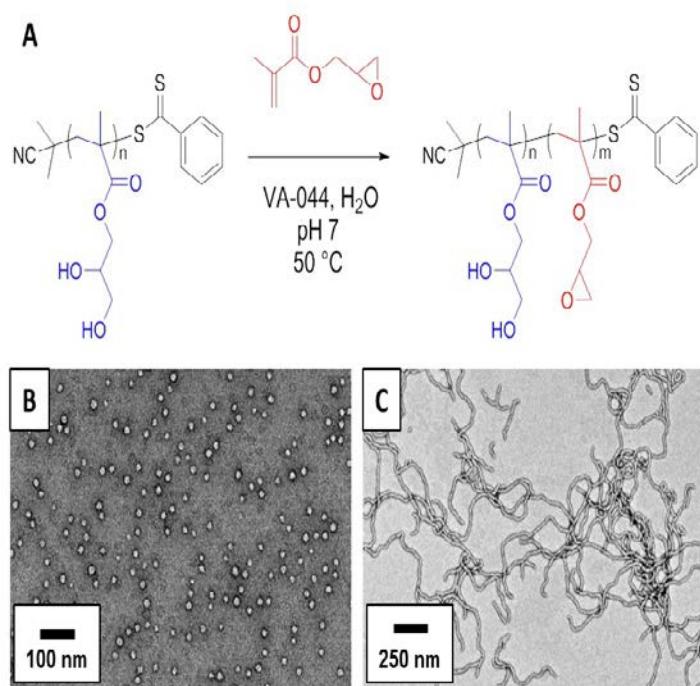


Figure 1 A) Synthetic route to prepare PGMA-PGlyMA latex particles, TEM images of B) PGMA₄₅-PGlyMA₃₅ spherical particles and C) PGMA₂₆-PGlyMA₅₀ worm-like micelles.

COLL 818

Time-resolved small-angle x-ray scattering studies of the micellar nucleation event during polymerization-induced self-assembly

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Reversible addition-fragmentation chain transfer (RAFT) dispersion polymerization of methacrylic monomers in a suitable solvent enables the *in situ* synthesis of diblock copolymer spheres, worms or vesicles. Polymerization-induced self-assembly (PISA) occurs when using a soluble macromolecular chain transfer agent (macro-CTA) to polymerize a miscible monomer to produce an insoluble second block, thus forming sterically-stabilized diblock copolymer nanoparticles. For a given copolymer, the final morphology is dictated by various parameters, including the mean degree of polymerization (DP) of the stabilizer block, the target DP for the core-forming block and the copolymer concentration. PISA syntheses have been studied using *in situ* small-angle X-ray scattering (SAXS), which has provided direct evidence for the evolution in copolymer morphology. In the present work, poly(stearyl methacrylate)₃₁-poly(benzyl methacrylate)₂₀₀₀ (PSMA₃₁-PBzMA₂₀₀₀) nanoparticles are targeted in mineral oil. Remarkably, the nascent particles that are formed during the micellar nucleation event are *non-spherical* (see Figure 1), even though the final copolymer morphology obtained at full conversion comprises well-defined spheres. Similar *non-spherical* nuclei have been observed for other PISA formulations, suggesting that these findings may be generic.

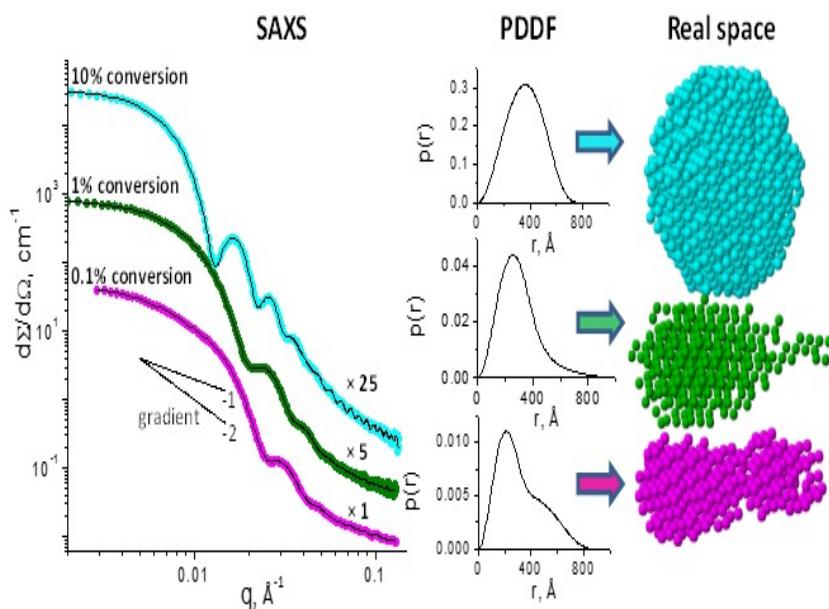


Figure 1. SAXS patterns recorded for PSMA₃₁-PBzMA₂₀₀₀ spheres in mineral oil (left), corresponding pair-distance distribution functions (PDDFs) obtained by indirect Fourier transformation of the experimental SAXS patterns (centre) and *ab initio* low resolution structure of the scattering objects derived from the SAXS data (right).

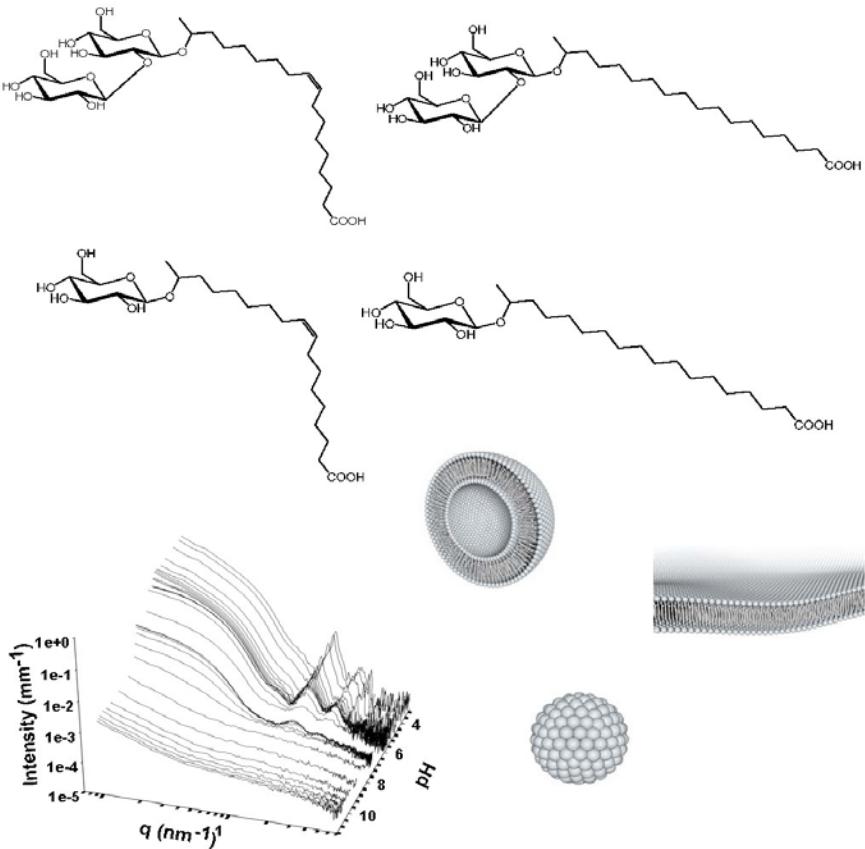
COLL 819

pH-resolved self-assembly of microbial glycolipids: Mechanistic insights

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Stimuli-responsive self-assembly is an active field of research due to the number of potential applications. Block copolymers and lipids are commonly designed to tune their self-assembly properties in solution as a function of temperature, pH and ionic force, etc. Typical self-assembled structures range from simple spherical to branched micelles, disks, vesicles, etc..., and where the morphological relationship between them is generally considered to rely on the molecular structure, according to the well-known packing parameter relationship. However, this model fails to describe many experimental facts.

Here we show the self-assembly properties of four COOH-containing glycolipids (Figure 1), biobased compounds produced by microbial fermentation of biomass and at which the surfactant industry is looking with interest due to their good biodegradability and low aquatic toxicity. All of them form micelles at basic pH but each one assembles into different structures below pH 7: micelles and twisted ribbons are respectively observed for monounsaturated and saturated sophorolipids (glucose beta1,2 disaccharide as hydrophilic headgroup) while vesicles and infinite sheets are respectively observed for monounsaturated and saturated glucolipids (glucose alone as hydrophilic headgroup). The use of pH-resolved in-situ SAXS (Figure 1) shows that the morphological variations and the pH-driven mechanism of formation only partially relies on the packing parameter but also on melting temperature of the lipophilic region, COOH/COO- ratio, hydration of the sugar headgroup, bilayer membrane flexibility just to cite some.



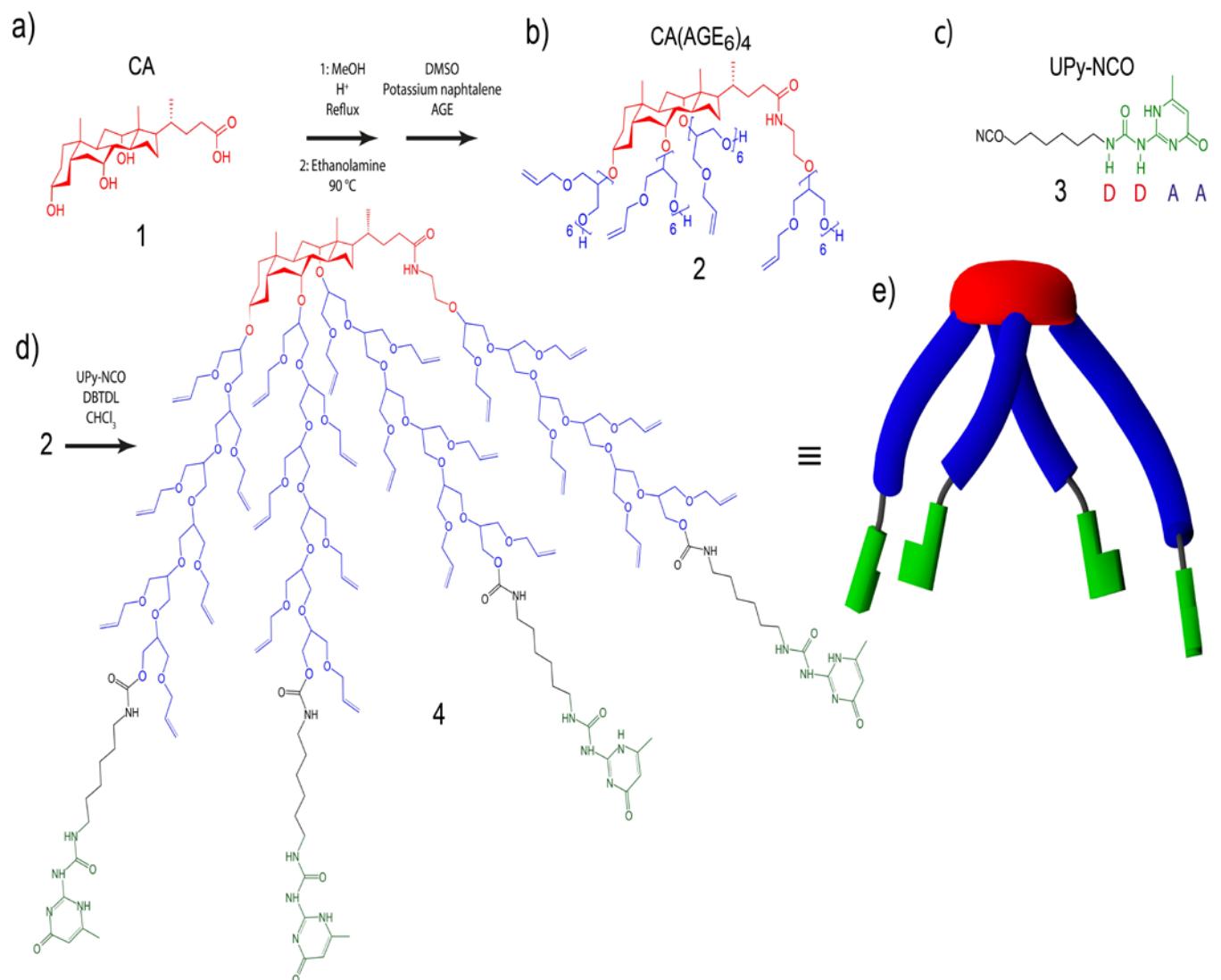
Microbial glycolipids studied in this work using in-situ SAXS

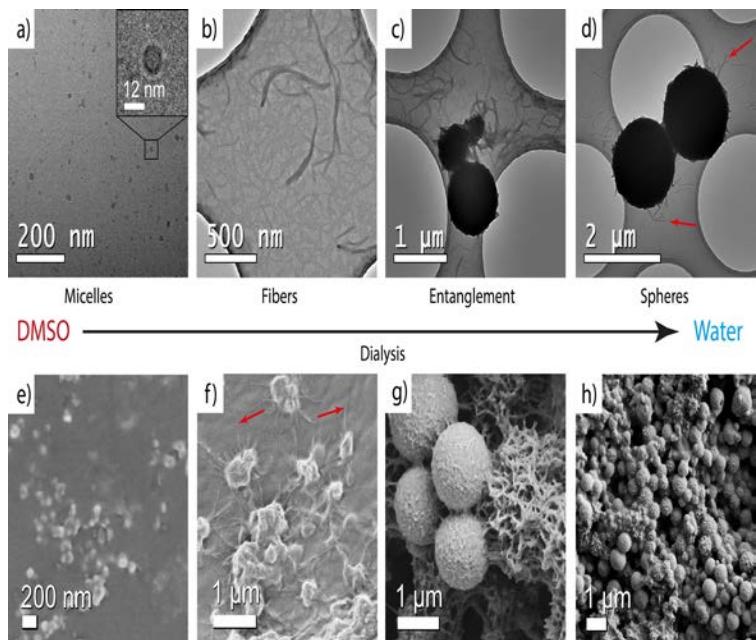
COLL 820

Hydrogen bonding asymmetric star-shape derivative of bile acid leads to supramolecular fibrillar aggregates that wrap into micrometer spheres

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We report that star-shaped molecules with cholic acid cores asymmetrically grafted by low molecular weight polymers with hydrogen bonding end-groups undergo aggregation to nanofibers, which subsequently wrap into micrometer spherical aggregates with low density cores. Therein the facially amphiphilic cholic acid (CA) is functionalized by four flexible allyl glycidyl ether (AGE) side chains, which are terminated with hydrogen bonding 2-ureido-4[1H]pyrimidinone (UPy) end-groups as connected by hexyl spacers, denoted as CA(AGE₆-C₆H₁₂-UPy)₄. This wedge-shaped molecule is expected to allow a rich variety of solvent-dependent structures due to the complex interplay of interactions, enabled by its polar/nonpolar surface-active structure, hydrophobicity of the CA in aqueous medium, and possibility to control hydrogen bondings between UPy's by solvent selection. In DMSO, the surfactant-like CA(AGE₆-C₆H₁₂-UPy)₄ self-assembles in nanometer scale micelles, as expected due to its nonpolar CA apexes, solubilized AGE₆-C₆H₁₂-UPy chains, and suppressed mutual hydrogen bonds between the UPy's. Dialysis to water leads to nanofibers with lateral dimension of 20-50 nm. This is explained by promoted aggregation as the hydrogen bonds between UPy's start to become activated, the reduced solvent dispersibility of the AGE-chains, and hydrophobicity of CA. Finally, in pure water the nanofibers wrap into micrometer spheres having low density cores.





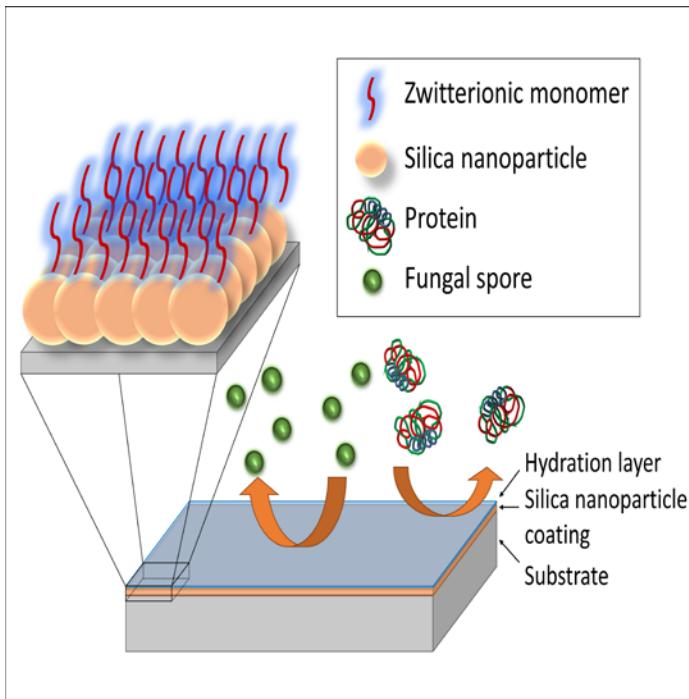
COLL 821

Self-assembly of zwitterionic sulfobetaine siloxane onto silica nanoparticles for application as a versatile antifouling coating system

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The growing need to develop surfaces able to effectively resist biological fouling has resulted in the widespread investigation of nanomaterials with potential antifouling properties. The ability of colloids and nanoparticles to be functionalised with a range of polymer chemistries is allowing the tuning of surface properties with fine control over the presentation of chemistries at the material interface. Here, we report the functionalisation of silica nanoparticles with a zwitterionic silanated sulfobetaine monomer for the preparation of hydrophilic low fouling coatings. Quartz crystal microgravimetry with dissipation monitoring (QCM-D) is presented as a new method through which to optimise self-assembly of sulfobetaine onto silica nanoparticles deposited as thin films, as a model towards solution based nanoparticle functionalisation. Functionalisation of nanoparticle films occurs rapidly and could be achieved over a wide pH range and at low zwitterion concentrations. Similarly, functionalisation of silica nanoparticle suspensions could be achieved under aqueous conditions with moderate grafting densities. Zwitteriated particles were used to prepare hydrophilic coatings via a simple spin-coating process. All functionalised particle surfaces presented a high degree of wettability and resulted in large reductions in adsorption of bovine serum albumin (BSA) protein. Prepared particle surfaces also showed a reduction in adhesion of fungal spores (*Epicoccum nigrum*) by up to 87%.

These results indicate the potential for functionalised nanosilicas to be further developed as versatile fouling resistant coatings that are highly scalable, able to be deposited using a range of coating techniques (e.g. spray coating, inject printing), and are suitable for use in diverse applications including biomedical and aquatic based industries.



Schematic of a hydrated silica nanoparticle coating presenting antifouling properties, prepared through functionalisation of nanoparticles with zwitterionic silanated sulfobetaine.

COLL 822

Self-assembled protein vesicles made from recombinant fusion proteins

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Protein vesicles incorporating functional, globular proteins have enormous potential in a number of bio-applications such as drug delivery systems, micro bioreactors, and mimicking artificial cells. We have designed globule-zipper-polypeptide protein complexes (mCherry-Z_E/Z_R-ELP), consisting of a model fluorescent globular protein (mCherry), high affinity leucine zipper pair (Z_E/Z_R), and thermo-responsive elastin-like polypeptide (ELP). These complexes self-assemble into vesicles under warming. In order to propose rational guidelines to engineer the protein vesicles, we have traced the phase transition of the recombinant fusion proteins as a function of concentration and temperature using characterization methods including dynamic light scattering, transmission electron microscopy and small angle neutron scattering. The fusion protein

complexes at a constant concentration undergo the phase transition from soluble monomers, through dynamic coacervates, to stable hollow vesicles as operating temperature (T_o) increases over transition temperature (T_t). Since the T_t is decreased with increasing protein concentration, diverse self-assembled structures from spherical particles to vesicles form with the increased average sizes as protein concentration increases at the same T_o . Also, the protein complexes can self-assemble into either single-layered or bi-layered vesicles according to the hydrophobic conformation of ELP domain. The phase diagram of mCherry-Z_E/Z_R-ELP complexes established in this study reveals the effect of difference in the T_o and T_t on the self-assembled protein vesicle size and structures, which provide a simple design rule to engineer the functional, globular domain-containing protein vesicles with desired size and structure for target applications. Functional demonstration of the design rule was applied to ScFvF5-Z_E/Z_R-ELP to create nanoscale vesicles that target HER2+ breast cancer cells.

COLL 823

Novel readily biodegradable disulfonate surfactants

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Alkylated diphenyl oxide disulfonate (ADPODS) surfactants, which are commercially available under Dow's trade name of DOWFAX™, are an important group of surfactants that are particularly useful for emulsion polymerizations and various other applications where harsh conditions, like high electrolyte concentration, strong acid or alkaline, or oxidizers such as sodium hypochlorite bleach, are present. To provide industries and consumers with an additional surfactant option that can deliver the desired performance features while minimizing the environmental impact, a new disulfonate based surfactant chemistry has been developed. These unique anionic surfactants are derived from 1,3-dichloro-2-propyl ethers, which are prepared by reacting 1,3-dichloro-2-propanol with a linear α -olefins under acidic conditions. Strecker sulfonation of the dichloroethers generates the disulfonates. A broad range (butene to octadecene) of α -olefins can be used to generate the intermediate dicloroethers, which allows a broad range of properties for corresponding disulfonate surfactants. The C₁₀ to C₁₆ analogues demonstrated good surface activity, effectively reducing surface tension to about 30 mN/m, providing good wetting to low energy surfaces, and generating moderately high and stable foam; great cleaning performance; and effectiveness in the emulsion polymerization of styrene-butadiene copolymers. The solubility of these new disulfonate surfactants in electrolyte solutions and the stability of sodium hypochlorite bleach were proven to be superior to conventional anionic surfactants and comparable with ADPODS surfactants. Following OECD 301F testing guidelines, the C₁₂ and C₁₄ surfactant samples were established to be readily biodegradable. The main components of the C₁₂ surfactant were shown practically non-toxic in the aquatic toxicity tests following the OECD guidelines. These results suggest that the new disulfonate

surfactants could be environment-friendly high performance anionic surfactants that are potentially useful in multiple applications.

COLL 824

Novel liposome-based Surface Enhanced Raman spectroscopy (SERS) substrate

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Single-molecule Surface-Enhanced Raman Spectroscopy (SERS) has traditionally relied on inserting probe molecules into highly enhancing “hot spots” (<10nm gap junctions) between gold and/or silver particles. Although this strategy leads to single molecule detection, the interactions between the probe molecule and enhancing medium often results in denaturation and inactivation of the probe molecule. To address this issue, we have constructed novel SERS substrates containing liposomes, which offer an ideal scaffold since encapsulated probe molecules retain biological and chemical activity. We present single nanoparticle SERS studies of a new construct in which probe molecules are encapsulated into surface-tethered liposomes that are conjugated to gold nanostars. The gold surface and gold nanostars offer enhancement capable of single molecule detection, while the core of the liposome provides an adjustable aqueous environment.

COLL 825

Block copolymer templated mono- and bimetallic catalysts for fuel cell electrocatalysis

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The invention of the proton exchange membrane fuel cell (PEMFC) occurred over a half-century ago and, in spite of extensive developments of its science and its components, its widespread commercialization remains a challenge. Currently, improvements in the durability, performance and manufacturing cost of PEMFCs are required – all of which can be addressed with advances in catalyst function. Platinum (Pt) for example has long been the default anodic and cathodic fuel cell catalyst, which makes resulting fuel cell devices less efficient due to Pt poisoning and slow kinetics for the oxygen reduction reaction (ORR). Recent work in our laboratories has shown that a block copolymer template-directed synthesis of mono- and bimetallic nanoparticle catalysts is an attractive method for preparing and studying high performance fuel cell catalysts. The content of this presentation will describe our investigation of the underlying principles for prescribing the size, spacing and composition of nanocatalysts that can be isolated from self-assembled block copolymers loaded with metallic anions.

The approach offers several advantageous synthetic features compared to solvothermal catalyst synthesis. The approach is highly flexible and allows for the preparation and screening of a variety of mono- and bimetallic catalysts particles (Pt/Au, Pt/Ir, Pt/Cu, etc.). The method allows for the fine-tuning of the catalyst activity by selection of the block copolymer template precursor. The equivalent exercise of isolating and refining catalysts by solvothermal or other techniques often requires a vigilant redesign of the experimental conditions (ligands, solvents, temperature, pressure, new metal salt precursors, etc.) that control the growth and reduction kinetics of the reagents that create the nanocatalysts. Accordingly, the electrocatalytic activity of block copolymer template-directed bimetallic catalysts is presented. Details for the methanol and formic acid oxidation reactions and tolerance to catalyst poisoning are discussed. Preliminary details on a structure–activity relationship between nanocatalysts and their self-assembled block copolymer templates are also presented.

COLL 826

Initial growth of Au nanostructures on TiO₂(110)-1x1 surface at elevated temperature

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Catalytic properties exhibited strong dependence on size and thickness of Au nano clusters dispersed on TiO₂(110) surface. Understanding the growth mechanism of the support nanostructures are important in both of fundamental science and industrial applications. It has been early reported that the Au clusters grow as quasi-2D clusters with one to two atomic layers in thickness aligned over 5C-Ti rows. It has also been reported that the missing oxygen vacancies on clean TiO₂ surfaces can be filled in short time by hydroxyl groups dissociated from residual water in UHV. Therefore, it is likely that there are fewer missing O vacancies on the TiO₂(110) during deposition of Au at RT. In this study, Scanning Tunneling Microscope (STM) , X-ray Photoemission Spectroscopy and low-energy ion scattering spectroscopy are used to study the initial growth of Au atoms on TiO₂(110) surface at elevated temperature of 600K at which water does not adsorb and O-vacancies present. In contrast to the early report, STM shows that Au deposition resulted in monomer-like features sitting on oxygen rows at ~600K, further deposition resulted 2D sheets growth restricted along O-rows with single atomic thickness. These observations indicate that missing oxygen vacancies play a role in initial growth of Au adatoms. Details will be presented.

COLL 827

Polymer-like nanowires

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We will discuss ongoing work in our laboratory on the analogies between ensembles of nanoscale crystals and ensembles of polymer molecules. These two classes of materials have been long considered distinct, most fundamentally due to their different growth mechanism and thermodynamics. Recent work shows that, for very thin nanowires, the analogies might extend beyond the mere aspect ratio.

One-dimensional nanostructures of Bi_2S_3 were found to grow with a kinetics resembling that of step-growth polymerization, but without termination and chain transfer processes: essentially a conventional “addition” process by which precursors would add to the growing tips of the nanowires and a “coupling” process by which the fully formed nanowires could couple together end-to-end.

Furthermore, these nanowire appear to display a conformation describable as a worm-like chain of remarkably small persistence length (17 nm).

Work since then has focused on (i) eliminating the traditional addition process to observe and characterize a completely non-classical growth process, preferably as a function of temperature and nanowire concentration, and on (ii) characterizing the dynamics of the nanowires to elucidate whether they possess conformational dynamics (and, therefore, conformational entropy) comparable to those of polymer molecules.

COLL 828

Functional and structural characterization of multi-functional gold nanoparticles

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We show a simple method to characterize the structure and function of gold nanoparticle carrying different functionalization groups on their surfaces. By combining size separation with online size measurements and centrifugal particle sedimentation measurements we could determine the mass and density of the functionalization layer at various ratios of functional groups bound to gold nanoparticles. We controlled the functionalization of the nanoparticles surfaces by checking their capabilities of binding human serum albumin. This method provides much-needed experimental information on the properties of multifunctional gold nanoparticles and on their behavior in biological systems.

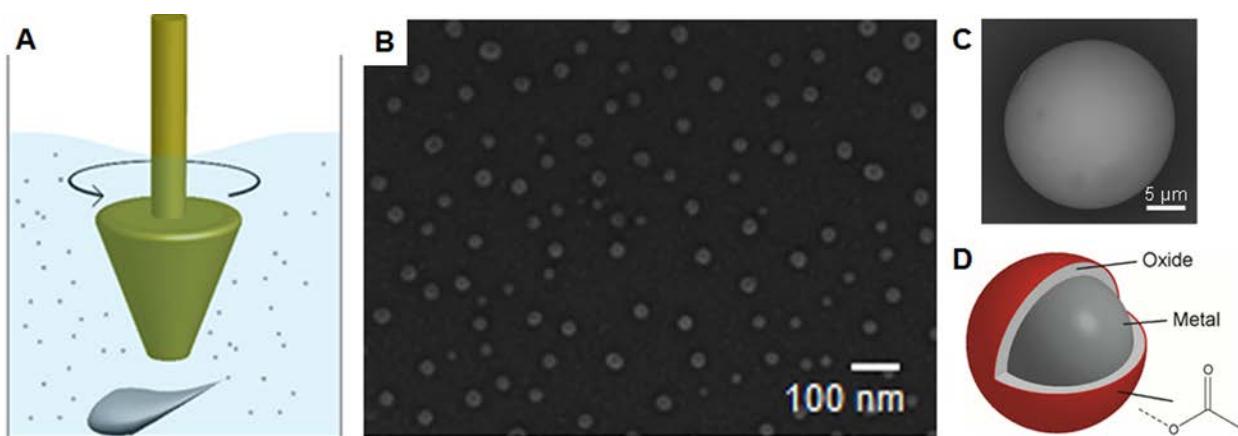
COLL 829

Frugal innovation: Synthesis and applications of undercooled metal particles

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Synthesis of colloidal metal particles is well studied, but little has been attained in the use of affordable approaches to attain quasi-stable states in good yields. The use of SLICE, an extension of droplet emulsion technique, to produce core-shell particles, of

structure; metal@oxide/acetate, from molten or liquid metal alloys is discussed. For molten metals, the produced particles are stable against solidification at ambient conditions leading to undercooling in >90 % yield. Besides synthesis, we report the use of these under-cooled metal particles for heat free soldering and manufacturing at ambient conditions. Our approach is based on gentle etching and/or fracturing of outer layers of the particles, through chemical or mechanical stress, initiating a cascade entailing fluid flow with concomitant deformation, combination/alloying, shaping, and, solidification. This facile and low cost technique for welding or fabrication allows for access to complex shapes at the meso- and micro-scale, and fabrication and/or joining at ambient conditions without heat, skilled manpower, advanced instrumentation, or, complicated sample preparation procedures.



COLL 830

Salt-induced color change and assembly of gold nanoparticles confined in a polymer brush matrix

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Polymer chains that are end-grafted to the substrate (polymer brushes) have been studied extensively throughout the last few decades. Using stimuli-responsive polymers makes the grafted polymers attractive candidates for sensor applications, as the surface-grafted brushes can be employed as templates for the immobilization of gold nanoparticles (AuNPs). Due to surface plasmon resonance of the AuNPs, the brush/particle hybrids exhibit interesting optical properties with potential applications in colorimetric sensing. In this work, citrate-coated AuNPs are embedded into surface-grafted poly(N-isopropylacrylamide) (PNIPAM) brushes. Previous research has shown that color variations of PNIPAM/AuNP can be induced by changing the temperature, which is attributed to the coil-to-globule transition of PNIPAM in water at ~32°C. However, it is unclear how salinity would affect the structure and color of PNIPAM/AuNP. This is an important aspect, because salt is ubiquitous in nature. We

aim to get a better under the effect of salinity on the assembly of AuNPs in surface-grafted PNIPAM brushes, and the color change associated with different types of salts. UV/vis spectroscopy, scanning force microscopy, and neutron reflectometry are employed to study the assembly and color change of AuNPs in PNIPAM brushes in presence of NaF, NaCl, NaBr and KCl. We find that the particle assembly and the salt-induced color change are ion-specific, and conclude that salinity is a key factor regarding technical applications of PNIPAM/AuNP sensor materials.

COLL 831

Chemical identity of surfactants control the electronic behaviors of the metallic core in gold nanoparticles

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Using conduction electron spin resonance (CESR) we demonstrate that the electronic properties of gold nanoparticles respond to changes in the chemical identity of thiolates bound to the surface of the particles. In particular, we demonstrate that both aromatic and aliphatic ligands can be used to control the Fermi Level of the metallic core of the particles. This is true, even for very subtle changes in ligand, such as the elongation of straightchain alkanethiolates.

COLL 832

Assessment of the physical stability of metal and metal oxide films for enhanced signal detection in colorimetric bioassays

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In this study, we characterize the planar surfaces of hybrid systems in every step of the bioassay process in an effort to demonstrate the significance of stability of nanofilms on the performance of bioassays; magnitude of enzymatic signal. In that regard, detection of a model protein, i.e., b-BSA bioassay was carried out on three different hybrid platforms; (1) poly(methyl methacrylate) (PMMA), was chemically modified before introducing silver thin films of thicknesses; 1 nm, 5 nm and 10 nm, (2) paper functionalized with silver nanowires (SNW), and (3) indium tin oxide (ITO) on terephthalate (PET). Bioassays for b-BSA in buffer was performed using microwave heating (MW) and at room temperature (RT, a control experiment). To assess the extent of the loss of either silver or ITO, scanning electron microscopy (SEM) and optical spectroscopy were done on the surfaces and measured the absorbance of the enzymatic product. PMMA platform exhibited significant loss of STFs (5 nm > 1 nm > 10 nm) from its surface while the amounts of ITO on PET at the end of the experiment were almost the same as those at the beginning of the experiment. Control experiments

(i.,e RT) witnessed a significant loss of STFs relative to those completed under MW heating. PMMA + 10 nm STFs and paper + SNW showed lowest level of detection (LLOD) for b-BSA, i.e., 10-10 M while ITO displayed LLOD of 10-11 M. These results show that hybrid platforms that display physical stability can be used as assay platforms and they can improve LLOD by 10 fold.

COLL 833

Size and shape dissolution of silver nanoparticles

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Silver nanoparticles are one of the most widely used commercial nanomaterials. Their dissolution into silver ions makes them potent antimicrobial agents well suited for incorporation into coatings on products such as washing machines and children's toys. In these applications silver ions are continually produced whether or not there is a need for disinfection. It would be far more efficient to tailor dissolution such that there is only silver ion release when there is contamination. Such control may also help to mitigate the unintended impact of these materials on natural environmental systems. Both goals require a quantitative understanding of silver nanoparticle dissolution. Towards this end we have developed synthetic methodologies that can produce libraries of uniform silver nanoparticles with various shapes, dimensions and surface chemistry. Studies of both the dissolution rate and equilibrium silver ion concentration, or solubility, helped clarify the importance of each parameter. We found a striking shape dependence to the dissolution rate of silver nanoparticles: high aspect ratio particles can have solubilities and dissolution rates up to an order of magnitude larger than spherical materials. Also, silver dissolution can proceed rapidly even when nanocrystals are coated with polymers; however, the surface coverage and polymer type influences both the rate and nanocrystal solubility. In agreement with prior work, we found that across a wide range of diameters, shapes and surfaces that the antimicrobial activity of these materials correlated with the equilibrium concentration of silver ions in a suspension and not with the concentration of total silver or nanocrystals. These results are not only fundamentally interesting, but also of practical importance to the safe and efficient application of silver nanoparticles.

COLL 834

Hidden electrostatic asymmetry of gold nanorods

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Gold Nanorods (AuNRs) are presumed to be centrosymmetric due to nearly cylindrical shapes of gold cores. Surface charge density of nanoparticles, however, may not equate with geometrical symmetry of the metallic core of the nanocolloids. Although non-linear optical (NLO) property such as second harmonic generation (SHG) is forbidden for centrosymmetric metal nanoparticles, many studies show that single AuNRs can also have SHG. Together with their linear properties, NLO properties of them were also reported and appeared as promising field for photonic applications. The defects and small deviations from the symmetric shape as well as from broken symmetry at interfaces have been adduced as the reason. Here, we have shown the fact that AuNRs have distinct asymmetric surface charge density, which needs to be known for adequate description of their optical properties. Electron microscopy, Kelvin probe force microscopy, and computational modeling data indicate that this anisotropy of electrostatic potential is associated with unequal distribution of cetyltrimethylammonium bromide capping ligand at the ends of AuNRs. Removal of excess of capping ligand on one of the ends by electron beam ablation leads to disappearance of asymmetry in plasmon resonance map taken by electron energy loss spectroscopy technique, which previously attributed to local environment. More importantly, we found that the charge polarization asymmetry in AuNRs is essential to have a strong SHG by comparison of optical response from two different composites with nearly isotropic and anisotropic AuNRs. This work explains previously baffling NLO response and will aid in interpretation of other various properties of metal nanostructures.

COLL 835

Comparative roles of Zr(IV) and Ni(II) hetero-metal substituted polyoxometalates in oxidation solutions

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The utilization of Wells-Dawson hetero-metal substituted polyoxometalates (POMs) in aqueous decontamination solutions against organic CWA simulants are described. The decomposition of an organophosphate contaminant with a catalytic solution of Zr(IV) substituted Wells-Dawson POM has been evaluated and compared with a Ni(II) substituted Well-Dawson POM solution. The evaluation was performed to understand the reaction mechanism and active catalytic species present in the solutions. Aqueous catalytic solutions were applied directly to the organophosphate contaminant and left to react without the utilization of a phase transfer agent. Analysis of the reaction

byproducts was performed with GC-MS and concentrations were determined via an internal standard method. Analysis of the catalytic species in solution was performed via ^{31}P -NMR, FTIR, and Raman spectroscopies. The structural flexibility from the sandwich type Zr(IV) hetero-metal substituted POM resulted in greater reactivity when compared to Ni(II) substituted POM. Mechanistic implications of these findings are discussed.

COLL 836

Multi-stage transformation and lattice fluctuation at AgCl-Ag nanoparticle interface

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The mechanical dynamics resulted from transformation reactions in solid state have an origin of the interface and volume change of grains down to atomic scale.

Understanding how structural evolution and mechanics are related in this scale is of fundamental interest but they are often difficult to trace. In this work, we use *in-situ* transmission electron microscopy (TEM) to directly study the reduction transformation at AgCl-Ag nanoparticle interface. Three stages of AgCl lattice fluctuation: steady state, compression, and relaxation, are identified by Fourier Transform and are correlated to the structural evolution. A quasi-layered growth to both vertical and lateral directions is observed during steady state of AgCl lattices whereas their kinetics differ by two orders. Real-time imaging shows that nucleation and growth of silver at the interface happens simultaneously. We show that the development of planar defects is associated with lattice compression. Depletion of AgCl origins from the interfacial region and is associated with lattice relaxation of AgCl. Grain rotation and temperature effects on lattice fluctuation are found insignificant by TEM simulation and dynamic range analyses. To understand why positive strain and AgCl depletion does not commence in the first two stages, we trace the topography and structure of decomposing AgCl nanoparticles by *in-situ* scanning transmission electron microscopy (STEM). Silver species are suggested to originate from both surface and interior of the crystal, and then transport to the interface. Such mass transport may have enabled the steady state and compression of lattice in this volume-shrinking shear transformation.

COLL 837

Novel sol-gel derived TiO₂-SiO₂ particle systems for direct ink writing compositionally tailored GRIN glasses

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Conventional diffusion-based production methods for gradient-index (GRIN) optics limit their final size to a few mm in diameter and only allow for monotonic radial gradients—limiting their use in many applications. Direct ink write (DIW) 3D printing provides a revolutionary approach to design functionally graded materials, such as GRIN optics. By blending two inks with different compositions within the printing nozzle, one can readily print a compositionally graded low density monolith, or green body. Then, using traditional ceramic processing, the resulting green body can be dried and sintered into a fully dense GRIN optic with a custom tailored refractive index profile. This presentation focuses on the development and characterization of novel, sol-gel derived TiO₂-SiO₂ particle formulations for use in DIW inks. Initial results show that we can use these inks to reliably fabricate uniform-composition, transparent, TiO₂-SiO₂ glass monoliths with varying weight percent of TiO₂. Ongoing efforts to blend the inks to achieve a GRIN optic are also described. Additionally, the role of particle morphology and chemistry are discussed as they relate to the benefits and challenges in preparing a transparent glass optic by this method.

COLL 838

New algorithm to model quantum growth dot dynamics

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The photophysical properties and applications of semiconducting quantum dots (QDs) remains an active and growing area of research. The development of new QDs made of novel materials and of various core/shell structures has been fervently pursued over that past twenty years, while an understanding of the mechanisms responsible for their properties, specifically their colloidal growth and formation, has lagged behind. A widely studied class of QDs is cadmium selenide (CdSe). CdSe QDs have generated remarkable interest in the past decade because of their applications in biological fluorescence imaging, medical imaging, quantum dot solar cells, quantum dot lasers, and even military tracking devices. Reaction schemes have been developed to synthesize CdSe QDs of many different shapes such as rods, tetrapods, teardrops, arrows, and spheres. However, despite all of these advances, the growth dynamics for CdSe QDs are still largely unknown. Here, we present a novel semi-empirical atomistic QD growth model (algorithm) for CdSe QDs in which reaction parameters can be adjusted (such as temperature, pressure, growth solution components, precursor oxidation state, etc.) independently from one another. This approach can be used to systematically test synthetic schemes to provide growth statistics. These growth statistics can then be tested experimentally using an in situ technique to provide insight into the accuracies of the modeling program. Modeling aspects, including the use of

charge equilibration techniques, as well as the effect of surface chemistries and QD symmetry, provide atomistic insight into the parameters most relevant to quantum dot growth. Using experimentally realized CdSe QD "magic sizes" as a basis for comparison, this new model provides new insight at a fraction of the computational cost of traditional ab initio or DFT approaches.

COLL 839

Damping of quantum dot acoustic phonons by chalcogenide surface ligands

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Ultrafast transient absorption spectroscopy is commonly used to investigate quantum dot (QD) excited state dynamics, but also has the capability to provide insights about the photoacoustics of exciton-phonon interactions. This presentation will describe a study of the effect of quantum dot ligand identity on phonon behavior using transient absorption spectroscopy. The transient absorption (TA) signals of colloidal cadmium chalcogenide QDs are modulated at the longitudinal acoustic (LA) and longitudinal optical (LO) phonon frequencies when the QD surface is passivated with native, aliphatic ligands. Upon ligand modification to shorter chalcogenide ligands, the TA signal is only modulated at the LO frequency. These results suggest that the LA phonon, the radial breathing mode of the QD, is damped when chalcogenide ligands passivate the QD surface. The chalcogenide ligand interface between the QD and its environment, which has previously been shown to enhance electron transfer, therefore also enhances mechanical energy transfer.

COLL 840

Microfluidic discovery platform: Toward nanoparticle functionalization through closed loop optimization

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Functionalization of nanoparticles to control physiochemical characteristics of the surface is the major challenge inhibiting transition of many nano-technologies, from optoelectronics to multifunctional composites, specialty coatings and electronics fabricated with nanoinks. The optimal interface reflects a complex interrelationship

between NP surroundings and the architecture of the functional canopy, which to date has been unraveled sequentially and through slow conventional experiments. Herein, we address this challenge via Microfluidic Discovery Platform (MDP). MDP borrows from “lab-on-a-chip” concepts to enable precise, computer control of reagents addition, sequential reactions, complex inline characterization (UV-Vis, SAXS), purification and product-separation on a low cost, custom printed fluidic platform. To demonstrate the efficacy of the MDP design, we demonstrate facet-specific diazonium functionalization of plasmonic nanorods. Diazonium coupling to form strong Au-C bonds replaces conventional weak Au-S coupling to provide enhanced thermal stability for processing, as well as new avenues to manipulate optoelectronic and plasmonic properties. However, current attempts indicate that the reaction is highly sensitive to time, temperature and reagent addition, which challenges batch-to-batch quality. We optimize MDP via fluid modeling and prototype fabrication with additive manufacturing and integrate it with spectroscopy to demonstrate in-line reaction optimization. Our approach will provide a basis to develop versatile and optically active nanomaterials such as compositionally graded ligand or plate-ring architectures, that would be exceedingly difficult in flask-based chemistry.

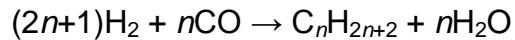
COLL 841

First steps in the Fischer-Tropsch reaction catalyzed by ultra-small ruthenium nanoparticles: A DFT study

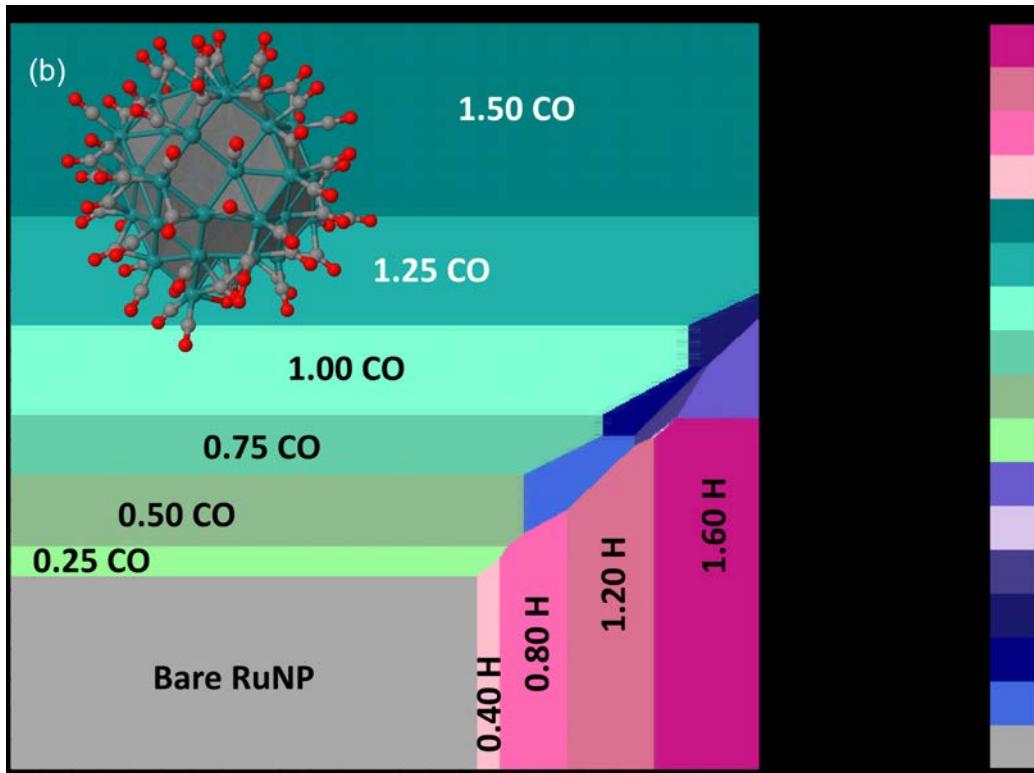
Lucy Cusinato², Luis M. M. Martínez-Prieto¹, Bruno Chaudret², Iker Del Rosa², Romuald Poteau³, romuald.poteau@univ-tlse3.fr. (1) Laboratoire de Physique et Chimie des Nano-objets, Institut National des Sciences Appliquées, Toulouse, Midi-Pyrénées, France (2) LPCNO, Toulouse, France (3) LPCNO @ IRSAMC (INSA, UPS, CNRS), Université de Toulouse, Toulouse Cedex, France

Provided that understanding at the atomic level reactive processes that occur on their surface allows the fine-tuning of nanocatalysts, first-principle calculations and simple models can guide their conception, both in terms of activity and selectivity, although it remains challenging.

As a paradigm of this complexity, we will consider ruthenium nanoparticles (RuNPs)-catalyzed Fischer-Tropsch synthesis (FTS), a catalytic process that converts a mixture of carbon monoxide and dihydrogen in the gas phase into mainly linear hydrocarbons and water:



A relevant computational approach requires considering an appropriate molecular model, in terms of structure and surface composition. Based both on ab initio thermodynamics results and on experimental titration and characterization, we will first give insights on the H and CO co-adsorption for an extended range of pressures and temperatures. The mechanistic consequences of this study on the very first steps of the FTS will be discussed, and supported by multi-step reaction studies.



H/CO co-adsorption free adsorption energy $\Delta_{\text{ads}}G(P_{\text{CO}}, P_{\text{H}_2})$ at 450K

COLL 842

Magnetic nanoparticles as contrast agents for reservoir imaging

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Magnetic nanoparticles have been extensively studied in the past decade as contrast agents for magnetic resonance imaging (MRI) and other biomedical applications. The novel use of magnetic nanoparticles in the oil industry as contrast agents in electromagnetic tomography, a reservoir imaging technique, offers an intriguing opportunity, but at the same time it is very challenging. This is due to the fact that the characteristic travel distance and residence time for those particles in the reservoirs are orders-of-magnitude greater than those in biological systems, and because reservoirs generally have much harsher conditions, such as high temperature, pressure, and salinity.

In the present work, we report the synthesis and characterization of core-shell magnetic

nanoparticles (CSMNPs) with high colloidal stability that can withstand the harsh reservoir conditions. The magnetic nanocores were dressed with organophilic and hydrophilic shells in order to solubilize them in oil and water, respectively. Specifically, the shells are sought to counterbalance the strong attractive magnetic interactions between the magnetic nanocores, and hence preventing the CSMNPs from agglomerating.

COLL 843

Characterization of nanoparticle interactions and thin film properties using MP-SPR

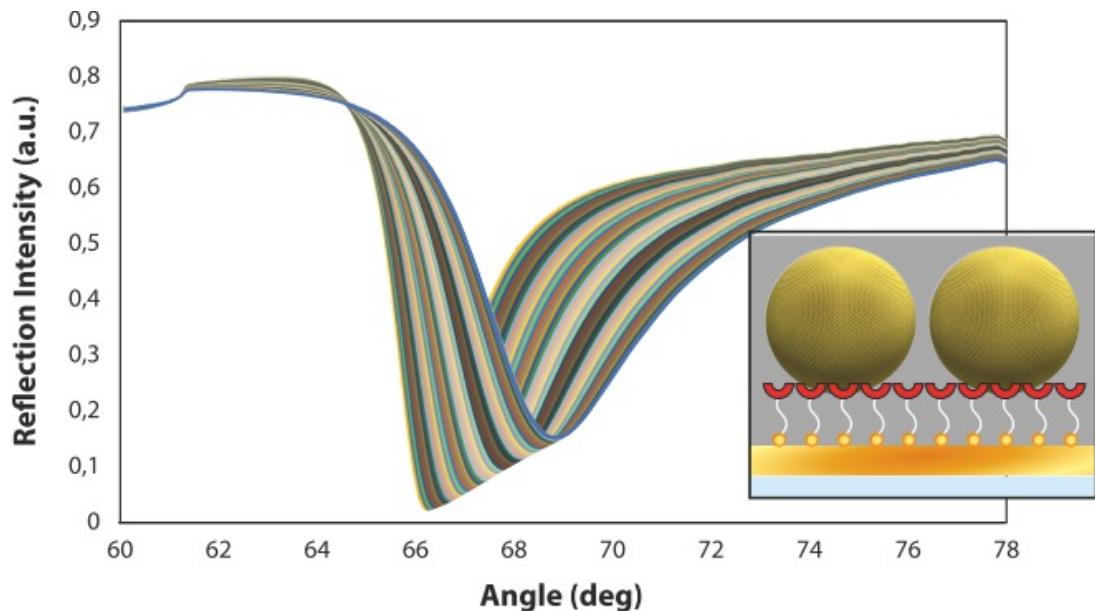
Niko Granqvist, **AnniKa Jokinen**, annika.jokinen@bionavis.com, Johana Kuncova-Kallio, Janusz W. Sadowski. BioNavis Ltd, Tampere , Finland

Surface Plasmon Resonance (SPR) is a popular method to measure molecular interactions, such as drug and protein affinity and binding kinetics in real-time and label-free. Multi-Parametric Surface Plasmon Resonance (MP-SPR) extends applicability of SPR from molecular interaction measurements to more fundamental studies of nanoparticle interactions, and materials characterization.

The MP-SPR instruments can perform measurements in a wide angular range and can record SPR curves at more than one wavelength, characterizing nanoscale films for both thickness and refractive index. *In situ* deposited polyelectrolyte multilayer, consisting of polystyrenesulfonate and polyallylaminehydrochloride (PSS:PAH), and CVD grown graphene layer were characterized using MP-SPR. Conformation of deposited lipid bilayers and vesicle layers were confirmed using thickness and refractive index information.

100% serum sample interaction and corona formation on liposome surface was studied using MP-SPR. The mass of adsorbed molecules on the polymer surface and the best antifouling surface was determined. Recently the mean size of bound nanoparticles was determined using the technology.

The MP-SPR method has shown good correlation with reference methods used in the studies such as quartz crystal microbalance (QCM), atomic force microscopy (AFM) and Raman, and with previous literature values for similar systems. High sensitivity of the method enables characterization of layers down to subnanometer thickness. As an non-invasive method without need for measurements in vacuum, MP-SPR is proven to be a fast and effective tool for characterization of nanoparticle interactions and nanoscale thin films in air and in liquid.



Binding of gold nanoparticles to a self-assembly monolayer was measured in real-time to reveal binding kinetics (*Vikholm-Lundin 2016*)

COLL 844

Controlled nanoparticle morphology transitions induced by high-pressure ice-segregation

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We present a method for controlling changes in particle morphology during ice segregation induced molecular assembly in gold and silver colloidal suspensions. Acrylate capped spherical silver nanoparticles (NPs) with a size distribution of 14 (+-) 2nm and BSA bioconjugated hexagonal gold NPs of sizes 51 (+-)13 nm were synthesized in aqueous phase and characterized using several techniques including transmission electron microscopy, surface enhanced Raman spectroscopy, electron dispersive spectroscopy, ultraviolet-visible spectroscopy, and X-ray diffraction. The colloids were then subjected to a process of directional solidification, performed in a specialized high pressure vessel under liquid nitrogen. Solid NPs were then harvested from the frozen colloids using a low-pressure sublimation chamber and characterized using the same methods mentioned above. The results show that we were able to modify the original morphologies to produce high numbers of monodispersed pyramidal gold and silver NPs, which is significant as earlier freezing processes tend to produce particles of widely dispersed sizes and shapes.

COLL 845

Inorganic-organic hybrid electrical devices based on nanoparticle arrays for switchable current and spin transport

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The fusion of metals and organics has long been known to produce dramatic electronic effects. In molecular electronics and nanoscale electronics, effects such as valence tautomerism and spin crossover that come from these inorganic-organic “hybrid” systems are diverse and have strong promise for a broad array of applications. However, designing and studying electronic devices is a challenge at the nano- to single-molecule scale, and while complex inorganic compounds can yield promising properties, tuning these results can be a synthetic challenge, and a further challenge exists in utilizing these compounds in electronic device settings.

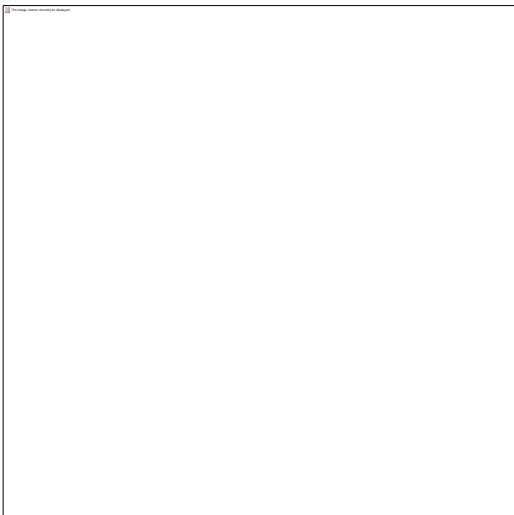
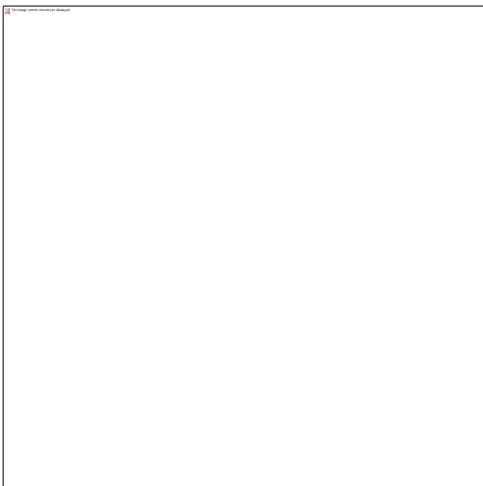
In this talk, we will detail work toward fabricating nanoparticle arrays and studying their current and spin transport. This fundamental test-bed is designed to usurp the synthetic difficulties of inorganic compounds, allowing for both nanoparticle and ligand to be altered *in situ*, thereby providing the opportunity to tune desired output as well as modify device properties in device configuration. First, we will detail the patterning and fabrication processes used to generate the nanoparticle devices. Careful utilization of lithography and self-assembly processes allow for nanoparticles to be patterned between predefined metal electrodes in a device. Then, we will show how changing the nanoparticle ligand overall impacts the transport properties of devices *in situ*. Simple modifications from switching insulating ligands, such as oleic acid, to more conjugated molecules are able to alter resistances of devices as well as observed spin properties, and further opens possibilities for studying more complex molecules. Overall, we will show how this platform allows for basic studies in charge and spin transport across nanoparticle matrices leading toward more advanced phenomena for potential application.

COLL 846

2µm Ultrathin silica shells doped with iron (III) for low threshold of CPS and color doppler ultrasound performance and notable biodegradability

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Silica particles have been developed for biomedical imaging contrast agents due to ease of synthesis and modification. Nevertheless, silica particles are inorganic and may not be fully biodegradable. We developed the ultrathin 2 μ m hollow silica particles doped with Fe (III) that demonstrated significant reduction of ultrasound imaging power. The iron doping provides not only capabilities of varying shell thickness for various applications, but also enhances biodegradability via Transferrin-Fe(III) chelating pathway. The ultrathin silica shells doped with 3 atomic percentage Fe (III), which is a half amount doping of the control thick shells, showing 69% thinner shells, are mechanically weaker so that easier to fracture to release the gas at lower insonation power. The threshold of CPS imaging of ultrathin shells switches down 72% compared with the control thick shells. The first signal in Color Doppler imaging shows up at MI=0.3 while the thick shells show the first signal at MI=1.



COLL 847

Superparamagnetic carrier particles for water purification, resources recovery and substance sensing in fluids

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By controlling size, shape and composition, the magnetic properties of iron oxide based nanoparticles can be controlled. There is a remarkably broad application potential for small particles with novel magnetic effects:

For instance, the particles can be engineered to behave superparamagnetically. They are strong magnets in an external magnetic field, but lose their magnetisation completely, once the field is removed. Thus, switchable magnets can be created. Micron sized composite particles were synthesised from these switchable magnetic nano-building-blocks that act as carrier particles in fluids.

It will be demonstrated how these superparamagnetic nanocomposite microparticles with a nanostructured adsorber on the particles surface act as magnetic scavenger particles to selectively remove and recover phosphate from waste water.

Moreover, a complex particle system consisting of these superparamagnetic nanocomposite microparticles, coated with luminescent metal–organic frameworks is presented. The novel composites combine the properties of both constituents:

superparamagnetism and luminescence. The magnetic properties can be exploited to magnetically collect the particles from dispersions in fluids and, by gathering them at one spot, to augment the luminescence originating from the MOF modification on the particles. The luminescence can be influenced by chemical compounds, e.g., by quenching observed for low concentrations of water. Thus, the new composite systems present an innovative concept of property combination that can be potentially used for the detection of water traces in organic solvents as a magnetically augmentable, luminescent water detector.

COLL 848

Colloidal gold nanorods uptake study on *C. fluminea* filter-feeding bivalve clams: Effect of aspect ratio and surface coating

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Bivalves are column water and sediment filter feeders and can be found in both freshwater and marine habitats. Filter feeders are a sub-group of organisms feed by straining suspended matter and food particles from water, typically by passing the water over a specialized filtering structure. As a result, they are highly susceptible to environmental pollutants such as heavy metals, organic pollutants, ENMs, etc. This

filtration mechanism makes them a good candidate to monitor and investigate a wide variety of contaminants in environmental studies. Prior studies have suggested that *C. fluminea* can uptake and accumulate ENMs based on size. However, none of these studies have investigated the effect of anisotropicity and aspect ratio of ENMs on uptake rate. In this research, uptake of suspended gold nanorods (AuNRs) by *C. fluminea* filter feeding bivalves in an environmentally relevant freshwater microcosm will be studied. AuNRs with aspect ratio of 1,4,8 and 20 coated by CTAB and BSA will be introduced to a microcosm containing *C. fluminea* clam. The overall uptake is determined and evaluated by the whole-body organism burden that will be later normalized by body mass. The uptake per body mass for each set of experiment is determined and its relation to the tested AuNRs dimensional and surface characteristics such as size, aspect ratio, and surface coating is investigated. To measure and quantify the AuNRs partitioning, several samples will be taken at time zero, time points with a specific interval, and at the end of the experiment. Supernatant suspension column, clams (tissue and shells), and glass beads are the media where the samples are taken. Vis-NIR spectroscopy and ICP-MS are the main characterization techniques. Primary results suggest that the size and aspect ratio are the most influential characteristics on uptake of AuNRs by clams. Larger and highly anisotropic AuNRs are uptaken faster compared to smaller and lower aspect ratio AuNRs.

COLL 849

Plasma modified catalytic micromotors

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Nano science and nano technology are the critical disciplines of the present influencing the miniaturization concept in analytical chemistry. The development of autonomous nano and micro motors has seen growing interest due to potential applications in both biomedical and environmental fields. Particular attention has been given to chemically powered catalytic micro-/nanomotors, based on different compositions and structures moving autonomously in the presence of hydrogen peroxide fuel (H_2O_2). The catalytic micro-and nanomotors can be prepared using different methods. Plasma method is one of the advanced methods to prepare micro-, nanomotor systems. This method is a solvent-free (dry), nontoxic and single-step process. In this work, the plasma coating methods were used to obtained a series of micro-, nanomotor systems for miRNA sensor applications. Materials (WO₃, W₅O₁₄ and Fe₃O₄) were modified with different dopant agents using rf rotating plasma under optimized conditions. RF rotating modified materials were coated with Platinum (Pt) by RF Magnetron Sputtering method to obtain a series micro-nanomotors. Characteristic properties of all micromotors were investigated by using SEM-EDS analysis and NIKON Eclipse Optic LV100ND Microscopy. The effect of fuel concentration (H_2O_2) and surfactant (Sodium Dodecyl Sulfate (SDS)) on the speed of micromotors were investigated. Moreover, potential

applications of these motors were explored for the detection of breast cancer as miRNA sensor.

COLL 850

Thermochemistry of MAX and MXene phases

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High temperature oxide melt solution calorimetry using $3\text{Na}_2\text{O} \cdot \text{MoO}_3$ solvent at 802°C was performed for a Ti_3AlC_2 -based MAX phase and its fluoride-etched terminated clay-like MXene. The enthalpies of formation from elements at room temperature are $-527.2 \pm 32 \text{ kJ/mol}$ for MAX and $-2202.1 \pm 5.4 \text{ kJ/mol}$ for corresponding MXene. The surface terminations (O, OH and F) and adsorbed cations (Li and Al) play a major role in the thermodynamic stabilization of MXene.

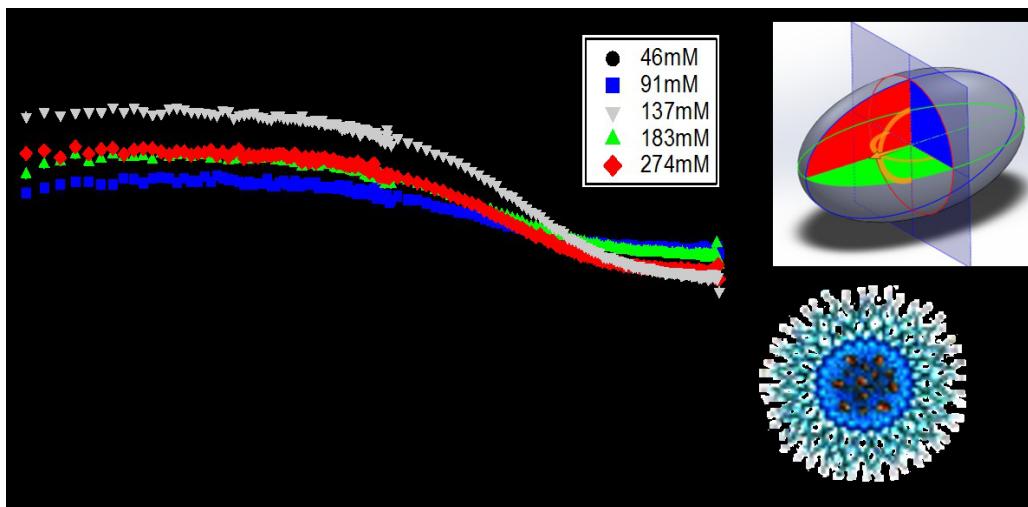
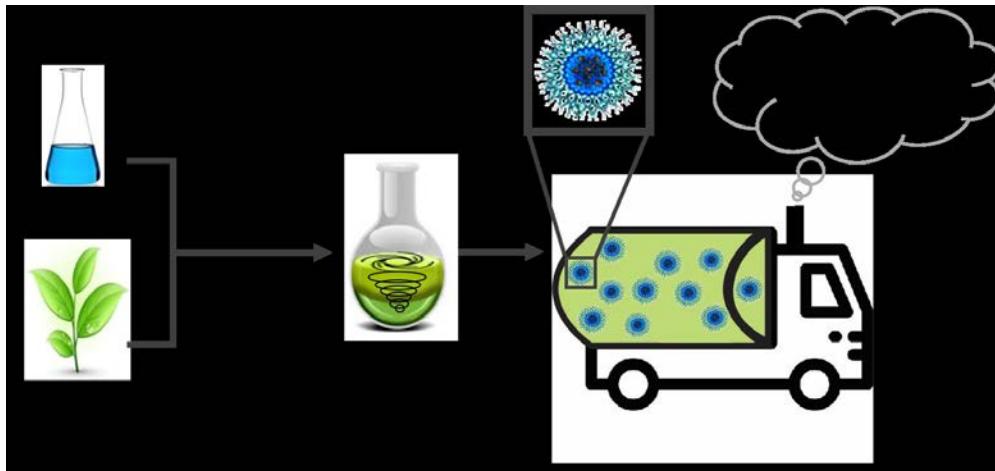
COLL 851

Incorporating oxygenates into diesel fuel systems via stable reverse micelles

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Adding oxygenates such as ethanol and water into ultra-low sulfur diesel (ULSD) can help to meet certain long-term goals in transportation such as superior emission profiles and lower carbon intensities. However, the incorporation of ethanol into diesel can be difficult as typical mixtures have a tendency to separate into two-phase systems that are not conducive to proper combustion and have an increased likelihood for corrosion. We have developed a method for using free fatty acids derived from a range of minimally processed waste streams to stabilize ethanol into ULSD by forming thermodynamically stable fuel emulsion systems that are directly usable as transportation fuels. We describe an analytical framework based on dynamic light scattering (DLS) and small-angle neutron scattering (SANS) that has been used to understand the structure and stability of a model platform for biofuel formulations consisting of ethanol, water, and surfactant in *n*-hexadecanes. We then apply this framework to quantitatively assess surrogate fuel systems consisting of ethanol, ultra-low sulfur diesel, and surfactant resulting from minimal processing of corn oil waste. These surrogate mixtures are shown to be stable over a range of concentrations, temperatures, and water levels. Our understanding of the sizes and shapes of the structures can be used for the

optimization of biofuel formulations that can meet industry standards for stability, cold-flow, and other performance requirements, while improving on the emissions.



COLL 852

Effect of viscosity on the propulsive motion of catalytic Janus motors

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There has been much interest in using catalytic Janus particles to make active motors that can move, carry and deliver cargoes. Many applications of such motors include moving objects through complex environments, including in the body for drug delivery. However, all previous experimental work using synthetic colloidal motors have been reported in water. The first step in understanding more complex environments is to

examine viscosified, but still Newtonian, fluids. Such systems are more easily examined both experimentally and theoretically.

We have experimentally studied the variation of the propulsion velocity of active colloidal particles which catalyze a chemical reaction asymmetrically on their surfaces as a function of solution viscosity. We find that the velocity inversely varies with viscosity with a saturation for higher viscosities. Additionally, the type of viscosifying agent used affects the interaction between fuel molecules and the motor and hence affects propulsion. A diffusion-reaction model has been proposed as an attempt to understand the observed experimental trends. By incorporating the fluid properties of the medium, these studies will be instrumental in understanding the future design considerations of motors swimming in complex environments.

COLL 853

Manipulating single molecular junctions using electrochemical environments

Yaping Zang, *yz3126@columbia.edu*, **Michael S. Inkpen**, **Latha Venkataraman**. APAM, Columbia University, New York, New York, United States

Rational manipulation and measurement of the conductance across single molecule junctions not only provides an ideal window for exploring conductance phenomena at the single molecular level, but also meets the requirement for junction functionality control. Creating different linker groups to the molecule by chemical synthesis is a commonly used method to tune the junction formation and molecular conductance. Here, by utilizing electrochemical gating in the scanning tunneling microscope based break-junction (STM-BJ) technique, we realized a new mechanism to create single molecule junctions. Specifically, we use electrochemical control to selectively create/destroy molecular junctions that could not be formed otherwise using thiol-terminated molecules. We enable the gate voltage-controlled selective molecule-electrode bond formation that allows us to investigate the electronic properties of disulfide bonds, which can only be stabilized under electrolytic environments. These results provide a novel strategy to create tunable molecular junctions and explore structure-function relationships for systems that are otherwise not accessible.

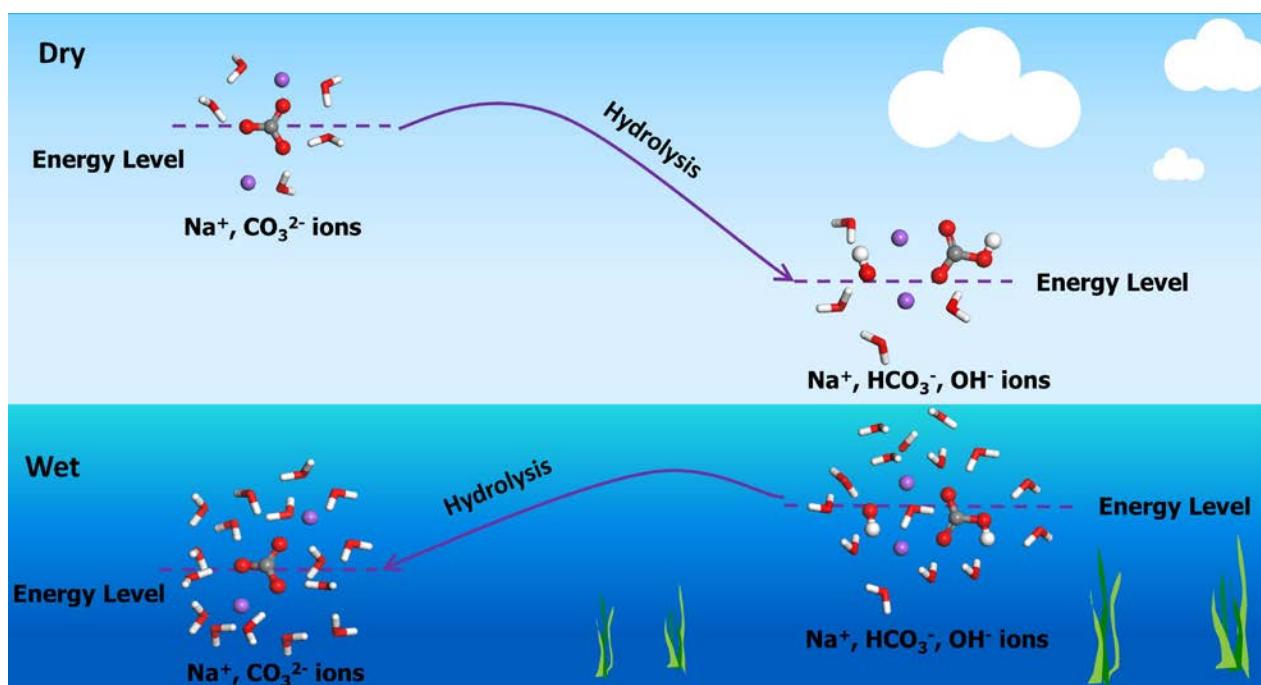
COLL 854

Effect of moisture on the hydrolysis of basic salts

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A great deal of information exists concerning the hydration of ions in bulk water. Much less noticeable, but equally ubiquitous is the hydration of ions holding on to several water molecules in nanoscopic pores or in natural air at low relative humidity. Such

hydration of ions with a high ratio of ions to water molecules (up to 1:1) are essential in determining the energetics of many physical and chemical systems. Here we present a quantitative analysis of the energetics of ion hydration in nanopores based on molecular modeling of a series of basic salts associated with different numbers of water molecules. The results show that the degree of hydrolysis of basic salts in the presence of a few water molecules is significantly different from that in bulk water. The reduced availability of water molecules promotes the hydrolysis of divalent and trivalent basic ions (S_2^- , CO_3^{2-} , SO_3^{2-} , HPO_4^{2-} , SO_4^{2-} , PO_4^{3-}) which produces lower valent ions (HS^- , HCO_3^- , HSO_3^- , H_2PO_4^- , HSO_4^- , HPO_4^{2-}) and OH^- ions. However, reducing the availability of water inhibits the hydrolysis of monovalent basic ions (CN^- , HS^-). This finding sheds some light on a vast number of chemical processes in the atmosphere and on solid porous surfaces. The discovery has wide potential applications including designing efficient absorbents for acidic gases.



COLL 855

Moisture-swing thermodynamics

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Moisture-controlled sorbents make it possible to remove CO_2 from ambient air. They provide a new approach to address CO_2 emissions from mobile sources like cars and airplanes. More broadly, sorbents with two sorbates, where one sorbate (here H_2O) controls the affinity of the second sorbate (here CO_2), offer an unconventional approach to gas separation. To this end we explore the properties of an amine-based anion exchange resin dispersed into a polypropylene matrix, which we prepared in alkaline

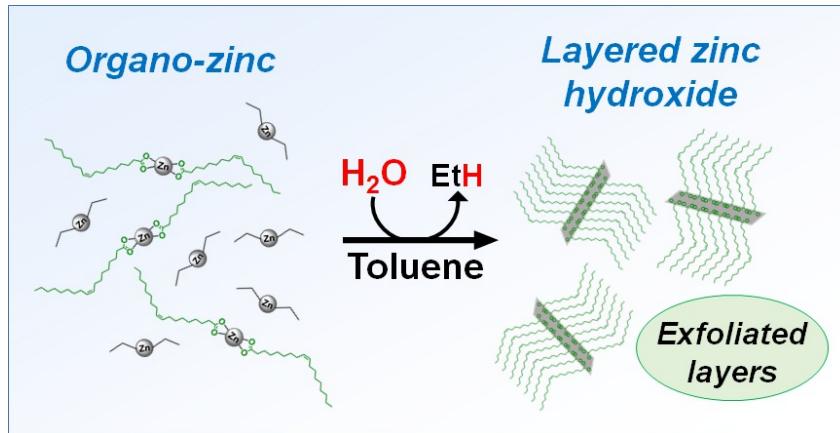
form to capture CO₂ at low concentrations (several hundred ppm of CO₂) from air. The sorbent binds CO₂ when dry. After exposure to moisture, the sorbent releases the CO₂ at a 500 times higher partial pressure. The moisture-swing cycle completes when the moist sorbent dries in ambient air and starts to absorb CO₂ again. This study focuses on the thermodynamic behavior of the sorbent- CO₂-water system and tries to establish an equation of state as a function of temperature, water and CO₂ concentration. Regular thermogravimetric analyzers (TGAs) can only monitor single sorbate systems; therefore, one of the main challenges that confronted this study was to build an appropriate experimental setup to control both of the strongly interacting sorbates and independently measure their loading on the sorbent. An experimental setup was designed and built to measure and control temperature, gas phase concentration of water vapor and CO₂, as well as the loading state of the sorbent with CO₂ and water. The sorption/desorption process can be described by a Langmuir model. The two sorbates, CO₂ and H₂O, strongly interact with each other on the sorbent, even though they do not compete for the same site on the sorbent material. An earlier model to fit a more limited data set suggested that the absorption and desorption free energy is only controlled by relative humidity, but is independent of temperature. However, the system's behavior at higher temperatures shows a clear deviation from this model. This study tries to extend the old model to different temperature and humidity conditions and validate the new model.

COLL 856

Organometallic route to layered zinc hydroxides and their exfoliated monolayers in apolar solvents

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Exfoliated 2-D inorganic materials are of fundamental interest and are useful for applications spanning catalysis, electronics and sensing. Here, a new method to make exfoliated and highly soluble layered zinc hydroxides (LZH) is presented. It applies the controlled hydrolysis of organometallic zinc precursors in the presence of zinc carboxylate complexes. The synthesis is achieved by reacting diethyl zinc with sub-stoichiometric equivalents of zinc carboxylates, optimally with [COOR]/[Zn] = 0.6, at room temperature and in organic solvents. Monolayers of layered zinc hydroxides, coordinated by oleate, are prepared by stirring the LZH in toluene, for 2 h. The exfoliated monolayers are characterized using both atomic force and transmission electron microscopies and show high solubilities in polar aprotic solvents (up to 23 mg/mL). Solution deposition of the LZH solutions onto a glass substrate, followed by annealing at 500 °C for 15 mins, enables the formation of 1 µm thick films of optically transparent zinc oxide.



COLL 857

Precision tunable nanomaterials from persistent micelle templates

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Porous and nanoscale architectures of inorganic materials have become crucial for a range of energy and catalysis applications, where the ability to control morphology largely determines the transport characteristics and device performance. Despite the availability of a range of block copolymer self-assembly methods, the conditions for tuning the key architectural features such as the inorganic wall-thickness have remained elusive. Toward this end, we have developed a solution processing method that enables fundamental studies with series of tunable isomorphic architectures. Here, porous samples may have the pore size and morphology held constant while varying the wall-thickness, or vice versa, have the wall-thickness and morphology held constant while varying the pore size. Orthogonal access to key morphological parameters will enable new model studies based upon materials prepared by self-assembly. The specific thermodynamic and kinetic criteria will be presented to enable persistent micelle templates and examples will be given for a range of (photo)catalytic materials. The accessible pore sizes span a wide range from mesopores to macropores and the resulting materials are thermally stable to >600 °C for access to crystalline inorganic materials.

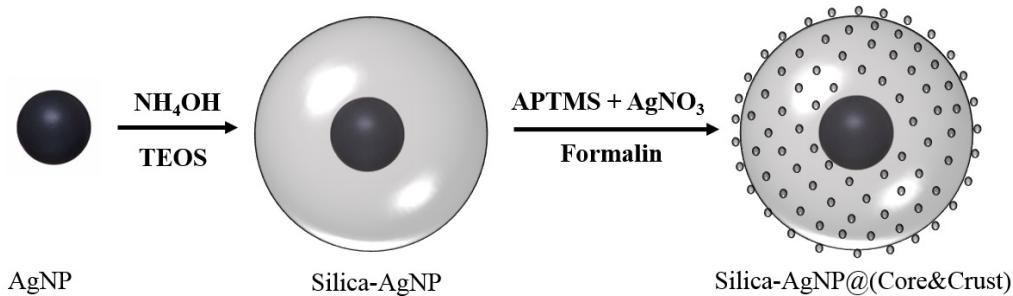
COLL 858

Facile, single-pot preparation of nanoporous silica with AgNPs at the core and crust for controlled Ag⁺ ion release

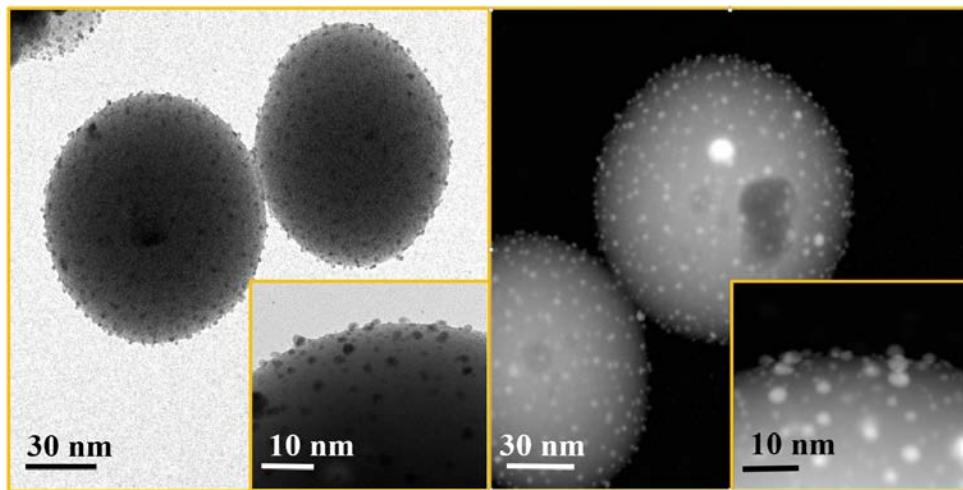
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The present study demonstrates a novel, facile and one-pot approach to develop silica nanoparticle with silver at its core and crust. A modified Stöbers method was used to make Silica-AgNPs@ Core & Crust (SACC). A significant reduction in the size of silica nanoparticle was seen, clearly 2-5 nm AgNPs was uniformly distributed on the surface while 10-20 nm AgNPs were seen in the center. A typical mesoporous silica from stöbers method was transformed to nanoporous silica by this modified stöbers method. Nanoporous silica was advantageous for slow and consistent silver release which was confirmed by Ag^+ ion release test. Antibacterial activities of the samples were carried out to investigate the disinfection performance of the samples on the Gram negative bacteria (*Escherichia coli*) using disk diffusion and LB-agar method. SACC showed prolonged silver release for more than 20 days and improved antibacterial properties even after 5 days of incubation.



Sematic illustration of the formation of SACC (Silica-AgNPs@ Core&Crust).



HRTEM and STEM images of SACC (Silica-AgNPs @ core and curst)

COLL 859

Selective electropolymerization of aniline on an ITO electrode using magnetic nanoparticles and a varying magnetic field

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Electrically conducting polymers, such as polyaniline, are increasingly being used in electronic devices over conventional metals and semiconductors due to their comparable conductivities, flexibility, and greater processing ability. For various electronic applications, the conducting polymer must be spatially deposited on a substrate in a specific pattern to perform a specific task. Numerous patterning techniques have been used to deposit conducting polymers in a desired manner; however, these methods are either too complicated, not practical, or do not provide the needed resolution for the intended application. In this research, polyaniline has been deposited on a flexible ITO electrode through an oxidative electropolymerization reaction. Magnetic nanoparticles have been positioned on the electrode using various magnetic fields in order to block the deposition of polyaniline in the corresponding patterns. In the unblocked regions, polyaniline forms on the electrode through the electropolymerization reaction, whereas on the regions blocked with magnetic nanoparticles no polyaniline forms. Polyaniline patterns have been formed in this way at technologically relevant resolutions and conductivities. The pattern of conducting polymer on the electrode has been found to change depending on the magnetic field shape and strength.

COLL 860

Morphology, structure, and optical properties of 2D SnS nanoplates synthesized via a hot-injection method

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Two dimensional (2D) layered materials such as graphene, metal dichalcogenides and black phosphorus are of increasing interest because of their unique optical and electronic properties. Black phosphorus has a variable band gap but is air-sensitive while graphene is limited by its zero bandgap. SnS has a similar crystal structure to black phosphorus but is stable in air. In addition, SnS is a *p*-type, 2D semiconductor with a direct band gap (~1.3 eV), indirect band gap (1.1 eV), and a high absorption coefficient ($>10^4 \text{ cm}^{-1}$). It has potential applications in transistors, photovoltaics, photocatalysis, and lithium ion batteries. We have synthesized 3-60 nm thick and up to approximately 10 micron wide SnS nanoplates via decomposition of tin(IV) diethyldithiocarbamate upon hot injection into oleylamine (300-340 °C). The reaction products are characterized using a combination of electron microscopy, energy dispersive X-ray spectroscopy, X-ray diffraction (XRD), atomic force microscopy, and

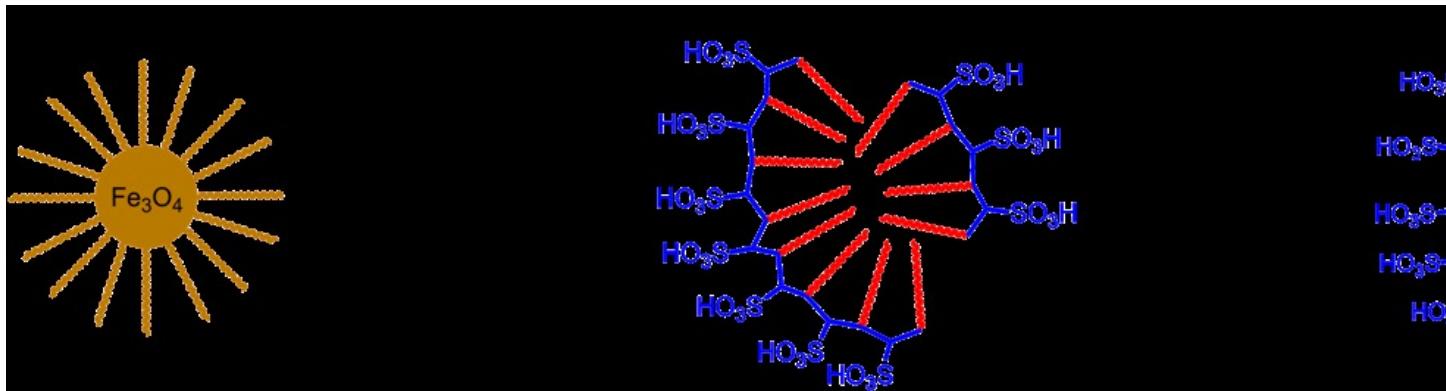
Raman spectroscopy. All characterization techniques confirm that the final reaction product is orthorhombic SnS (e.g., after 60 minutes at 340 °C). At low temperatures (300 °C) and short synthesis times (3 minutes) we also observe the presence of tin disulfide (SnS_2) which suggests that decomposition of tin(IV) diethyldithiocarbamate first produces SnS_2 . SnS_2 is subsequently reduced, likely by oleylamine, to SnS. The SnS nanoplate surfaces are covered with oleic acid ligands, which sterically stabilizes their dispersions in organic solvents. These ligands could be exchanged with K_2S to charge stabilize them in water and other polar solvents. Orthorhombic SnS grows preferentially as plates, with the [001] direction normal to the plate surfaces. In fact, when plates are large (>1 micron) XRD from films cast from colloidal dispersions in toluene show predominantly the (004) diffraction. The nanoplate size affects their optical properties. The flat surface on large nanoplates make them highly reflective when compared to smaller (<1 micron) nanoplates as confirmed with reflectance and transmission measurements. Nanoplates are polarizable in electric fields and their dispersions respond to electric fields. They form spontaneous patterns in dispersions confined between two electrodes that are biased with respect to each other.

COLL 861

Synthesizing and screening high mobility nanoparticles

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Nanoparticle interactions are a major challenge for any innovation that relies on the introduction of functional nanoparticles into complex environments. The effects of different coatings (PAA and PAMPS) on quantum dot and iron nanoparticle transport and retention in both uniform and heterogeneous porous media have been successfully measured. The studies concluded that for amphiphilic stabilized nanoparticles, e.g. nMag-PAMPs, the free polymer in solution plays a significant role in the enhancement of the mobility of the nanoparticles and was proved that different polymers can be used as co-injection materials to alter the behavior of the nanoparticles. The effect of the size of nanoparticles was studied by using PS beads functionalized with taurine to emulate the active surface of the nMag-PAMPs. The attachment profiles of different sizes show differences in both the mass attached and the rate of attachment, moreover this model is also affected by the introduction of co-injection agents. The oil and gas industry relies on the ability of nanoparticles to reach the intended site of interest and thus understanding the interactions of nanoparticles is important to further expand the use of nanotechnology.



Schematic representation of the bilayer formation.

COLL 862

Surfactant-induced shape changes in oil droplets caged in deformable polymer shells as templates for the synthesis of anisotropic polymer particles

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We report characterization of surfactant-induced changes in the shapes of oil droplets ‘caged’ inside covalently crosslinked and semi-permeable polymer shells fabricated by the reactive/covalent layer-by-layer assembly of poly(2-vinyl-4,4-dimethylazlactone) (PVDMA) and poly(ethyleneimine) (PEI). The filling of micrometer-scale PEI/PVDMA capsules with hydrophobic and water immiscible oils, followed by extraction into water, yields spherical polymer ‘cages’ partially-filled with smaller spherical oil droplets. These ‘caged’ oil droplets are observed to undergo large transformations in shape upon the addition of a model anionic surfactant (SDS) to yield ‘caged’ droplets that exhibit complex and anisotropic particles with unique shapes and apparent six-, five-, four- and three-fold symmetries. These transitions appear to be driven by surfactant-induced changes in the wetting behaviors of the droplets with the walls of the capsules and are accompanied by large changes in the shapes of the surrounding capsules. The first part of this presentation will discuss factors that influence the extent of these stimuli-responsive shape changes and the distributions of colloidal droplet shapes, including the concentration and charge of the surfactant, the diameter of the polymer capsules and the thicknesses of their walls, and the sizes of the caged oil droplets. Our results reveal these shape changes to be reversible upon the addition of cationic surfactants. These transformations also appear to be general, and are observed in ‘cages’ partially filled with a variety of different isotropic and anisotropic (liquid crystalline) oil droplets. We demonstrate that photopolymerization of droplets of vinyl monomers ‘caged’ in these capsules provides means to template the synthesis of micrometer-scale polymer particles with unique anisotropic shapes that mimic those of the enclosed oil droplets. Finally, we demonstrate that crosslinked polymer ‘cages’ that are reductively

degradable enable the subsequent removal of the surrounding cages and the isolation of 'cage-free' anisotropic colloids with complex and novel geometries.

COLL 863

Synthesis and chemical transformation of nickel nanoparticles embedded in silica

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Ni nanoparticles (NPs) catalyze many chemical reactions, including dry methane reforming, the oxygen evolution reaction, and the Suzuki coupling reaction. However, in many of these reactions, the Ni catalyst becomes contaminated or decomposes in a short period of time, resulting in downtime and high material and labor costs. Therefore, there is a need to develop new Ni NP catalysts with improved durability. Deposition of silica (SiO_2) onto many kinds of inorganic NPs has been shown to improve the chemical, optical, and thermal stability of the composite NPs. Furthermore, porous SiO_2 shells can provide some protection of the core NPs, while also allowing the reactants to contact the core NP.

The objectives of this study were to deposit SiO_2 overcoatings on ~25 nm Ni NPs to create composite NPs for use in catalysis and to analyze chemical and structural transformations that occur during the formation of composite SiO_2 -overcoated Ni ($\text{SiO}_2\text{-Ni}$) NPs. During deposition of SiO_2 in a reverse microemulsion, the Ni NPs were etched into many smaller NPs with diameters of ~2 nm and distributed throughout ~30 nm porous SiO_2 NPs. Etching of the Ni NPs is attributed to the use of NH_4OH as a base catalyst for deposition of SiO_2 from tetraethyl orthosilicate (TEOS). Ethanol is generated as a byproduct, which modifies the phase behavior of the mixture over the course of the overcoating reaction and results in a monodispersed product. The stability of $\text{SiO}_2\text{-Ni}$ NPs was also studied under high temperature oxidizing and reducing environments because applications in catalysis often utilize oxidizing or reducing environments and high temperatures. The structure of the $\text{SiO}_2\text{-Ni}$ NPs remained significantly unchanged after both oxidation and reduction, which suggests structural durability when used for catalysis. The synthetic approach of etching using NH_4OH is also potentially applicable to other catalytically active core NP materials.

COLL 864

Carboxylate decomposition: A critical step in high temperature synthesis of metal oxide nanocrystals

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The thermal decomposition of metal carboxylates in organic solution is a widely applied and general method for the synthesis of metal oxide nanocrystals. While these reactions are known to produce highly uniform nanocrystals with narrow size distributions, a detailed mechanism to describe their formation process, comparable to those used to design organic molecules, has yet to be developed. A mechanistic understanding of the formation process would facilitate systematic tuning of nanocrystal shapes, dimensions, and forms, providing a gateway towards synthesis of a broader range of materials. In order to achieve full optimization of nanocrystal production by this method, the role of organic constituents in their formation must be considered. To this end, we have monitored the synthesis of iron oxide nanocrystals from iron carboxylates in order to establish the relationship between carboxylate deoxygenation and nanocrystal nucleation and growth. We have characterized not only the nanocrystals themselves, but also the organic decomposition products using gas and liquid phase analysis. Further, we have demonstrated how these organic by-products, notably CO, can be exploited to deposit graphite on the nanocrystal surfaces. These graphite-encapsulated nanocrystals are promising materials for applications in magnetic separation.

COLL 865

Synthesis and characterization of metal-doped synthetic melanin nanoparticles

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To date, synthetic melanin has received considerable attention in the development of functional biomaterials inspired by natural systems. While the integration of synthetic catechol-based materials with metals has been widely explored for diverse applications, few studies have focused on the fundamental chemical properties of these materials such as polymerization kinetics, influence the identity of the metal ion on polymerization rates, upper limits of metal ion incorporation into synthetic melanin, magnetic properties, and their relationships to MRI. Herein, we utilized self-oxidation polymerization to prepare a series of metal- loaded synthetic melanin nanoparticles (SMNPs) via a pre-doping strategy that involves mixing dopamine with different metal ion salts prior to dopamine polymerization. The resulting SMNPs show a notably higher level of metal content compared with post-synthetic metal doping strategies. We choose Fe(III)-loaded SMNPs as an example, to investigate the parameters that influence the final particles' morphology as well as the Fe(III) loading. Importantly, we found that the high and controllable content of iron enables the systematic investigation of magnetic properties via magnetometry which reveals details of the local anisotropy and coupling

interactions that are vital to understanding the magnetic nature these materials and how they can be optimized for MRI contrast. In addition, we developed a metal displacement method to prepare a series of Gd(III)-loaded SMNPs with tunable metal loadings and ultra-high relaxivity ($75 \text{ mM}^{-1} \text{ s}^{-1}$ and $10.3 \text{ mM}^{-1} \text{ s}^{-1}$ at 1.4 T and 7 T, respectively). We performed a systematic investigation to demonstrate the high relaxivities are attributed to a high hydration state of the Gd(III) at the particle surface, fast rate of water exchange and negligible antiferromagnetic coupling between Gd(III) centers throughout the particles.

COLL 866

Effect of solution composition on Pu oxide nanoparticle morphology

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Plutonium is highly susceptible to hydrolysis, with a tendency to form intrinsic nanocolloids in a wide variety of aqueous media. This tendency has been considered a nuisance in laboratory-scale Pu chemistry, and has significant implications on the mobility of Pu in the environment. Pu colloids were first described as large, amorphous polymers but modern studies have revealed aggregates of nanocrystalline Pu-oxide particles typically under 10 nm in diameter. Different structures have been observed, with some studies indicating mixed oxyhydroxide clusters, while others have determined crystalline Pu oxide structures with no evidence of Pu-OH bonds. Limited data are available concerning the influence of the solution matrix on the structure, size, and aggregation behavior of Pu nanoparticles. The present work aims to determine how different counter-ions and co-ions impact the properties of Pu colloids formed by hydrolysis of Pu(IV) in mildly acidic and circum-neutral pH solutions. Pu colloid solutions were prepared by adding Pu(IV) in HCl to 1 M salt solutions (NaClO₄, NaNO₃, NaCl, LiCl, CsCl, MgCl₂, SrCl₂, BaCl₂) yielding total Pu concentration of 1×10^{-4} M. Each sample was characterized by transmission electron microscopy (TEM) and Pu L_{III}-edge X-ray absorption spectroscopy (XAS). Results of these experiments will be discussed.