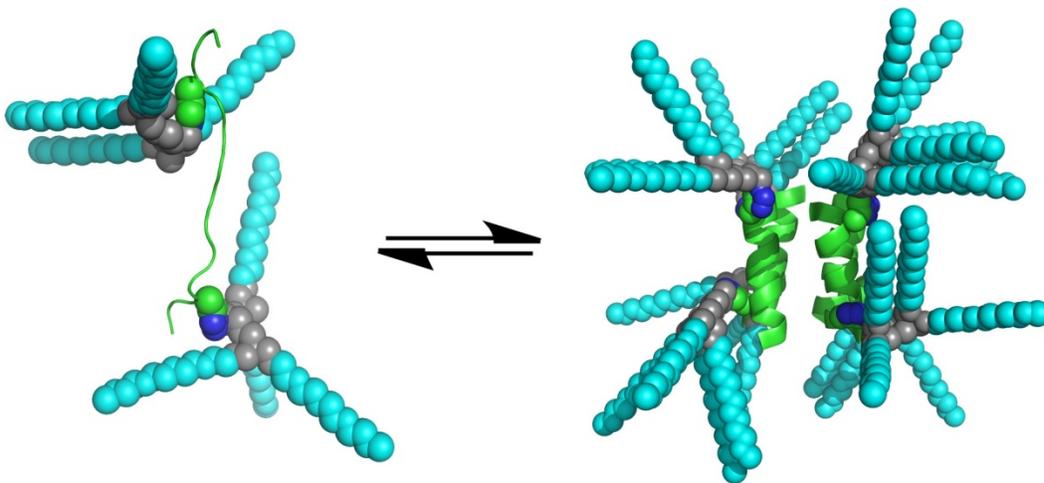


COLL 1

Dendronized helix bundle assemblies designed de novo

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Peptides that recapitulate the structural and functional properties of natural helix bundle motifs serve as models of nanoscale biological structures and as building blocks for synthetic biology. To mitigate the material properties of these peptides, we have developed synthetic approaches to conjugate dendrons to minimalist peptide models of proteins. Understanding how dendrons affect the structure of the peptides is desirable for the design of hybrid biomaterials. Our approach to developing this understanding involves critically testing rules for the de novo design of peptides that mimic protein folding and assembly in the context of dendron-peptide conjugates. Dendronized peptides that fold and assemble into helix bundles have been identified through spectroscopic studies. These results and subsequent structure-activity relationships will be presented.



COLL 2

Mimicry of biorecognition motifs with peptidic foldamers

Samuel H. Gellman, *gellman@chem.wisc.edu*. Univ of Wisconsin, Madison, Wisconsin, United States

Folded proteins perform diverse functions in biological systems. Most of these operations require the polypeptide chain to adopt a specific conformation. Over the past two decades there has been growing interest in the prospect that protein functions

might be recapitulated and perhaps even improved upon with unnatural oligomers that manifest discrete folding preferences. Such systems are referred to generically as "foldamers". Protein-inspired foldamers include molecules with backbones built from extended subunits such as beta-amino acids ("beta-peptides") or gamma-amino acids ("gamma-peptides"). Newer efforts have involved heterogeneous peptidic backbones, i.e., backbones in which different types of subunits are combined, such as "alpha/beta-peptides" and "alpha/beta/gamma-peptides". Some of these systems, alpha/beta-peptides in particular, allow mimicry of information-rich surfaces displayed by natural polypeptides. The resulting foldamers can inhibit specific protein-protein interactions, or they can augment signaling through polypeptide-activated receptors. Recent results in this area will be described.

COLL 3

Functional coiled-coil peptides controlled assemblies

Alexander Kros, *a.kros@chem.leidenuniv.nl*. Leiden University, Bodegraven, Netherlands

Both in nature and in the laboratory, α -helical coiled coils are formed by the binding of two or more α -helical peptides in a specific manner producing a stable complex in aqueous solution and its stability can be tuned by external parameters like pH, temperature and ions. This versatility arising from a simple helix has resulted in many functions of coiled coils in nature, and has inspired many advances in synthetic biology and supramolecular chemistry. The functions of coiled-coil domains that have been elucidated to date have predominantly been binding, structural and dynamic. It is our long-term goal to understand and harness the emergent properties of complex biological systems. Our approach towards this is the use of biologically inspired modules, for the prescriptive self-assembly of functional synthetic systems. Inspired by examples from nature, we developed coiled coil amphiphiles in order to design (responsive) assemblies with a defined shape and size. Examples on how these assemblies can be used for vaccine applications will be discussed. Furthermore, based on a complementary lipidated coiled coil, we designed an efficient membrane fusion system that is functional in live cells. Initial studies suggest that cargo can be delivered into the cytoplasm of cells by avoiding endosomal pathways, which would revolutionize drug delivery.

COLL 4

Thermodynamics of surface-tethered peptide-polymer conjugates

Scott P. Carmichael, **M. Scott Shell**, *shell@engineering.ucsb.edu*. Chemical Engineering, UC Santa Barbara, Santa Barbara, California, United States

We discuss a simulation approach to understanding the behavior of mobile but surface-tethered peptides that are functionalized with polymers. Such systems mimic the

behavior of peptide amphiphiles in which polymers are used to stabilize folded peptide helical states that prevent undesired peptide-peptide interactions and assembly into beta-sheet structures. We use a novel coarse-graining technique to develop simple models that recapitulate the basic and assembly driving forces. Simulations show that functionalization with polymers can stabilize helical states, but the behavior is highly dependent on the specific amino acid at which the polymer is attached. In some cases, polymer functionalization can destabilize the fold and actually promote aggregation. We show that these unexpected results are actually well-understood in terms of a simple theory that accounts for the entropy of a polymer near an impenetrable surface.

COLL 5

Combating diseases with peptide – polymer conjugate

Harm-Anton Klok, *harm-anton.klok@epfl.ch. STI-IMX-LP, EPFL, Lausanne, Switzerland*

Peptide – synthetic polymer conjugates are an exciting class of nanomedicines. On the one hand, polymer conjugation provides opportunities to enhance and guide the cellular internalization of biologically active peptide therapeutics. On the other hand, synthetic polymers are also powerful platforms that allow to present multiple copies of biologically active peptides, which allows to harness multivalency effects and generate therapeutically-active peptide-polymer conjugates. This presentation will attempt to illustrate both of these points with a number of case studies, which include amongst others (i) polymer-modified HIV fusion inhibitors that show increased stabilities as compared to the unmodified peptides while maintaining activity and (ii) multivalent HIV entry inhibitors based on side-chain peptide – polymer conjugates which allow to augment the activity of the peptide.

COLL 6

Carving pi-ways into biomaterials: electronic delocalization via peptide self-assembly

John D. Tovar, *tovar@jhu.edu. Johns Hopkins Univ, Baltimore, Maryland, United States*

This contribution will describe recent work to incorporate pi-conjugated molecules of interest for organic electronics into self-assembling oligopeptides of interest for biomaterial applications. The assembly process leads to the formation of supramolecular polymers fashioned into 1-D nanomaterials ca. 10 nm in diameter. Using this general platform, a series of energy transport examples will be discussed, spanning transistor-based gating for carrier mobility and photonic activation for exciton transport. Prospects for using these hybrid electronic biomaterials to elicit biological adhesion or other specific responses in an externally tunable manner will be addressed.

COLL 7

Colloidal effects in virus stability

Francesco Stellacci, *francesco.stellacci@epfl.ch*. Institute of Materials, EPFL, Lausanne, Switzerland

In this talk, recent results obtained in my group and throughout the research community on the effect of nanoparticles on the chemical stability of a few viruses will be discussed. In particular the possibility of controlling and manipulating such stability with simple colloidal objects such as nanoparticles and small molecules will be discussed. When possible, mechanisms will be hypothesized and tested.

COLL 8

Self-assembly of nanoparticles in chiral and other superstructures

Nicholas Kotov, *kotov@umich.edu*. University of Michigan, Ann Arbor, Michigan, United States

Intrinsic ability of nanoparticles (NPs) to self-organize is evident in many studies. The mechanisms of these processes are not well understood and include many surprises. One of the enigmatic aspects of these processes is the ability of large number of NPs to form mesoscale superstructures with high complexity. In this presentation, I will address classification based on the dimensionality of the assemblies and inter-NP interactions. Practical aspects of nanoparticle self-organization phenomena assessing their potential utility in different areas of technology starting analytical chemistry to understanding the origin of homochirality on Earth will be elaborated.

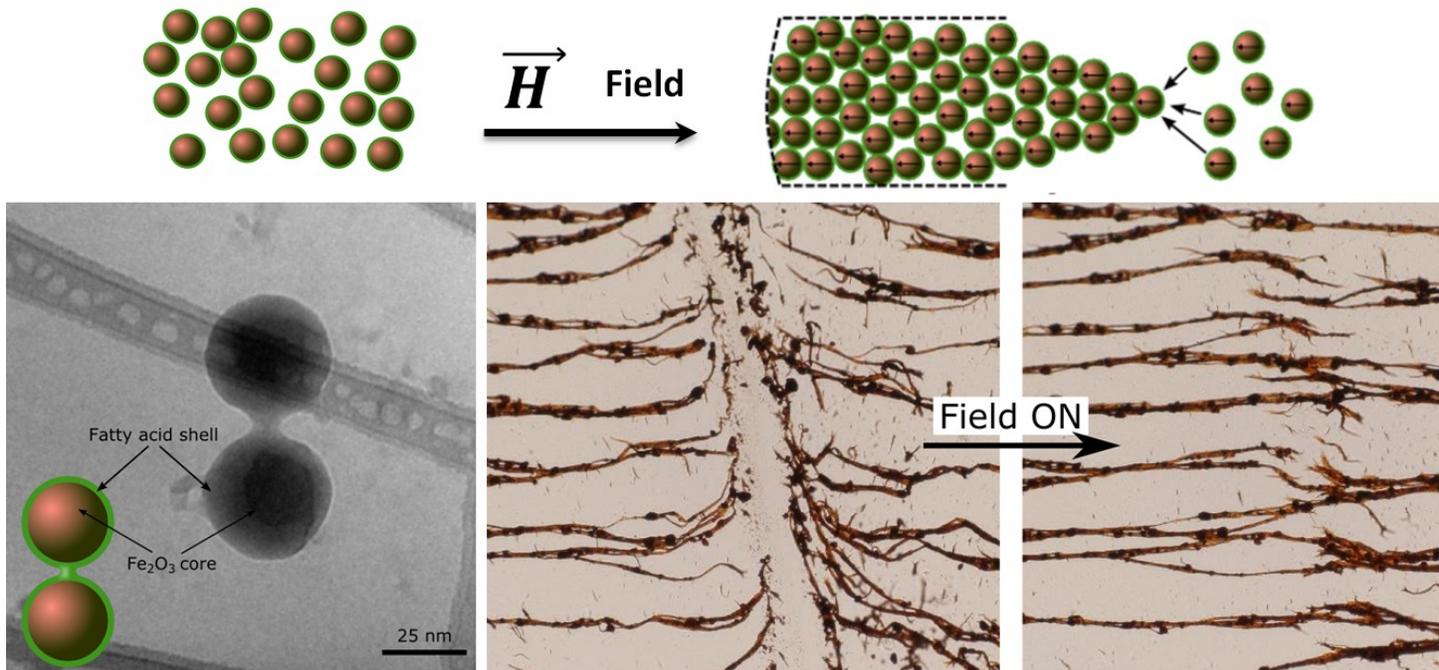


COLL 9

Ultraflexible reconfigurable magnetic nanoparticle filaments and networks by nanocapillary lipid bridging

Orlin D. Velev¹, odvelev@ncsu.edu, **Bhuvnesh Bharti**¹, **Anne-Laure Fameau**², **Michael Rubinstein**³. (1) *Chemical Biomolecular Engineering, North Carolina State University, Raleigh, North Carolina, United States* (2) *National Institute of French Agricultural Research, Nantes, France* (3) *UNC Chapel Hill, Chapel Hill, North Carolina, United States*

Dispersions that respond to external stimuli can find applications in a wide range of industrial and environmental processes. We will present a new smart gel system containing ultraflexible filaments assembled from magnetically responsive nanoparticles and biologically derived lipids. The super-paramagnetic nanoparticles used as structural units are covered by condensed, surface-anchored lipid shells, which on contact form nanocapillary liquid bridges between them. Initial burst of magnetic field collects the particles into filaments by magnetophoresis. After switching off the field the particles retain their structural arrangement by a soft attractive potential induced by the liquid-like bridges. The soft and reversible capillary binding on contact and the fluidity of the nanobridges provide extraordinary high flexibility and reconfigurability of the filaments. The formation of liquid menisci was correlated to the thermodynamic phase of the lipid shell around the particles, its fluidity and nanoparticle wettability. The liquid bridges allow for easy particle rolling and sliding; thus the resulting ultrahigh flexibility was measured to be orders of magnitude higher than any other linear structures reported to date. We demonstrate that despite of their high linear density, the persistence length of the filamentous chains remains comparable to one of bio-molecules, verifying the ultraflexible nature of the assembled chains. These new soft and magnetically responsive structures can be dynamically reconfigured and programmed. The control of nanoparticle binding through soft, "snappable" bridging provides a facile means of creating self-repairing networks and potentially in magnetically self-repairing gels. Such flexible magnetically responsive structures can be used in future applications beyond smart gels, such as micrograbbers and microbots with ultrasoft joints, and other types of reconfigurable soft matter.



Schematic of the NP assembly, example of nanocapillary bridging and binding, example of chain self-repair.

COLL 10

Colloidal design and optimization for assembly of complex crystals

Sharon C. Glotzer, *sglotzer@umich.edu*. Department of Chemical Engineering, University of Michigan, Ann Arbor, Michigan, United States

Through enthalpic functionalization and entropic "shaping", colloidal nanoparticles may be tailored for self assembly into complex crystals isostructural to atomic and molecular crystals, and displaying aperiodicity, chirality and other desirable -- but difficult to realize -- characteristics. We present studies of several experimental and theoretical systems and discuss predictive design and optimization strategies to yield complex structures via simple rules.

COLL 11

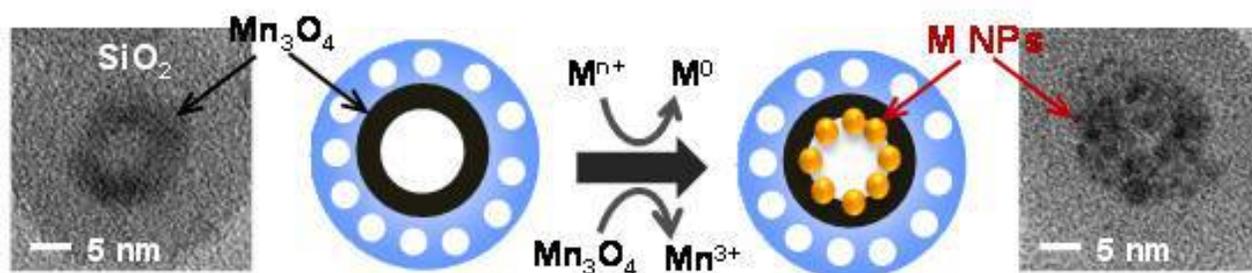
Selective and differential functionalization of interior surface of hollow nanoparticles for nanoreactor applications

Soo Min Kim, **Dong-Gyu Lee**, **In Su Lee**, *insulee97@postech.ac.kr*. Dept of Chemistry, POSTECH, Pohang, Gyeongbuk-do, Korea (the Republic of)

Hollow nanoparticles that encapsulate catalytic species inside the permeable porous shell of chemically inert materials are promising candidates for nanoreactors that

efficiently catalyze the chemical reactions of selected molecules while preserving the exposed surface area of the entrapped catalysts even under harsh reaction conditions or during the recycling process. Therefore, selective and differential functionalization of the internal space of the hollow nanoshell is the important and challenging topic which is demanded for fully exploiting the potential of the hollow nanoparticle in the nanoreactor application.

In this presentation, I would like to report a post-synthetic functionalization protocol based on galvanic replacement at the Mn_3O_4 surface, which leads to the high-density deposition of ultrafine catalytic metal nanoparticles, including Pd, Pt, Rh, Ir, and their alloys, on a Mn_3O_4 -layer-coated interior surface of the hollow silica nanosphere.[figure1] The hollow nanoreactor fabricated using the proposed method exhibited highly enhanced activity, selectivity, and recyclability in catalyzing the hydrolytic oxidation of silanes, which are attributable to the synergistic combination of the porous silica nanoshell and the oxide-immobilized catalyst system. I will also discuss further extension of the utility Mn_3O_4 -involved galvanic replacement process for differently decorating interior and exterior surfaces of hollow carbon nanospheres with catalytic nanocrystals, which exploits the effect of the variable oxidation state of manganese oxide on reaction behavior.



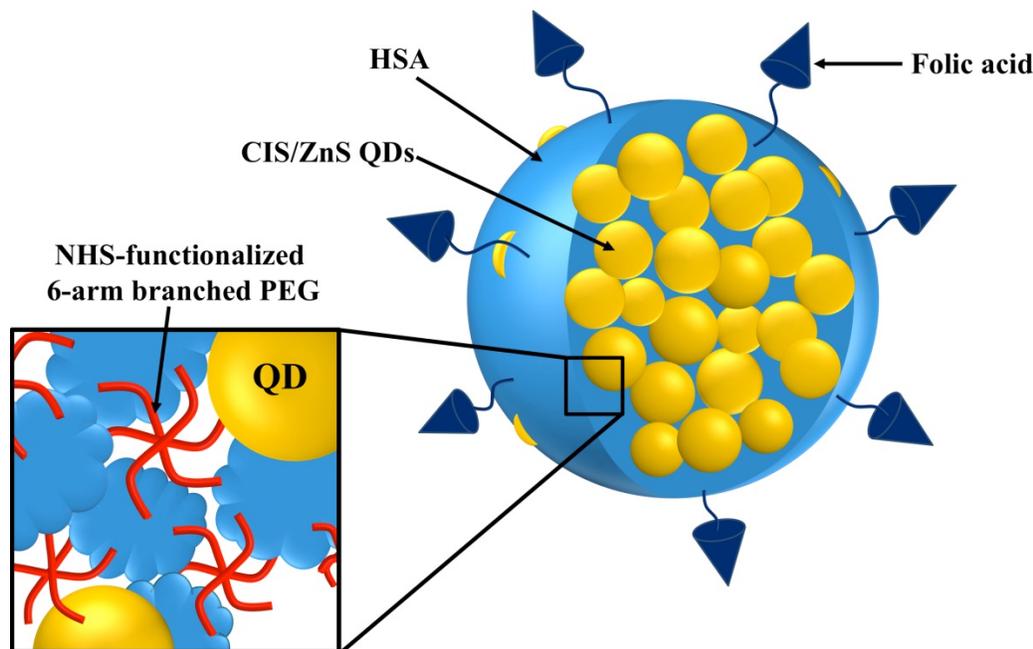
COLL 12

Protein-based organic/inorganic hybrid nanocapsules for In vivo delivery applications

Yoon Sung Nam, *yoonsung@kaist.ac.kr*, Jeong Yu Lee. KAIST, Daejeon, Korea (the Republic of)

Human serum albumin (HSA) is highly abundant in the blood plasma and transports fatty acids, hormones, bilirubin, and other small molecules. It has a long half-life in serum (about 20 days), making the protein attractive for in vivo systemic delivery of therapeutic agents. However, non-specific binding of molecules to the hydrophobic patches of HSA often leads to undesirable aggregation because of uncontrolled changes in the interfacial properties of the protein. Here I will introduce serum-stable HSA-based hybrid nanocapsules using six-arm-branched polyethylene glycol (PEG) as

a cross-linker. The HSA/PEG hybrid nanocapsules are prepared by emulsifying an organic solution of amine-reactive six-arm-branched PEG into an aqueous solution of HSA. The successful formation of nanocapsules are kinetically determined by several processes: diffusion of PEG molecules out of the organic phase, adsorption of HSA onto the emulsion surfaces, and cross-linking reactions between PEG and HSA at the organic/aqueous interface. The nanocapsules are employed as in vivo delivery carriers for paclitaxel and inorganic nanocrystals. In several types of cells, the surface modification of nanocapsules with a cell-penetrating peptide or cancer-targeting molecule greatly facilitates cellular uptake and apoptosis-inducing effects of paclitaxel. Furthermore, the targeted anti-tumor activities of the paclitaxel-loaded nanocapsules in a mouse tumor model suggest that the shell cross-linked nanocapsules are very promising oil-free nanoscale delivery vehicles for water-insoluble anti-cancer agents. In addition, cadmium-free CuInS/ZnS quantum dots, and monodisperse iron oxide nanocrystals are encapsulated within the shell as an imaging probe. I will discuss physicochemical properties of the prepared hybrid nanocapsules in relation with their cytotoxicities and in vivo destinations. This study demonstrates that the HSA/PEG hybrid nanocapsules can be utilized as a biocompatible, cell-targeting platform for in vivo systemic delivery of various therapeutic and imaging agents.

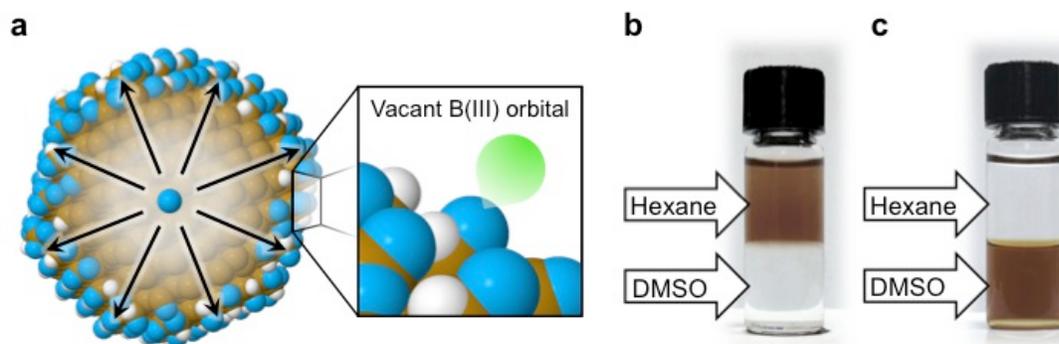


COLL 13

Interface engineering for nanocrystal stability in media spanning hexane to water

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Size-tunable optical properties and the ability to process thin films using scalable, cost-efficient printing techniques have long made colloidal nanocrystals (NCs) an attractive candidate for next-generation optoelectronics. Much of the recent progress in this direction hinges on the ability to manipulate the NC surface. Conventional solution synthesis yields NCs with ligands bound to metal surface atoms through a labile acid-base complex. The electrically-insulating native ligands are thus routinely exchanged to produce conductive NC arrays for devices such as solar cells, light-emitting devices, transistors, and photodetectors. Just as surface manipulation has launched metal-based NCs to the forefront of optoelectronic technology, it is the inability to do so with the covalent surface of group IV NCs that has greatly hindered progress. In this work, we demonstrate a Lewis acidic boron surface chemistry of gas-phase synthesized Si NCs that provides the same solution-phase versatility as their metal-based counterparts. This represents an immense step toward an abundant, non-toxic alternative to Pb and Cd-based NCs. These Si NCs are also uniquely suited for investigating the mechanism of colloidal stability that has been observed after metal-based NCs are stripped of ligands or ligand-exchanged for ionic ligands. We find the electrostatic mechanism previously invoked to be incomplete. An alternative model is proposed from which we demonstrate stable Si NC colloids in media that runs the gamut from hexane to water.



a) A depiction of a silicon nanocrystal terminated with Lewis acidic boron groups and photographs of the nanocrystals functionalized with oleylamine and stabilized in hexane (**b**) and stabilized in DMSO without functionalization (**c**).

COLL 14

Design of stimuli-responsive nanogels for bioapplications

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San Sebastian, Spain (2) Department of Bioengineering and Institute for Biomedical Engineering, Imperial College, London, United Kingdom

Nowadays, advanced nanoscale carriers for drug delivery are receiving tremendous attention in nanomedicine. The need for drug nanocarriers that efficiently target diseased areas in the body arise because drug efficacy is often altered by nonspecific cell and tissue biodistribution, and because some drugs are rapidly metabolized or excreted from the body. In this sense, much attention has been directed to environmentally responsive crosslinked colloidal particles, known as nanogels, considering their unique property to swell rapidly in a thermodynamically good solvent, responding to external stimuli such as temperature, ionic strength, magnetic field, biomolecules, or pH, among others. Furthermore, their small size allows them to overcome various biological barriers and achieve passive and active targeting, which reduce adverse reactions in tumour therapy. What is more, due to their porous structure they are able to contain small molecules inside and release them by changing their volume. These properties make them interesting and suitable materials to be used as nanocarriers in drug/gene delivery.^{1,2}

During the last few years, our research group has been focused on the design of multi-responsive nanogels able to combine multiple stimuli for advanced bio-applications.³⁻⁵ In this talk, our most recent approaches will be presented showing special interest in the synthesis strategies, and also in the colloidal characterization of the nanogels.

ACKNOWLEDGEMENTS

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COLL 15

Shape engineering substrate-based plasmonic nanostructures

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Breakthroughs in the shape engineering of metallic nanostructures have led to the elucidation of some very fundamental atomic-scale mechanisms. The study of such fundamental events is typically carried out using solution-dispersed metallic

nanostructures which act as seeds for additive processes reliant on homo/heterogeneous nucleation (HN) or subtractive processes, such as galvanic replacement reactions (GRRs). While much is understood, mechanistic insights are often difficult to attain from reactions carried out on solution-dispersed templates. Here, we present an alternative platform for investigating these fundamental chemical processes whereby surfactant-free templates are immobilized on a substrate. The platform gives rise to a new set of substrate-based nanostructures while allowing for growth modes which are far less convoluted than current modalities. It combines substrate-based techniques with solution-based synthetic procedures in a manner which allows an impressive colloidal chemistry to occur directly at the substrate surface. Kinetically controlled heterogeneous nucleation of Ag onto Au is shown to modulate crystal growth modes. Synergistic protocols, involving both HN and GRRs, are shown to form periodic arrays of (i) nanoshells with tunable composition, (ii) nanoframes and (iii) structures with a particle-in-a-shell geometry exhibiting tunable gaps. The resulting photonic surfaces formed from these arrayed nanostructures have compositions and shapes engineered to realize the plasmonic resonances and near-fields as predicted by FDTD (finite difference time domain) simulations. These studies aim to establish the mechanistic framework and synthetic protocols required to place shape-engineered substrate-based plasmonic nanostructures at site-specific locations, a capability which will enable the fabrication of advanced sensing devices with plasmonic elements as the active component.

COLL 16

All-optical control of localized plasmonic resonance using photoalignment and liquid crystals

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Large shifts in the plasmonic resonances of a thin film of gold nanorods (GNRs) are induced through the modulation of the local refractive index of the neighboring dielectric medium. This change is enabled through light-induced surface reorientation of a nematic liquid crystal in contact with a nanometer-thin photoalignment layer coating the GNR film. The presence of isolated and well distributed GNRs, both before and after the photoalignment layer deposition, is shown through atomic force and scanning electron microscopy. Exposure of the photoalignment layer to polarized light is shown to reorient aligned nematic liquid crystal molecules to an orthogonal direction, thereby changing the local refractive index of the medium in close proximity to the GNR film. This large change in the local dielectric strength is shown to cause a broad red shift of the localized plasmonic longitudinal resonance and almost no shift in the local transverse resonance. A light induced planar to twist reorientation produces a localized refractive

index variation in the environment around the GNRs; this affects the position of the LPR, yielding a shift of about 100 nm. Active control of the LPR of GNRs represents a crucial step toward the realization of active photonic devices based on plasmonic nanomaterials.

COLL 17

Unique temporal and spatial biomolecular emission profile on individual zinc oxide nanorods

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Zinc oxide nanorods (ZnO NRs) have emerged in recent years as extremely useful, optical signal-enhancing platforms in DNA and protein detection. Although the use of ZnO NRs in biodetection has been demonstrated so far in systems involving many ZnO NRs per detection element, their future applications will likely take place in a miniaturized setting while exploiting single ZnO NRs in a low-volume, high-throughput bioanalysis. We investigate temporal and spatial characteristics of biomolecular fluorescence on individual ZnO NR systems. Quantitative and qualitative examinations of biomolecular intensity and photostability are carried out as a function of two important criteria, time and position along the long axis (length) of NRs. Photostability profiles are also measured with respect to the position on NRs and compared to those characteristics of biomolecules on polymeric control platforms. Unlike uniformly distributed signal observed on the control platforms, both fluorescence intensity and photostability are position-dependent on individual ZnO NRs. We have identified a unique phenomenon of highly localized, fluorescence intensification on the nanorod ends (*FINE*) of well-characterized, individual ZnO nanostructures. When compared to the polymeric controls, biomolecular fluorescence intensity and photostability are determined to be higher on individual ZnO NRs regardless of the position on NRs. We have also carried out finite-difference time-domain simulations whose results agree well with the observed *FINE*. The outcomes of our investigation will offer a much needed basis for signal interpretation for biodetection devices and platforms consisting of single ZnO NRs and, at the same time, contribute significantly to provide insight in understanding biomolecular fluorescence observed from ZnO NR ensemble-based systems.

COLL 18

Theoretical study of the chirality and electronic structure of helical silver nanowires

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Metal nanoparticles with a chiral geometry exhibit unusual optical properties such as a strong circular dichroism (CD) signal in the visible or near IR region. The interaction of biomolecules with noble metal nanoparticles can produce plasmonic helical metal nanoparticles. These DNA-templated metal clusters are a fluorescent species and have potential applications as sensors. The theoretical investigation of these structures demonstrate that helix pitch, helix radius, nanoparticle length, interparticle distance can have an effect on the optical properties of these structures. In this work, TDDFT methods were employed to examine the evolution of the extinction and circular dichroism spectra with geometrical parameters and the length of silver atom chains on the optical properties of neutral bare silver helical nanostructures. Calculations of excited states to determine optical absorption and CD spectra were performed using the SAOP/TZP level of theory. In our model, the geometry of the helical silver chain is dependent on the Ag-Ag-Ag bond angle and the Ag-Ag-Ag-Ag dihedral angle. The influence of different geometrical structures on the optical absorption and CD spectra were studied for helical and planar Ag₈. Silver nanowires Ag_n ($n = 4, 6, 8, 10, 12$) were examined to determine the effect of the helical chain length on the electronic properties. The results show that planar clusters exhibit zero circular dichroism signals, whereas when the metal atomic chain loses planarity and obtains a helical organization, strong CD signals arise. The intensities of the CD peaks for these structures are strongly affected by the shape and length of the helix. Our theoretical results are compared with experimental results on DNA-silver complexes.

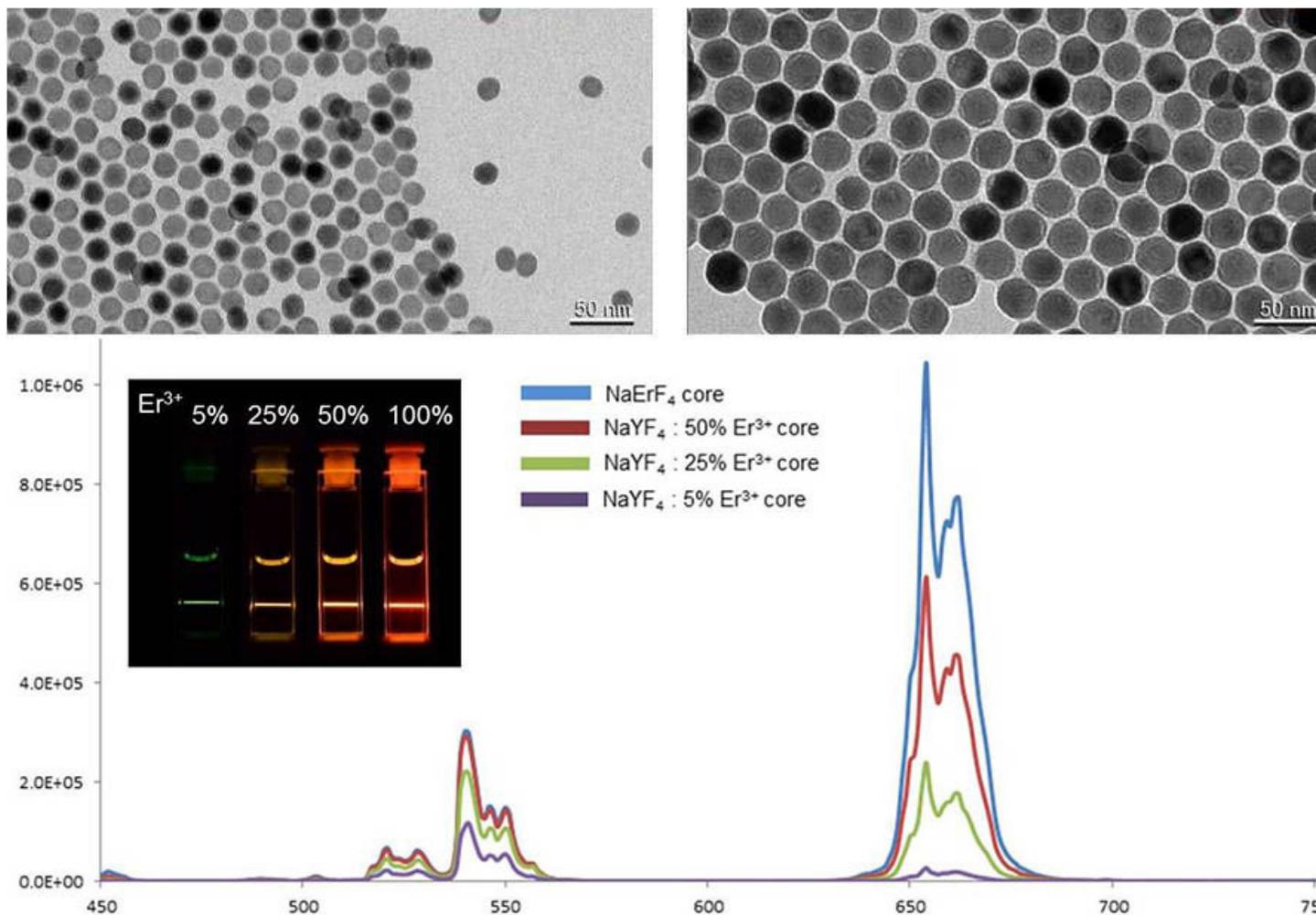
COLL 19

Unprecedented upconversion efficiency in lanthanide nanocrystals via uniform, optically inert shells

*Noah Johnson, Sha He, **Adah Almutairi**, aalmutairi@ucsd.edu. UC San Diego, La Jolla, California, United States*

Lanthanide-doped nanocrystals' unique ability to upconvert multiple low-energy (near infrared, NIR) photons to a high-energy (UV or visible) photon, as well as their lack of blinking and high photostability, suggest that they could revolutionize bioimaging, photovoltaics, and displays. However, concentration quenching and surface quenching have greatly limited these nanostructures' performance. As surface quenching dominates upconversion, especially when nanocrystal sizes are on the order of the excited state energy migration distance (below 20 nm), much research is devoted to enhancing their efficiency by shielding (core-shell structures) or coupling with plasmonic nanostructures. Optically inert shells should decouple dopant concentration quenching from surface quenching, but current methods of epitaxial shell deposition yield anisotropic coatings that are generally too thin in some regions to achieve this goal. We have found that uniform ~10 nm-thick NaLuF₄ shells (Figure, top; left, core; right, core-shell) allow incorporation of a greater concentration of activators within the core, yielding unprecedented upconversion efficiencies (Figure, lower panel). We are currently exploring the mechanism underlying this unexpected phenomenon by measuring the lifetime of emission. Further, we are pursuing upconversion of 800 nm

NIR, which is more biocompatible than the 980 nm that is most efficiently absorbed by current upconverting nanostructures, and in vivo imaging by downconversion to wavelengths > 1000 nm.



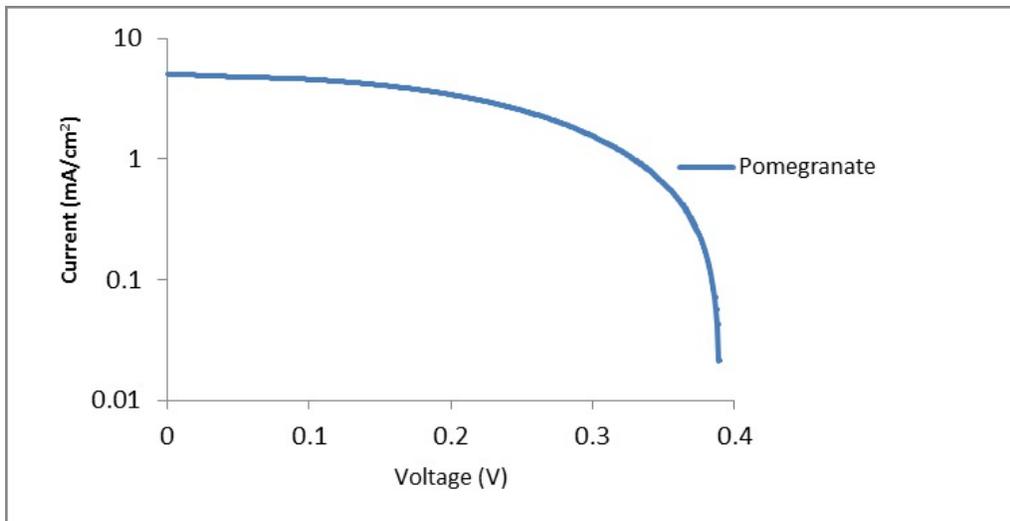
COLL 20

Creation of natural dye sensitized solar cell

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This research focuses on improving the methodology of producing chlorophyll dye-sensitized solar cells by the process of amalgamation with anthocyanin dyes to maximize cell efficiency and power production at the most economical cost and mass

manufacturing process. The methodology of producing a dye-sensitized solar cell divided into three sections: dye extraction, TiO_2 paste application, and solar cell structure. These three important factors contribute significantly to the maximization of a dye-sensitized solar cell. This research conducted explores different ways of improving the current-voltage potential of the solar cells. The performance of the solar cells in terms of efficiency, voltage, and current were tested with 1.5 AMU solar simulator as the light source. The experimental results show that Pomegranate anthocyanin dye produced the greatest photoelectric conversion efficiency (η) up to 2%, an open-circuit voltage (V_{oc}) of 339 mV, and a short-circuit current density (J_{sc}) of 5 mA/cm².

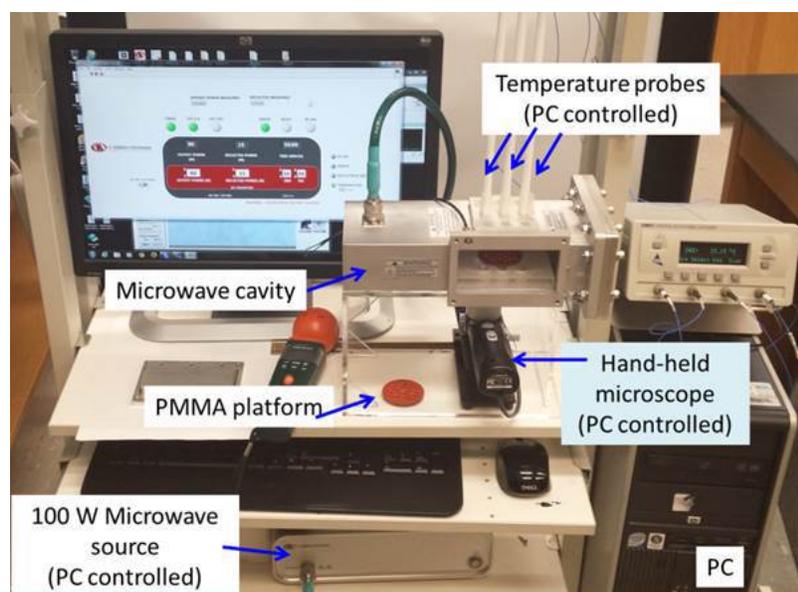


COLL 21

Rapid and sensitive assessment of biological and environmental samples using microwave-accelerated bioassay technique

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Microwave heating has found its way into a wide range of applications in various disciplines, including food industry chemical synthesis, drug discovery, bactericidal and fungicidal sterilization and most recently rapid bioassays. In this work, we have developed a small and portable monomode microwave cavity powered by an external and solid-state microwave generator to be used in the applications of Microwave-Accelerated Bioassays (MAB) technique. We have also designed novel circular bioassay platforms with 21-, 94- and 204-well sample capacity, which were modified with silver nanoparticle films (SNF) for use with our monomode microwave cavity. The circular bioassay platforms and the monomode microwave cavity are designed for on-site and rapid analysis of biological and environmental samples. We present the results of two sandwich-ELISA for shigatoxin (STX1) and glial fibrillary acidic protein (GFAP) performed using our system and compare the results obtained to the “gold standard” ELISA carried out without microwave heating (i.e., conventional technique). Our results show that ELISA for STX1 and GFAP can be completed in less than 5 minutes using the MAB technique, as compared to 5 hours using the conventional technique. The lower level detection and the dynamic range in both MAB technique and the conventional technique were similar, which proves the effectiveness of the new tools developed for MAB technique.



Monomode microwave cavity and circular bioassay platforms used in rapid ELISA

COLL 22

Physical measurements of hydrophobin air-filled bubbles and oil-filled blobs

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Cerato-ulmin (CU) is a small, hydrophobic protein from the hydrophobin family. All hydrophobins have a low molar mass of about 10 kDa. They are extracted from fungi and each has a conserved pattern of disulfide bonds established between 8 cysteine residues. CU is an amphipathic molecule with well-confined hydrophilic and hydrophobic patches, reminiscent of Janus colloids. Through self-assembly into amphiphilic membranes, hydrophobins are able to convert hydrophilic surfaces to hydrophobic ones and vice versa. CU shows unusual ability to stabilize cylindrical air bubbles and oil blobs and can be used for oil spill remediation and clean-up. In this work, various hydrocarbon-based oils and air were encapsulated by CU in aqueous solution. The appearance of the CU shapes was investigated using optical microscopy. The thickness of the CU biomembrane was estimated from mass balance and analysis of bubble and blob images. More precise dimensions can be obtained by small-angle X-ray scattering, which reflects not only the thickness of the bubbles and blobs, but also their shape and size. The dynamic behavior of bubbles and blobs, as well as their stability as a function of time and temperature, was investigated by multi-angle dynamic light scattering. The dynamic surface tension and dilatational modulus of the bubble and blob surfaces were characterized using a home-built microtensiometer.

COLL 23

Interactions of aromatic compounds with water-air and water-phospholipid interfaces

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Interactions of water soluble aromatic compounds at and near water interfaces are important for many biological and environmental systems. This is especially true for cell membranes, where molecular physics occurring near water-phospholipid interfaces and inside phospholipid bilayers is vital for cellular function. This presentation describes interface sensitive experiments examining the role of aromatic molecules, such as phenylalanine, in altering interfacial properties and function. Interfacial partitioning,

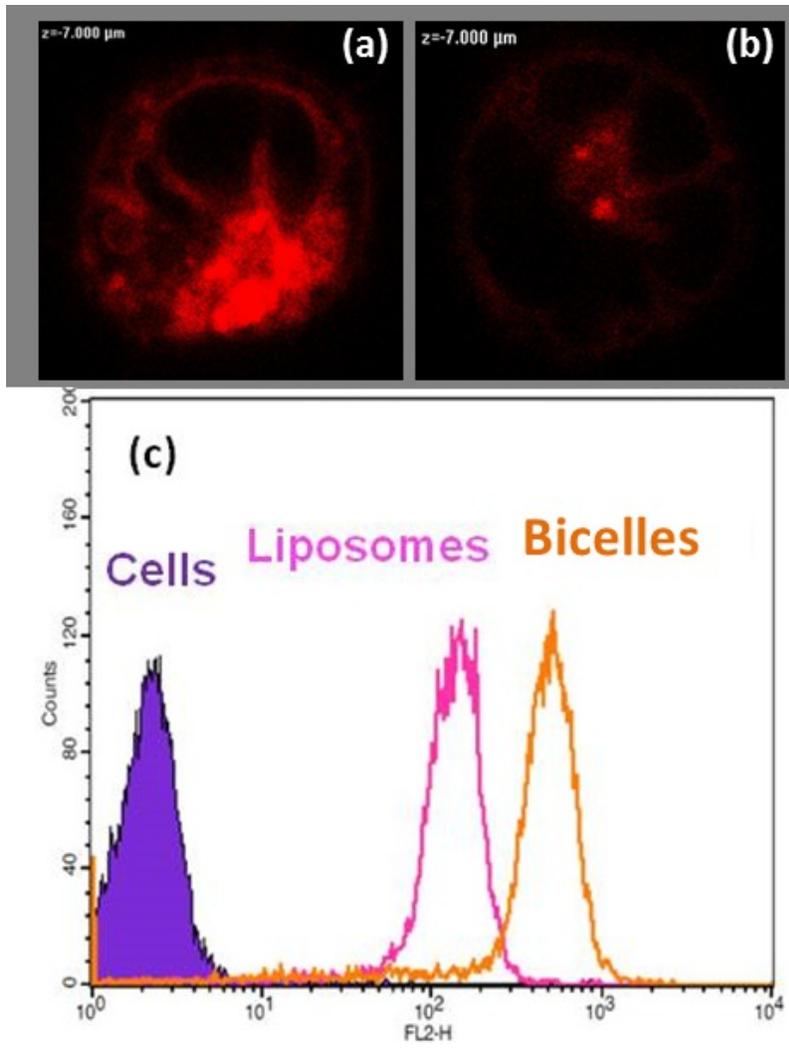
organization, aggregation and permeability are all considered in light of biological functions and diseases.

COLL 24

Cellular uptake mechanisms as controlled by nanostructures of a lipid mixture: Comparison between bicelles and vesicles

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It has been reported that the cellular uptake of nanoparticles is morphologically dependent. Experimental verification on this topic requires a good control over the uniformity of various nanoparticle morphologies made of the same materials. In the past, we were able to self-assemble disk-like bicelles and oblate vesicles in a lipid mixture composed of a zwitterionic long-chain 1,2-dihexadecanoyl-*sn*-3-phosphocholine (DPPC), a zwitterionic short chain 1,2-dihexanoyl-*sn*-glycero-3-phosphocholine (DHPC) doped with small quantities of charged long-chain 1,2-dihexahecanoyl-*sn*-glycero-3-phospho-(1'-rac-glycerol) (DPPG) and a PEGylated lipid, 1,2-distearoyl-*sn*-glycero-3-phosphoethanolamine-N-[methoxy(polyethylene glycol)-2000] (DSPE-PEG2000). The structures of bicelles and vesicles are confirmed by small angle neutron scattering through appropriate model fitting. It shows that the cellular uptake of bicelles is 3 ~ 5 folds of that of the vesicles. Moreover, four uptake pathways have been examined for both nanoparticles, i.e., clathrine-mediated, caveolae-mediated, macropinocytosis and microtubules, respectively. The result shows that vesicles only take the former two mechanisms, while bicelles take all four pathways, to be internalized in the cells. This understanding furthers our knowledge of the cell-nanoparticle interaction which may advance the design for drug delivery nanocarriers.



Fluorescence confocal optical micrographs of CCRF-CEM cancer cells after incubating with NR-containing (a) bicelles and (b) liposomes (i.e., vesicles). The flow cytometry results of the CCRF-CEM cancer cells after incubation with individual nanoparticles in both cases, respectively are shown in (c).

COLL 25

Investigating effects of Al^{3+} on structure and fluidity of lipid membranes: FRAP and molecular dynamics

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Aluminum is the most common metal in the earth's crust, yet the ion Al^{3+} is a well-known neurotoxin. It derives toxicity from the structural changes it induces in lipid membranes upon binding, including increasing bilayer rigidity, facilitating vesicle fusion, and inducing vesicle rupture. However, the mechanism for these processes is not well understood. We implement Fluorescence Recovery After Photobleaching (FRAP) and Molecular Dynamics (MD) simulations to better understand the mechanism of the system. We provide a quantitative analysis of the effect of increasing Al^{3+} concentration on membrane diffusion in both zwitterionic and anionic membranes, as measured by both FRAP and MD. We also investigate the coordination structure of Al^{3+} with phosphatidylcholine lipid head groups, and report Al^{3+} coordination to the phosphate groups and acyl chain carbonyl groups. Our results indicate that addition of Al^{3+} to membranes causes an overall increase in rigidity and decrease in diffusion for zwitterionic membranes, and possibly a transition to gel phase in anionic membranes. Understanding Al^{3+} -membrane interactions is important for a better understanding of the mechanism of aluminum toxicity in biological systems.

COLL 26

Characterization of solid-supported ultrathin films using MP-SPR

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Surface Plasmon Resonance (SPR) has been used already for a few decades for label-free detection and characterization of biochemical kinetics and affinities of many different types of analytes. However, the physical phenomenon is not limited to biochemistry, but is applicable to other nanoscale characterization of thin films [1]. Multi-parametric surface plasmon resonance (MP-SPR) is a new approach to the physical phenomenon, which utilizes full SPR angular spectral measurement and among other things allows new type of thin film characterization methods to be used. MP-SPR can be used to characterize ultrathin nanoscale films for both thickness and refractive index with two methods. It is possible to characterize the films either by measuring them in two different media with high RI difference, such as air and water [1,2], or by measuring the films with two or more wavelengths of light [2,3]. The method effectiveness has been extensively demonstrated using different ultrathin films systems [2-4].

Stearic acid (SA) LB films showed approximately 2.5 ± 0.2 nm thickness with both 2M and 3W methods, and linear increment with increasing layer number. Similarly the polyelectrolyte multilayer consisting of polystyrenesulfonate and polyallylaminehydrochloride (PSS:PAH) was characterized to grow in 3-3.5 nm steps per layer pair. Lipid bilayers spread from vesicles showed typical thickness of approximately 5 nm. The refractive index of all studied thin films correlated well to earlier literature values. Ex-situ depositions of nanofibrillated cellulose (NFC) by spin coating were characterized by the 2W method to form 14 ± 3.4 nm layers. These films were also characterized for their swelling behaviour, which correlated well with QCM based swelling characterization.

Both of the methods are in good agreement with reference methods used in the studies such as QCM, and with previous literature values obtained with different measurement methods. Thus the MP-SPR based characterization methods for ultrathin films appear to be effective, especially for applications requiring both measurement of the film properties and interactions of different compounds with the film.

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COLL 27

Production of highly dispersed silver nanoparticles recovered from photographic film wastes using a simple green method

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This work represents new method to prepare highly dispersed silver nanoparticles with high yield from waste materials. A simple green route was used for producing silver nanoparticles by reducing silver salt using natural gum, starch and/or glucose in alkali media. The gum had the ability to reduce silver in better control of the silver particle size and stability. Transmission electron microscopy (TEM), dynamic light scattering (DLS) and UV–vis spectroscopy were employed to characterize the synthesized Ag nanoparticles. The results indicated the successful synthesis of nano silver particles with average particle size of 5–10 nm. The produced silver nanoparticles showed good resistance to stomach synthetic fluid (0.5 M HCl).

COLL 28

AFM-based fabrication and probing of metallic nanostructures

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A number of applications from electronics to solar energy use metal nanostructures to either make electrical connections or to modify the properties of the materials. AFM-based methods allow the precise fabrication of nanostructures with well defined locations. AFM-based nanoshaving followed by electroless deposition has been used to fabricate silver and copper nanowires. The effect of AFM patterning parameters as well

as solution deposition conditions have been investigated in order to understand the deposition process and optimize the resulting structures. Electrical properties of the metallic films have also been investigated.

COLL 29

Controlling the electronic structure and chemical reactivity of small nanoparticles through atomic composition

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Tuning catalytic activity through electronic structure modification is a grand challenge in the field of heterogeneous catalysis. Recent synthetic advances have produced very small ($\leq 2\text{nm}$), ligand-protected, nanoparticles with quantized, molecule-like electronic structures. Such nanoparticles have shown high catalytic activity for a variety of reactions. The small size and molecule-like electronic structure of these nanoparticles allows the investigation of fundamental questions like: how will the inclusion of a few heteroatoms (dopants) impact the electronic structure and chemistry of the resulting mixed-metal nanoparticle. The inclusion of heteroatoms will likely occur at specific, energetically favorable locations, and the nanoparticle's electronic structure will likely experience unique perturbations. Here we show that the electronic structure and chemical reactivity of small Au nanoparticles can be controllably perturbed by incorporation of heteroatoms (dopants). Electronic structure perturbations were studied with density functional theory (DFT) and experimental techniques such as optical absorbance and luminescence spectroscopy, X-ray photoelectron spectroscopy, non-aqueous electrochemistry, and *in situ* spectroelectrochemistry. Composition-dependent chemical reactivity was studied using electrochemical techniques. These results provide a route to control the electronic structure and chemical reactivity of small nanoparticles, and they help further the concept of "rational" catalyst design.

COLL 30

Behavior of $\text{U}_{24}\text{Py}_{12}$, a uranyl cage cluster, upon addition of salt to aqueous solutions

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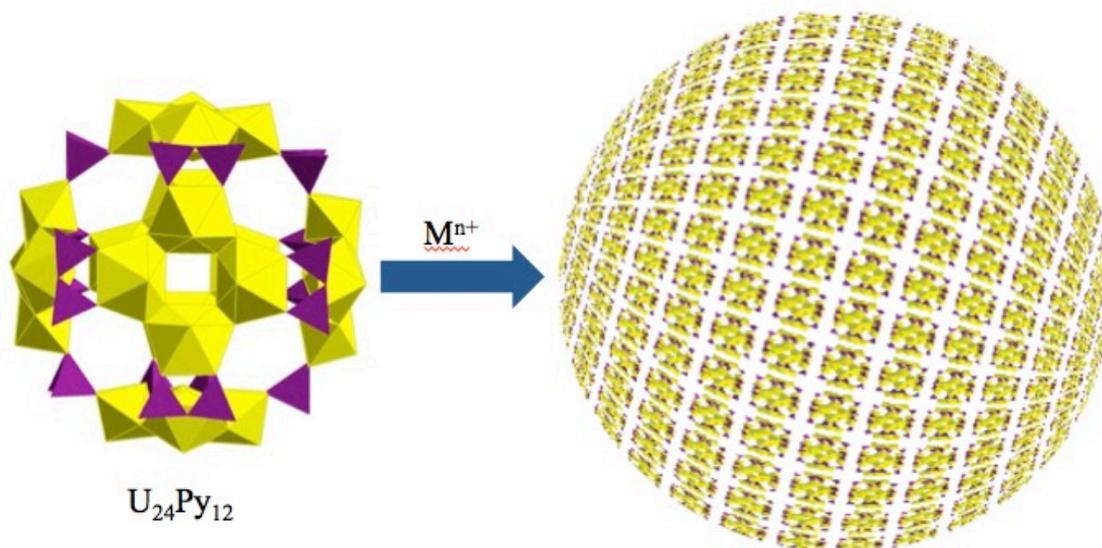
Uranyl peroxide cage clusters include a large family of more than 40 published clusters composed of various sizes and incorporating various ligands including pyrophosphate and oxalate¹. Previous studies have shown that these clusters can be used to separate

uranium from aqueous solution², with potential implications for use in the advanced nuclear fuel cycle. Because of the potential applications of these novel structures, it is important to have a fundamental understanding of the behavior of these clusters, including more complex environments where other ions are present.

Here we will discuss the behavior of a specific cluster, $U_{24}Py_{12}$, and its behavior when aqueous solutions are spiked with mono-, di-, and trivalent cations. The resulting solutions will be analyzed using dynamic light scattering and ultra-small angle X-ray scattering to demonstrate the species in solution. Precipitates that occur upon spiking the cluster solutions will be analyzed using powder X-ray diffraction, X-ray fluorescence spectrometry, and Raman spectroscopy. The results of these analyses demonstrate the impact of cation size and charge on the aqueous behavior of uranium macroions.

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COLL 31

Real time microfluidic investigation: The role of seed age on gold nanorod formation

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We report a real time investigation into the effect of the seed age on the growth of gold nanorods using a microfluidic reaction set up. Through SAXS and UV-Vis analysis we observe the gold seed nanoparticles aging in accordance with Ostwald ripening. A seed solution is then aged *in-situ* and injected directly onto a microfluidic cell to initiate rod growth. Gold nanorod formation is tracked in real time using in-line UV-Vis-NIR monitoring and a decrease in yield with increasing age time is observed. We then show that by diluting the gold seed solution immediately following synthesis the rate of aging can be greatly reduced and nanorods synthesized continuously, in high yield. These results suggest that the age and nature of the seed is critical for the controlled formation of gold nanorods.

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COLL 32

Investigation of the surface effects of Ag nanoparticles in solution as a result of a NSF-TUES related funding opportunity

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An undergraduate exploratory lab that introduces students to a semester-long study of nanoparticle systems led to a larger investigation in the research laboratory to understand the stability and ultimately surface-related pH effects of Ag nanoparticles in solution. Silver nanoparticles were synthesized using the sodium borohydride reduction method and were investigated during formation by using UV-Vis spectroscopy and monitoring changes in pH. In addition scanning transmission electron microscopy (STEM) was used to analyze the size and morphology of the Ag nanoparticles in solution both during and post formation. The ITC, UV-Vis and zeta-potential data of both formation and post formation studies have been investigated in order to make correlations between pH, size and shape of the nanoparticles, their corresponding λ_{\max} and potential surface effects. The data suggests that as the nanoparticles form and the solution returns to thermal equilibrium that a direct correlation between the temperature and the pH of the AgNPs solution exist, indicating a products-related pH response. Herein the investigation of solution based Ag nanoparticles provides a significant opportunity to probe the surface effects and hence stability of these particles.

COLL 33

Dissolution and antibacterial efficiency of silver nanoparticles: Influence of particle size, shape, and surface chemistry

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The behavior of nanoparticles is usually influenced by their size, shape and surface chemistry. Identifying the influence of these attributes on their behavior is important not only to the fundamental understanding the physics and chemistry of materials on the nanoscale, but also to the design of nanomaterials with optimal performance in their applications.

Nanosilver is one of the most extensively used nanomaterials due to their excellent antimicrobial activity. Silver nanoparticles undergo oxidative dissolution in water. The dissolution profile of silver nanoparticles influences both their performance in many applications and the impact to ecosystem after released to the environment. The influence of the size, shape and surface chemistry of silver nanoparticles on their dissolution chemistry has not been well understood so far. The lag in effort on this important issue is partially due to the difficulty in varying one particle attribute while keeping other attributes unchanged in the synthesis of silver nanoparticles.

We developed several synthesis methods to produce a large library of monodisperse silver nanoparticles with independently tunable size, shape and surface chemistry. The high monodispersity of the samples and independent tunability of each attribute enabled us to unambiguously identify the influence of these particle attributes on their dissolution profile and antibacterial efficiency. It was found that silver nanoparticles dissolve very fast in the beginning and then slow down with time. The dissolution stops after a period of time when equilibrium is reached. The size, shape, functional group and molecular weight of the protective agent of silver nanoparticles all have dramatic influence on their dissolution rate, solubility and antibacterial efficiency. The antibacterial efficiency of silver nanoparticles is closely related to the concentration of silver ions released from the dissolution of silver nanoparticles.

COLL 34

Study of interparticle interactions between gold nanoparticles using liquid cell electron microscopy

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The ability to control the self-assembly of colloidal nanoparticles as nanoscale building blocks to create complex structures is crucial for realizing the full potential of nanoparticles in technological applications. To be able to achieve such level of control at the nanoscale, the nature of the relevant forces that govern how individual colloidal

particles behave in the presence of other particles must be understood. Here, we have used *in situ* liquid cell TEM to investigate the role of interparticle forces that determine the outcome of gold nanoparticle assembly. After observing selective self-assembly of gold nanoparticles, we analyzed the assembly dynamics to extract the mathematical form of the interaction potential between the particles. The spatial and temporal resolution offered by liquid cell TEM enables such analysis in the nanoscale which has been difficult to achieve with optical tweezer and confocal microscopy experiments. We then applied the knowledge gained and varied the experimental conditions to yield non-assembly and non-selective assembly. In our work, we demonstrated the use of liquid cell TEM as a technique to quantitatively analyze the interactions between colloidal nanoparticles.

COLL 35

Size-focusing synthesis of gold nanoclusters with *para*-mercaptobenzoic acid

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Etching methods are now widespread for preparation of atomically monodisperse thiolate protected gold nanoparticles. Etching methods are not widespread, however, in the production of water-soluble gold nanoparticles. Reported is a new method for etching or size-focusing of large gold nanoparticles utilizing *para*-mercaptobenzoic acid. We observe preferential formation of three large gold nanoparticles with approximate masses of 22kDa, 53kDa and 88kDa. Based on the stability of these masses against further etching, they appear to be especially stable sizes. These sizes are not prominent after etching challenges with organosoluble ligands, and the 53kDa and 88kDa sizes appear novel. The overall trend in particle size distribution over time is also unusual, with larger sizes dominating at longer time points.

COLL 36

Constructing 0, 1, and 2D silvers within interlayer spaces of titania nanotubes

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Zero-, one- and two-dimensional silvers were successfully nucleated and grown within the narrow interlayer spaces of titania nanotubes (Ti-NT). Silver clusters were uniformly deposited between the 1-2 nm gaps between the titanate layers from liquid solution. Manipulating the solution chemistry, the formation of 1D silver nanorods can be induced within the interlayer gap. Pretreatments of the Ti-NT are required to prepare 2D silver nano-islands. Detailed microscopy and spectroscopy studies indicated that the structure and chemistry of the silver are strongly influenced by the confinement. Furthermore,

these materials display very interesting optical properties and the confined 2D silvers exhibit strong plasmon effects.

COLL 37

Iridium-triggered facet transformation of Au nanocrystals via spontaneous oxidation-reduction process

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Shaped metal nanoparticles have received high attention for their unique properties relying on the facet structures. To induce different facets over a metal nanoparticle, strategies for shape evolution were widely studied. Although gold is relatively stable among all precious metals, gold nanoparticles are partially etched under certain reaction condition such as presence of oxygen in reaction mediate or disproportionation reaction by Au^{3+} ions. Thus, facets of Au nanoparticles can be post-modified via oxidative etching. [1, 2] However, precisely controlled formation of highly pure and monodispersive nanocrystals is rather tough due to the difficulty in optimizing etching and growth rate. In our work, a facile method of Ir-triggered facet transformation over Au single crystals and polyhedra at nanoscale was developed. By the addition of IrCl_3 , suspended gold nanoparticles totally dissolved due to oxidative etching. Interestingly, gold nanoparticles come back in 6 hours while they all become (111) facet-dominated shape such as octahedra, tetrahedra and triangular plates. These retrieved nanoparticles are always in high purity and uniformity. According to the results of X-ray absorption, a chloride-assisted mechanism can be proposed to explain the spontaneous oxidation-reduction process.

COLL 38

Capillary migration of spheres on curved fluid interface

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We study migration of 10 micron PS microspheres at fluid interfaces with well-defined curvature fields. The particles migrate along curvature gradients to sites of high curvature. Particles “sense” the host interface shape via the contact line boundary condition, which can, in principle, either obey an equilibrium contact angle or be pinned. We derive capillary energies for both cases. For pinned contact lines, particle roughness makes a nanoscopic quadrupolar distortion in the interface, which couples to the curvature field. The resulting capillary energy is linear in the deviatoric curvature. For equilibrium contact lines, the capillary energy is negligible. We compare the energy

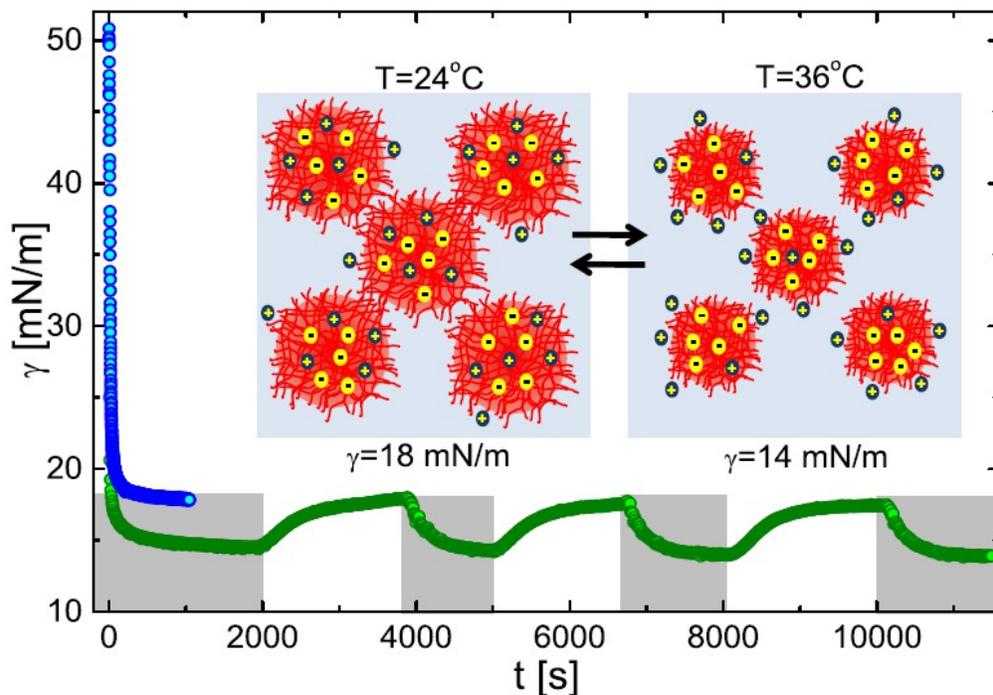
dissipated by particle migration to prediction, finding excellent agreement with the expression for pinned contact lines. This phenomenon provides a macroscopic read-out for nanometric surface roughness.

COLL 39

Interactions between soft microgel particles at fluid interfaces

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We studied the adsorption and interactions of poly(NIPAM) particles (Volumetric Phase Transition at 32°C/90°F) at Air-Water and Oil-Water interfaces. Experiments with a Langmuir Trough in combination with characterization of the molar mass, allowed measuring the hitherto unknown equation of state. From it, we found that adsorbed particles are strongly stretched, giving rise to discernable surface pressures even at low coverage densities. Combining these results with measurements of how the surface pressure of a Pendant Bubble evolves in a freshly created pNIPAM solution, allowed to analyze the adsorption kinetics. Diffusive transport and the creation of a (growing) adsorption barrier as the adsorption proceeded, were corroborated. Remarkably, the final area per particle was practically the same for all bulk pNIPAM concentrations; suggesting a drastic change in the adsorption barrier and/or net adsorption energy as the coverage density reaches this value. Additional experiments at the Oil/Water interface using Pendant Drops afforded well-defined variations of both temperature and droplet area. Cycling between 24°C (75°F) and 36°C (97°F) indicated a full reversibility of the surface pressure, while large stepwise reductions in the droplet area resulted in surface pressure responses without a relaxation time. These findings suggest that the pNIPAM particles adsorb irreversibly. Remarkably, raising the temperature from 24°C to 36°C gave a significant increase in surface pressure, in spite of the considerable shrinkage of the particle in the bulk liquid. This trend will be tentatively explained.



Response of the interfacial tension of a poly(NIPAM) coated aqueous drop in oil, to changes in temperature. Green circles: drop created at 36 and cycled between 36 and 24 degrees C. Blue circles: drop created at 24 C. Grey areas denote the part of the temperature cycle at 36 C while blank spaces correspond to 24 C. The inset shows a schematic of the proposed particle conformations in the aqueous phase at the two temperatures.

COLL 40

Molecular characterization of surfactant adsorption at the surface of emulsion particles

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Emulsions are very important in many industries including: oil refinery, cosmetics and food. The stability and properties of the emulsions are determined by the oil/water interface, which can be stabilized with surface-active species, such as surfactants or nanoparticles. The behavior of these species at the oil/water interface is known to effect emulsion formation and stability and can also be dependent on various other parameters such as concentration, ions, and additional cosurfactants and polymers. This presentation will describe our vibrational sum frequency scattering spectroscopy studies of surface-active species at the emulsion interface with a specific focus on the surfactant AOT. Its molecular structure, solvation and alkyl chain conformation as measured at the surface of a reverse emulsion particle suspended in an organic solvent, regular emulsion particle suspended in water and at the planar organic/water

interface will be discussed as will the effect of counterion and particle size on the interfacial properties.

COLL 41

Understanding Pickering emulsions using multiscale simulations

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Although Pickering emulsions are becoming extremely popular in the academic community, few applications benefit from such interesting systems. We argue that better understanding their fundamental properties, especially related to their stability, will enable a host of practical applications. The stability of Pickering emulsions is related to structural and dynamical properties of interfacial nanoparticles. Our group has investigated such properties by means of multi-scale simulations (from atomistic to coarse-grained, to phenomenological). We considered several nanoparticle types, including spherical and elliptical, Janus or homogeneous with different amounts of hydrophilic/hydrophobic surface groups. We focused on (a) the effect of particle properties on self-assembled aggregates structure, (b) systems of different composition, (c) particles properties as a function of droplet size, and (d) particles with grafted polymers of varying lengths and chemical features. For a given system composition, we investigated the effect of increasing nanoparticle density. We will present a survey of our recent results, quantified in terms of interfacial tension reduction, radial distribution function, order parameters, contact angle, self-diffusion coefficient, etc. The goal is to identify properties that could be tested experimentally and propel the practical utilization of these fascinating systems.

COLL 42

Tracking nanoparticles in 3D – techniques and applications

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The ability to track nanoparticles with nanoscale precision in three dimensions enables the study of particle-particle and particle-interface interactions in complex media. These are important in fields as diverse as cell biology and oil recovery. A complete understanding of the physics involved requires 3D measurements that are precise and accurate in both space and time. Making such measurements becomes increasingly difficult as the particle diameter, d , decreases – diffusion coefficients scale as $1/d$ and the number of photons available decreases as d^3 . In other words, the smaller the particle, the faster it moves, and the dimmer it becomes. We have developed both

single- and multiple-particle tracking methods. We will discuss the spatial and temporal resolution limits of these approaches with reference to nanoparticles at oil-water interfaces and at silica-water or silicone-water interfaces in nanofluidic confinement.

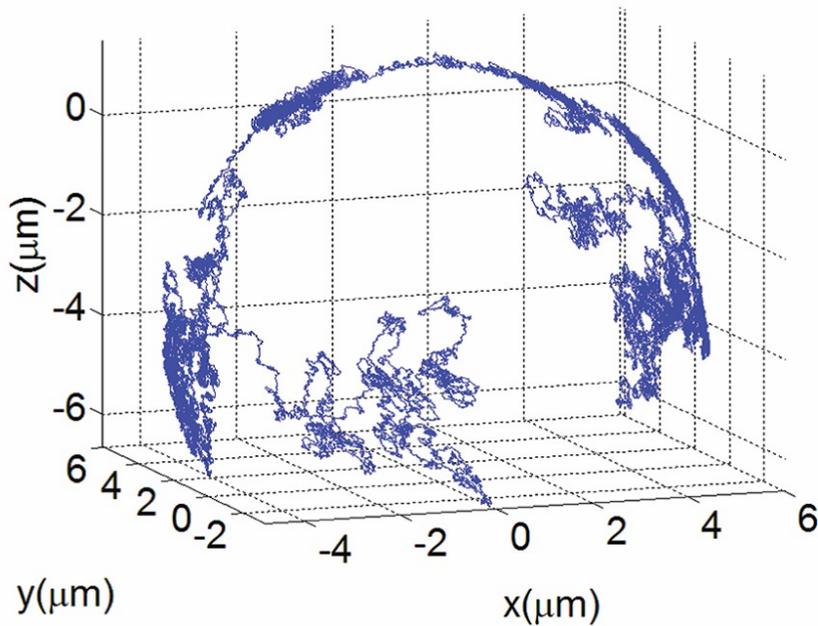


Figure 1. 3D tracking of a 200-nm-diameter polystyrene particle diffusing at the surface of a silicone oil droplet in water. The 3D trajectory shows the profile of the oil droplet.

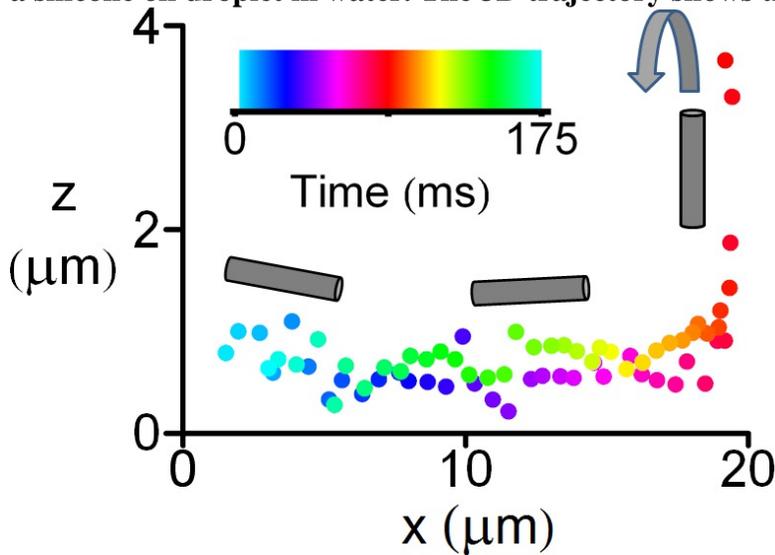


Figure 2. A rodlike magnetic nanoparticle (grey cylinder) switches direction and rotates at $x = 20 \text{ mm}$ under an applied magnetic field. The particle is tracked along a 3D trajectory in the image plane with centroid analysis (x) and perpendicular to the image plane with through focus depth analysis (z). The depth analysis allows calibration of the near-surface

viscous drag the particle experiences. Time is encoded in the color of the data points.

COLL 43

Spontaneous emulsification and interface formation induced by colloids

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In this talk I will present recent progress in our understanding of experimentally observed thermodynamically stable Pickering emulsions: emulsion droplets stabilized by colloidal particles that adsorb at the oil-water interface. Contrary to the 'classical' Pickering emulsions that are intrinsically unstable or metastable, we found proof that under some conditions, Pickering emulsions are the thermodynamic equilibrium state of oil-water-colloid mixtures [1]. In particular, recent findings regarding the influence of static [2] and dynamic [3] factors that influence stability will be discussed. In another system, one that consists of floppy colloids with a broken symmetry, a variety of two-dimensional structures were found: bubbles, sheets and shells. These are other examples where effectively, interface is being created. However, different from the situation in Pickering emulsions, shells are 'hollow' – both inside and outside consist of water. An attempt will be made to explain the directionality that underlies the stability of these two-dimensional structures.

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COLL 44

DNA-functionalized nanoparticle assembly

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The selectivity of DNA recognition inspires an elegant protocol for designing versatile nanoparticle (NP) assemblies. We use molecular dynamics simulations to analyze dynamic aspects of the assembly process and identify ingredients that are key to a successful assembly of NP superlattices through DNA hybridization. A scale-accurate coarse-grained model faithfully captures the relevant contributions to the kinetics of the DNA hybridization process and is able to recover all experimentally reported to date binary

Superlattices. With multi-scale modeling we show that through very slow cooling, DNA functionalized nanoparticles can assemble into superlattices with a specific crystal habit, providing a nanoscale analogue to the crystallization behavior exhibited by conventional atomic crystals. We also describe directed assembly of nanoparticles at interfaces.

COLL 45

Capillary foams: A new pathway toward functional porous materials

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Liquid foams are a familiar part of everyday life from beer and frothed milk to bubble baths; they also play important roles in industrial processes like enhanced oil recovery and the production of lightweight foam packaging, cushions, and insulation. Here we report the discovery of a new class of foams, obtained by frothing a suspension of colloidal particles in the presence of a small amount of an immiscible secondary liquid. A unique aspect of these new foams, which we call capillary foams, is that the suspended particles mediate spreading of the minority liquid around the gas bubbles. The resulting mixed particle/liquid coating can stabilize bubbles against coalescence even when the particles alone cannot. Moreover, the coated bubbles become immobilized in a network of excess particles in the liquid bulk that connected via bridges of the minority liquid and are held together by capillary forces, much like the water-bridged grains of wet sand in a sand castle. We demonstrate that the formation of capillary foams is a general phenomenon by exploring a diverse set of particle/liquid combinations and by rationalizing the results with a simple free energy model. In addition to their many possible applications as liquid foams, capillary foams can serve as precursors for hierarchically-structured solids with porosity on different length scales and with significant application potential in their own right. We conclude by discussing some of the functionalization options arising from the presence of the minority liquid.

COLL 46

Organized assemblies of colloids formed at the interfaces of micrometer-sized droplets of liquid crystal: Enabling the synthesis of patchy and nonspherical particles

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This presentation will describe the use of liquid crystal (LC)-in-water emulsions for the templated assembly of either spherical or non-spherical particles with organized, chemically-distinct domains located on the surfaces of the particles. The approach involves the positioning of solid colloids at the surfaces of the LC emulsion droplets, via interactions mediated by the elasticity of the LC and topological defects that form

predictably at surfaces of water-dispersed LC droplets. Specifically, we have found that three key interactions underlie organized assemblies formed by colloids at the curved surfaces of water-dispersed nematic LC microdroplets: (i) a long-range attraction of the adsorbed colloids to regions of the droplet interface at which splay distortion of the LC is at a maximum (splay attraction), (ii) inter-colloid quadrupole—quadrupole elastic interactions (the result of a quadrupolar topological defect structure about the colloids), and (iii) electrostatic repulsion between colloids. These three interactions promote formation of hexagonal arrays of colloids at well-defined locations on the LC droplet interface. In contrast, for the case of colloids at a flat aqueous—LC interface, the splay attraction is absent and the electrostatic repulsion keeps colloids separated under conditions of low ionic strength in the aqueous phase. Thus, the influence of splay attraction on the curved LC droplet interface is two-fold. It both overcomes repulsive interactions to promote the ordering of colloids on the surfaces of LC droplets, and plays a key role in determining the morphology of the assembly formed. Overall, the results to be discussed in this presentation provide guidance for the design of chemically patchy particles (including Janus particles) by advancing our understanding of the directed assembly of colloids at interfaces of LC droplets.

COLL 47

Artificial organelles: Cellular expression and assembly of polypeptide microdomains

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INTRODUCTION: By using synthetic biological materials to assemble structures, process information, and harness energy, it is becoming possible to engineer new structures, such as artificial organelles. Towards this goal, our recent reports focus on protein polymers that reversibly phase separate into microdomains within live cells. Depending on their peptide sequence, they stimulate sorting or assembly of co-expressed proteins. We also developed microdomains that specifically intervene in clathrin-mediated endocytosis.

METHOD: Elastin-like polypeptides (ELPs) are protein polymers, of the sequence (VPGXG), that self-associate above a transition temperature, which depends on X and I . Utilizing ELP phase separation, we hypothesized that receptor tyrosine kinases can be reversibly clustered, thus modulating the activity of these important trans membrane proteins. In response to ligand, epidermal growth factor receptors (EGFR) auto-phosphorylate, internalize, and signal for cell survival. Due to its importance in cancer proliferation and the availability of clinically relevant kinase inhibitors, human EGFR was used to test this hypothesis. EGFR morphology was assessed as a function of temperature using both live and fixed cell imaging assayed by indirect

immunofluorescence and fluorescent protein tags respectively.

RESULT: A small library of EGFR ELP fusions was characterized, many of which display temperature-dependent changes in morphology. Most notably, phase separation was associated with the clustering of EGFR fusions into microdomains that rapidly internalized within the cell. These microdomains can be visualized during live cell imaging using a co-transfected green fluorescent protein fused to a related ELP. Most importantly, these internalized microdomains showed evidence of phosphorylation.

CONCLUSION: Via genetic engineering, it is possible to express ELP fusions with trans membrane proteins that gain the ability to phase separate as a function of temperature. With additional study, this technology may become a tool for the controlled manipulation of biological signaling pathways. These tools may enable the dissection of cellular signaling pathways, the high throughput selection of small molecule inhibitors of desirable specificity, and the engineering of synthetic biological components for cellular therapies.

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COLL 48

Self-assembling peptide materials for hydrogen sulfide delivery

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Hydrogen sulfide (H₂S) is now widely recognized as the third gasotransmitter (in addition to nitric oxide and carbon monoxide), and it has significant therapeutic potential. However, for successful therapeutic use of H₂S that avoids potential off-target effects, efficient delivery to a site of interest must be attained. We present here a strategy to achieve localized delivery of H₂S using peptide-based gels. The gels are comprised of peptides derivatized with S-arylothiooximes—a functional group that releases H₂S in response to cysteine. The functionalized peptides self-assemble in aqueous solution to form long cylindrical micelles, and entanglement of these cylindrical micelles leads to gelation in aqueous solution at 1 wt. %. We present here the synthesis, mechanical properties, H₂S release rate, and biological evaluation of these unique gels.

COLL 49

Photons, chemicals, and electric fields as functional stimuli in supramolecular materials

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Supramolecular self-assembly is an emerging strategy to design soft materials with functions that benefit from the molecular versatility of organic matter. One of their important characteristics is their ability to combine dynamic behavior and high degrees of order brought about by noncovalent interactions. The dynamic nature allows them to self-repair, respond strongly to external stimuli, and transform their structure in response to specific conditions in their environment. A second important feature is the possibility of using noncovalent interactions to integrate the necessary functions of supramolecular systems. This lecture will describe a broad cross section of such systems that include supramolecular networks that respond strongly to electric fields revealing ferroelectric behavior. Other systems to be described respond to visible photons to generate hydrogen fuel as a result of functional integration through noncovalent bonds of light harvesting assemblies with catalysts. A third variety of assemblies respond to added molecules that can bind biomolecules thus allowing supramolecular systems to switch their bioactivity toward cells that are in contact with them.

COLL 50

3D cell entrapment as a function of the weight percent of peptide-amphiphile hydrogels

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The design of scaffolds which mimic the stiffness, nanofiber structure, and biochemistry of the native extracellular matrix (ECM) has been a major objective for the tissue engineering field. Furthermore, mimicking the innate three dimensional (3D) environment of the ECM has been shown to significantly alter cellular response compared to traditional two dimensional (2D) culture. We report the development of a self-assembling, fibronectin-mimetic, peptide-amphiphile nanofiber scaffold for 3D cell culture. The PR_g peptide-amphiphile was used for this study as studies in our group have shown that it outperforms other RGD based peptide functionalized surfaces. More important, PR_g peptide-amphiphile hydrogels have been shown to support increased cell adhesion, proliferation, and ECM secretion as 2D substrates and outperform PuraMatrix hydrogels and PEG hydrogels functionalized with fibronectin. To form such a scaffold, 5 mol% of the bioactive PR_g fibronectin-mimetic peptide-amphiphile was mixed with 95 mol% of a diluent peptide-amphiphile (E2) whose purpose was to neutralize electrostatic interactions, increase the gelation kinetics and promote cell survival. We then varied the weight percent (wt%) of the hydrogels and investigated for

the first time the effect of the wt% on the 3D cell entrapment in peptide-amphiphile hydrogels.

The mechanical properties and hydrogel microstructure were characterized for various wt% formulations of the 5 mol% PR_g - 95 mol% E2 peptide-amphiphile mixture. Atomic force microscopy verified the fibrillar structure of the gels and confocal microscopy showed that the projected area of void space was decreased as the wt% of the hydrogels was increased. The elastic modulus of the gels increased with increased wt% and the presence of entrapped cells in the gels decreased the elastic modulus by approximately 40% for both the 0.5 and 1.0 wt% peptide-amphiphile hydrogels. While both formulations supported cell proliferation, the 0.5 wt% gels supported significantly greater fibroblast cell proliferation throughout the gels than the 1.0 wt% gels. However, the 1.0 wt% hydrogels promoted greater increase in expression of fibronectin and type IV collagen ECM proteins compared to the 0.5 wt% formulations.

This study suggests that this fibronectin-mimetic scaffold holds great promise in the advance of 3D culture applications and cell therapies.

COLL 51

Targeting collagen strands by triple helix hybridization

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Collagen, the most abundant protein in mammals, plays a crucial role in tissue development and regeneration. Since elevated collagen remodeling activity is associated with numerous pathologic conditions (e.g. tumor, fibrosis, arthritis), ability to target unstructured collagens in diseased tissue could lead to new diagnostics and therapeutics, as well as applications in regenerative medicine. In this talk, I will present a new strategy for targeting denatured collagens that is based on triple helical hybridization between collagen strands (of diseased tissues) and synthetic collagen mimetic peptide (CMP). This hybridization results in robust collagen specific binding *in vivo* which allows detection of degraded collagens present in normal tissues undergoing fast remodeling (e.g. bones and cartilage) and those in diseased tissues with persistent wound healing activity (e.g. tumor, arthritis). I will describe various experiments designed to elucidate the mechanism of the hybridization as well as those verifying the CMP's collagen binding capacity both *in vitro* and *in vivo*. Due to its neutral and hydrophilic nature, the CMP is an extremely inert peptide with high serum stability. It is also a structurally simple peptide that can be readily conjugated to various imaging and therapeutic modalities. The CMP offers an entirely new way to target the microenvironment of diseased tissues which could lead to new opportunity for management of pathologic conditions associated with high level of collagen degradation and remodeling.

COLL 52

Design evolution of an antibacterial bioadhesive inspired by cationic peptide hydrogels

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Surgical site infections cause significant postoperative morbidity and increased healthcare costs. Materials that can be applied to damaged tissue during surgery that thwart infection would be clinically useful. We have reported that hydrogels having inherent antibacterial activity can be prepared from self-assembling cationic beta-hairpin peptides (*Biomaterials* **2012**, 33, 8907; *Biopolymers Peptide Science*, **2013**, 100, 637). Depending on the exact amino acid composition of the peptide, gels having potent activity against drug-resistant strains of bacteria can be prepared. Although useful in certain applications, these gels lack significant adhesive character, which precluded their use in tissues that experience significant load. However, a detailed understanding of the peptide gel's antibacterial mechanism of action has enabled the subsequent design of polymer-based, syringe-injectable bioadhesives that are capable of killing bacteria on contact (*Nature Communications*, **2014**, 5, 4095, 1). These hydrogel adhesives are prepared by mixing polydextran aldehyde and branched polyethylenimine during delivery from a dual barrel syringe. Crosslinking between the aldehyde and amine components defines the cohesive nature of the gel while schiff base bond formation between the gel and the extracellular matrix defines its adhesive quality. These adhesives kill both Gram-negative and Gram-positive bacteria, while sparing human erythrocytes. An optimal composition of 2.5 wt % oxidized dextran and 6.9 wt % PEI sets within seconds forming a mechanically rigid (~1700 Pa) gel offering a maximum adhesive stress of ~ 2.8 kPa, on the order of fibrin glue. A murine infection model showed that the adhesive is capable of killing *S. pyogenes* introduced subcutaneously at the bioadhesive's surface, with minimal inflammatory response. The adhesive was also effective in a cecal ligation and puncture model, preventing sepsis and significantly improving survival.

COLL 53

Self-assembling antimicrobial nanofibers based on supramolecular peptide assemblies

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Peptide-based supramolecular assemblies represent an emerging and important class of biomaterials that have been extensively utilized in various biomedical fields, including drug delivery, vaccination and 3-D cellular scaffolds. *Surprisingly, such peptide assemblies have rarely been directed toward antimicrobial therapy development which has been considered as an urgent biomedical problem to tackle along with cancer therapy and tissue regeneration.* In this work, we present the first example of *de novo* designed multidomain peptides (MDPs) that form self-assembling antimicrobial

nanofibers (SAANs) with a broad-spectrum antimicrobial activity. SAANs, the 'nucleus' of our antimicrobial therapeutic platform, are supramolecular assemblies of *de novo* designed β -sheet-forming MDPs with a general formula of $K_x(QL)_yK_z$. Unlike most AMPs that exist as a monomer prior to their binding with lipid membranes, MDPs can be formulated into supramolecular nanofibers through proper balance of the number of lysine residues and repeating units of the (QL) domain. ***The formation of SAANs offers a huge advantage over previously designed monomeric AMPs in that the assembled nanofibers exhibit enhanced cell penetration and protects individual peptides against proteolysis while dramatically reducing their toxic and reactogenic effects on eukaryotic cells.*** To our knowledge, this is a unique set of properties, which has yet to be evaluated for its antimicrobial potential. This study details a design strategy to optimize supramolecular AMPs for minimal cytotoxicity, enhanced proteolytic stability, potent cell penetration and effective antimicrobial activity, thereby facilitating their application for systemic anti-infective treatments.

COLL 54

Ultrasonic modification and functionalization of surfaces and particle

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With Ultrasound one can create bubbles, which collapse providing shortly extreme pressures and temperatures. As hydrophobic surfaces favour bubble formation one may use this process to functionalize and to pattern surfaces. In this contribution I will demonstrate by video microscopy and scanning force microscopy that bubbles can be guided by a patterned surface allowing a lateral control of the impact of cavitation. The latter exists in creating a nanoporous surface that can be simultaneously loaded by drugs. This in turn enables control of adhesion and proliferation of cells adjacent to the surface. Additionally depositing a responsive polymer film on the surface enables controlled release which in turn may be used in biomedical devices as well as in anticorrosion or antifungal coatings.

As a typical bubble nucleus has dimensions around 100 nm, one expects different behavior for particles larger or smaller than this dimension: Larger particles may be roughened or split (depending on size), smaller particles may be arranged at the bubble surface and sintered due to high local temperatures. In all cases defects may be created that may serve as catalytic centers as well as fluorescent centers

COLL 55

Functionalization of gold nanorods

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Gold nanorods are of great interest for many engineering and biological applications. In virtually all cases, applications require chemical functionalization of the nanorod surface. In this talk I will discuss the methods to functionalize gold nanorods with many different sorts of molecules, polymers, and "hard shells". The most intriguing aspect of an anisotropic shape such as a rod is that one could functionalize just the ends of the rods or just the sides of the rods. There are scattered reports of this in the literature; I will highlight recent progress in this area.

COLL 56

Hybrid platforms based on metal nanoparticles-doped filter paper for sensing and catalysis

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Cellulose-based materials are widely used in analytical chemistry as platforms for chromatographic and immunodiagnostic techniques. The numerous advantages (3D porous structure, flexibility, biocompatibility and biodegradability, low cost, among others) presented by this material make a valuable substrate for sensing, catalysis, etc. With the aim of developing a versatile platform, we present a simple and general strategy for the immobilization of metal nanoparticles on filter paper; where the strong van der Waals forces and hydrophobic interactions between the particles and the substrate are responsible of the nanoparticle permanent immobilization. The final application of these cellulose based substrates is determined by the nature of the nanoparticles (Figure 1). For instance, we have demonstrated that the self-assembly of Ni/NiO nanoparticles on filter paper allows the selective immobilization of proteins containing polyhistidine tags (His-tag) and its further use for immune-capture of live bacteria or for performing enzymatic reactions (Figure 1 (2)). In the case of doping with Pd nanoparticles, the hybrid platform have been tested for several model reactions displaying efficient catalytic activity and excellent recyclability and reusability(Figure 1 (1)). Additionally, the use of Au nanoparticles has allowed to obtain a bifunctional platform with catalytic and, at the same time, sensing capabilities allowing the real-time monitoring of chemical reactions on its surface through Surface Enhanced Raman Scattering (SERS) technique (Figure 1 (3)).

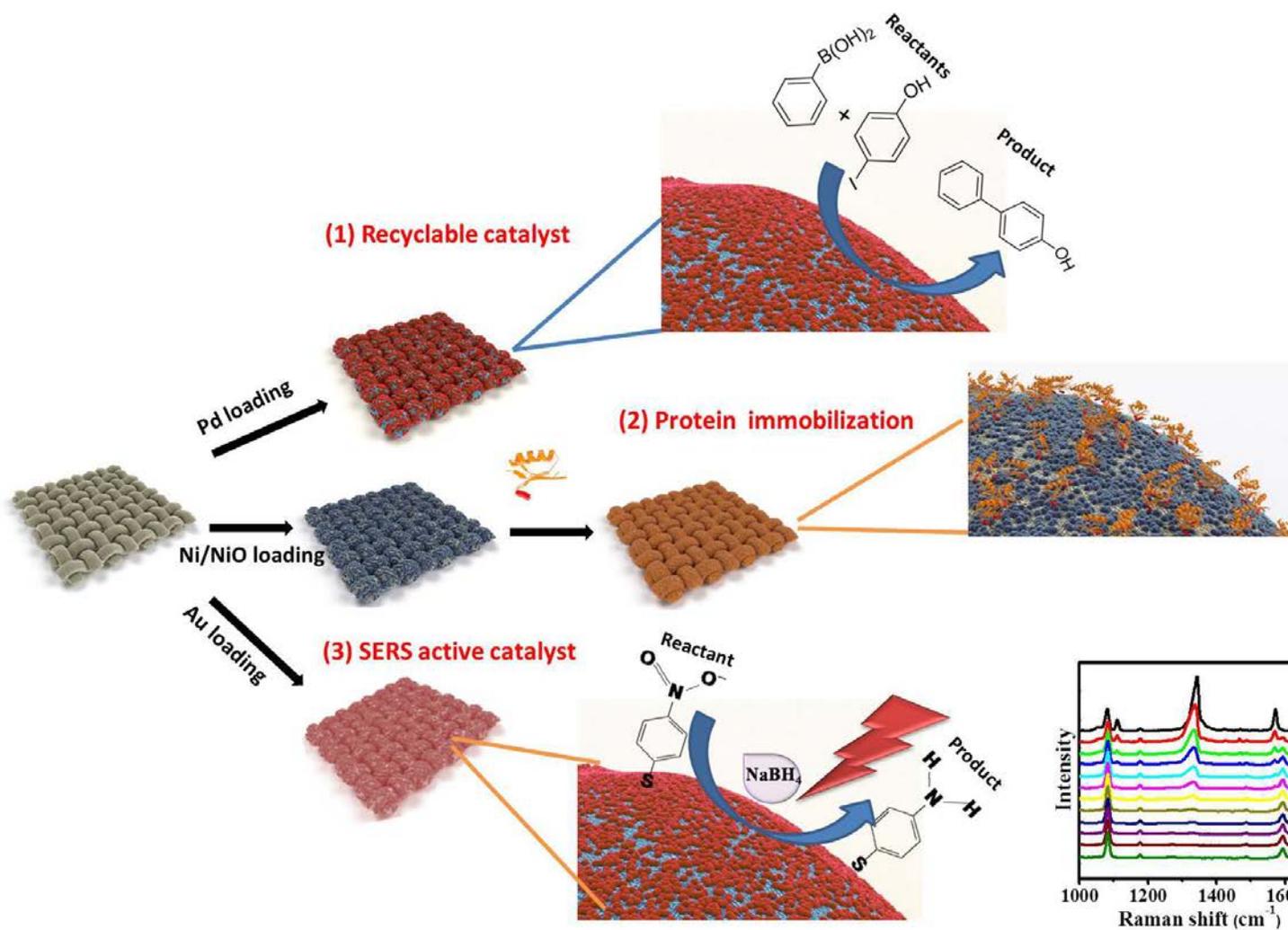


Figure 1. Schematic representation of the nanoparticle-doped filter paper preparation. (1) Pd-doped filter paper for catalysis. (2) Ni/NiO nanoparticles on filter paper for selective immobilization of proteins containing polyhistidine tags (His-tag). (3) Au-doped filter paper with bifunctional activity (catalysis and SERS sensing).

COLL 57

Dynamically self-assembling nanoflasks

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Nature has long inspired chemists with its abilities to stabilize ephemeral chemical species, to perform chemical reactions with unprecedented rates, yields, and selectivities, and to synthesize complex molecules and fascinating inorganic nanostructures with seemingly effortless ease. What natural systems consistently exploit - which is yet fundamentally different from how chemists perform reactions - is

their aspect of nanoscale confinement. Inspired by Nature, we design several different types of synthetic confined environments and subsequently study how chemical species behave inside them. One type of confined spaces is nanopores of colloidal crystals which self-assemble from nanoparticles functionalized with chromophore units upon exposure to specific wavelengths of light. We have shown that these nanopores can behave as “nanoflasks” by selectively capturing different chemical species from solution when nanoparticles self-assemble. Inside the nanoflasks, chemical reactivity of the captured species is altered - we have shown, for example, that the dynamically self-assembling nanoflasks can significantly accelerate chemical reactions, unusual stereochemistries can be induced, and that the trapping process can protect reactants from undesired side reactions.

COLL 58

Compact coatings for quantum dots that resist nonspecific binding to proteins, cells, and tissues

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Quantum dots are a class of light-emitting nanocrystal used for high-sensitivity multi-color imaging of molecules and cells. A major ongoing challenge is to coat these particles with a ligand shell that is compact in size, stable, and resistant to nonspecific binding to biological structures. Here we report a new series of multidentate molecular and polymeric ligands that fulfill these needs, which we have designed by optimizing the nanocrystal binding domains and hydrophilic domains for colloidal dispersion. The binding domains have a tunable number of thiols or imidazoles and the hydrophilic domains incorporate sulfobetaine and ethylene glycol oligomers that resist nonspecific interactions with proteins, cells, and tissues. Using these materials we have generated stable quantum dots with just a 1-nanometer radial increase in hydrodynamic size arising from the coating. We have further developed a universal technology for phase transfer to aqueous solvents compatible with a diverse range of molecular and polymeric ligand coatings to reproducibly yield homogeneous nanocrystals with high stability and high quantum yield. We expect that these materials and techniques will be broadly applicable for generating quantum dot probes with substantially reduced size and increased target specificity for molecular imaging applications in complex cells and tissues.

COLL 59

Functional nanoparticles: Synthesis and biomedical applications

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The talk focuses on the synthesis and biomedical applications of composite nanoparticles containing noble metal and iron oxide. Using solution phase based reduction chemistry, we have synthesized a series of monodisperse oleylamine-coated nanoparticles of Au and Pt. These noble nanoparticles can serve as seeds for the production of composite dumbbell-like NM-Fe₃O₄ (NM = Au, Pt, or PdPt) nanoparticles. Once deposited on an electrode, these dumbbell nanoparticles serve as HRP-mimic catalyst for electrochemical reduction of H₂O₂, making it possible to detect H₂O₂ released from different cells for cell characterization. These dumbbell nanoparticles can also be functionalized selectively on the noble metal and iron oxide sides with a special antibody, peptide and an anticancer agent. They have shown much improved target-specificity and are promising for medical diagnostic and therapeutic applications.

COLL 60

Multicoordinating amphiphilic polymers provide compact, highly stable, and reactive semiconductor and metal oxide nanocrystal-conjugates

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We introduce a new set of multifunctional and multi-coordinating polymer ligands that combine one or more metal-chelating groups adapted to several metal and metal oxide nanocrystal surfaces. The ligand design relies on the introduction of a large but controllable number of amine-modified metal-anchoring groups, along with hydrophilic moieties and reactive functionalities onto poly(isobutylene-*alt*-maleic anhydride) chain, via a one-step nucleophilic addition reaction. We further demonstrate that when applied to quantum dots this design is fully compatible with a novel and mild photoligation strategy to promote the in-situ ligand exchange and phase transfer of hydrophobic QDs to aqueous media under borohydride-free conditions. This strategy provides compact and reactive nanoparticles that are suitable for use in sensor design based on energy and charge transfer interactions. The resulting nanoparticles are coupled to cancer targeting peptides and used to probe intracellular uptake.

COLL 61

Intracellular sensing of ion concentration with nanoparticles

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Colloidal particles with fluorescence read-out are commonly used as sensors for the quantitative detection of ions. Regardless the sensing mechanism the particles act as carriers. Surface chemistry of the particles thus determines their interaction with cells, in particular pathway of uptake, intracellular location, as toxicity. Different surface chemistry for particle functionalization will be compared, which can be applied to

different particle geometries such as spheres, rods, etc. It also will be explained how surface chemistry can interfere with read-out. Besides delivery and intracellular location of particle-based fluorophores also other experimental difficulties such as crosstalk of the fluorescence read-out with pH, and spectral overlap of the emission spectra of different fluorophores will be discussed.

COLL 62

Smart photon management for organic photovoltaic

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In this talk, I will present the research progress of the organic photovoltaic (OPV) employing photonic nanostructures to boost device performance. There are two major parts: 1. OPV devices incorporated with plasmonic nanostructures; 2. Visibly transparent OPV (TOPV) incorporated with distributed bragg reflecting layer (DBR).

1. There are several approaches to utilize the surface plasmon to enhance the efficiency of the organic photovoltaic device. Firstly, we incorporated gold nano particles (NPs) into both buffer layers (e.g. PEDOT:PSS layer) and the photo-active layer. The plasmon resonance of gold NPs could be easily tuned so as to match with the absorption spectrum of different polymers, and this concept is proved to work well in both large band gap polymer solar cells and low band gap polymer solar cells. Secondly, we studied the surface plasmonic effects of large-area metallic grating on patterned active layer. About 10% of short current density improvement is obtained, and PCE achieves 7.73% for the plasmonic inverted solar cells with the low band gap polymer as the active layer. An observable improvement in PCE is mainly ascribed by the surface plasmonic and scattering effects due to the electrode (Ag) grating. Finally, we combined the above two strategies together and studied the dual plasmonic effect in the polymer solar cells.

2. The visibly transparent OPV (TOPV) has attracted lots of attentions recently due to its unique applications that conventional solar cells fail to deliver. However, the transparency and device efficiency are intrinsically contradicting each other. Here, we solve this problem by incorporating DBR that selectively passes the visible spectrum while reflects the IR spectrum. The TOPV device efficiency increases about 30% with scarifying little visible transparency.

COLL 63

Nanoscale oxynitrides with tunable composition and absorption spectra

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This presentation will focus our efforts to synthesize and characterize zinc-gallium oxynitride ((Ga_{1-x}Zn_x)(N_{1-x}O_x)) nanocrystals. This family of materials has potential applications in solar water splitting. (Ga_{1-x}Zn_x)(N_{1-x}O_x) is a solid solution of ZnO and GaN. Remarkably, although both constituent semiconductors absorb light in the ultraviolet, the mixture can absorb visible light with a band gap that varies with composition (value of x). The origin of this effect is not currently understood. We have developed a synthesis of oxynitride nanocrystals with a wide range of compositions (0.2<x<0.99) using nanocrystals with simpler composition as precursors. I will discuss our current efforts to understand the relationship between composition, elemental distribution, and electronic structure in these materials.

COLL 64

Light extraction from organic light-emitting diodes using plasmonic scattering layers

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Organic light-emitting diodes have been successfully commercialized for display applications. However, efficiency remains a roadblock to lighting applications, the largest contribution to loss failure to extract emitted light due to waveguiding in the device and substrate. This reduces overall external quantum efficiencies to less than ~ 25%. For waveguiding in the device, which is the larger effect, one of the primary strategies to improve light extraction is the incorporation of scattering layers into the device architecture and implementations with TiO₂ nanoparticles embedded in a silica matrix have nearly doubled the outcoupling of light [1]. Here, we will discuss the construction and application of nanotextured silver scattering layers as an alternative with the idea that the very high scattering cross-sections for silver nanoparticles are advantageous in that less recycling of light into the lossy regions of the device is needed. We will present modeling that supports this hypothesis and describe approaches to implementing suitable silver scattering layers and integrating them with organic LEDs. The extraction efficiency, spectrum and angular distribution of extracted light will be documented and compared with control devices containing no scattering layer.

[1] H.-W. Chang et al., "Organic light-emitting devices integrated with internal scattering layers for enhancing optical out-coupling", *Jnl. of the Society for Information Display* **2011**, 19/2, 196-204.

COLL 65

Nanostructured plasmonic antenna systems and catalytic electrode materials for enhancing solar water splitting

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The world energy consumption is projected to be 28 TW in 2050. There is an average of 1.2×10^5 TW of solar energy potentially available on earth, and only 1 hour of solar energy illumination can fully address the 28 TW energy challenge. Solar energy can be harvested for direct water splitting to produce hydrogen gas through photoelectrochemical (PEC) reactions. Since Fujishima and Honda's first experiment demonstrating direct water splitting using TiO_2 photoelectrode, this "holy grail" has been sought for more than three decades and is presently being intensely investigated. We present here solar energy driven water splitting reactions using kinds of nanostructured materials including surface plasmon enhanced photocatalyst and new catalytic anode materials for water electrolysis. Several enhancement configurations are developed to help address the challenges of plasmon enhanced water splitting systems, while preserving the electrochemical stability of the plasmon antenna under harsh conditions. We will also present newly-developed nanostructured electrode material to decrease the energy cost of the water splitting reaction.

COLL 66

Molecular imprinted polymers for plasmonic sensing

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A major limitation of nanosensors is irreproducible and changing surface functionality. Because surface recognition layers can exhibit variability as a function of temperature, matrix, shelf life, and pH; surface chemistry and quality control measures that promote both nanomaterial stability and responsiveness are vital and motivate our investigations. In this presentation, the synthesis of perm-selective molecular imprinted polymers (MIP) and plasmonic nanomaterials as well as the use of these materials for direct, qualitative and quantitative detection of small molecules will be demonstrated using localized surface plasmon resonance (LSPR) spectroscopy and surface enhanced Raman scattering (SERS). Detection of three drug molecules will be evaluated and the magnitude of the plasmonic responses will be shown to correlate with the number of binding sites in the MIP and hydrophilic interactions between the MIP and plasmonic nanomaterials. Future studies could focus on exploiting the nanomaterial and MIP hydrophilic driven aggregation for increased SERS enhancements for complex sample analysis and for SERS-based MIP biosensor development.

COLL 67

On the possibility of the para-aryl-dithiols cross-linking plasmonic nanoparticles as dithiolates

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Para-aryl-dithiols (PADT, HS-(C₆H₄)_n-SH, n=1, 2 and 3) that contain two distal end -SH groups have been used extensively in molecular electronics, surface-enhanced Raman spectroscopy (SERS), and quantum electron tunneling between gold and silver nanoparticles (AuNPs and AgNPs). One common belief is that these dithiols cross-link noble metal nanoparticles as monolayer dithiolate spacers. Discussed in this presentation is our finding that PADTs are in predominantly monothiolate forms on AuNP or AgNP even in highly concentrated NaOH (6M) solutions. No PADT induced nanoparticle cross-linking were observed under any of the tested experimental conditions. Combined experimental and computational Raman investigation revealed a critical, but entirely overlooked pitfall in the existing Raman and SERS studies of PADT thiol deprotonation in solution and on NPs. The Raman activity of the S-H stretching feature is vanishingly small in PADT monothiolate, therefore, PADT monothiolate can be readily mistakenly identified as PADT dithiolate. Methods for improving the reliability of Raman and SERS spectral interpretation will be discussed.

COLL 68

Air-stable droplet interface bilayers

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Droplet interface bilayers are versatile model membranes useful for synthetic biology and biosensing; however, to date they have been for the most part confined to fluid reservoirs. Here, we demonstrate that when two or more water droplets meet on an oil-infused substrate, they exhibit noncoalescence due to the formation of a thin oil film that gets squeezed between the droplets from the bottom up. We show that when phospholipids are included in the water droplets, a stable droplet interface bilayer forms between the noncoalescing water droplets. As with traditional oil-submerged droplet interface bilayers, we were able to characterize ion channel transport by incorporating peptides into each droplet. We demonstrate the ability of these air-stable droplet interface bilayers ("airDIBs") to incorporate ligand-gated ion channels via fusion of microsomes, which enables the biosensing of airborne matter.

COLL 69

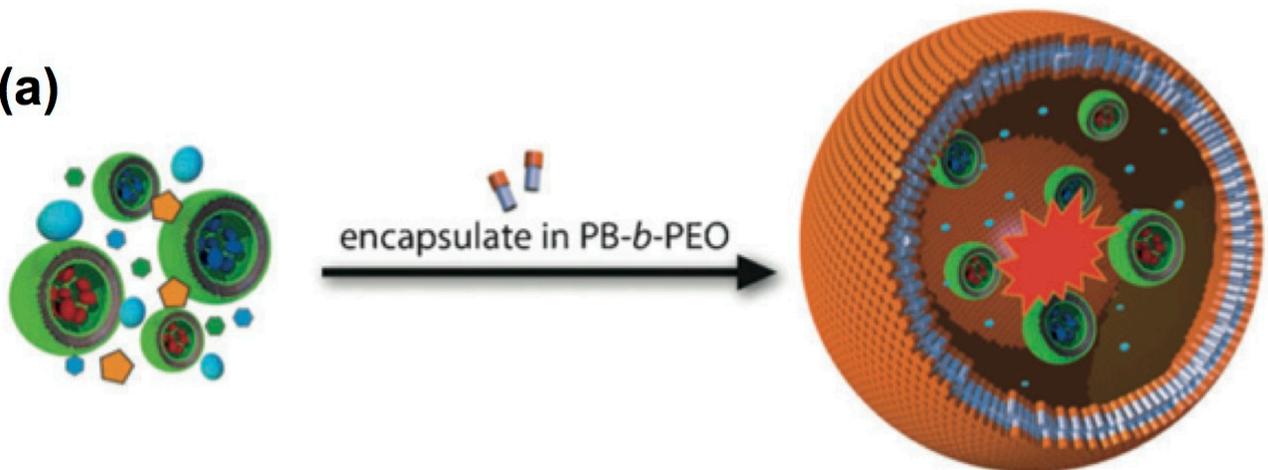
From compartmentalized polymersomes to biomimetic artificial cell

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The goal of this research line at the biology/chemistry/biophysics interface is the development of micrometric **multicompartmental addressable capsules**, which can serve as hosts for biological entities, such as enzymes. The sequestration of individual biomolecules in these robust self-assembled polymer-based host systems, would offer a controlled environment to disentangle complex reaction pathways on introducing selected reactants in a controlled dose or sequence while enzyme activity can be monitored. This can be considered a “bottom-up approach” to Synthetic Biology, harnessing a synthetic minimal cell acting as a functional platform and allowing integration of multiple components in a much simpler and controlled form than natural cells

In this paper, we aim at mimicking the complexity of eukaryotic cells that possess a multicompartmentalised structure, via which the cell gains spatiotemporal control over its processes, allowing it to physically separate reaction components and pathways by confining them to different organelles. In order to construct a model system that would allow the study of the effect of compartmentalisation on multistep processes, we have developed a functional and structural cell mimic via a self-assembly approach. A polymersomes-in-polymerosome multicompartment system, containing enzyme-filled semi-porous PS-*b*-PIAT nanoreactors that act as artificial organelles, was prepared to mimic the organisational structure of the cell. A three-enzyme cascade reaction that requires the presence of natural cofactors was used to mimic a natural reaction pathway, where the three different enzymes were confined to both the cytosol and different organelle compartments of the cell mimic. A profluorescent substrate was used to show that the reaction exclusively takes place in the cell-mimics. Furthermore, we demonstrate that the fluorescent reaction product can be locally produced and retained in organelle mimics containing the final enzyme of the cascade reaction. In addition, the use of confocal fluorescence to follow reaction kinetics and to prove that a multicompartmentalized enzymatic reaction is taking place inside single colloidal objects is also in itself a technological challenge of major importance

(a)



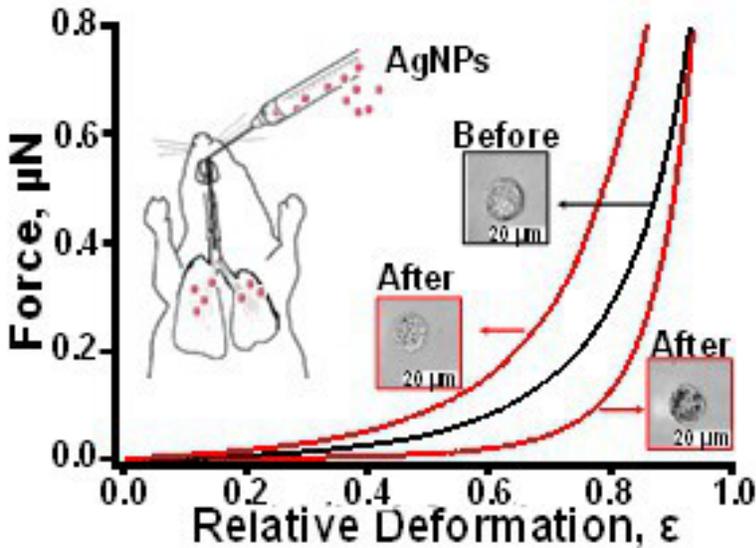
COLL 70

Probing interactions between nanoparticles and cellular membrane via single cell mechanics

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Single cell mechanics, derived from atomic force microscopy-based technology in conjunction with *in vivo* exposure, provides a new and effective readout for monitoring nanoparticle-cell interactions, as such nanocytotoxicity. Macrophages represent a major defense mechanism by which inhaled particles are removed from the respiratory tract. Cellular mechanics has previously been shown to be a sensitive indicator in human aortic endothelial cells' disruption upon *in vitro* exposure to nanomaterials. This study extends the single cell mechanics approach to probe the cytotoxicity of nanomaterials upon *in vivo* exposure. Materials included 20 and 110 nm silver nanoparticles (AgNPs), which were pre-dispersed in designated solvents. Instillation by rats was completed at a dosage of 0.5 mg AgNPs/kg body weight, and then the bronchoalveolar lavage was collected one day later to harvest living macrophage cells. The intracellular AgNPs exhibit a high degree of variation among AMs due to intake and intracellular physiochemical status of AgNPs, and as such, subsequent single cell mechanics are measured from representative cells from each subpopulation. These measurements indicate a multitude of effects, ranging from reduction of membrane fluidity, increase of membrane elastic compliance, ion flux dysfunction, to cytoskeleton damage and cell death. The impact depends on the aggregation and solubility of AgNPs. This investigation reveals that single cell based studies are a necessary and valuable tool to

probe *in vivo* pulmonary nanotoxicity. The advantages and limitations of this single cell based approach in the context of nanotoxicity are also discussed.



COLL 71

Rigidity signals drive differential ROCK signaling to regulate invadopodia activity

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Rho-associated kinase (ROCK) activity increases due to extracellular matrix (ECM) rigidity in the tumor microenvironment and drives cancer cell migration and invasion via actomyosin contractility. Invasion through cross-linked tissues is facilitated by actin-rich adhesive protrusions called invadopodia that proteolytically degrade the ECM. We have previously shown that ECM degradation by invadopodia is dependent on matrix rigidity and traction forces generated by non-muscle myosin II (NM II) suggesting that invadopodia activity is regulated by rigidity signals transmitted through cellular contractility. However, ROCK exists in two isoforms that may participate in other signaling pathways to regulate invadopodia activity independent of force generation. In particular, the ROCK substrate LIM kinase (LIMK) has been shown to regulate invadopodia activity to drive cancer cell invasion. Therefore, we hypothesized that rigidity signals induce differential ROCK activity to regulate invadopodia. Using siRNA to specifically inhibit each ROCK isoform, we investigated the contractile and invasive responses of an aggressive head and neck carcinoma cell line using polyacrylamide gels of different rigidities that span reported values for the mechanical properties of increasing grades of human tumor tissues. We found that only ROCK1 inhibition

decreased traction forces while both ROCK1 and ROCK2 inhibition decreased ECM degradation. We also found that downstream ROCK signaling through both NM II and LIMK was dependent on matrix rigidity and regulated by ROCK1 and ROCK2, respectively. Therefore, our data suggest that matrix rigidity activates differential ROCK activity through two non-redundant signaling pathways that converge to regulate invadopodia activity and may contribute to invasive behavior by cancer cells in response to the mechanical properties of the tumor microenvironment

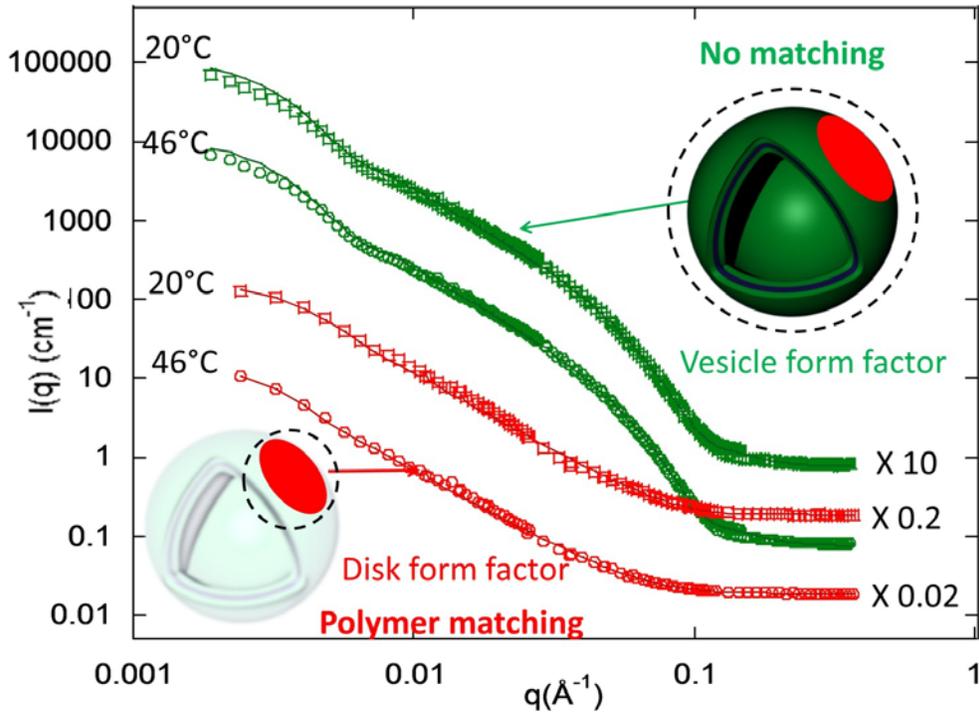
COLL 72

Phase separation in hybrid polymer/lipid vesicles: a rationale to obtain lipid or polymer raft-like nanodomains

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Hybrid vesicles resulting from the combined self-assembly of both amphiphilic copolymers and phospholipids may be viewed as an advanced vesicular structure compared to their liposome and polymersome forerunners, as the best from the two different systems can be integrated in a single hybrid vesicle and could be used in different fields such as: nano-reactors for enzymatic reactions, improved cell membrane mimics,[1, 2] etc... To afford such design, different parameters controlling both the self-assembly and membrane structure must be tuned. However, the exact mechanisms governing phase-separation of the membrane into domains analogous to lipid rafts in cells are not known so far. In this work, using different lipids and copolymers to form Giant Hybrid Unilamellar vesicles, we show that hydrophobic mismatch existing between polymer and lipid phase boundaries as well as the fluidity of the lipid phase are of prime importance on the membrane structuration.

Moreover, we prove that Hybrid polymer/lipid Large Unilamellar Vesicles (LUV) presenting lipid or polymer "raft-like" nanodomains can be obtained, as evidenced by small angle neutron scattering (SANS) (Figure 1) and time resolved fluorescence spectroscopy. To obtain such level of structuration, the idea was to limit the line tension at the lipid/polymer boundaries. The stabilization of the domains resulting from phase separation of the two components was allowed by using a vesicle-forming copolymer with a membrane thickness close to the lipid bilayer thickness. This study should clarify the elementary bricks necessary to modulate membrane properties of these new self assembled hybrid structures, in an optimized fashion regarding to different field of applications.



SANS data of PDMS-*g*-(PEO)₂/d₆₂-DPPC (80/20 wt. ratio) hybrid vesicles at 20°C and 46°C in polymer matching and no matching conditions. Solid lines: fitting curves.

COLL 73

Methods for rapid synthesis of nonaggregated nanozeolite Y

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Nano zeolite has advantages of large external surface area, short diffusion path and less coke formation over micron-sized zeolites. With these improved properties, nano zeolite has applications in synthesis of structured zeolite materials (membrane, film), optical and chemical sensing, catalysis and biomedical targeting.

Synthesis of nonaggregated nano zeolite requires clear-solution synthesis method, which needs large amount of organic structure directing agent, low alkali cation content and low crystallization temperature. Several studies have reported successful synthesis of nanozeolite Y, but long crystallization time of 4-5 days and low yield are limiting its industrialization.

In this study, supernatant obtained after hydrothermal synthesis has been used as the reactant. After regular clear solution synthesis, large amount of unreacted nuclei still remains in the supernatant. With microwave heating, 9% yield of nanozeolite particle is achieved in 1 hour. By recycling the supernatant, total yield reaches 70% after 8 batches. However, as recycling time goes more than 6 batches, large particles of dense zeolite framework, like LTA, SOD, start to form.

COLL 74

Design of suitable protocols to evaluate metal oxide nanoparticles in unmodified commercial sunscreens

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The potential applications of metal oxide nanoparticles in pharmaceutical or cosmetic products have attracted significant amounts of research and have dramatically increased in the number of marketed products for many decades. Unfortunately, most existing analytical techniques are unsuitable to detect and characterize metal oxide nanoparticles in unmodified commercial sunscreens because they require dilution or modification of unmodified products containing nanoparticles, leading to aggregation and/or agglomeration effects. Here, the most appropriate sample preparation technique prior to characterizing the physico-chemical properties of commercial sunscreens without interfering as-received product characteristics using field emission-scanning electron microscopy/energy-dispersive X-ray spectroscopy (FE-SEM/EDS) was explored. Two techniques which were blade-coating and spin-coating deposition were investigated for their ability to deposit the unmodified sunscreens on substrates. Comparing to the blade-coating deposition, spin-coating deposition was found to be a better promising technique for depositing unmodified sunscreens due to their broader application with different sunscreen textures. FE-SEM results indicated that edges and dimensions of nanoparticles containing for all as-provided samples were partly obscured by the formation of multilayer agglomerates of non-volatile organic components. The EDS analysis revealed that some sunscreens comprised titanium dioxide (TiO₂), zinc oxide (ZnO) and other inorganic constituents such as silicon dioxide (SiO₂) and aluminium oxide (Al₂O₃). X-ray diffraction (XRD) investigation demonstrated that TiO₂ particles containing in sunscreens were rutile phase while the ZnO particles were wurtzite phase. The metal oxide nanoparticles found from the XRD analysis was in reasonable agreement with those found from the EDS studies. In conclusion, FE-SEM, EDS and XRD can detect and provide complementary characterization information regarding nanoparticles within a complex matrix of sunscreens.

COLL 75

Local and long range structure in metal oxide nanoparticles

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X-ray absorption fine structure (XAFS) and X-ray diffraction (XRD) have been used to characterize both local and long range structure in a series of nano-scaled metal oxide systems. Their unit cell lattice parameters have been observed to contract systematically with crystallite size and composition relative to that observed for the macro-scaled crystallite structure. In rocksalt NiO, the contraction in a_0 is approximately 0.2% for 25 nm nano-crystallites but proportionally smaller in solid-solution $Zn_xNi_{1-x}O$ and $Cu_xNi_{1-x}O$ ($0 \leq x \leq 0.3$), in which larger guest cations (Zn^{2+} and Cu^{2+}) substitute for the smaller Ni^{2+} . While both Zn^{2+} and Cu^{2+} form homogeneous solid solutions in NiO, with random guest substitution, the copper cation undergoes a small Jahn-Teller distortion in the solid solution while no difference in $Zn^{2+}-O^{2-}$ and $Ni^{2+}-O^{2-}$ coordination and bond lengths are observed for $Zn_xNi_{1-x}O$. Both nano-scaled PdO and $Cu_xPd_{1-x}O$ ($0 \leq x \leq 0.75$) show contractions in a_0 and c_0 unit cell parameters, with cell contractions increasing with decreased particle size. Reports of lattice differences between macroscaled and nanoscaled oxide crystallites are controversial. However, to date many describe a lattice expansion for nanoparticles with decrease in crystallite size. For example, the contraction is not intrinsic to the rocksalt structure since NiO exhibits a contraction whereas both forms of ZnO (rocksalt and wurtzite) show a slight expansion. Instead the ionic v.s. covalent nature of the oxide lattice must be considered in determining the effect of nano-scaled changes in local and long range crystal structure.

COLL 76

Fabrication of abundant Zn vacancies in ZnO for p-type conductivity, room-temperature ferromagnetism and high photocatalytic activity

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ZnO has been attracting intensive interests in optoelectronics, nanoelectronics, spintronics and photocatalytic applications. Stable p-type and room-temperature-ferromagnetic ZnO is particularly important for the advent of such innovative technologies, but its fabrication remains a great challenge for decades. Theoretically, the metal vacancy can cause inherent p-typeness and ferromagnetism, however the Zn-vacancy-mediated p-typeness and ferromagnetism have not been realized because it is quite difficult to engineer and manipulate the metal defects in a stable and reliable way. Herewith, abundant Zn vacancies (7.5 mol%) were successfully introduced into undoped ZnO by a simple solvothermal method followed with thermal calcination, and undoubtedly proved by both characterizations and computations. The presence of Zn vacancies led to some new properties in ZnO, such as p-type conductivity, room-temperature ferromagnetism and high photocatalytic activity. The formation process of abundant Zn vacancies during the synthesis of ZnO was also discussed. This work demonstrates that metal defects can be easily engineered in undoped metal oxides, which may trigger many unexpected behaviors and thus widen the synthetic approach and application of functional materials in energy fields.

COLL 77

Application-scale size-selective fractionation of iron oxide nanoparticles using CO₂-expanded liquids

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Iron oxide nanoparticles exhibit highly size-dependent physicochemical properties that are extremely important in applications such as catalysis, biomedicine, environmental remediation and data storage. These size-dependent properties need to be effectively harnessed on a large scale for these particles to be used in any industrial application. The synthesis of monodisperse iron oxide nanoparticles can be a prohibitively expensive process on a large scale. A more viable alternative could be the use of cheaper synthesis procedures followed by a size-selective processing technique. While previous studies have shown that there are many techniques available to fractionate nanoparticles, these techniques prove to be inefficient at fractionating iron oxide nanoparticles cheaply, in large quantities, and in an environmentally friendly manner. An application-scale apparatus capable of fractionating large quantities of iron oxide nanoparticles into distinct fractions of different sizes and size-distributions has been developed. The iron oxide nanoparticles coated with oleic acid used in this study were synthesized using a simple and inexpensive coprecipitation technique. This apparatus uses hexane as a CO₂-expanded liquid to controllably precipitate nanoparticles inside a 1L high-pressure reactor where the compressible gas used to expand the solvent is carbon dioxide (CO₂). Similar systems have been used previously to carry out size-selective fractionation studies on gold nanoparticle dispersions at a smaller scale. This study presents this new apparatus and, for the first time, demonstrates the successful fractionation of metal oxide nanoparticles with initial nanoparticle concentrations in the gram-scale. The operation of this apparatus, along with analysis of the obtained fractions using transmission electron microscopy (TEM) and dynamic light scattering (DLS), are highlighted in this study. The use of this simple apparatus could provide a pathway to separate large quantities of iron oxide nanoparticles based upon their size for use in applications such as catalysis will also be highlighted.

COLL 78

Improvements of TiO₂ nanoparticle dispersion stability in nonpolar solvents by long chain fatty acid functionalization

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TiO₂ nanoparticles have many potential applications, but the high surface polarity makes the nanoparticles less compatible with hydrophobic matrices. Highly pure

anatase TiO₂ nanoparticles were synthesized by a hydrolysis precipitation method and the surface TiO₂ nanoparticles was functionalized with oleic acid by a one-step modification method. The functionalization of TiO₂ nanoparticles and morphological properties were confirmed by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and transmission electron microscopy (TEM). Dynamic light scattering (DLS) measurement evaluated dispersion stability behaviors of oleic acid functionalized TiO₂ nanoparticles and TiO₂ nanoparticles in polar and nonpolar solvents. Oleic acid functionalized TiO₂ nanoparticles and TiO₂ nanoparticles showed spherical shaped anatase phase of (101) lattice planes with diameter sizes ranging from 3 to 10 nm. Compared to TiO₂ nanoparticles without the functionalization, the oleic acid functionalized TiO₂ nanoparticles could form highly stable suspensions in nonpolar solvents due to increased affinity between oleic acid functionalized TiO₂ nanoparticles surface and nonpolar media. Oleic acid functionalization TiO₂ nanoparticles showed the most stable dispersion in chloroform. Based on our findings, by this simple effective surface functionalization of TiO₂ nanoparticles using oleic acid, a stable colloidal solution of TiO₂ nanoparticles can be attained in nonpolar solvents. Therefore, this oleic acid functionalized TiO₂ nanoparticles method is an economical technique to control aggregate formation and strongly enhance compatibility between hydrophilic TiO₂ nanoparticles and hydrophobic media in order to obtain desired properties of TiO₂ nanoparticles to final materials without changing any properties of the nanoparticles in variety of applications such as polymer composites, foods, cosmetics, personal care products, biotechnologies, electrical and medical devices.

COLL 79

Mobility of antiscalant-modified BaSO₄ particles through saturated proppant pack

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Formation brine in Marcellus Shale typically contains high concentration of barium as indicated by flowback/produced water quality. When injection fluid used for hydraulic fracturing is rich in dissolved sulfate, BaSO₄ will precipitate in the subsurface and may be transported back to the surface during the flowback period. The attachment of barium sulfate to the proppant that is injected with hydraulic fracturing fluid to enhance the productivity of a gas well will influence the permeability of the proppant pack and well productivity. This study is designed to evaluate the fate and transport of BaSO₄ particles under the conditions that are relevant for gas extraction in Marcellus Shale. It was found that the mobility of barite particles through proppant is very limited at high ionic strength typical of deep brines, which is due to the agglomeration of barite particles and reduced electrostatic repulsion between barite and sand. Breakthrough of barite through the sand column is much faster in the presence of sulfonated polymeric phosphine carboxylic acid (SPPCA) even at high salinity conditions. Such behavior is most likely due to the reduction in size and/or surface charge (zeta) potential of barite particle that would precipitate in the presence of SPPCA. SEM images of barite particles

illustrates that the presence of scaling inhibitors result in the decrease in particle size and more spherical morphology. Particle size shown in the SEM image is consistent with the particle size distribution measured by light scattering.

The findings of this study indicated that it is possible to control potential reduction in well permeability in the case when high sulfate fluid is used for hydraulic fracturing in Marcellus Shale.

COLL 80

Enhanced photodecomposition activity induced by nanodimensional cerium oxide domains on titania surfaces

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Titanium dioxide (titania) is a widely-studied photocatalyst. Prior investigations have examined the ultraviolet photodecomposition of methanol on titania using Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS). In the current study, methanol was used as a probe molecule to examine the effects of added cerium oxide (ceria) on the ultraviolet surface photochemistry of titania. Titania was decorated with different amounts of cerium oxide using deposition precipitation with cerium (III) nitrate as the cerium oxide precursor and titania P25 as the substrate. A series of decorated titania materials were prepared, with weight loadings predicted to develop surface coverages of approximately 0.25, 0.5, 1, and 2 monolayers of cerium (IV) species. XRD results confirmed that the 0.25 and 0.5 monolayer samples contained no crystallites corresponding to cerium oxide species, while the 1 and 2 monolayer materials contained CeO₂ crystallites with sizes on the order of 4 nm. The dried and calcined solids were placed in the DRIFTS reaction cell and a mixture of methanol in N₂ (1:1000) flowed through the solid powder to create the adsorbed methanol species. Strong peaks due to CH₃ infrared absorption were observed at approximately 2830, 2850, 2930, and 2950 cm⁻¹, corresponding to physisorbed methanol as well as methoxy (chemisorbed methanol) species. After adsorption of methanol, bare and decorated titania solids were then exposed to ultraviolet light in the presence of oxygen, and the integrated area of the CH₃ infrared absorption band before and after irradiation was used as a measure of the decomposition. The bare titania, 0.5, and 1 monolayer samples lost 40-60% of the CH₃ integrated intensity after UV irradiation whereas the 0.25 and 2 monolayer samples lost 82% and 99%, respectively. These results as well as those from flow reactor studies and the intensity dependence studies to gain further insight into the nature of the modified surface reactivity.

COLL 81

Thiol adsorption on metal oxide nanoparticles and surfaces

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Thiols are known to adsorb on a variety of metal surfaces and nanoparticles, including gold. Self-assembled monolayers have also been proposed for corrosion protection of reactive metals. While extensive work has been performed related to thiol adsorption on metals, fewer studies have been carried out related to metal oxides. In this work, fluorescence and X-ray photoelectron spectroscopy (XPS) have been used to investigate the adsorption of thiols, including 2-naphthalene thiol and methanethiol, on a variety of metal oxide nanoparticles having typical average particle sizes of 20-30 nm. Examples of nanoparticles that adsorb thiols include ZnO and ZrO₂. Comparison is made to experiments on single crystalline ZnO(0001) and oxidized polycrystalline zirconium. A novel method of forming oxidized gold nanoshells is also presented, along with initial results related to thiol adsorption on these nanoparticles. In this case, reaction of the thiols with the nanoshells results in reduction of the oxidized gold nanoshell and oxidation of the thiol. This work may have applications for chemical sensing and gas filtration.

COLL 82

Highly uniform gadolinium oxide nanoparticles as remarked remarkably enhanced MRI contrast agents for cellular MR imaging

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Magnetic resonance imaging (MRI) is one of the most central noninvasive imaging techniques in clinical diagnosis. Images are produced from the response of water protons to a strong external magnetic field. However, since water proton relaxation times are similar for normal and abnormal tissues, contrast agents are typically used to induce changes in relaxivity and improve the resolution. Current contrast agents are made from toxic materials, which have limitations to their achievable resolution. Through the use of engineered nanomaterials it will be possible to improve the MRI resolution and reduce toxicity. This proposal describes the synthesis of anisotropic, monodisperse and size-tunable gadolinium oxide nanostructures, capable of being applied in-vivo as enhanced T1 MRI contrast agents. The MRI properties studies were fulfilled by varying different parameters, such as polymer molecular weight, hydrophilic surface coating and nanoparticle core size. The longitudinal relaxivity of PAMPS_{LA} coated gadolinium (Gd) oxide nanoparticles resulted approximately 20 times higher than clinically approved Gd contrast agents. The polymer-coated gadolinium oxide nanoparticles are biocompatible based on our in vitro cytotoxicity study in which showed no significant effect on cell viability up to a concentration of 600 µM of gadolinium. Owing to the large enhancement in relaxivity, we were able to use the nanoparticles as in vitro cellular MR labels; these showed high cellular uptake while increasing the signal intensity on the T1-weighted

image, which is very promising for cellular labeling. This study demonstrates that water-soluble biocompatible gadolinium oxide nanostructures are potential candidates for an enhanced MRI contrast agents suitable for non-specific cell labeling, which makes the visualization of labeled cells in-vivo possible.

COLL 83

Cr:ZnGa₂O₄ nanoparticles with controllable size and persistent luminescence

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Monodispersed nanoparticles (NPs) of 0.2 mol% Cr³⁺-doped ZnGa₂O₄ were synthesized via a hydrothermal process and characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscopy (TEM) and photoluminescence (PL). A general facile synthetic procedure has been demonstrated to synthesize these NPs size-controllably. Additionally, persistent luminescence upon UV-Vis excitation has been observed up to two hours from these NPs. It will also be discussed with their persistent luminescence for application as multimodal probe for near-infrared luminescence and real-time monitoring in a noninvasive manner.

COLL 84

Controlled synthesis of inorganic nanostructures using soft stretchable substrates

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We describe the synthesis of nano/micron-scale inorganic structures using soft elastomeric substrates. Elastic deformations, such as those caused by tensile strain, enable the reversible modification of critical surface-chemical features (e.g., geometry and molecular density) of these “soft” substrates providing a convenient method to dynamically control the surface energy of the crystal growth substrate and the arrangement of the inorganic structures on their surface. We use this capability to control the surface nucleation and growth of hard, crystalline materials that possess functional (e.g., electronic or optical) properties. The morphology of these crystals is controlled by the rational manipulation of their spatial arrangement during growth through deformations of the elastomeric substrates. This approach enables modulation of mass transport, which in surface growth is dominated by crystal proximity effects, to rationally control morphology without the need for surfactants or other approaches. Specifically, we report the surface-chemical patterning of silicones, such as polydimethylsiloxane, and the use of these materials as substrates for the mineralization of rippled metal chalcogenide nanocrystalline films and metal oxide nanocrystals. The hybrid hard-soft materials we report are difficult to fabricate directly using other

approaches and their physical properties are potentially applicable to soft sensors and electronics and mechano-responsive optical materials.

COLL 85

Electrostatic repulsion between colloids at the oil-water interface

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The electrostatic interaction between colloidal particles dispersed in fluids has long been described by the Gouy-Chapman theory, in which charges are screened by a double layer of counter-ions. In contrast, electrostatic interactions between colloids at an oil-water interface are significantly stronger and surprisingly long-ranged. Particles that normally exhibit repulsion at separations on the order of one hundred nanometers when dispersed in water repel strongly at micrometer separations when spread at the interface. The measured repulsion between colloids at an oil-water interface and the relative changes as a function of electrolyte were found to be in quantitative agreement with predictions with recent models that use the Langevin–Poisson–Boltzmann equation that incorporates steric effects and the polarization saturation of the medium. These results support the hypothesis that a condensed layer of counterions contributes to the electrostatic interaction between colloidal particles at an oil–water interface.

COLL 86

Janus particles as dynamically tunable solid surfactants

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Janus particles are biphasic colloids that have two sides with distinct chemistry and wettability. Because of their amphiphilic nature, Janus particles present a unique opportunity for stabilizing multiphasic mixture such as emulsions. Inspired by a special class of molecular amphiphiles that are responsive to environmental stimuli, we synthesize stimuli-responsive Janus particles that drastically change their shape and in turn their surfactant properties. We show that these Janus particles can stabilize different types of emulsions depending on the solution pH and composition of the multiphasic mixtures. We demonstrate that these emulsions can be inverted to the opposite type by inducing transitional phase inversion via pH change. We also demonstrate that multiple emulsions can be stabilized with these Janus particles in one-step emulsification. These multiple emulsions exhibit triggered release behavior in response to changes in the solution pH. Our study not only presents a new class of colloidal materials that will further widen the functionality and properties of Janus particles as dynamically tunable solid surfactants but also shows the versatility of Janus particles in stabilizing multiphasic mixtures.

COLL 87

Bicompartmental phase transfer vehicles based on colloidal dimers with anisotropic structural and interfacial properties

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Colloidal particles have been used extensively for stabilizing oil-water interfaces in petroleum, food, and cosmetics industries. They have also demonstrated promising potential in the encapsulation and delivery of drugs. Motivated by challenging applications that require protecting and transporting active agents across the water-oil interfaces (such as in situ cracking of hydrocarbon molecules), we report our successful design, synthesis, and validation of a unique type of bi-compartmental targeting vehicle that can encapsulate catalytic molecules, find and accumulate at oil-water interface, release the catalysts towards the oil phase, and perform hydrogenation reaction of unsaturated oil. This vehicle is based on colloidal dimers that possess both structural and interfacial anisotropies between two compartments. We encapsulate active species such as fluorescent dye and catalytic molecules in one lobe which consists of uncrosslinked polymers, while the other polymeric lobe is highly crosslinked. Although dimers are dispersible in water initially, the uncrosslinked lobe swells significantly upon contact with a trace amount of oil in aqueous phase. The dimers then become amphiphilic, migrate toward, and accumulate at the oil-water interface. As the uncrosslinked lobe swells and eventually dissolves in oil, the encapsulated catalysts are fully released. We also show that hydrogenation of unsaturated oil can be performed subsequently with high conversion efficiency. By further creating the interfacial anisotropy on the dimers, we can reduce the catalyst release time significantly. Our work demonstrates a new concept in making colloidal emulsifiers and phase-transfer vehicles that are important for encapsulation and sequential release of small molecules across phase boundaries.

COLL 88

Self-organisation of colloidal particles at liquid interfaces

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The behaviour of monodisperse silica particles at oil-water interfaces has been studied by microscope observations. Particles of different sizes and/or hydrophobicity and their mixtures have been spread at the planar liquid interface to give one- or two-component particle monolayers. It is found that the single component monolayers of very hydrophobic particles show long-range order due to strong particle repulsion through the oil. Similar behaviour is observed on curved liquid interfaces, i.e. at the surface of droplets in particle-stabilised emulsions, which affects the mechanism of stabilisation in such emulsions.

The binary mixtures of large (3 μm diameter) and small (1 μm diameter) very hydrophobic particles form two-dimensional super lattices (binary colloidal alloys) with

different structure depending on the number fraction of small particles, f at a planar liquid interface (Fig. 1a,b). A rich variety of two-dimensional hexagonal super-lattices of large and small particles can be obtained in this system due to strong and long-range electrostatic repulsions through the non-polar oil phase. Binary monolayers of large very hydrophobic and large or small hydrophilic silica particles at a planar octane-water interface have shown interesting selective attraction between very hydrophobic and hydrophilic particles. By tuning the composition and packing geometry of the mixed monolayer, we have found that a variety of two-dimensional hexagonal superlattices of mixed clusters are formed, stabilized by short-ranged electrostatic induced dipole interactions (Fig. 1c,d). Our results suggest that it should also be possible to obtain similar cluster structures for other types of binary monolayers, e.g. metal-dielectric composites, with unique electromagnetic properties and potential applications in opto-electronics.

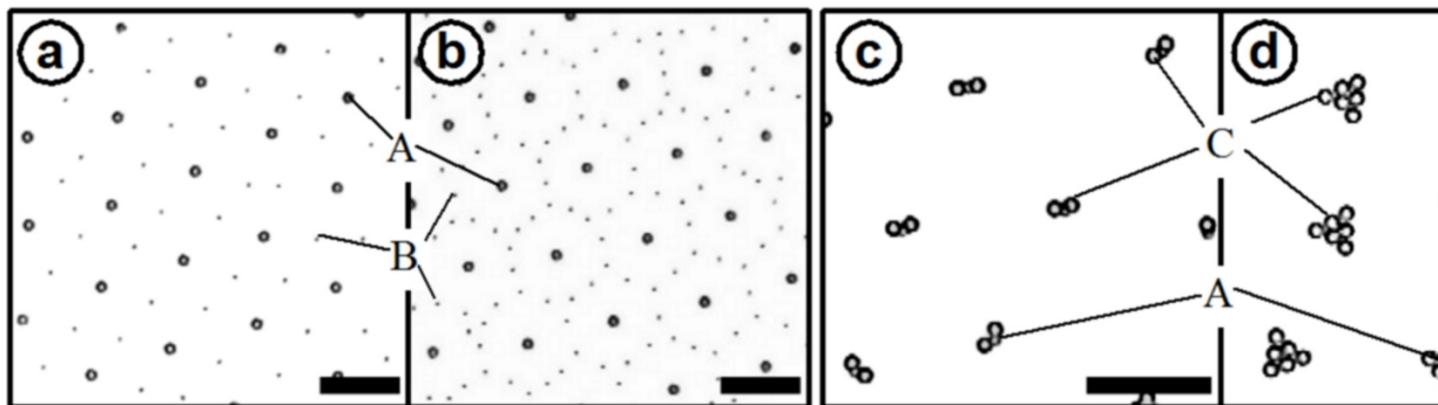


Fig. 1 Images of two-component silica particle monolayers at the octane-water interface. (a, b) Superlattices of large (A) and small (B) very hydrophobic particles at $f \approx 2/3$ and $f \approx 5/6$, respectively. (c, d) Superlattices of mixed clusters of very hydrophobic (A) and hydrophilic (C) silica particles. The scale bars are $25 \mu\text{m}$.

COLL 89

Particle transport at oil/water interfaces driven by spatially varying surfactant adsorption or desorption kinetics

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Surface tension gradients produce flows, known as Marangoni flows, from regions of low surface tension to regions of high surface tension. Marangoni flow is responsible for the familiar tears of wine phenomenon and “soap boat” experiments in a kitchen sink. Marangoni stresses lead to tip streaming phenomena for surfactant solutions in

extensional flows, and they influence bubble shape and dynamics. We investigate Marangoni flow as a mechanism for the transient convection of particles adsorbed at the interface between an oil and a flowing surfactant solution, in response to changes in the bulk surfactant concentration. Model experiments are conducted in a stagnation point, radial flow cell to establish a well-controlled flow field for convective diffusion of surfactant to or from the oil/water interface. When a surfactant-free solution is displaced by a flowing surfactant solution, the surfactant adsorption rate varies in position and time, producing transient surface tension gradients that increase the interfacial speed, and thus the speed of adsorbed particles entrained in the interface, in the direction of flow. When surfactant is rinsed from the system, spatial gradients in desorption rates reverse the direction of the interfacial flow, and entrained particles transport against the direction of the bulk flow. The generated particle speeds depend on the surfactant concentration in a manner that is consistent with the scaling of adsorption or desorption kinetics. The distances traversed by particles during the surfactant transients may be of significance to cleaning or other applications that involve flow of surfactant solutions over a mobile interface.

COLL 90

Thermodynamics of Janus particles in 2D confinement

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Colloidal particles with a suitable surface wettability can be confined to liquid interfaces with a capillary energy that is thousands of times the thermal energy. These systems offer a platform for fabricating new materials and an effective route to emulsion stabilization. Stability of particle-stabilized emulsions, i.e., Pickering emulsions, is influenced by the flow behavior and mechanics of the particle-laden interfaces as well as the phase behavior under deformation. Hence, a fundamental understanding of the factors that affect the properties of these self-assembled structures at the interface can be exploited in designing emulsions with superior stability.

Shape anisotropy of colloidal particles can be used to tune the interparticle interactions and assembly behavior. For example, a network of ellipsoidal particles formed by capillary effects at the water/decane interface was found to result in a more elastic monolayer compared to that formed by its spherical counterparts [1]. Additionally, interfacial packing and orientation of cubic and peanut-shaped particles has been studied to better understand the high coalescence-stability of the oil droplets covered by these particles [2].

While these geometrically anisotropic particles have recently been investigated in the literature, the influence of chemical anisotropy on properties of interfacial monolayers has received less attention. We have investigated the properties of air/liquid interfaces decorated with colloidal particles of various chemical anisotropies. Our work elucidates

the impact of particle wettability and amphiphilicity on the viscoelastic nature of these interfacial films. We find that changing particle wettability can alter the monolayer response to deformation. Moreover, the orientation of amphiphilic particles at the interface has consequences for stability and stiffness of interfacial particle films.

COLL 91

Remotely triggered colloidal disassembly from particle-laden microbubble

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Self-assembly of colloidal particles at fluid-fluid interfaces is exploited for emulsion stabilization, tunable nanomaterials, and nanocomposites with complex morphologies. Disassembly of interfacial particle monolayers is equally important, for instance for green catalytic processes. Current methods require physico-chemical modification of the system, for instance by tuning the pH or electrolyte concentration. We demonstrate controlled disassembly from the interface of particle-laden microbubbles. We use ultrasound waves as remote trigger to drive the bubbles into oscillations, which cause violent interface deformations accompanied by particle ejection. We visualize ejection events at the single particle level using high-speed video microscopy. Measurements of the area density of particles and of the acceleration of the bubble interface reveal that the interplay of two mechanisms is responsible for particle expulsion: tangential stresses in the interface upon compression, and the body force acting on the particles due to the large radial acceleration of the interface. Non-linear bubble dynamics can also be exploited to design complex particle expulsion scenarios, such as non-spherical oscillations and jetting, with relevance to directed particle delivery in microreactors.

COLL 92

Measurements and models of reversible adsorption of nanoparticles at the oil-water interface

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We observed the reversible adsorption and desorption of 5 nm diameter gold nanoparticles at the oil-water interface. The extent of adsorption can be controlled by changing the pH or the ionic strength of the aqueous solution.[1] Imaging experiments using optical microscopy also demonstrated the spontaneous formation of particle-laden drops. The number of drops decreases with increasing pH of the aqueous solution (desorption of the particles from the interface) and increase with the number of particles in the system. We developed a robust model based on perturbation theory to explain both the spontaneous formation of drops and the reversible adsorption/desorption of the nanoparticles from the interface. The model, which is in terms of the total Helmholtz free energy change in the system, allows us to relate the extent of adsorption to the particle-

particle interaction potential. The model allows us to predict the physicochemical conditions where emulsification is favorable and we verify these predictions in our experiments.

[1] M. Luo, G. Olivier, and J. Frechette, "Electrostatic interactions to modulate the reflective assembly of nanoparticles at the oil-water interface", *Soft Matter*, 8, 11923-11932, 2012.

COLL 93

Breaking Lord Rayleigh's Rule: Linked photochemical reactions that double the resolution of a lens

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Lord Rayleigh taught us that the minimum resolution of projection optics is his constant (k) times the ratio of the wavelength of the propagating light (λ) and (NA), the numerical aperture of the lens. $R = k\lambda/NA$. Rayleigh's constant is generally agreed to be 0.25. We have successfully printed gratings with a pitch that exceeds his resolution limit by nearly a factor of 2. This was accomplished with a photo resist formulation that includes a photoacid generator and a new photobase generator that produces amine through two linked reactions. That is, a latent photobase generator reacts with a photon to produce a photobase generator that then reacts with a second photon to produce base. If the kinetics of these reactions are properly adjusted, exposing the resist using a mask with a grating pitch of G produces a developed image with a grating pitch of 2G. In this way, chemistry can be employed to formally overcome what has always been considered a limit imposed by physics.

COLL 94

Designing precursors for the deposition of inorganic nanostructures by CVD, SPMCS and EBID

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Nanostructures can be deposited from organometallic and inorganic precursors by a variety of techniques including chemical vapor deposition (CVD), surface plasmon

mediated chemical solution deposition (SPMCSD) and electron beam induced deposition (EBID). Precursor choice requires consideration of the reaction conditions and possible decomposition mechanisms for the particular method. Examples will be chosen from CVD of metal nitride nanoparticles and films, CVD of metal oxide nanorods, SPMCS of metal nanoparticles on nanostructured Ag substrates and EBID of high metal content deposits.

COLL 95

Dynamic substrate control: Dual-tone hydrogel photoresists

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In vivo, natural tissues are rarely physically or mechanically homogenous, but rather exhibit a range of elasticities and textures/topographies. Additionally, cells in native tissues reside in a dynamic environment in which the physical environment may change spatially and/or temporally (i.e., during tissue remodeling). Hydrogels are extensively investigated as two- and three-dimensional scaffolds for cells because of their high water content, tunable mechanical and physicochemical properties and their ability to be formed in the presence of biological materials such as cells, proteins and DNA. Therefore, hydrogels in which both topography and elasticity are dynamically tunable undoubtedly represent an important tool for investigating the synergistic effects of inhomogeneities in the physical environment on cell behavior, and better mimic the native microenvironment for tissue engineering applications.

Many strategies and materials to produce hydrogels with controllable and patternable elastic moduli and topographic features have been explored, including techniques such as photolithography, micromolding and microcontact printing. Although physically and mechanically patterned materials are obtained, these techniques generally allow *either* topographic patterning or elastic patterning, but no hydrogel with controlled variations in both topography and elasticity has been reported. Secondly, most of the demonstrated hydrogel patterns are static or predefined, and cannot be altered dynamically, especially once cells have been introduced into the scaffold. Finally, topography control is typically exerted in a “one-way” manner.

Here we report a photodegradable hydrogel substrate in which the elastic modulus and hydrogel topography are precisely controlled using light. We exploit changes in hydrogel crosslink density induced via photodegradation to create hydrogels exhibiting complex patterns of both elasticity and topography. These photodegradable hydrogels can act as both positive and pseudo-negative photoresists, depending on exposure time and wavelength. By carefully controlling the aspect ratio (surface area to depth) of micropatterned features, unique swelling-induced ordered microstructures can be formed on the surface. These dual-tone hydrogel photoresists therefore allow dynamic

tunability in both topography and elasticity, enabling the fabrication of complex and anisotropic biomaterials.

COLL 96

Chemical lift-off lithography by collapsing soft-material molds

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Soft-materials, e.g., polydimethylsiloxane (PDMS), are widely utilized in conventional soft lithography for feature patterning and material transferring over a large area. Lateral diffusion, however, restricts the feature resolution that can be achieved through stamping related techniques. Chemical lift-off lithography (CLL), on the other hand, can selectively remove alkanethiol molecules from self-assembled monolayers (SAMs) on gold surfaces with high pattern fidelity through a “subtractive” stamping process. The collapsing phenomenon of soft-material mold is combined with the CLL process in this research. The intentionally induced mold collapsing process creates much smaller final features than those carried by the original molds. In addition, the unique patterns fabricated through this strategy can be applied to the creation of various bio-recognition arrays for related sensing applications.

COLL 97

Atomic picture of nuclear decay in stable 2D radioactive films

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While macroscopic radioactive decay is well understood and has been utilized for decades; nanoscale effects of radioactive decay have barely been explored. We have synthesized one atom thick films of radioactive iodine-125 on gold that are stable in ambient conditions and can be handled safely. STM supported by simulation shows the atomic-scale structure of the films and the appearance of individual atoms of tellurium-125, the radioactive decay product. Using XPS we have verified the chemical composition of our samples and characterized the oxidation of daughter tellurium atoms. Electron spectroscopy reveals a multitude of low energy secondary electrons from the decay process. These lower energy electrons are the main drivers of radiation-induced chemical reactions, biological damage and radiation therapy. Therefore, 2D radioactive films offer a platform for understanding the microscopic details of these processes. Furthermore, the geometry of metal-supported 2D films more than quadruples the secondary electron yield making patterned monolayer films or coated nanoparticles spatially well-defined sources of higher intensity, tunable secondary electrons.

COLL 98

J-aggregate formation of cationic cyanine dyes on clay minerals

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A light-harvesting system composed of more than 100 chlorophylls collects light energy and transfers to a light reaction center in natural photosynthesis. We demonstrated efficient energy transfer reaction between two dyes co-adsorbed on clay minerals which was used as host materials. In the dye / clay complex, dye do not aggregate even under high density condition due to "Size-Matching Effect".¹ On the other hand, not only efficiency of the energy transfer but also concentration of the light energy is important such as light-harvesting in natural photosynthesis. Whitten and co-workers reported that fluorescence from cyanine forming J-aggregate on clay nanosheet was efficiently quenched.² However, this J-aggregate structure was unknown.

In this work, we investigate J-aggregate formation behaviors of cyanine dye (Figure 1(a)) on clay nanosheet (saponite) to reveal the J-aggregate structure. Absorption spectra of cyanine / clay complex at low and high dye loadings were shown in Figure 1(b).

Absorption peak of adsorbed monomer species was observed at low dye loading. This monomer species disappeared instead of appearance of long-wavelength species that showed ca. 50 nm red-shift with increase of dye loading. Fluorescence spectral shape of long-wavelength species was sharp compared to monomer species (shown in Figure 1(c)). Stokes shift of long-wavelength species was decreased compared to that of monomer species (487 cm⁻¹ to 224 cm⁻¹). These characteristics indicate that long-wavelength species is the J-aggregate formation of cyanine dye. Aggregation number and slip angle of J-aggregate on the clay was calculated to be 8 ~ 50 and was 16.3 ~ 22.1 degree from shift width of absorption spectra with an expansion Kasha theory.³ It was concluded that cyanine dye formed linear J-aggregate densely adsorbed on the clay nanosheet.

Ref.

1. Takagi, S. *et al.*, *Langmuir*, **2013**, 29, 2108.
2. Whitten, D. *et al.*, *Langmuir*, **2002**, 18, 7706.
3. Kobayashi, T, *J-Aggregates*, **2012**, vol. 2.

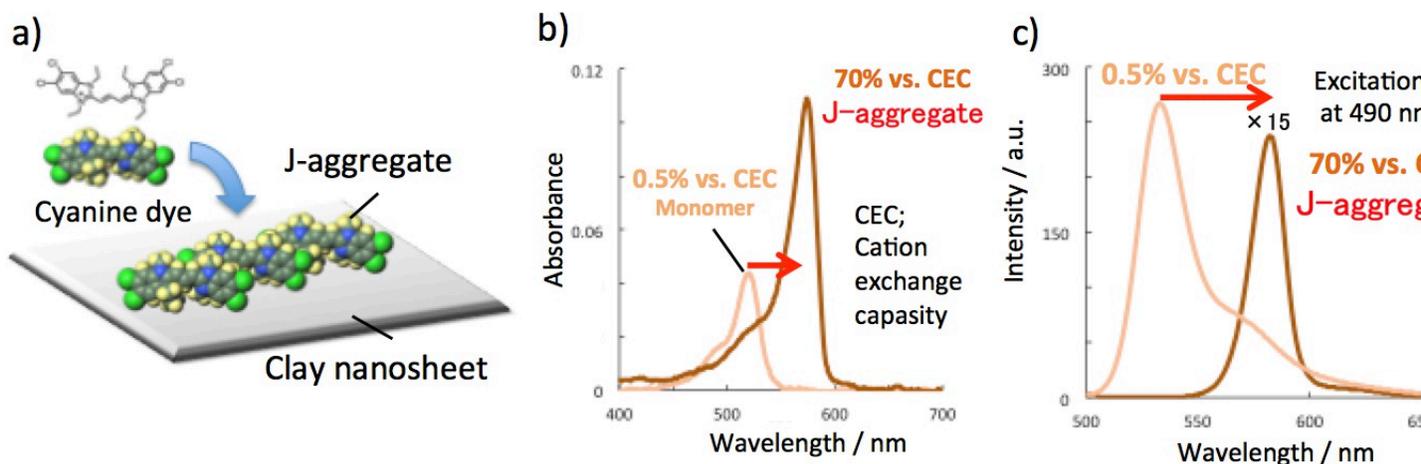


Figure 1 Image of cyanine dye adsorbed on clay nanosheet (a), absorption spectra (b) and fluorescence spectra (d) of cyanine / clay complex.

COLL 99

Dynamics of binary mixtures of cationic and anionic microgels at the air water interface

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When a droplet of colloidal dispersions dries on a solid surface, a thin ring-like stain is typically left, wherein most of the solid material is deposited after evaporation. In contrast, when the dilute dispersions of the microgel which is composed of poly(*N*-isopropylacrylamide) were dried, a thin film was formed and the film showed iridescent color. In microscopic scale, the microgels were arranged to non-close packed structure. So far, there were many studies of drying phenomena in order to control the properties of the resultant films. However, to the best of our knowledge few works have been reported on drying mechanism of the microgel dispersions in detail. If the key factor of forming mechanism was revealed, we would be able to control the assemble structure of microgels. Therefore, we have investigated the forming mechanism of the microgel. We found that the microgels were spontaneously adsorbed at the air/water interface, and then they were arranged at the interface. In addition, when the cationic and anionic microgels were mixed, they assembled into chain-like structures at the air water interface (**Figure 1**). The forming mechanism, the structure of microgel strings, and the other approaches related to the assembly of cationic and anionic microgels will be discussed at the poster presentation.

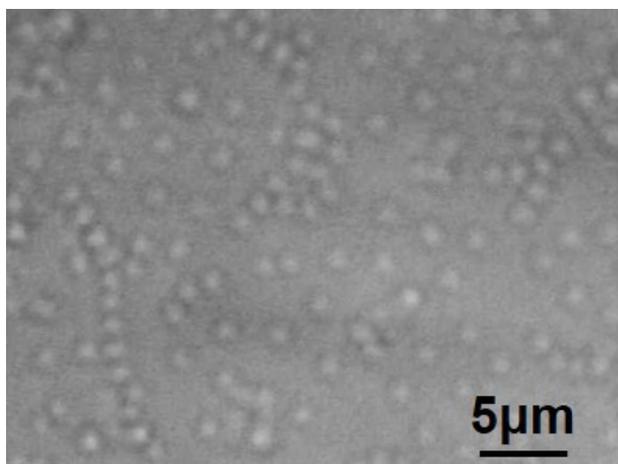


Figure 1. Observation at the air water interface when cationic and anionic microgels were mixed.

COLL 100

Solvent-free functionalization of multiwalled carbon nanotube buckypaper with amines

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Buckypaper (BP) is a thin film of carbon nanotube (CNTs) network, formed by nanotubes strongly aggregated through van der Waals forces. It attracted special attention due to its high porosity, specific surface area and flexibility. BP promises a number of applications, for example, in the development of efficient sensors based on functionalized BP. We developed a novel approach for the covalent functionalization of BP based on multiwalled carbon nanotubes (MWNTs) with amine molecules of variable structure, which helps to avoid contamination with detergents and solvents. The technique proposed consists in a solvent-free one-step treatment of BP with volatile amines under reduced pressure at 160-180 °C. After the reaction, the excess amine is removed from the sample by simultaneous heating and pumping out. The functionalized BP samples were characterized by means of Fourier-transform infrared, Raman and X-ray photoelectron spectroscopy, thermogravimetric analysis, as well as by scanning and transmission electron microscopy and atomic force microscopy (AFM). AFM imaging found important morphological differences between pristine and functionalized BP samples due to the presence of functionalizing molecules in the amine-treated materials. The suggested mechanism of covalent bonding of amines is through their nucleophilic addition to pentagonal and other structural defects at closed ends and sidewalls of pristine MWNTs. In addition to its simplicity, our approach allows for obtaining amine-functionalized BP material without contamination with other chemical

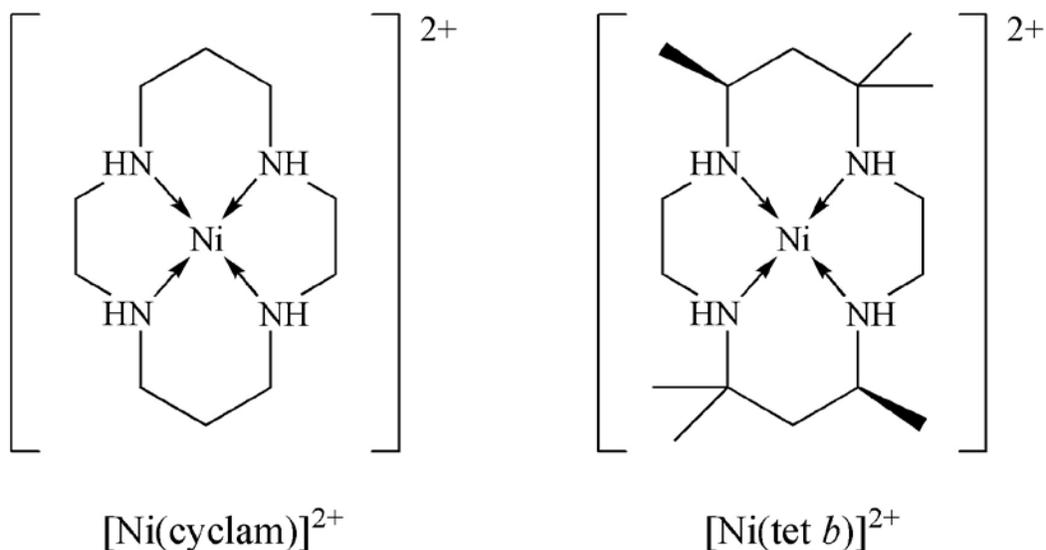
substances (e.g., solvents and condensing reagents), which is especially important for a variety of applications spanning from nanoelectronics to nanomedicine. We appreciate financial support from the grants UNAM-DGAPA-IN100112 and CONACyT-127299. I. J. R.-C. thanks CONACyT and Posgrado en Ciencia e Ingeniería de Materiales UNAM for a doctoral fellowship.

COLL 101

Coordination functionalization of graphene oxide and nanodiamond with nickel(II) tetraazamacrocyclic complexes

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The existence of carboxylic groups on the surface of graphene oxide (GO) and nanodiamond (ND) offers rich possibilities for the covalent, ionic and coordination functionalization of these important classes of carbon nanomaterials, and thus for broadening the spectrum of their useful properties and potential applications. For example, the attachment of tetraazamacrocyclic complexes to GO is extensively studied with an emphasis on hybrid nanomaterials for the uses in organic photovoltaics, spin electronics and electrocatalysis. In the present work, we explored the possibility of coordination functionalization of GO and ND with Ni(II) complexes of 1,4,8,11-tetraazacyclotetradecane (cyclam) and *rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (tet *b*). Both $[\text{Ni}(\text{cyclam})]^{2+}$ and $[\text{Ni}(\text{tet } b)]^{2+}$ exist in diamagnetic square-planar tetracoordinated state in neutral and acidic media, however, are known to adopt a folded hexacoordinated conformation upon coordination with carboxylate ions in basic media (thus becoming paramagnetic complexes). It is the latter property which was employed by us for the attachment of $[\text{Ni}(\text{cyclam})]^{2+}$ and $[\text{Ni}(\text{tet } b)]^{2+}$ to COOH groups of GO and ND. The nanohybrids obtained were characterized by using electron paramagnetic resonance, Fourier-transform infrared, Raman and X-ray photoelectron spectroscopy, thermogravimetric analysis, scanning electron, transmission electron and atomic force microscopy. Additional information about structure and properties of the macrocycle–GO nanohybrids was obtained from density functional theory calculations (DMol³ numerical-based DFT module, Materials Studio 6.0 package from Accelrys Inc., PBE GGA functional with Grimme dispersion correction, in conjunction with the double numerical basis set DNP). Financial support from UNAM (grants DGAPA-IN100112 and IN101313) and CONACyT (grant 127299) is greatly appreciated. N. A.-C. and L. V. H.-H. are indebted to the Doctorate Program in Chemical Sciences of UNAM and CONACyT for a Ph. D. fellowship.



COLL 102

Characterization of covalently-functionalized mesoporous silica nanoparticles by solution-phase NMR methods

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Mesoporous silica is a porous nanomaterial that is widely applied in current endeavors such as catalysis, environmental remediation, and biological applications. These nanomaterials possess unique and advantageous properties such as very high surface areas, variable pore diameters and volumes, and a surface that can be functionalized via coupling reactions with a variety of chemical moieties. A grand challenge of these materials is being able to obtain useful molecular level information about chemical structures and dynamics of the ligands on the surface in a solution-phase (aqueous) environment. Many applications of these materials will be in aqueous solution, so investigating these materials in an aqueous, solvated medium is critical. Ligand structure and dynamics were probed using a suite of solution-phase NMR methods including 1D ¹H NMR, diffusion measurements and Nuclear Overhauser Effect spectroscopy (NOE), the ligands have been probed using a suite of methods. Overall, the data suggest that some ligands on the surface of these materials are dynamic entities capable of hydrolysis, adsorption and rapid chemical exchange processes. Several ligands were explored including molecules with amino- and carboxyl-functionalities. These ligands appear to have different dynamics depending on their ability to form single or multiple siloxane bonds with the mesoporous silica nanoparticle surface.

COLL 103

DFT study of noncovalent complexes of phthalocyanines with spherical fullerenes and short nanotube models

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Noncovalent hybrids of phthalocyanines (Pcs) with fullerenes and carbon nanotubes (CNTs) is a subject of considerable research effort in the development of efficient organic photovoltaic cells, heterogeneous catalysts, gas sensors, field effect transistors, lithium batteries, among other aspects. Despite of theoretical studies play an important role in the elucidation of structure and properties of the nanohybrids, the number of relevant research reports is limited due to a large molecular size of both Pcs and carbon nanoclusters. The goal of the present work was to provide information on the noncovalent interactions of free Pc ligand (H_2Pc) and its copper(II) (CuPc) and zinc(II) (ZnPc) complexes with spherical fullerenes C_{60} and C_{80} (I_h isomer), as well as with short closed-cap models of single-walled CNTs (SWNTs) by using DFT calculations. The armchair and zigzag SWNT models ANT and ZNT were derived from C_{60} and $I_h C_{80}$ to form armchair (5,5) and zigzag (10,0) nanotubes, composed of 120 and 140 carbon atoms, respectively. The results were obtained by using the DMol³ numerical-based DFT module (Materials Studio 6.0 from Accelrys Inc.). We employed PBE GGA functional with Grimme dispersion correction, in conjunction with the double numerical basis set DNP. Full geometry optimization and calculation of electronic parameters was performed by using the quality and convergence criteria set to 'fine', along with all-electron core treatment, Fermi orbital occupancy, and the global orbital cutoff of 4.4 Å (as defined by the presence of Cu and Zn atoms). The calculated energies of complex formation span from -17.90 (for H_2Pc+C_{60}) to -37.12 kcal/mol (for $ZnPc+ZNT$); the interaction strength increases with increasing the size of carbon nanocluster, as well as, generally, with increasing atomic mass of the central atom. In all the complexes studied, Pc molecule notably bends to embrace carbon nanocluster and thus to increase the contact area. The optimized geometries are analyzed in terms of close contacts between the interacting components and N-M-N angles in the coordination sphere of Pcs. The HOMO-LUMO gap energies calculated are governed by the gap value of isolated carbon nanocluster rather than by the nature of central atom. The plots for HOMO, LUMO and spin density are presented. Financial support from UNAM (grant DGAPA-IN101313) and CONACyT (grant 127299) is greatly appreciated.

COLL 104

Label-free detection of RNA by using liquid crystals

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Detection of RNA is more challenging than DNA because it can be easily degraded by RNase. Thus, RNA has to be reverse-transcribed to cDNA before detection and sequencing can be conducted. Herein, we report an optical method to detect RNA directly by using liquid crystals. The principle is based on the disruption of a thin layer of liquid crystal in contact with RNA hybridized with immobilized PNA on a solid surface. In the presence of metal ions, RNA is able to hybridize with surface-immobilized PNA probes, and forms a RNA/PNA/metal ion complex. This complex is able to influence the orientation of liquid crystals near the surface, and cause a ordering transition in the bulk liquid crystal. By using this method, we can detect 10fM lac Z RNA from total RNA of *E.coli*.

COLL 105

Interaction of a Ni(II) tetraazaannulene complex with spherical and elongated fullerenes: A DFT study

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Noncovalent nanohybrids of nickel(II) complex of 5,14-dihydro-6,8,15,17-tetramethyldibenzo[*b,l*][1,4,8,11]tetraazacyclotetradecine (NiTMTAA) with carbon nanotubes (CNTs) is a more complex and interesting case in structural terms as compared to the related materials functionalized with porphyrins and phthalocyanines. Saddle-shaped NiTMTAA molecule adsorbed can adopt different, energetically non-equivalent orientations with respect to CNT, depending on whether CH₃ or C₆H₄ groups contact the latter. The main goal of the present work was to provide information on the interactions of NiTMTAA with simple single-walled CNT (SWNT) models. We employed three dispersion-corrected DFT functionals: M06-2X and LC-BLYP as implemented in Gaussian 09 package, and PBE-G as implemented in Materials Studio 6.0. We considered one armchair (A) and one zigzag (Z) short closed-end SWNT models (also referred to as 'elongated fullerenes'), derived from C₆₀ and C₈₀ hemispheres. The geometries obtained with M06-2X and LC-BLYP functional were very similar. In most complexes, the interaction between NiTMTAA and SWNT was noncovalent. The exception was the geometry of one complex with Z, in which a new C-C covalent bond spontaneously formed: one carbon atom forming this bond belongs to the pentagon of the nanotube tip, and another one is the γ -C atom of NiTMTAA. In an attempt to explain this phenomenon, we performed an additional series of calculations with fullerene C₆₀, as well as with *I_h* and *D_{5h}* C₈₀. In the case of C₈₀ *I_h*, from which (10,0) Z model is derived, we found again the covalent bonding with NiTMTAA in M06-2X calculations. Apparently, the possibility of addition has to do, on one hand, with the reactivity of pentagonal defects responsible for spherical curvature and kinks of pristine nanotubes, and on the other hand, with the reported reactivity of the γ -C atom of transition metal complexes of TMTAA. In the case of PBE-G calculations, all the complexes were noncovalent. The general trend was that the 'embracing' contact of *o*-phenylene rings of NiTMTAA with SWNT gives rise to stronger complexation due to π - π interactions.

Financial support from UNAM (grant DGAPA-IN101313) and CONACyT (grant 127299) is greatly appreciated. L. V. H.-H. is indebted to the Doctorate Program in Chemical Sciences of UNAM and CONACyT for a Ph. D. fellowship.

COLL 106

Imaging of liver cells using water soluble CdTe quantum dots

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Quantum dots have received significant attention for their potential in bio-imaging applications. One drawback to their use is maintaining emission intensity in an aqueous environment, without adding significant diameter to the crystal. Here, highly luminescent, water-soluble cadmium telluride (CdTe) quantum dots were synthesized by a standard high temperature injection in organic solvent, followed by conversion to aqueous media by surface functionalization reactions. These nanocrystals exhibit intense bandgap emission, which is retained throughout the water solubility reaction. This added intensity is due to the incorporation of an alkanethiol during the initial synthesis. The characterization of the optical properties and crystal size was performed using ultraviolet-visible absorption, fluorescence spectroscopy, and x-ray diffraction. The nanocrystals underwent surface modifications to become water soluble, followed by exposure to a buffalo rat liver cell culture. The cells were imaged using fluorescence microscopy at different exposure times. Results indicate the quantum dot emission intensity was present over a period of several days.

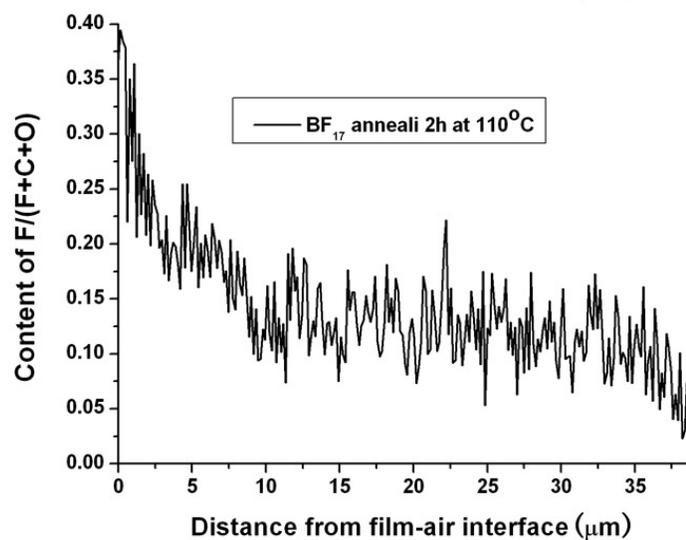
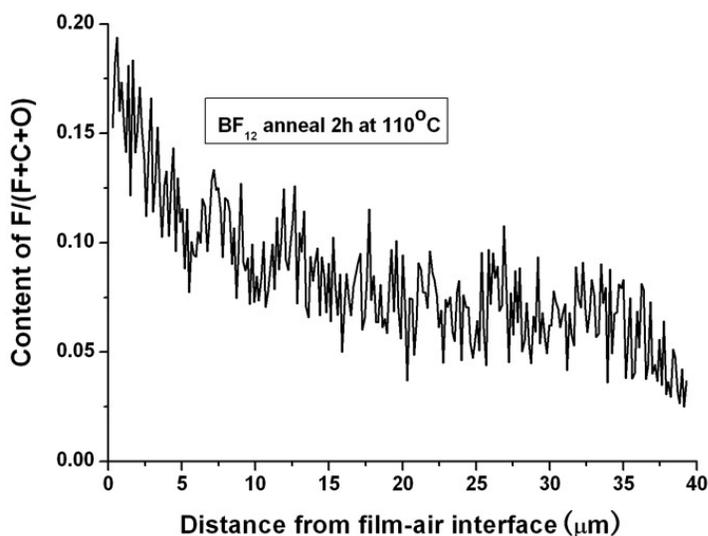
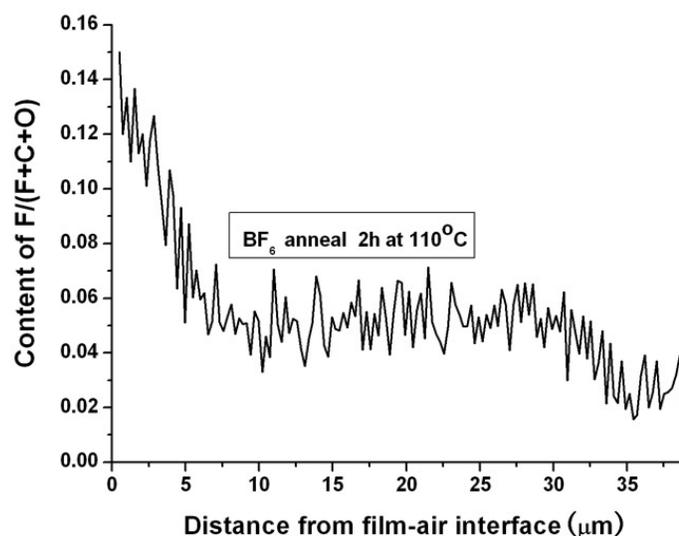
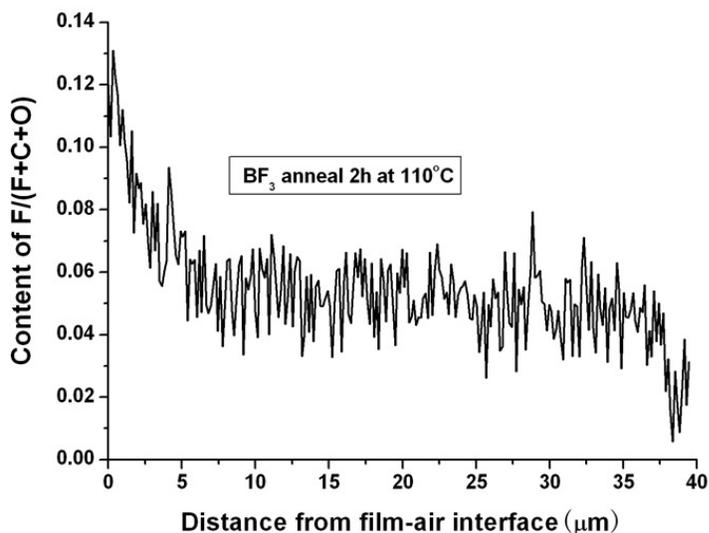
COLL 107

Effects of composition on the gradient structure and surface properties of fluorinated polyacrylates latex blends film

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The main driving force provider of the formation of self-organization gradient structures in the fluorinated/non-fluorinated polyacrylate latex blends system are the difference of the surface free energies(SFE) of the polymers, which mainly provided by the fluorine-containing alkyl chain segments. In this work, four different fluorinated acrylate(F₃MA; F₆MBA; F₁₂MA; F₁₇MA) with different fluorine-containing alkyl were chose to copolymerization with butyl acrylate(BA) and methyl methacrylate(MMA) by emulsion polymerization methods, then, four copolymers emulsion with similar fluorine monomer content, T_g and particle size were obtained. The four fluorinated copolymer were blend with the same non-fluorinated polyacrylate(PMMA-co-BA) at the same rate. The four blend latex(BF₃; BF₆; BF₁₂; BF₁₇) were filmed at room temperature and annealed 12h

at 110°C. The effect of perfluoroalkyl chain length on the surface property and gradient structure of fluorinated polyacrylates latex blends film were discussed by AFM, SEM-EDS and contact angle method. The results showed that with the extension of fluorine alkyl chain segments in system, the hydrophobicity and oleophobicity of the film-air interface and the concentration gradient of fluorine across the thickness of the blend film were improved.



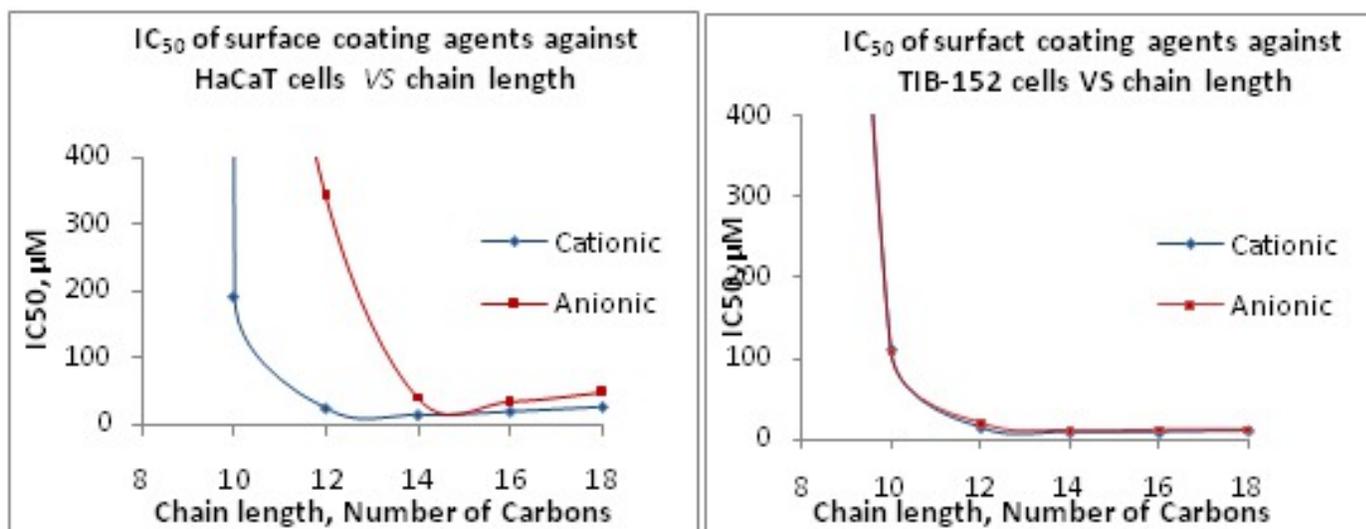
The content of F/(F+C+O) of the four kind of blend films anneal 2h at 110 °C

COLL 108

Effect of chain length, number of chains, and charge on the in vitro cytotoxicity of surface coating agents used for nanoparticles

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The research and application of nanotechnology have grown tremendously in the last decade. Surface coating agents, or surfactants, are an integral part of most nanoparticles for shape and size control during synthesis and surface protection and stability. Therefore, the study of the toxicity of nanoparticles must consider the effects of the surfactants used. Here we report the *in vitro* cytotoxicity of both cationic (alkyl ammonium salts) and anionic (alkyl sulfates) surfactants in two cell lines: human skin keratinocytes (HaCaT) and blood T lymphocytes (TIB-152) with the consideration of chain length, number of chains and charge. Both cationic and anionic surfactants with chains length of ≤ 8 carbons are essentially not cytotoxic on both cell lines. The cytotoxicity of the surfactants increases with the increase of the chain length from 10 to 12 carbons, and then levels off from 12 to 18 carbons except for the cationic surfactants on HaCaT cells where the leveling off chain length is 14 carbons. The cationic didodecyl (12) surfactant is slightly more cytotoxic than the mono-dodecyl surfactant, while the cationic dioctadecyl (18) surfactant is not cytotoxic due to micelle formation in the concentration range tested. For HaCaT cells, the cationic surfactants are more cytotoxic than the anionic surfactants with the same chain length, but for TIB-152 cells, both cationic and anionic surfactants are on the same cytotoxicity level. Both of these two classes of surfactants are more cytotoxic to TIB-152 cells than to HaCaT cells. There appears to be a threshold concentration for some surfactants that cytotoxicity is not observed until a certain concentration, where it appears suddenly.



COLL 109

Fluorescent organic nanodots for sensing metals and a targeted immunofluorescence labeling

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Fluorescent materials are used to investigate a biological mechanism of a cell. The fluorescence labeling, as one of the analytical techniques, is commonly used to study the structure of living cells. Organic molecules or inorganic semiconductors are currently used in these fields. However, they both have serious drawbacks. Organic molecules lose their fluorescence intensity by self-quenching and inorganic quantum dots are toxic to a bio cell. Thus, we developed a new fluorescent material to overcome these problems by using a heterocyclic structure of the excited state intramolecular proton transfer since the molecular structure showed remarkable photophysical property and anticipate it is applied in the fluorescence labeling. The organic solution is injected to the diacetylene vesicles of diameter of few 100 nm. As expected, synthesized nano assembly has the fascinating optical property.

COLL 110

Electrochemical and photocatalytic activity analysis of TiO₂-NiO/TiO₂

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TiO₂-NiO/TiO₂ bilayer films were prepared and tested through electrochemical analysis and photocatalytic activity on acid orange 7 (AO7) degradation with the presence and absence of UV light. The film preparation started with the first layer of TiO₂, which was prepared from commercial TiO₂. Ni(OH)₂ was incorporated into TiO₂ for the second layer deposition. Ni(OH)₂ was subjected to 300 °C calcination temperature before being mixed with sol TiO₂, which was later used to coat for the second layer. TiO₂-NiO/TiO₂ bilayer films were prepared by spin-coating method. In characterization methods, the anodic peak of AO7 was tested by cyclic voltammetry technique and the crystal structure of TiO₂-NiO was analyzed by XRD. The energy storage of TiO₂-NiO/TiO₂ film was proven by electrochemical process that the changes in the potential of TiO₂-NiO/TiO₂ film rapidly shifted at 1 h but ITO, TiO₂ and TiO₂-NiO did not show the same behavior. For the photocatalytic activity, TiO₂-NiO/TiO₂ showed photocatalytic properties even without illumination implying that there was possibility of energy storage during the illumination.

COLL 111

Studies on the mechanisms of forced transport of dye through solution modifications to a polymerized surface

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The design and implementation of a controlled macromolecular chemical transport system could greatly advance switchable chemical reactions and be applicable for targeted drug delivery, intelligent inks, and nanotechnology. To better understand the mechanisms of function for a switchable macromolecular transport system, preliminary work has been completed that studies the transport of bromothymol blue (BB) facilitated by cetylpyridinium bromide hydrate (CPBM) to a silica surface that has been modified with Poly(styrene-co-maleic anhydride), a pH switchable polymer. Ultraviolet spectroscopic trials were conducted measuring the absorbance of BB and CPBM at two pH levels, while holding BB at a constant 1×10^{-5} M, varying CPBM between 1 and 10×10^{-5} M. Under acidic conditions at pH 3.5, BB and CPBM were attracted to the silica surface, however CPBM had a lower surface concentration, varying from 0.7 to 1.7 times lower. Additionally as the concentration of CPBM was increased, the time to surface of the BB and CPBM also increased by doubling in time at an 8 fold concentration increase. Under basic conditions at pH 9.5, initial attraction of the BB was observed to the silica surface above a concentration of 3×10^{-5} M however; as CPBM concentration increased at the surface, the BB concentration decreased. A concentration of 4.5×10^{-5} M of CPBM was needed before a low concentration of BB would remain on the silica surface. The difference in attraction under both acidic and basic conditions was due to columbic repulsion between the negatively charged BB and the negatively charged surface. The surface coverage of the bound polymer also was noted to play a role in attraction of the BB and CPBM, with a lower surface coverage having a greater attraction of BB and CPBM. Further work is to be completed by investigating the reversibility of BBs attraction/repulsion to the silica surface using polyelectrolytes as vehicles of removal as well as further work done on the effect of surface coverage of the bound polymer on the silica surface.

COLL 112

Adsorption of poly(vinyl alcohol) onto polydimethylsiloxane substrates: Formation of continuous films, honeycomb structures, and fractal morphologies

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Polydimethylsiloxane (PDMS) is extensively used in analytical systems, biomedical devices, and electronic devices. However, its hydrophobicity hinders some of its applications by causing incompatibility with biological media and fouling that ultimately results in device failure. In this research, surface hydrophilization of PDMS was carried out by adsorption of poly(vinyl alcohol) (PVOH, 99% hydrolyzed, M.W. = 89-98 kDa) from aqueous solution. PDMS of different molecular weights, from 162 Da to 116 kDa, were covalently attached to silicon wafer substrates. All the substrates were characterized using ellipsometry, contact angle goniometry, and atomic force microscopy before and after each step. Interestingly, adsorbed PVOH thin films were only continuous on PDMS layers of 2 kDa and showed “dewetted” morphologies, such as honeycomb structures and fractal features, as the underlying PDMS molecular

weight increases and decreases. The instability of the adsorbed PVOH thin films is likely caused by chemical and/or physical surface “defects”: lower molecular weight PDMS resulted in incomplete surface coverage exposing silanol groups while larger molecular weight PDMS covered the silicon wafer substrates completely with significant roughness. *In situ* imaging confirms that various PVOH morphologies are formed upon exposure to air, not in solution. The unique structural features of adsorbed PVOH thin films are likely the direct result of PVOH crystallization upon dehydration and are dependent on surface defects.

COLL 113

Role of substrate receding contact angle in deposit patterns of sessile droplets containing stabilized gold nanoparticles

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Self-assembled monolayers (SAMs) of gold nanoparticles (AuNPs) have many applications including imaging, lithography, sensing, and catalysis. A simple and effective way to form this type of SAMs is to deposit sessile drops containing AuNPs onto desired substrates. However, colloids in solution typically form non-uniform deposit patterns upon solvent evaporation, commonly known as “coffee rings.” While many studies exploring drying dynamics have been performed, little attention has been paid to ensure the chemical and physical homogeneity of the substrates. This devalues the results, as even the slightest surface heterogeneities cause localized droplet pinning and distort final deposit patterns. We have adapted a system for creating molecularly smooth and chemically homogeneous substrates. Plasma oxidation was used to remove surface contaminants from silicon wafers, creating superhydrophilic surfaces functionalized with silanol groups. The wafers were then modified through silanization using tris(trimethylsiloxy)chlorosilane for varying amounts of time in the vapor phase resulting in substrates with different degrees of hydrophobicity. Steric stabilization of AuNPs was accomplished by conjugation with poly(vinyl alcohol) (PVOH) in aqueous solution. Microliter-sized droplets containing PVOH-AuNPs were cast and dried on clean and modified silicon wafers. Macroscopic deposit patterns were characterized using optical microscopy and nanoparticle packing within each deposit pattern was analyzed using atomic force microscopy (AFM). The deposit pattern on superhydrophilic clean silicon wafer is extremely uniform, consisting of a monolayer of closely packed AuNPs. On the other hand, deposit patterns on modified substrates all consist of “rings” whose size and width vary as a function of substrate receding contact angle. This is the first time that particle packing pattern within dried deposit is correlated to substrate dynamic contact angles, especially receding contact angle, using AFM analysis.

COLL 114

Smooth and uniform thiol-functionalized substrates for bioconjugations

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Thiol-functionalized substrates were fabricated by reacting silicon wafers with either mercaptopropylalkoxysilanes or thiol-functionalized polydimethylsiloxanes. The two approaches and the reaction variants used within allowed us to prepare thiol-functionalized substrates with a wide range of density and flexibility/accessibility. Unfortunately, the thiol layers as prepared were rough and non-uniform due to disulfide bond formation between reagent molecules. Reducing agents, such as dithiothreitol, applied either during or subsequent to the modification reactions were found necessary to generate smooth and uniform thiol layers. The thiol-functionalized substrates were subsequently evaluated as platforms for conjugations of molecules of biological interest. In one system, vinyl-terminated poly(ethylene glycol) was “clicked” to the substrates via thiol-ene photochemistry to minimize non-specific protein adsorption. In a parallel system, proteins were covalently attached to the thiol-functionalized substrates via disulfide bond formation or thiol-disulfide exchange reaction. In addition to protein activity assays, the substrates are characterized using ellipsometry, contact angle goniometry, and atomic force microscopy before and after each reaction.

COLL 115

Probing the hydrodesulfurization properties of cobalt-nickel phosphides: Supported catalysts and encapsulated nanoparticles

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The need for improved hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) catalysts is being driven by increasingly demanding requirements for ultralow sulfur fuels and by the fact that sulfur levels in crude oil have been trending upward over recent decades. Current industrial catalysts are based on molybdenum sulfide (MoS₂) and its highly anisotropic structure severely limits the number of exposed active sites. Transition metal phosphides (e.g. Ni₂P/SiO₂) are a new class of materials with promise to have improved properties relative to sulfided Ni-Mo/Al₂O₃ catalysts. The addition of a second metal can have large effects on the electronic and surface properties of a catalyst, which in turn can heavily influence its catalytic properties. Cobalt-nickel phosphide catalysts (Ni_{2-x}Co_xP, 0 ≤ x ≤ 1) are being investigated to determine the effect of cobalt on the HDS properties of bimetallic phosphides of nickel. Catalysts prepared via conventional preparation methods using metal phosphate precursors supported on silica, and reduced by temperature programmed reduction (TPR) are compared with solution-prepared metal phosphide nanoparticles that were subsequently encapsulated in a mesoporous silica shell to form core@shell nanostructures. Infrared spectra of adsorbed CO on the catalyst surfaces show two significant peaks, one is attributed to CO bound to surface nickel atoms, while the second, smaller peak is attributed to CO

bound to surface phosphorous atoms. As cobalt is added into the crystal lattice, there is a shift to lower wavenumbers of the absorbance due to CO bonded to surface nickel atoms. This may indicate electron donation from cobalt to nickel, making for more electron-rich binding sites. The catalysts were tested for HDS activity and selectivity using dibenzothiophene and 4,6-dimethyldibenzothiophene. The trends in catalyst activities and turnover frequencies with Co content will be described and discussed in the context of the characterization results.

COLL 116

Capacitance and hydrogen evolution reaction characterization of electrodeposited nickel alloy thin films

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With the global energy demand growing, there is greater need for production of energy. One of the ways of producing this energy is creation of hydrogen gas to store energy, however, this technique is not yet economically favorable compared to many other energy sources. One reason for this is the current use of platinum in hydrogen production. As a result, we are exploring other less costly metals for use as hydrogen producing catalysts. With the technique of electrodeposition, different nickel alloy thin films were created to characterize their structure, composition, and hydrogen production capabilities. Characterization was completed using atomic force microscopy (AFM) to measure roughness, scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS) to measure composition, and cyclic voltammetry to measure electrochemical capacitance. Linear sweep voltammetry was used to perform the hydrogen evolution reaction (HER), a reaction that produces hydrogen gas as a product. The use of these characterization techniques and HER measurements could help further understanding of the production of hydrogen and help fuel cells become more economically favorable using these earth-abundant metals.

This material is based upon work supported by the National Science Foundation under NSF-RUI Grant No. DMR-1104725, NSF-MRI Grant No. CHE-0959282, NSF-MRI Grant No. CHE-1126462, and the Hope College Jacob E. Nyenhuis Faculty Development fund.

COLL 117

Quantitative characterization of methanol oxidation catalysis on dealloyed NiCu films

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The topic of catalytic nanoporous materials has seen a surge of interest in the past decade. With Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS), the surface area, topography, and composition of these nanostructures can be characterized. The accessibility of these instruments has generated interest involving the interactive effects of surface topography and catalytic activity of binary alloys. The research conducted involved electrodepositing, dealloying, and characterizing various nickel-copper binary alloys on a Au substrate for methanol oxidation applications. By dealloying copper out of a NiCu alloy using Controlled Potential Electrolysis (CPE), a high-surface area nanoporous material was fabricated. The composition and capacitance of the NiCu alloys (before and after the dealloying step) were characterized via SEM/EDS, and Cyclic Voltammetry (CV) respectively. Utilizing Chronoamperometry (CA), the oxidation of methanol was analyzed before and after dealloying to determine whether porosity enhanced the catalytic efficiency.

This material is based upon work supported by the National Science Foundation under NSF-RUI Grant No. DMR-1104725, NSF-MRI Grant No. CHE-0959282, NSF-REU Grant No. PHY/DMR-1004811, and the Hope College Dean for Natural and Applied Sciences Office.

COLL 118

Nickel phosphide hydrotreating catalysts on phosphorus-modified oxide supports

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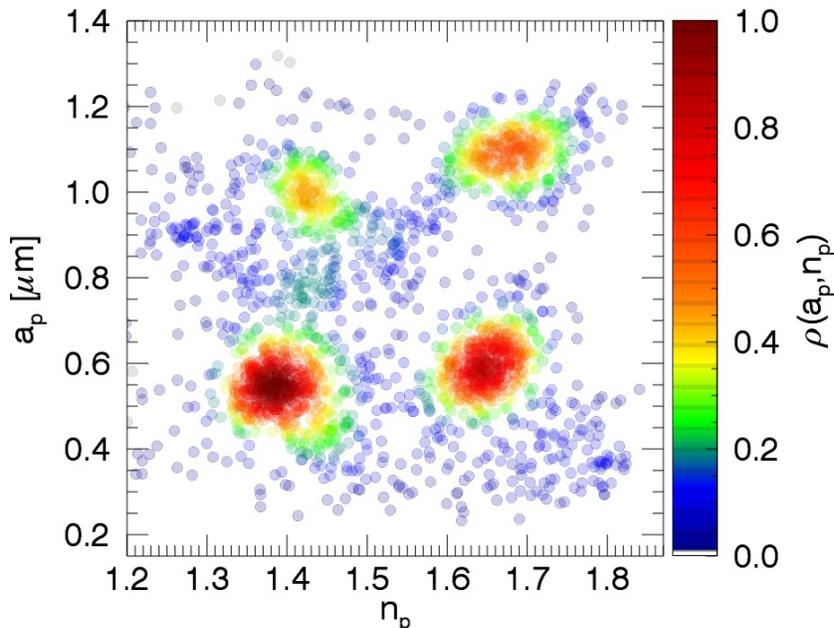
The synthesis and hydrotreating properties of nickel phosphide supported on phosphorus-modified alumina, amorphous silica-alumina (ASA), and silica have been investigated. The utility of nickel phosphides on Al-containing supports for hydrodenitrogenation (HDN) and hydrodesulfurization (HDS) catalysis is hindered by the formation of AlPO_4 on the support during catalyst synthesis. A series of modified supports have been prepared by forming a thin layer of P_2O_5 on the supports prior to synthesis of the Ni_2P , with the goal of improving the catalytic properties of the nickel phosphide catalysts. X-ray photoelectron and FTIR spectroscopies were used to characterize the P_2O_5 overlayer formed on the supports. P-treatment inhibited interactions between the support and impregnated Ni and P salts, allowing for the formation of Ni_2P at lower temperatures and phosphorus loadings than on unmodified supports. The Ni_2P catalysts were characterized by X-ray diffraction to determine the average crystallite size and phase purity. The catalytic properties of Ni_2P on the P-modified supports were investigated in high-pressure reactor studies using a mixed carbazole / benzothiophene feed and the results of these measurements will be related to those for Ni_2P on the unmodified supports.

COLL 119

Total holographic characterization of colloidal suspensions

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Total holographic characterization uses holographic video microscopy to measure the size, refractive index and three-dimensional position of individual colloidal particles moving freely through their fluid medium. The detailed information derived from these measurements have applications in product development, quality assurance and manufacturing process control in industries as diverse as consumer products, food, cosmetics, medical diagnostics, pharmaceutical manufacturing, petrochemicals, among others. Based on the Lorenz-Mie theory of light scattering, holographic characterization yields a particle's size to within a nanometer and its refractive index to within a part per thousand. These data are available for each particle in the microscope's field of view and for each snapshot in the holographic video stream. No other particle characterization technique provides such a wealth of information. The analysis is fast enough that population statistics on tens of thousands of particles can be amassed in minutes. Holographic characterization therefore yields insights into the composition of inhomogeneous and multicomponent colloidal dispersions that cannot be obtained in any other way. Holographic tracking data, obtained at the same time, yields insights into individual colloidal particles' responses to external forces, their interactions with bounding surfaces and their interactions with each other. In combination with optical micromanipulation, these measurements provide an unprecedented view into the stability and dynamics of colloidal dispersions.



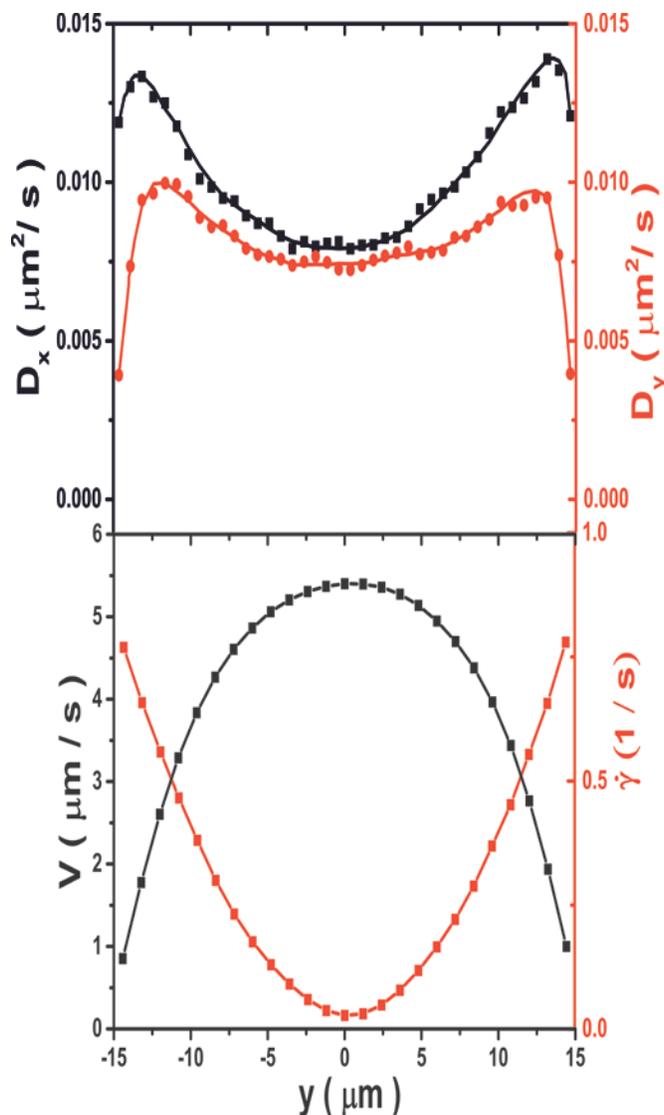
Real-time analysis of 5,000 spheres from a blend of 4 populations. Total Holographic Characterization distinguishes particles in situ on the basis of size and composition.

COLL 120

Effects of shear and walls on the diffusion of colloids in microchannels

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Colloidal suspensions flowing through microchannels were studied for the effects of both shear flow and the proximity of walls on the particles' self-diffusion. Use of hydrostatic pressure to pump micron-sized fluorescent silica spheres dispersed in water-glycerol through poly(DiMethylSiloxane) channels with a cross section of 30x26 micron, allowed to vary the Péclet number (Pe) from 0.01 to 50. To obtain the diffusion coefficients, image-time series from a Confocal Scanning Laser Microscope were analysed with a method that, after finding the particle trajectories, subtracts the instantaneous convective displacements and then measures the slopes of the Mean Squared Displacements in the flow (x) and shear (y) directions. The thus obtained D_x and D_y , which should be equal to the free diffusion coefficient in the dilute limit regardless of shear, both increase strongly with Peclet number (for $Pe > 10$) in a concentrated suspension. This effect of the shear-induced collisions is counteracted by the contribution of the wall, which causes a strong local reduction in D_x and D_y .



Upper graph: Diffusion coefficients in the flow (x) and shear (y) directions as a function of the lateral (y) position position in the channel. Lower graph: Local velocity and shear rate in the same channel. The walls are located at $y = \pm 15$ micron. Symbols represent experimental data while lines are to guide the eye.

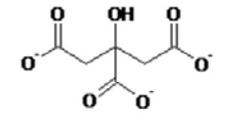
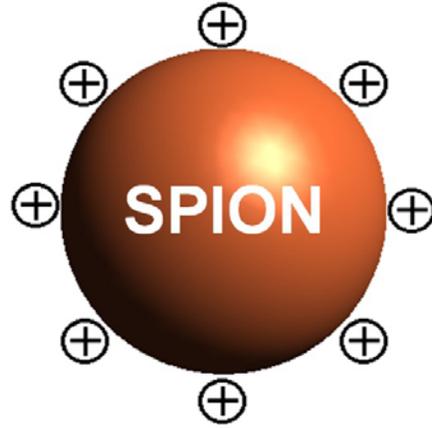
COLL 121

Glutathione-coated luminescent gold nanoparticles: A surface ligand for minimizing serum protein adsorption

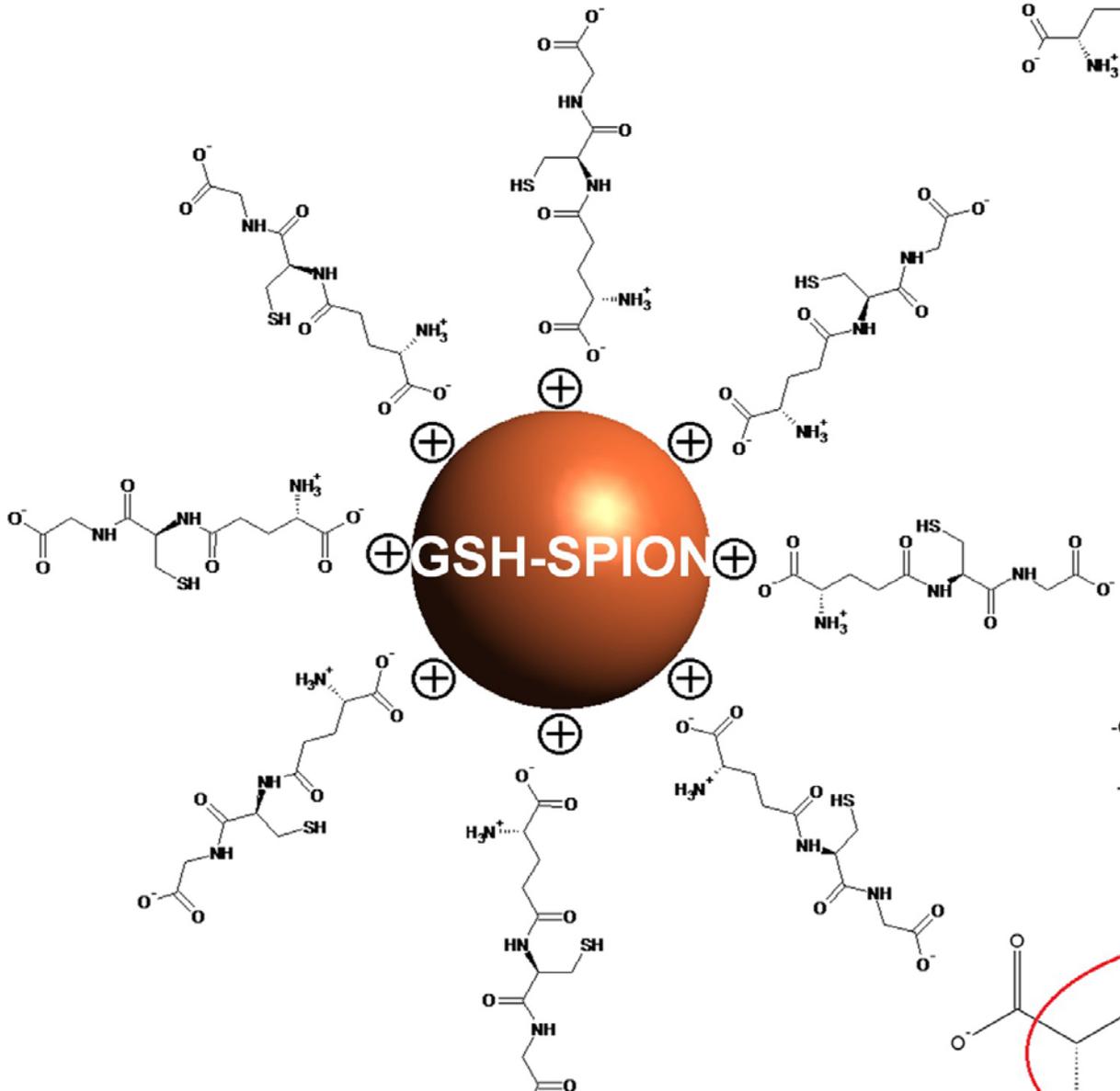
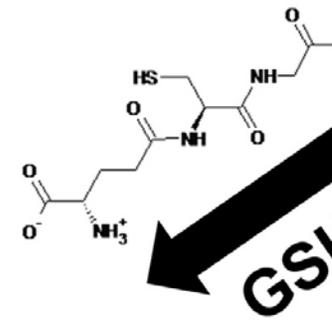
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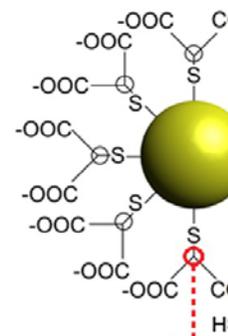
Glutathione-coated luminescent gold nanoparticles (GS-AuNPs) of ~2 nm are known for their high resistance to serum protein adsorption. Our studies illustrate that these GS-AuNPs can serve as surface ligands to significantly enhance the physiological stability and lower the serum protein adsorption of superparamagnetic iron oxide nanoparticles (SPIONs), in addition to rendering the NPs the fluorescence property. After the integration of GS-AuNPs onto the surface of SPIONs to form the hybrid nanostructures, these hybrid nanoparticles' protein adsorption was about 10-fold lower than those of the pure glutathione-coated SPIONs suggesting that GS-AuNPs are capable of providing a stealth effect against serum proteins.



Citrate



GS-Au



Schematic illustration of how the ultrasmall luminescent gold nanoparticles and superparamagnetic iron oxide nanoparticles were integrated.

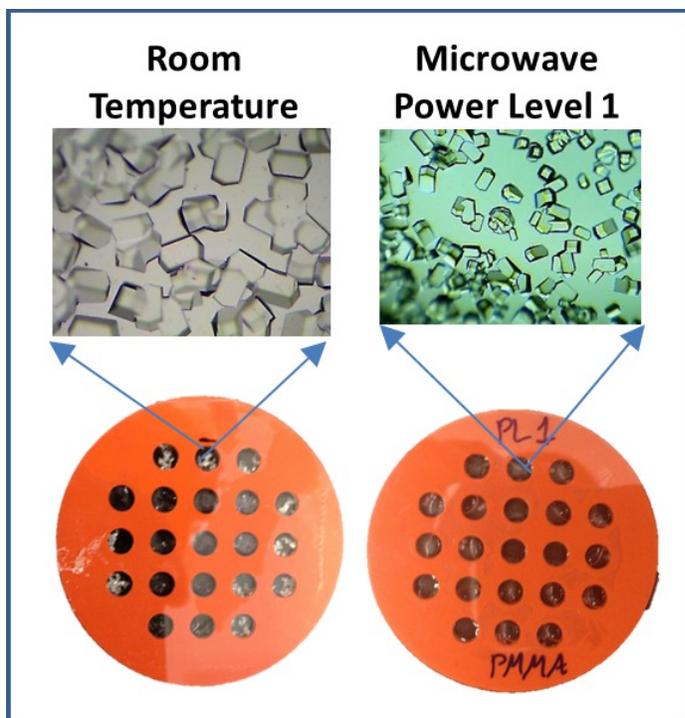
COLL 122

Crystallization of proteins on iron nanocolumns using metal-assisted and microwave-accelerated evaporative crystallization for improved size distribution

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In response to the growing need for new crystallization techniques that facilitate for rapid processing times along with control over crystal size and distribution, the Aslan Research Group has recently demonstrated the use of Metal-Assisted and Microwave-Accelerated Evaporative Crystallization (MA-MAEC) technique in conjunction with silver nanostructures deposited onto circular crystallization platforms.

In this work, we employed the MA-MAEC technique with iron nano-columns (height: 50, 100 and 200 nm, average distance between the columns = 140, 175 and 175 nm, respectively) to control the size distribution of protein crystals by initiating the growth of protein crystals between the iron nano-columns. Using the MA-MAEC technique, we observed a narrower size distribution and a decrease in the size of lysozyme crystals grown on iron nano-column deposited circular crystallization platforms as compared to grown on platforms without iron nano-columns, which can be directly attributed to the iron nano-columns. Moreover, similar results were observed for lysozyme crystals grown on iron nano-columns at room temperature. These observations prove that the MA-MAEC technique and iron nano-columns can offer alternative means for control over crystal size and distribution of biological molecules.



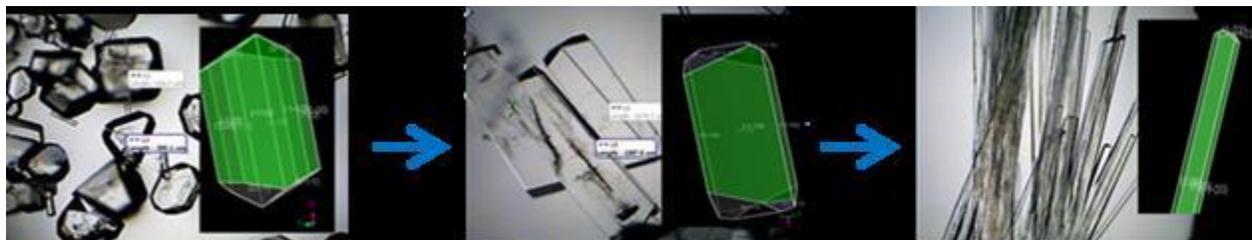
COLL 123

Crystal engineering of L-alanine in the presence of multiple amino acid additives using metal-assisted and microwave-accelerated evaporative crystallization

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In this work, we investigated the L-alanine's crystal structure under the influence of a mixture of multiple hydrophobic and hydrophilic amino acid additives using our Metal-Assisted and Microwave-Accelerated Evaporative Crystallization (MA-MAEC) technique. Our experimental results show that the incorporation of a mixture of multiple additives to L-alanine solution inhibits the growth rate of L-alanine's {120} face and significantly changes the morphology of L-alanine crystals. The use of the MA-MAEC technique afforded for up to 5-fold reduction in time of crystallization of L-alanine in the presence of a mixture of amino acid additives, as compared to control experiments carried out without microwave heating and metal nanoparticles. To elucidate our experimental observations, computational theoretical simulations (Materials Studio 7.0 software) were carried out. In this regard, the built-in method was used to calculate the thermodynamic energy of L-alanine's unit cell with and without the incorporation of additives. The surface docking method was used to study the interactions of the additives with the surface of L-alanine crystals. Results from the theoretical simulations corroborated with experimental results, and showed that the hydrophobic amino acid

additives results in a difference in energy between pure L-alanine and L-alanine with the adsorption of additives.



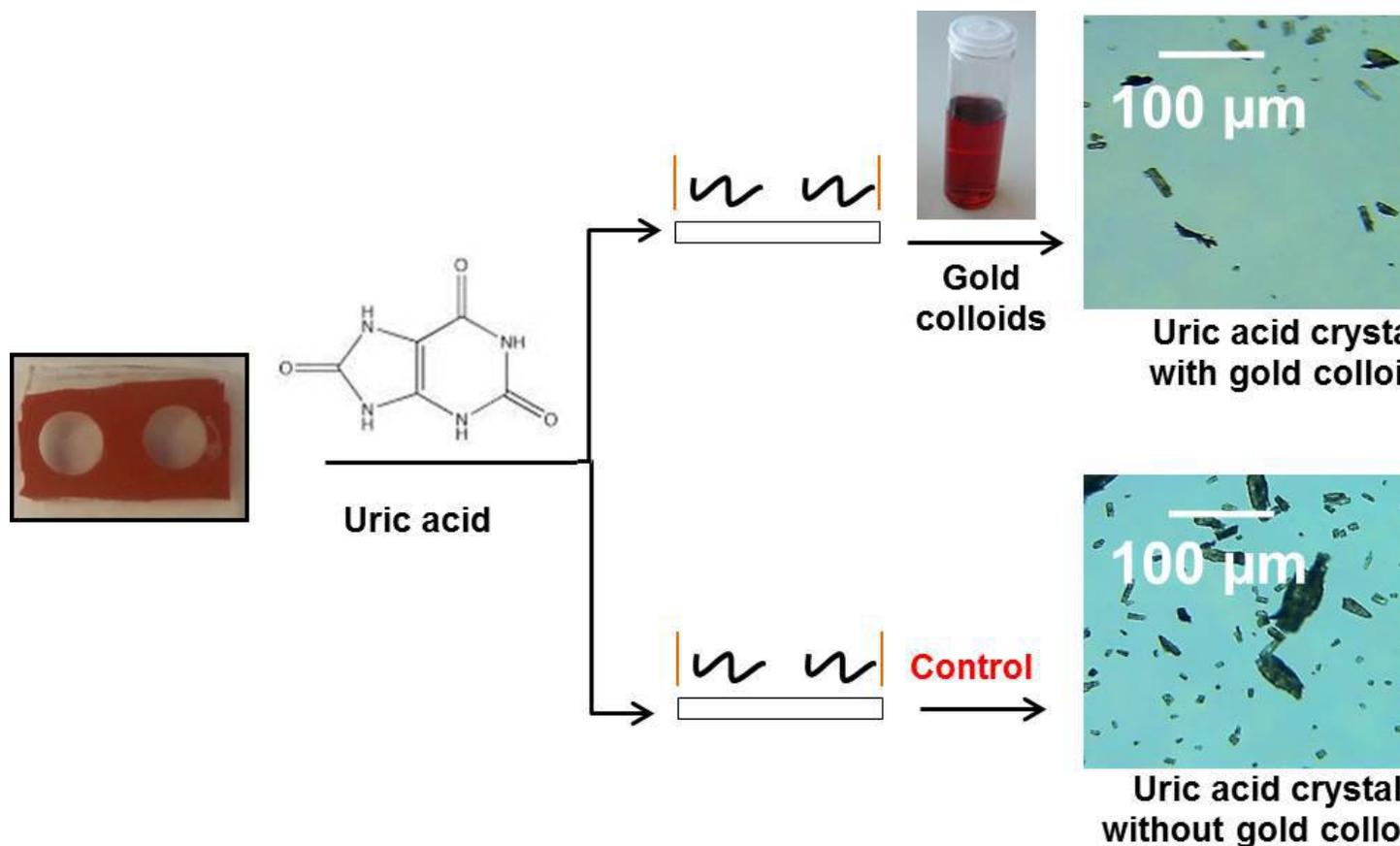
The morphology of L-alanine crystals can be engineered by additives

COLL 124

De-crystallization of uric acid crystals in synovial fluid using gold colloids and low power microwave heating

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In this study, we demonstrated a unique application of our Metal-Assisted and Microwave-Accelerated Evaporative Crystallization (MA-MAEC) technique for the de-crystallization of uric acid, which causes gout in humans when monosodium urate crystals accumulate in the synovial fluid found in the joints of bones. Our technique was based on the use of metal nanoparticles (i.e., gold colloids) with low microwave heating to accelerate the de-crystallization process. This study was conducted to investigate whether MA-MAEC can offer an alternative solution to the treatment of gout, given the shortcomings of the existing treatments. In this regard, de-crystallization of uric acid was performed in a two-step process; (i) crystallization of uric acid on glass slides, which act as a solid platform to mimic a bone, (ii) de-crystallization of uric acid crystals on glass slides with the addition of gold colloids and low power microwave heating, which act as “nano-bullets” when microwave heated in a solution. We observed that the size and number of the uric acid crystals were significantly reduced within 5 minutes of low power microwave heating. In addition, the use of gold colloids without selective microwave heating (i.e. control experiment) did not result in the de-crystallization of the uric acid crystals, which proves the utility of our MA-MAEC technique in the de-crystallization of uric acid.



Depiction of the experimental procedure for de-crystallization of uric acid crystals

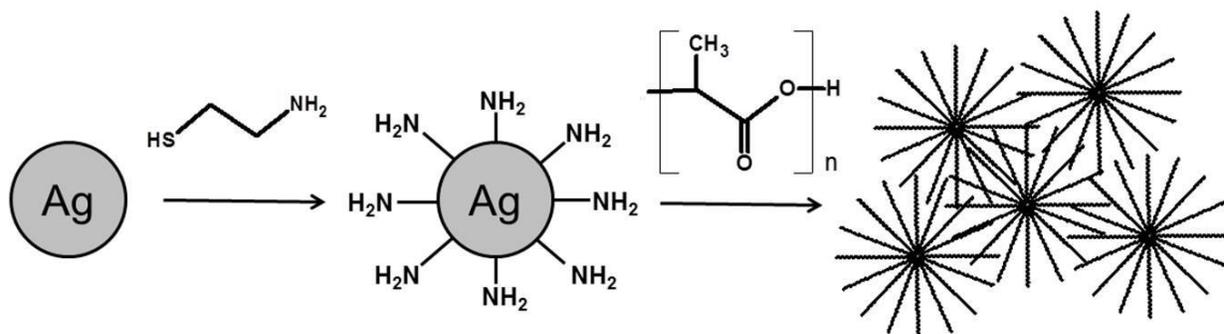
COLL 125

Biodegradable polymer materials containing stabilized silver nanoparticles

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In this work, silver/polymer composite materials containing colloidal nanosilver were obtained and characterized. All materials were prepared using commercially available polymers and nanosilver ($d=100-150$ nm). On the first step, silver nanoparticles (AgNPs) were modified by surface thiolation with 2-aminothiol. Then the surface amino groups reacted with end carboxyl groups of poly(DL-lactide) and poly(DL-lactide-co-glycolide) in the presence of diisopropylcarbodiimide. This method resulted in covalent bonding of the polymer chains to the AgNPs surface. Polymer-coated AgNPs remained finely dispersed and did not agglomerate in the polymer matrix. Chemical and structural characteristics of the obtained materials were studied by instrumental methods. Presence of silver crystals was proved by XRD. The diffraction pattern of Ag[111] at $2\theta=38^\circ$ was broad, which is typical for nanoparticles. Contents of silver in the polymers were 0.10-0.12%. UV-vis spectra of the dispersions of the composites contained

absorption bands of surface plasmon resonance at 472-479 nm. Strong red shift of this band can be explained by the Ag surface modification with polymers. The synthetic method reported in this work might be used in manufacture of optical materials or biodegradable biomaterials.



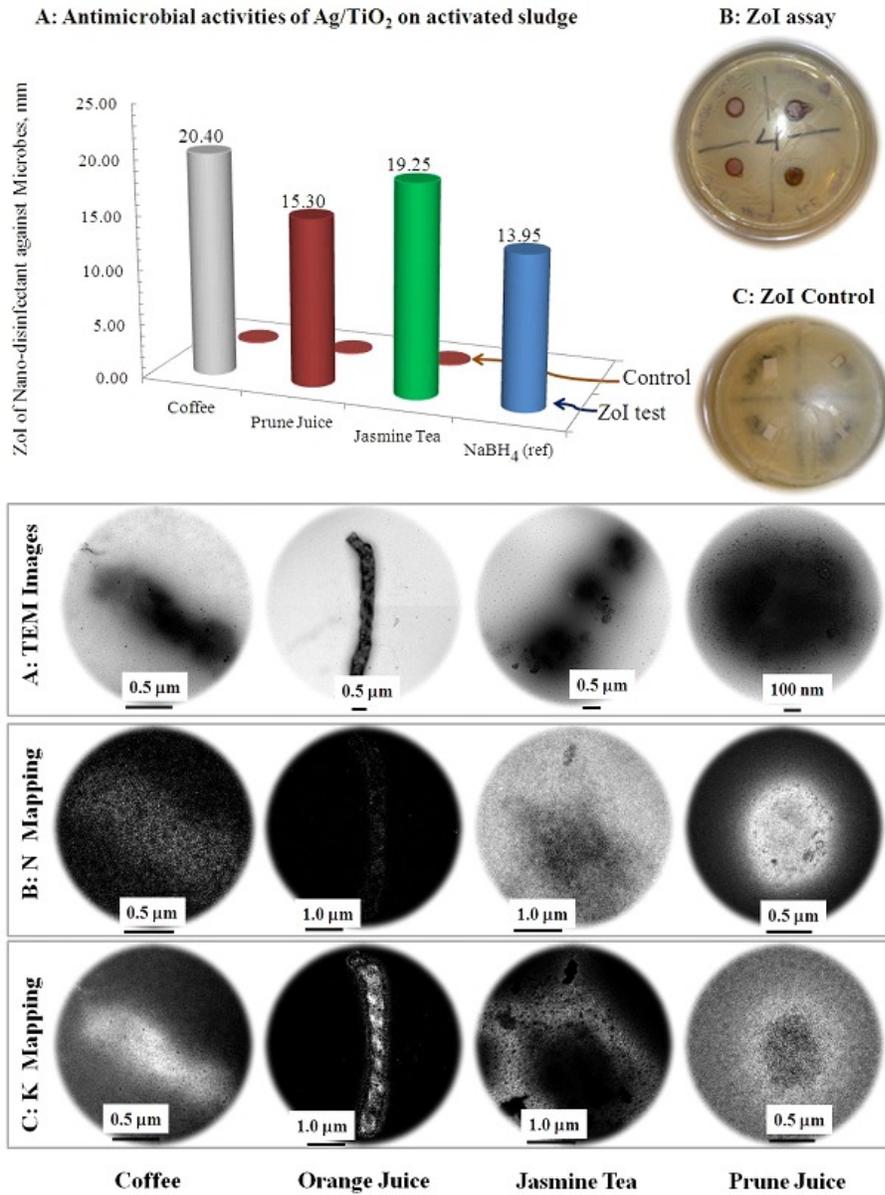
COLL 126

Characterization and bioapplication of nanoscaled materials derived from green chemistry

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Series of nanoparticles (NPs) were derived using green colloidal chemistry. Natural products, such as green tea, coffee and vitamin C were used as both dispersing and reducing agents. The catechin content of the natural extracts was then analyzed by using high performance liquid chromatography to evaluate four major flavanol derivatives. These derivatives were used in production of NPs, such as silver and silver-titanium. These NPs were formed through reduction oxidation (Redox) reaction, followed by the diffusion and aggregation. To determine crystalline phase, morphology and particle size and its distribution, the NPs were characterized using the state-of-the-art methods. It was also found that the NPs as disinfectants exhibited wide-spectra of activity toward Gram-negative/positive bacteria. The potency of bactericidal activities against Gram-negative bacteria was found to be 2.5 ppm within 2 hrs. The microbe cell membranes were damaged upon addition of the NPs. Some cytoplasmic membrane peeling may occur as the incubation time was increased and the leakage of reducing sugars and proteins was determined by EELS. The antioxidant quotient was evaluated by two standard assays, the Trolox equivalent antioxidant capacity (TEAC) and oxygen radical absorbance capacity (ORAC). The antioxidant quotient (promotes cell survival) and ROS (promotes the cell death) have opposite contributions towards inhibition of

microbes. The net contribution towards inactivation is the difference between these two factors.



Zone of inhibition of microbe cells (Top panel) and EELS mapping to determine the elemental leakage (Bottom panel).

COLL 127

How small molecules self-assemble into nanofibers and form hydrogels

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Self-assembly occurs extensively at all length scales, ranging from small molecules, protein filaments, to macroscopic objects. In the recent two decades, particular attentions has been paid to hydrogels, which can be used in a variety of applications ranging from light harvesting, tissue engineering, drug delivery, etc. Although it is known how to form hydrogels via self-assembly, relatively little attention has been paid to the thermodynamic behavior of the assemblies. There is limited information about how small molecules grow into nanofibers and how the nanofibers form a hydrogel. This problem may also be related to the onset of neurodegenerative diseases due to the formation of amyloid plaques. To gain a better understanding of the self-assembly process, we investigate a class of novel self-assembly molecules, which share the same self-assembly motif as the amyloid plaques. We study the temperature dependence of the self-assembly of these hydrogelators using various techniques, such as dynamic light scattering (DLS), NMR, rheology, and small angle neutron scattering (SANS). DLS yields information on the initial stage of fiber formation. SANS is used to determine the organization of the supramolecular assemblies (e.g., mesh size of the network). We believe a better understanding of the physics of self-assembly process may facilitate the design of nanofibers/hydrogels for applications in biology and medicine.

COLL 128

Computational study of hydroxyproline-pectin cross-linkage for drug delivery

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The objective of this research was to better understand the association between hydroxyproline and pectic polysaccharides in order to develop a prospective model for a pectin-based drug delivery system capable of site-specific or extended release drug delivery. Pectic polysaccharides are ubiquitous in nature, present in the cell walls of plants, where they are found in cross-linkages with other macromolecules. Cross-linkages between pectin and hydroxyproline-rich proteins, such as elastin, contribute to the structure, elasticity, and porosity of plant cell walls. Linkages between cell wall polypeptides and polysaccharides have previously been studied and used to develop pharmaceutical coatings that delay or prolong the release of medication. Ionic interactions and hydrogen bonding are known to account for the physical stability of the cross-linkages that exist between cell wall polysaccharides and polypeptides. In this research, atomistic-level computational models were constructed with Spartan to

develop an archetype of the formation of cross-linkages between hydroxyproline residues and polymers of galacturonic acid, the primary constituent of the homogalacturonan family of pectic polysaccharides. Electrostatic potential maps of hydroxyproline residues of various lengths were generated with Density Functional Theory with the EDF2 6-31G* functional in aqueous media using the Spartan computational suite, and were compared to similarly generated electrostatic potential maps of galacturonic acid polymers to determine the most likely sites of interaction between the molecules.

COLL 129

Tmpyp containing nanoparticles with enhanced photo –physical properties

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The design and synthesis of water compatible porphyrin nanoparticles (NPs) with enhanced photo-physical properties is emerging as an important research focus because such NPs find potential application in the biomedical field serving as agents for photo dynamic therapy and biological imaging. Furthermore, they are also intriguing building blocks for nano structured devices such as oxygen sensors and photonic systems. In this poster, we described a strategy to construct photo-active porphyrin spherical NPs composed of a supramolecular complex between tetrakis(4-N-methylpyridyl)porphyrin (TMPYP), cucurbit[7]uril (CB[7]), and poly(propylene glycol) monobutyl ether (PPG). TMPYP is a well-known photosensitizer, however, it typically self-stacks in water via aromatic interactions resulting in attenuated photophysical properties. In marked contrast, these TMPYP containing NPs exhibit attenuated porphyrin stacking and thus show enhanced photo-physical properties (in terms of both absorption and fluorescence). These NPs have been characterized by means of TEM, UV-vis spectroscopy, fluorescence spectroscopy, and singlet oxygen generation studies.

COLL 130

Optical characterization of purified noble metal nanoparticles

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As nanotechnology becomes part of the everyday vernacular, there is a growing need to fully characterize and purify nanomaterials, especially those that will be used in biomedical applications. Noble metal nanoparticles can be synthesized using a variety of methods including reduction by citrate ions or through the use of bacteria. The resulting nanoparticles can be characterized using UV-Vis spectroscopy and analyzed

to determine average particle size as well as size distribution. This work will compare the reproducibility and characterization of noble metal nanoparticles using different synthetic methods and purification techniques.

COLL 131

Green synthesis of magnetic nanocomposites formulated with Indian medicine to perform cancer theranostic study

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A colloidal approach was used to produce magnetic nanocomposites (MNCs) composed of gold (Au) and iron oxides (Fe_3O_4 , **Fig. A**). The as-prepared Au- Fe_3O_4 MNCs exhibited tunable fluorescence, in addition to the MNC being cost-effective to produce, with surface templating flexibility, homogeneity in size and composition at the molecular level. The MNCs were engineered using a three-step procedure: (i) production of ultrafine Au- Fe_3O_4 MNPs with tunable size and architecture; (ii) formulation with traditional Indian medicine (tIm) to form a core-shelled structure (tIm@Au- Fe_3O_4 , **Fig. B**); and (iii) evaluation of MNC-core shell cytotoxicity against Chinese hamster ovarian cancer cell lines. The stoichiometry (initial molar ratio of the Fe^{3+} and Fe^{2+} precursors) was maintained in the final MNCs, demonstrating control of dimension, composition and magnetism. In this present approach, the MNCs incorporated with tIm exhibit biocompatibility and efficacy upon tIm release. In essence, the system exhibits “trojan horse” mode of activation and cell inhibition to enhance their biocompatibility as cancer theranostic agents. Other pharmacologic approaches using antitopoisomerase I inhibitor, such SN-38 can be similarly used to deliver on-target and inhibit cell division upon activation of external magnetic field (**Fig. C**).

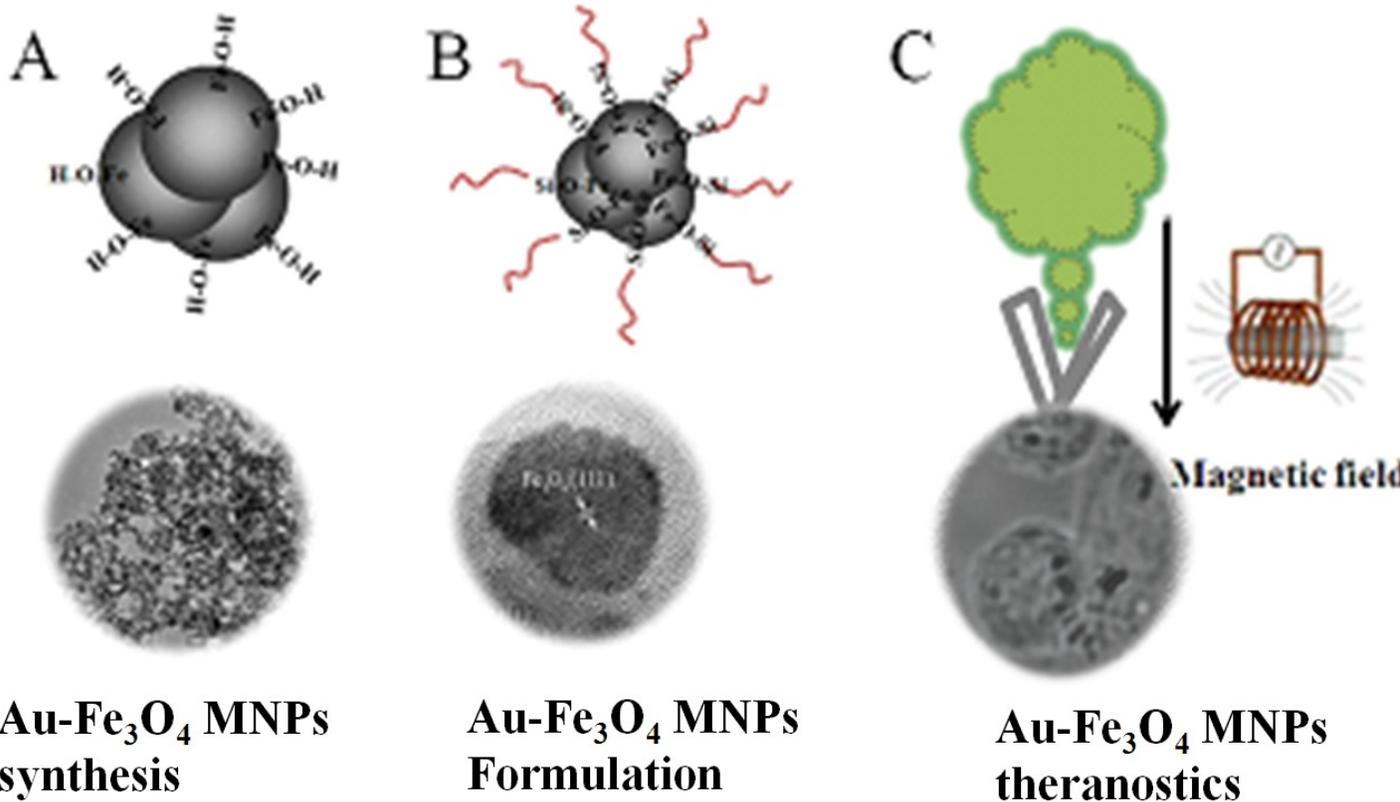


Figure. Magnetic nanocomposite (MNCs, Au-Fe₃O₄) used in cancer theranostic, A: nanosynthesis via a reverse emulsion approach; B: functionalization of MNCs with traditional Indian medicine to adjust the biocompatibility between MNCs and cancer cells; and C: Cancer theranostic analysis of MNCs binding to tumor.

COLL 132

Plasmonic nanocrystal solar cells utilizing strongly confined radiation

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The superior light extinction properties of plasmonic nanostructures make these materials attractive candidates for enhancing the performance of photovoltaic devices. Such enhancement is predicted to be particularly prominent in the case of small-diameter metal nanoparticles, where radiation modes are strongly confined. Unfortunately, the energy of surface plasmon (SP) emission becomes difficult to collect if the nanostructure size falls below 20 nm, as it efficiently couples to lattice phonons, resulting in the generation of heat. Here, we explore the feasibility of converting such

near-field radiation of 5-nm Au nanoparticles through resonant coupling to an array of PbS semiconductor nanocrystals. We demonstrate that the key to an efficient conversion of the SP emission into photovoltaic energy lies in the judiciously designed architecture of nanoparticle solar cells that reduces carrier scattering on Au dopants and simultaneously improves the stability of heat-prone plasmonic films. The contribution of the near-field emission in Au nanoparticles towards the charge carrier generation was manifested through the observation of an enhanced short circuit current and improved power conversion efficiency of prototype (Au, PbS) solar cells, as measured relative to PbS-only devices.

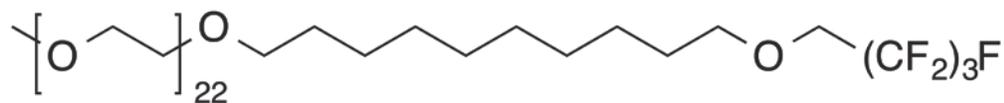
COLL 133

Structure and behavior relationships among semifluorinated linear, dibranched and miktoarm amphiphiles

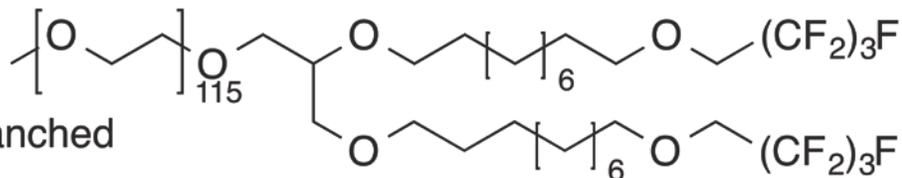
William Tucker¹, *wtucker@chem.wisc.edu*, **Aaron McCoy**¹, **Samantha Fix**³, **Melissa Stagg**¹, **Matthew Murphy**¹, **Sandro Mezzozz**². (1) *University of Wisconsin-Madison, Madison, Wisconsin, United States* (2) *School of Pharmacy, University of Wisconsin-Madison, Madison, Wisconsin, United States* (3) *University of North Carolina - Chapel Hill, Durham, North Carolina, United States*

Semifluorinated functionalities offer new possibilities in the design of self-assembling systems. Linear, dibranched and miktoarm amphiphiles containing hydrophilic, lipophilic and fluorophilic moieties were synthesized and characterized in an attempt to elucidate the relationship between structure and aggregate behavior in aqueous solution. For both linear and dibranched amphiphile architectures there was an exponential decrease in critical aggregation concentration (CMC) and a logarithmic increase in core microviscosity with increasing length of the fluorocarbon segment. For miktoarm amphiphiles, core microviscosity and CMC showed little variance. The linear surfactants showed enhanced kinetic stability, dissociating more slowly in the presence of human serum than did the dibranched amphiphiles or miktoarm amphiphiles. Encapsulation studies with the hydrophobic drug paclitaxel (PTX) showed that the ability to solubilize and retain PTX increased with the presence of and with the increasing size of the fluorocarbon moiety.

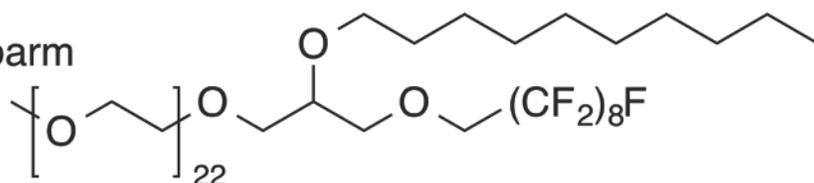
Linear



Dibranched



Miktoarm



Examples of linear, dibranched and miktoarm amphiphiles studied

COLL 134

Effect of pH on the adsorption of cationic polyacrylamide to polyacrylic acid

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Inorganic particles are used as filling materials in papermaking industry. To reduce its specific surface area, papermakers aggregate the particles by using flocculants such as polyacrylamide (PAM) or other polyelectrolytes. Filler particles are generally dispersed with the use of polyacrylic acid (PAA) as a dispersing agent. Therefore, to understand the adsorption behaviors of flocculants to dispersed inorganic filler particles, it is important to examine the interactions of these two polyelectrolytes. We investigated the adsorption of cationic polyacrylamide (C-PAM) to PAA at a pH ranges from 7 to 9. Characteristics of PAM and PAA are altered by pH of the dispersion. We used a particle charge detector (PCD) to measure the charge density of C-PAM. A quartz crystal microbalance with dissipation was employed to evaluate the adsorption characteristics of polyelectrolytes. Results indicated that the charge density of C-PAM decreased at elevated pHs. It was also shown that C-PAM adsorbed on PAA with a loose and bulky structure at a pH 7, while it adsorbed in compressed shape at higher pHs. (This work was supported by the Energy Efficiency & Resources of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Ministry of Trade, Industry & Energy, Republic of Korea.)

COLL 135

Role of alpha-hemolysin's phosphocholine binding pocket and cholesterol in lipid membrane adsorption and nanopore formation

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Lipid binding of alpha-Hemolysin (α HL), a nanopore-forming toxin secreted by the bacterium *Staphylococcus aureus*, has been extensively studied in the context of lysosomes and red blood cells. Evidence from these studies indicates that cholesterol enhances conditions for adsorption, heptamerization, and formation of a functional pore, particularly in the presence of membrane lipids that possess a phosphocholine (PC) headgroup. Crystallographic studies have also delineated a PC binding pocket in the cap of α HL that selectively assists with protein adsorption. We report results from Langmuir monolayer experiments that examine the adsorption and insertion steps of the α HL protein nanopore. Upon association, the protein increases the monolayer surface pressure. A series of α HL point mutants in the PC binding pocket is used to evaluate changes in exclusion pressure as a function of head group composition. Our data also shed light on the nature of the cholesterol enhancement among phosphocholine containing lipids and show surface structure rearrangements that occur upon α HL binding, as revealed by Brewster Angle Microscopy.

COLL 136

Surface equilibrium and kinetic dynamics of alpha hemolysin on red blood cell membranes

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Alpha-hemolysin (α HL), a protein toxin produced by *Staphylococcus aureus*, kills cells and tissues through a multi-step process that involves lipid membrane adsorption, monomer aggregation, and transmembrane pore formation. Although the basic molecular mechanisms of lytic pore assembly and insertion are generally understood, less is known about the toxin surface concentration, exposure time, and the equilibrium partition constant associated with lethality. Our work examines these factors in rabbit erythrocyte (rRBC) membranes. We utilize rRBC lysis assays, cellular fluorescence imaging, and fluorescence correlation spectroscopy to show that: (1) α HL monomer adsorption to rRBC membranes is rapid; (2) the adsorption mechanism has two distinct rates; (3) a minimum of 1000 seconds is required aggregate monomers and begin lysis after exposure; (4) the monomer equilibrium adsorption constant is relatively small; and (5) the saturation surface coverage on rRBC membranes is ~ 100 α HL molecules/ μm^2 .

COLL 137

Morphological and electrochemical characterization of Laponite/polyaniline/graphene and graphene oxide nanocomposite materials

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Graphene intercalation compounds with electroactive polymers such as polyaniline have demonstrated promise in supercapacitor device applications as electrode materials. We are currently investigating the morphological and electrochemical properties of Laponite/polyaniline/graphene and graphene oxide powders and films in order to better understand this complex material system. Crystallinity and morphological studies were carried out using powder X-ray diffraction, scanning electron microscopy, atomic force microscopy, and surface area analysis. Distribution and mixing of materials was further investigated with energy dispersive X-ray maps and optical microscopy. Electrical characterization includes cyclic voltammetry, galvanostatic charge-discharge, and impedance spectroscopy. A deeper understanding of material distribution and interfacial interactions and their effects on the electronic-transport capabilities within the bulk composite will facilitate implementation of these materials into devices.

COLL 138

Morphosynthetic studies of polyaniline/graphene oxide/Laponite nanoscaffolds

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Recent research has revealed that polyaniline-graphene oxide (PAGO) composites with conductive polymer strands located at the surface and between graphene oxide sheets exhibit high capacitance and superior cycling stability for supercapacitor applications. We are currently exploring the effect that specific morphosynthetic conditions (such as time, concentration, temperature, and oxidant) have on PANI morphology, guest-host interactions, and capacitance response. SEM, FTIR, and XRD studies indicated successful syntheses of PAGO composites using vanadium oxide as an oxidant. Infrared spectroscopy studies verified that PANI was in the conductive emeraldine salt form and confirmed strong interactions between PANI and GO heterointerfaces. Morphological studies of PAGO composites indicated that we can control PANI coverage on GO surfaces through both time and initial aniline concentration. Laponite nanoparticles were also employed as structure-directing agents within these PAGO composites to improve colloidal dispersion, water processibility, and film formation. These morphosynthetic studies offer important insight to optimize supercapacitor performance.

COLL 139

Study of selective heavy metal removal from seawater

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The global distribution and impact of heavy metals on marine organisms and human health are of great concern due to their persistent, non-biodegradable and toxic nature. Many of the heavy metals found in coastal water and harbours near populated urban areas are strongly associated with anthropogenic activities. Their ecological impacts on marine environment are well documented and their tendency to bio-accumulate in the food chain poses a real health threat to the population. Long-term consumption of heavy metal tainted foods is known to cause neurological disorder, organ damages and even increased cancer risk. Large scale district cooling projects utilizing seawater is expected to increase heavy metal release (i.e., copper and chromium) into coastal water. A new salt-tolerant, fouling-resistant adsorbents based on mesoporous silica were successfully designed to selectively remove a target pollutant or class of pollutants from contaminated water. Two particular adsorbents were capable respectively of removing ninety percent of copper and chromium ions from seawater in the presence of other contaminating metal ions (i.e., Ni²⁺, Zn²⁺, Cl⁻, SO₄²⁻). The adsorbent can be regenerated by a simple acid wash and the recovered metal ions are of sufficient purity (> 80%) to allow for recovery and reuse.

COLL 140

Interaction of ligand-capped metal nanoparticles with t2D atomic layered nanomaterials

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Two dimensional (2D) atomic layered nanomaterials exhibit some of the most striking phenomena in modern materials research and hold promise for a wide range of applications including energy and device technology. More recently, graphene oxide-metal nanoparticle hybrid materials have been of increasing interest due to their potential applications in biological and environmental industries. Our research specifically targets the preparation of metal nanoparticle catalysts supported on 2D nanomaterials, including graphene oxide and bismuth selenide nanosheets, using the strategy of pre-formed nanoparticle self-assembly. This strategy is especially useful for fine tuning the size and monodispersity of metal nanoparticles that have a direct influence over the catalytic activity of the hybrid materials. Ultimately, the use of aforementioned 2D supports, having extremely high surface area to volume ratio, excellent electric conductivity, and unique characteristics of enhancing mass transport of reactants to catalysts, would maximize the activity of surface-assembled metal

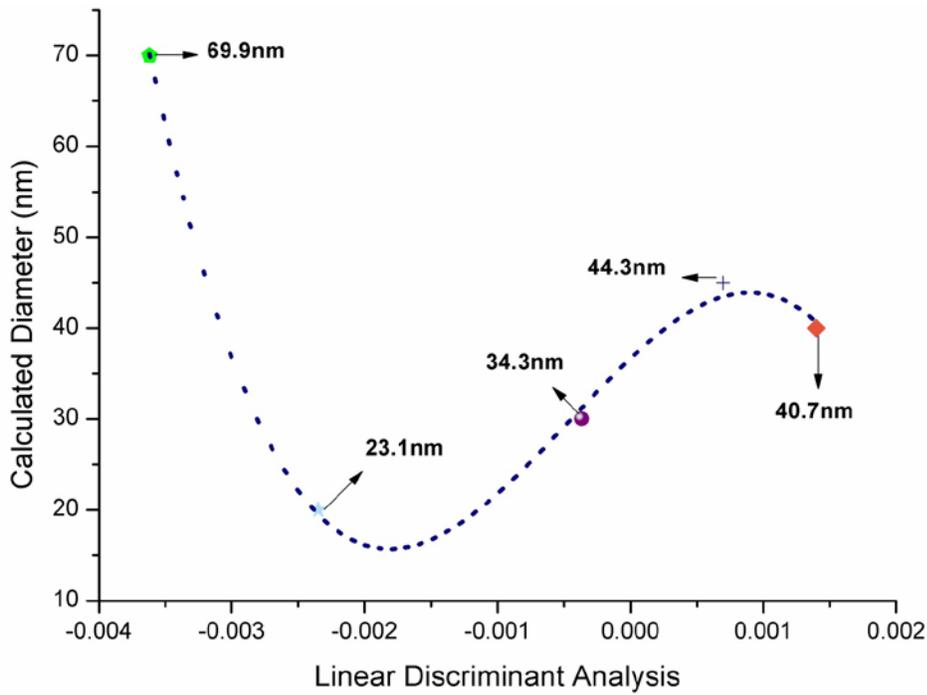
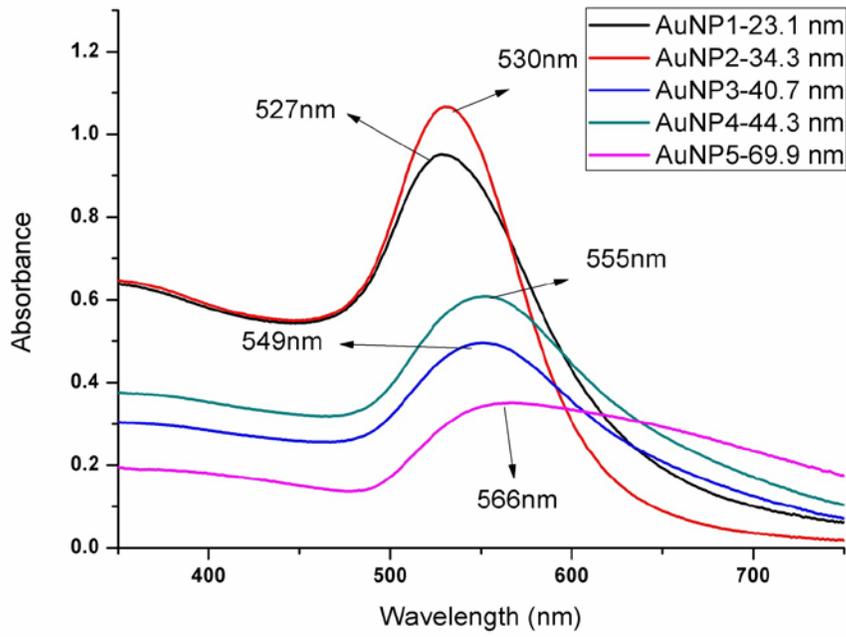
nanoparticle catalysts. As an initial step, the current research aims at understanding the interaction between ligand-capped gold and palladium nanoparticles on graphene oxide nanosheets. For this task, hydrophobic and hydrophilic ligand-capped nanoparticles with different core sizes are synthesized and mixed with graphene oxide. By varying the functional groups on the ligands between alkyl, aromatic, amine and/or alcohol groups, we are able to induce different interactions such as Van der Waals, π - π stacking, dipole-dipole, and hydrogen bonding. The solvent and concentration effects on the interactions between the nanoparticles and graphene oxide were also tested. The adsorption of metal nanoparticles onto the surface of graphene oxide was monitored using UV-vis spectroscopy and transmission electron microscopy (TEM). Once the metal nanoparticles are anchored onto graphene oxide, the surface ligands are partially removed by annealing the nanoparticles at higher temperature, which enable the nanoparticles to act as supported catalysts. For understanding the catalytic behaviors of the produced 2D supported metal nanoparticles, model organic reactions such as oxidation of benzylic alcohols and hydrogenation of alkynes are investigated.

COLL 141

Gold nanoparticles size characterization using PCA and LDA techniques by UV-Vis spectroscopy

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The particle size plays a critical role in nanoparticle properties and therefore property characterization of related nanoparticles is an essential task in particle sizing. Herein, the hydrodynamic diameters of different gold nanoparticle were measured by using dynamic light scattering (DLS) spectroscopy and these experimentally measured diameters were compared with the theoretically found ones by using principal component (PCA) and linear discriminant analysis (LDA) methods. These two methods were compared with regard to determination of the clusters of the similar sized nanoparticles by using UV-Vis spectra in the region of 350-750 nm obtained from UV-Vis spectrophotometer. Surface plasmon resonance peaks and diameters of different nanoparticles are expressed as polynomial functions of weights of dominant eigenvectors. When the results of the two techniques are compared, LDA technique clearly discriminates the nanoparticles from each other, and approximates the diameter and resonance peak of a nanoparticle much better than PCA technique.



Dynamic observation of NIH3T3 cells adhesion behaviors on binary self-assembled monolayers modified gold surfaces

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Cell adhesion is crucial to cell behaviors including survival, growth and differentiation. In recent years, quartz crystal microbalance with dissipation detection (QCM-D) was used to study cell-surface interactions during cell adhesion process owing to its advantage on obtaining real-time viscoelastic changes. Combined with optical microscope (OM) observation, cell morphology and corresponding viscoelastic changes can be obtained concurrently. Self-assembled monolayers (SAMs) are known for their convenience and versatile to modify the surface. A series of zeta potential can be obtained by introducing mixed functional groups of amine and carboxylic acid to the substrate. On this serial surface, the adhesion rate of NIH3T3 was found to be significantly affected by the zeta potential. In this work, the effect of zeta potential to the adhesion process of NIH3T3 and its surface-cell interaction were monitored with a combined system of OM and QCM-D. NIH3T3 cells were seeded and cultured on the SAM-modified gold-coating quartz crystal in the QCM-D window chamber for in situ OM observation at 37°C. Time-lapsed images were obtained by OM for observing the changes in cell morphology and mobility. In addition, after 4h in situ examination of cell attachment, cells were fixed and then dehydrated for scanning electric microscope (SEM) investigation in low vacuum mode to examine their finer feature. The QCM-D results show that with increasing negative charge on the surfaces, the cell attachment process induces less frequency and dissipation shifts indicating less cell-substrate interaction. Moreover, the in situ OM observation shows that mobility was increasing as the surface potential reduced. On the other hand, more-stretched cell morphologies were observed with stronger positive surface potential indicating stronger cell-substrate interaction.

COLL 143

Ag nanoparticle nucleation vs. shell growth

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Au nanoparticles are inorganic nanoparticles that have very unique properties, which give them a wide variety of applications such as bio-labels, diode lasers, and solar cells to name a few. The field of nanoparticle research has seen dramatic growth in recent years. Several theories have been proposed and some widely accepted about nucleation and growth of nanoparticles but it has yet to be confirmed experimentally if nanoparticles form by the nucleation theory. According to the theory it takes less energy to start forming a shell around existing nanoparticle rather than form a new core. In this project a Ag shell was grown at a slow rate around Au nanoparticles. Ag was chosen to

grow around the Au nanoparticles because they have nearly identical lattice structures. Due to their similar lattice structures it takes very little energy for the Ag to form a shell around the Au nanoparticle. The amount of energy it takes for Ag nanoparticles to nucleate as opposed to growing a shell was determined by monitoring plasmon absorption of Au cores, Au/Ag core/shell composites, and forming isolated Ag particles. The results of the experiments showed that shell growth does require lower amounts of heat and time of exposure than that of nucleation of new cores. This provides first experimental evidence that Ag nanoparticles form according to the classic theory of nucleation.

COLL 144

Improving the catalytic activity of metal semiconductor nanocomposites

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As time continues, the need for alternative energy sources continues to grow. Hydrogen has a great potential to be the next generation fuel. Using a previously published system for Hydrogen production through catalytic water splitting as a basis, a nanocrystal composite was designed with a gold core and semiconductor shell to absorb visible light, which would allow the transfer of electrons to occur from the gold to the shell thus creating special charge separation. Significant charge separation within the nanocrystal must be maintained to have efficient catalysis. Au/CdS/CdSe nanocrystals were made and tested with methyl viologen, a model system that would show us there was a successful energy transfer when exposed to visible light. The purpose of this research was to improve the catalytic activity of metal semiconductor nanocomposites in order to produce renewable clean energy in the form of Hydrogen gas.

COLL 145

Preparation of highly efficient Winsor-IV type microemulsions for rapid wood penetration

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Winsor-IV type microemulsions possess a highly efficient ability for rapid wetting/penetrating lignocellulosic biomass based on their ultralow surface tension and kinematic viscosity. In the present study, a cost-competitive surfactant-oil-water (SOW) system, namely sodium dodecyl sulfate (SDS)/pentanol/water/sodium

chloride/dodecane system was selected and reasonable formulations for Winsor-IV type microemulsions under fixed surfactant concentration were acquired by applying a novel and efficient titration method. Compared with the traditional phase behavior scanning method, this method was designed by optimizing the ratio between the quantity of surfactant and co-surfactant. Later, prepared microemulsions with relatively low surface tensions or kinematic viscosities were screened out for comparison of their respective abilities in wood penetration and also for investigation of the synergistic effects between surface tension and kinematic viscosity.

COLL 146

Variations in intermolecular interactions in the microtubule associated protein tau revealed by atomic force microscopy

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Tau is a neuronal microtubule associated protein (MAP) with several well-established functions, which include promoting microtubule polymerization and stabilizing them against depolymerization, and controlling the spacing between microtubules in axons. In addition, tau has been linked to a variety of neurodegenerative disorders with pathologies characterized by aberrant aggregation of the protein, so an understanding of the nature of intermolecular interactions between tau and the biochemical changes that lead to aggregation is of particular importance. In the present work, atomic force microscopy was used to investigate interactions between layers of tau protein immobilized on silicon nitride AFM tips and flat mica substrates through force-distance curves. In their ability to bind tau, silicon nitride and mica substrates are thought to mimic microtubules, enabling the study of tau-tau interactions in biologically relevant conformations. When collected in low ionic strength conditions, force-distance curves show that tau layers on these surfaces produce long range repulsive interactions characteristic of polymer brush-like layers, while also experiencing intermolecular attraction at specific tip-surface distances. When the ionic strength of the aqueous environment is increased, there is an overall decrease in the measured tau interactions, demonstrating that the effect is primarily electrostatic in nature. These results suggest that a previously-reported 'electrostatic zipper' model of tau interactions is strongly dependent on the initial experimental conditions. Finally, a series of truncated tau constructs were examined to determine which regions of the protein participate in long-range repulsive and shorter-range attractive protein-protein interactions. The force-distance curves collected on these samples suggest that acidic regions in both the N- and C-terminals of the protein contribute to intermolecular attraction. These results are significant because they contribute to an understanding of tau's function when bound to microtubules and point to putative mechanisms for tau aggregation in vivo.

COLL 147

First principles characterization of nontronite clay surfaces with varying Fe(II)/Fe(III) composition

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Naturally occurring surfaces that exhibit structural iron in different oxidation states are known to be capable of heterogeneous reduction/oxidation (redox) reactions, and this reactivity influences the transport and fate of redox active aqueous contaminants. To date, little molecular-level understanding of this class of geochemical reactivity is available. The main objective of the current study is to obtain structural, electronic and thermodynamic characterization of the oxidized and reduced iron-bearing clay surfaces. We are particularly interested the edge-surface (110) of NAu-1. Several ratios of Fe(II)/Fe(III) in the structure of NAu-1 are studied in the realm of density functional theory (DFT) and employing a Hubbard U term to treat the strongly correlated Fe d states. In the style of Reuter *et al.*, the DFT results are used in a thermodynamics framework to calculate surface free energies across ambient temperature and pressure conditions.

COLL 148

Effect of solvent on the growth of isotropic/anisotropic core/shell nanoparticles via alternating layer techniques

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Colloidal semiconductor core/shell nanoparticles are of interest because their high photoluminescence quantum yields (QY), size-tunable emission and high photostability. The formation of isotropic/anisotropic shells is important in maintaining and augmenting such exceptional spectroscopic properties. In this work, the influence of different mixtures of solvents (such as amines), are studied as to increase the synthetic yield of the shell for core/shell nanoparticles when using selective ionic layer adsorption and reaction (SILAR) based techniques for shell growth. Conversion of shell precursors to surface-adsorbed equivalents should be maximized for effective control of shell growth. Here, UV-vis and photoluminescence spectroscopy are applied to monitor shell growth. Additionally, during the shell growth, the free precursor concentration is measured by Inductively Coupled Plasma Mass Spectrometry (ICP-MS), and fitted with Langmuir isotherm model which reveals the influence of different solvents on the fractional occupation of shell precursor equivalents on the QD surface. The binding affinities of the solvent molecules to the QD surface are also studied to understand the influence of such interactions on shell growth. This study is important for understanding

the mechanism of growing the core-shell nanoparticles via SILAR technique and further could be applied to synthesize isotropic/anisotropic core/shell nanoparticles in an advanced and controllable manner.

COLL 149

Nanoparticle mediated remote activation of thermophilic enzymes with alternating magnetic fields

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Noninvasive, remote, control over biological processes is an exciting field. This can be accomplished by using nanoparticles as radiofrequency antennas to absorb energy and selectively heat local areas to initiate biological processes. In this work, gold coated magnetite particles were conjugated to thermolysin, a metalloprotease that can withstand high temperatures. The conjugates, mixed with a protein substrate, were exposed to alternating magnetic fields in a solenoid while monitoring the temperature for bulk heating. Remote digestion of the protein substrate was compared to bulk heated samples to determine if the enzymes were locally heated.

COLL 150

Template synthesis of gold nanoparticles using an organic molecular cage

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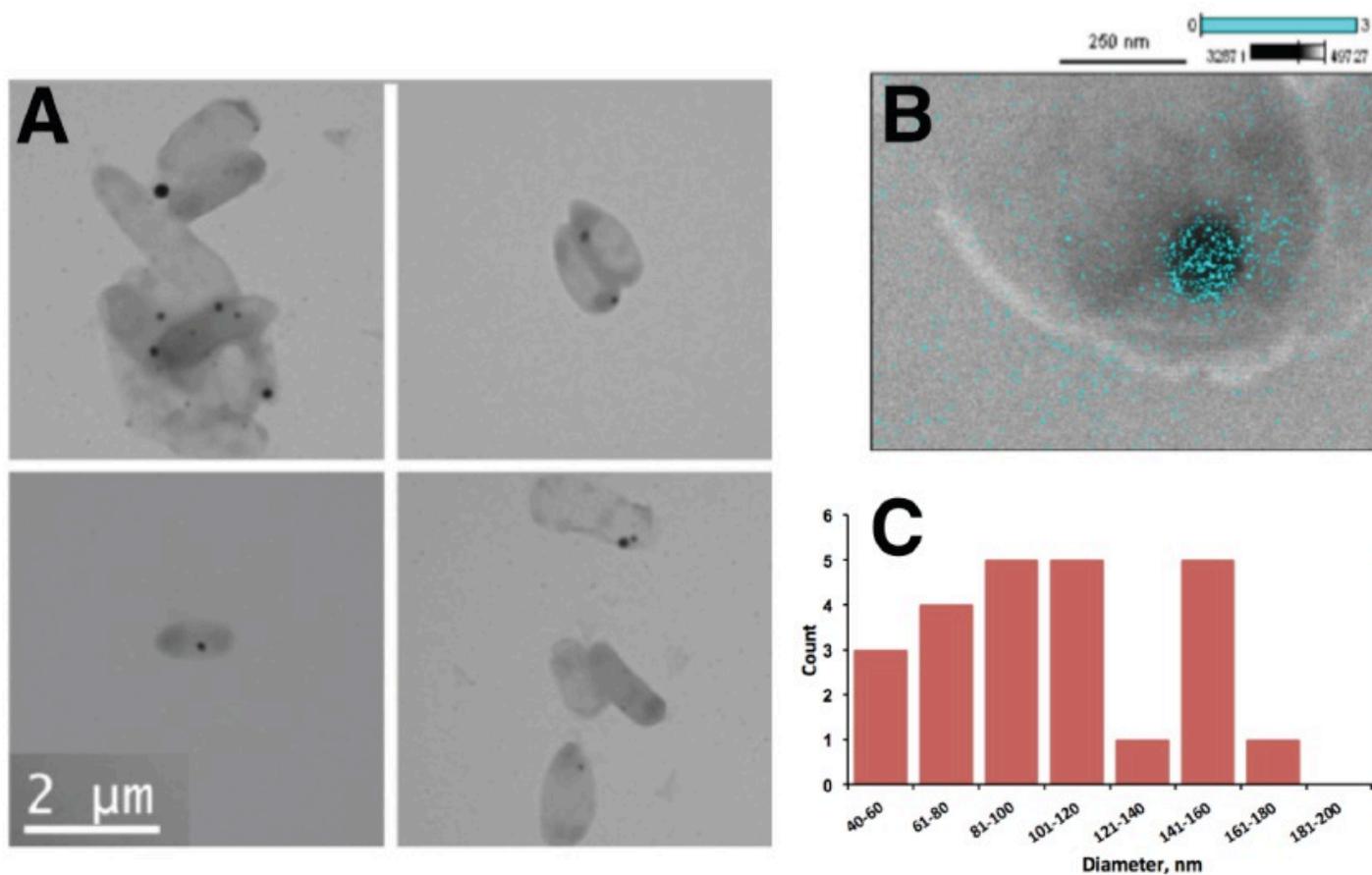
The size-dependent optical and electronic properties of gold nanoparticles (AuNPs) have long been of interest in the context of nanoscience and nanotechnology. Often, control over NP size, shape, and distribution has advanced through the use of small organic ligands, dendritic architectures, or polymers as templates or stabilizers. In this work, we will describe a recent development utilizing a novel “cage-template” approach for the synthesis of monodisperse nanoparticles within a well-defined cage molecule with a spatially confined cavity. The resulting cage-encapsulated AuNPs are shown to be very stable and have excellent solubility in a wide range of organic solvents, providing the potential for further assembly study and catalysis applications.

COLL 151

Progress toward clonable inorganic nanoparticles

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Green fluorescent protein revolutionized cellular optical microscopy by enabling clonable fluorescent contrast. Cellular electron microscopy lacks a similar clonable contrast tool. Naturally occurring cellular mechanisms for processing inorganic ions into nanoparticles represent a potential source of clonable nanoparticles. Herein we characterize the selenium (Se) and tellurium (Te) nanoparticles produced by a bacterium that tolerates ordinarily toxic concentrations of Se. The bacterium was recently isolated from roots of an Se hyperaccumulator plant *Stanleya pinnata*. Structure and cellular ultrastructure determined by electron tomography shows the nanoparticles as intracellular, of narrow dispersity, symmetrically irregular and without any observable membrane or structured protein shell. Protein mass spectrometry of fractionated soluble cytosolic material with selenite reducing capability identified nitrite reductase and glutathione reductase or close homologues as NADPH dependent candidate enzymes for the reduction of selenite to zerovalent Se nanoparticles. *In vitro* enzymology with commercially sourced glutathione reductase revealed that the enzyme catalyzes NADPH dependent reduction of selenite to zerovalent selenium nanoparticles. The disappearance of the enzyme as determined by protein assay during nanoparticle formation suggests that glutathione reductase is entombed in the nanoparticles whose formation it catalyzes. By lowering the concentration of NADPH, the size of the Se nanoparticles may also be controlled. In aggregate, we suggest that enzymes like the ones producing the Se nanoparticles identified here possess many of the attributes desired of a clonable nanoparticle system, such as precursor reduction, nanoparticle retention and size control of the nanoparticle at the enzyme site. Most notably, the particles appear to be naked and exposed to cytosol.



COLL 152

Role of surface groups in cycloaddition reactions over ZIF-8 films

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Zeolitic Imidazolate Frameworks (ZIFs) have gained notoriety of late for catalytic activity in reactions such as cycloadditions, transesterifications, Knoevenagel reactions, and Friedel Crafts acylations. However, the exact role of Lewis acidic and basic surface groups in these reactions remains unclear. In this study, direct characterization of surface groups of ZIF-8 was employed during the adsorption and reaction of gases involved in the above reactions with a specific emphasis on the cycloaddition of epichlorohydrin and CO_2 . Using a combination of X-ray photoelectric spectroscopy (XPS) and temperature programmed reaction spectroscopy (TPRS), the role of outer surface groups of ZIF-8 was compared to that of inner pore sites. ZIF-8 nanoparticle films were mounted in a UHV chamber in these studies to facilitate the study of surface

group interactions. An understanding of the role of the surface groups in catalysis is important in developing ZIFs as more effective and efficient catalysts.

COLL 153

Adsorption and interaction of alcohols with ZIF-8 films and the role of surface groups

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Zeolitic imidazolate frameworks (ZIFs) have emerged as an excellent class of porous materials with the potential for numerous applications in energy-related gas storage, biofuel catalysis, and sensor development. Much of the work to this point has focused on the synthesis and investigation of the bulk properties of microcrystalline ZIFs. In this study, we focus on the role of surface groups in the adsorption of alcohols, specifically methanol and butanol, by nanoporous ZIF-8 thin films. X-ray photoelectron spectroscopy (XPS) was employed to determine the identity of the surface-terminating groups upon alcohol adsorption. In parallel, we investigated the adsorption of alcohols of various sizes (methanol and butanol) by ZIF-8 films using temperature programmed desorption studies (TPD). Under low-temperature and low-pressure conditions, we measured the uptake of methanol and butanol by the film, and compared native uptake to that of amorphized ZIF-8 films in order to discern specific adsorption sites at inner pore sites from adsorption at outer surface groups. We also examined the binding of water for comparison. An investigation of the interplay of bulk and surface adsorption will help shed light on future work on the storage and use of alcohols.

COLL 154

Rational design and control of functional molecules on single metal nanoparticles

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Through synergizing the responsiveness of functional molecules to external excitations and the nanoscale modulation of light via surface plasmons on metal nanoparticles, hybrid molecule-nanoparticle systems can function as smart nanomaterials for a wide range of applications such as biochemical detection, drug delivery, and energy conversion. However, accomplishment of this synergy still relies on the improved understanding of molecule-nanoparticle interactions and capability of controlling functional molecules on metal nanoparticles. Herein, using photoswitchable azobenzene (AZO) as model molecules, we report our recent advances in designing, measuring and controlling single molecules or precise molecular assemblies on single

metal nanoparticles. Specifically, we have extended the directed and self-assembly strategies that we learned from the studies of molecules on atomically flat Au thin films to Au nanoparticles. Advanced characterization tools that integrate scanning tunneling microscopy and plasmon-enhanced optical spectroscopy have been employed to measure the structures, dynamics, and functions of AZO as single molecules or precise molecular assemblies on single Au nanoparticles. The photoswitchable molecule-nanoparticle interactions and their effects on the optical properties of the hybrid molecule-nanoparticle systems are also investigated. The experimental data coincide with theoretical calculations. Our single-molecule and single-nanoparticle studies help eliminate the inevitable heterogeneity from ensemble measurements and provide a new insight into the structure-property relations of hybrid molecule-nanoparticle systems.

COLL 155

Nanoporous hydrogen-reduced bismuth vanadate coupled with electrocatalysts as high-performance photoanodes for solar fuels

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We have developed the nanoporous hydrogen-reduced bismuth vanadate (H-BiVO_{4-x}) thin films coupled with Ni-B_i electrocatalysts as photoanodes for photoelectrochemical (PEC) water splitting. The photoanodes yield a large (~300 mV) cathodic shift in the onset potential for sustained PEC water oxidation at pH 7 with the kinetics equivalent to that for the sulfite oxidation. Moreover, the photoanodes exhibit high performance even in the low-bias regime (i.e., < 0.8 V vs RHE) and achieve the maximum power point for solar water oxidation at potential as low as 0.75 V vs. RHE with a photocurrent density of 2.25 mA/cm². Based on systematic experiments and calculations, we attribute these improved PEC performances to the enhanced charge separation, carrier density and conductivity in the photoanodes.

COLL 156

Ultrafast and temperature-dependent optical properties of Au₆₇, Au₁₀₂ and Au₁₄₄ clusters

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Optical properties of atomically mono-dispersed gold clusters have received vast research attention in recent years as they show properties of a transition region in metal and molecule. To understand the influence of cluster's structure and symmetry on the optical properties, temperature-dependent absorption and ultrafast luminescence dynamics of hexane thiol protected Au₆₇, Au₁₀₂ were studied and compared with Au₁₄₄. Interesting absorption spectral features were observed with decreasing temperature. These changes in the absorption spectra were modeled with electron-phonon and exciton-phonon interactions and they found to differ significantly from one cluster to another. Earlier we studied smaller clusters such as Au₂₅ (sphere and bi-icosahedral) and Au₃₈, and in this study we focused on bigger clusters such as Au₆₇, Au₁₀₂ and Au₁₄₄. In low symmetry clusters, optical information is not rich even at low temperatures due to overlapping transitions as in the case of Au₆₇ and Au₁₀₂ clusters. However, in higher symmetry cluster like Au₁₄₄ optical information is rich at low temperatures with discrete electronic states. In principle, optical information should diminish with cluster size. But, we observed a different scenario that we can assign to the symmetry of cluster. In addition, the oscillator strength of transitions has increased with decrease in temperature that was modeled with electron-phonon interactions. Also for Au₁₄₄ cluster staple motifs that protect are quite similar, making the strength of electron phonon larger than Au₆₇ and Au₁₀₂. Ultrafast luminescence measurements have shown fast relaxation from core-gold to shell-gold.

COLL 157

Fabrication of inverse opal films with stop bands in the full spectral range of visible light using co-assembly technique

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Periodic microstructures are important in terms of photonic applications, which involve reflection of specific wavelengths of visible light. Self-assembly is a simple technique and a good alternative to complex and expensive lithographic methods used in the production of photonic materials. Co-assembly is a newly introduced technique that involves the simultaneous assembly of the colloids and the filling of the interstitial sites by a sol-gel precursor (such as tetraethyl orthosilicate). The self "healing" ability of this technique allows for the fabrication of defect free inverse opal structures. We have successfully used co-assembly to fabricate inverse opal structures with voids of different sizes ranging from 283.5 nm to 430.7 nm. This was accomplished by tuning the size of the poly(methyl methacrylate) (PMMA) colloids using emulsion polymerization. Co-assembly, of the PMMA colloids with the tetraethyl orthosilicate allowed for the fine-tuning of the stop band of the inverse opal structures in the spectral range from 400 nm to 900 nm.

COLL 158

Electric-field assembly and propulsion of chiral colloidal clusters

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Chiral molecules with opposite handedness exhibit distinct physical, chemical, and biological properties. They pose significant challenges as well as opportunities in understanding the phase behavior of soft condensed matter, designing enantioselective catalysts, and manufacturing single-handed pharmaceuticals. Microscopic particles, arranged in a chiral configuration, could also exhibit unusual optical, electric, and magnetic responses that are essential to build metamaterials with exotic properties. Here we report a surprisingly simple method to assemble achiral building blocks, the asymmetric colloidal dimers, into a family of chiral clusters. Under a perpendicularly applied AC electric field, two to four lying dimers associate closely with a central standing dimer and form both right- and left-handed clusters on a conducting substrate. Although the assembly is initiated by an electrohydrodynamic flow, the final configuration of the cluster is primarily determined by the dipolar interactions between constituent dimers. Our theoretical model accounting for interactions between induced dipoles reveals that in-plane dipolar repulsions between petals favor the achiral configuration, while out-of-plane attractions between the central dimer and surrounding petals favor a chiral arrangement. It is the competition between these two interactions that dictates the final configuration. The theoretical chirality phase diagram vs dimer bond length and lobe diameter ratio is found to be in excellent agreement with experimental observations. We further demonstrate that the broken symmetry induces an unbalanced electrohydrodynamic flow surrounding the chiral clusters. As a result, they behave like micro-propellers and rotate in opposite directions according to their handedness. The assembly mechanism reported here could be applied to other types of asymmetric particles under electric fields. Such chiral colloids could be used for fabricating metamaterials, model systems for chiral molecules and active matter, and propellers for microscale transport.

COLL 159

Effect of surfactants on cyclopentane hydrates: Structure and properties

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Clathrate hydrates are crystalline inclusion compounds in which water molecules form hydrogen-bonded water cages that can trap small guest molecules. The crystal growth rate and mechanical properties of clathrate hydrates can be affected by the presence of surfactants. For this study, a Micromechanical Force apparatus was used to measure several clathrate hydrate properties, including the crystal growth rate, the strength of the hydrate shell, and the cohesion force between two hydrate particles, both with and without surfactants present. Interfacial tension measurements were also performed to

compare the surface activity of the surfactants at various concentrations. Understanding these changes is integral to the development of a more accurate model for hydrate formation and aggregation in production conditions, where there may be natural surfactants present in addition to chemicals added to prevent corrosion, scale, waxes or hydrates. Two surfactants were used in this study, an anionic and a cationic surfactant, Dodecyl Benzene Sulfonic Acid (DDBSA) and Polysorbate 80, respectively. It was found that the strength of the hydrate shell decreased significantly with the addition of both surfactants, and that the concentration did not have a large effect. Both of the surfactants also decreased the cohesion force below the value for pure hydrates, and the magnitude of this effect was concentration-dependent. The growth rate of the hydrates was also found to decrease with the addition of surfactants.

COLL 160

Properties of Fe₃O₄@chitosan nanoparticles at oil/water interfaces

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The self-assembly of nanoparticles at interfaces is a promising strategy for the synthesis of new materials. Here, an oil/water interface is stabilized using superparamagnetic Fe₃O₄@Chitosan nanocomposites. The effects of particle concentration, oil/water volume ratio, pH, and oil polarity on the stability and morphology of the resulting emulsion are studied. It is found that exceptionally stable Pickering emulsions are formed in non-polar hexane whereas unstable emulsions are found in polar hexanol. These results are interpreted in terms of the three-phase contact angle of the Fe₃O₄@Chitosan nanocomposites at the oil/water interface. Because the stabilization of emulsions using two or more different nanoparticles is relatively underexplored, a citrate-stabilized Au nanoparticle hydrosol was added to the Fe₃O₄@Chitosan suspension. Emulsions of hexane and hexanol are stabilized with both Fe₃O₄-Chitosan nanocomposites and citrate-stabilized Au nanoparticles. Preliminary results indicate that unstable Pickering hybrid emulsions can be used to create thin films composed of both Au and Fe₃O₄ nanoparticles with unique optical and magnetic properties. Film morphology is analyzed using transmission electron microscopy and atomic force microscopy. Optical properties are characterized using UV/Vis spectrophotometry. The film's magnetic susceptibility and electrical conductivity are measured over a range of temperatures. This work highlights the capacity of the oil/water interface as a promising technique for the efficient self-assembly of nanomaterials with novel properties.

COLL 161

Unique photoisomerization behavior of a dicationic azobenzene derivative on a clay nano-sheet

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A dicationic azobenzene derivative (4,4'-Bis(*N,N,N*-trimethylammonium)azobenzene, Azo^{2+}) was synthesized to develop novel reaction induced by a strong host-guest interaction between cationic molecules and anionic clay. The distance between two cations at both ends of the *trans* Azo^{2+} isomer was designed to be equal to the average distance between anionic sites on a clay (Saponite) surface. Remarkable changes on the photoisomerization behavior were observed against the water solution when the Azo^{2+} adsorbed on the clay. A quantum yield of the *trans*→*cis* photoisomerization decreased exceedingly to one-tenth, while one of the *cis*→*trans* photoisomerization increased about 10%~20%. We suggest that an electrostatic attraction between the cation in the Azo^{2+} and the clay anion hindered *trans*→*cis* transformation like as a “pinning”, and this force accelerated the *cis*→*trans* transformation. This novel reaction on the clay successfully generated almost all (~100%) of the *trans* isomer by a visible light irradiation.

COLL 162

Elucidating reaction pathways for thermoelectric materials fabricated by bottom-up solution-phase solid-state synthesis

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Fabrication of technologically-relevant compounds via a modified polyol process has been investigated because this bottom-up approach has a propensity for tailoring nanoscale features and has potential to reduce manufacturing costs. This research has investigated reaction pathways for the formation of Bi_2Te_3 and PbTe compounds fabricated by this solution-phase solid-state synthesis. These thermoelectric materials have excellent alternative energy potential, most notably for the conversion of waste heat into usable electricity. The synthetic method studied here uses sodium borohydride to reduce starting materials from metal ions to atoms while mixing them together in a high boiling point polyol solvent (tetraethylene glycol) to form intermetallic nanoparticles. The thermoelectric nanoparticles were characterized by powder x-ray diffractometry, scanning electron microscopy and energy dispersive x-ray spectroscopy. By synthesizing a range of samples as a function of temperature and time, the growth mechanisms for PbTe and Bi_2Te_3 were determined elucidating changes in crystal structure, morphology, and elemental composition. These growth mechanisms were then compared to investigate which stages were unique to the compound being generated and which were common to the synthetic method. Findings showed the formation of intermediate stages and revealed the importance of other variables, such as reduction rate, conjugate anion of the starting reagent, and the reaction atmosphere. Results highlighting these effects will be presented. Specifically, the formation of a PbTeO_3 intermediate was isolated and its formation is dependent on the presence of

oxygen in the conjugate anion of the metal salt. Also, the reduction rate of the tellurium starting material could be controlled eliminating the intermediate tellurium nanowires observed during the formation of the bismuth telluride. These types of experimental investigations of wet-chemical methods to produce materials with energy-related applications are fundamental to determine the feasibility of this approach to fabricate nanomaterials with reduced production costs and improved energy transport properties.

COLL 163

New approach for scientific research on RO membrane

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Reverse osmosis (RO) membranes are regarded as the most powerful tools to solve global water problems, since they make it possible to supply high-grade water with low cost and low energy consumption. RO membrane technologies have made great progress in last 50 years. However, still more improvement of membrane performance is required to achieve lower energy consumption and higher water quality in seawater and brackish water desalination field.

Fundamental and scientific researches for RO membranes on investigating physical and morphological properties to obtain further excellent performance have been executed. In our past work, pore size analyses by positron annihilation lifetime spectroscopy (PALS) study showed that there is the correlation between the pore size and the solute removal performance. Analyses by solid state nuclear magnetic resonance (NMR) provided much information on chemical structure and precise water content of polyamide layer of RO membranes, and molecular dynamics (MD) simulation based on the NMR data resulted in good agreement with pore size measured by PALS. The study gave us a parameter to control solute removal ratio of RO membrane for achieving higher water quality.

However, solute permeation through RO membranes would be affected by not only physical and morphological property but also chemical property. It is much important to investigate affinity between solutes and RO membrane. In this work, a new approach to define surface properties of RO membranes, Inverse gas chromatography (IGC), was conducted. Analyses of polyamide layer by IGC gave us surface energies relating dispersive and non dispersive interaction between polyamide and solutes. We will discuss the analytical results and its affection to the membrane performance in the presentation.

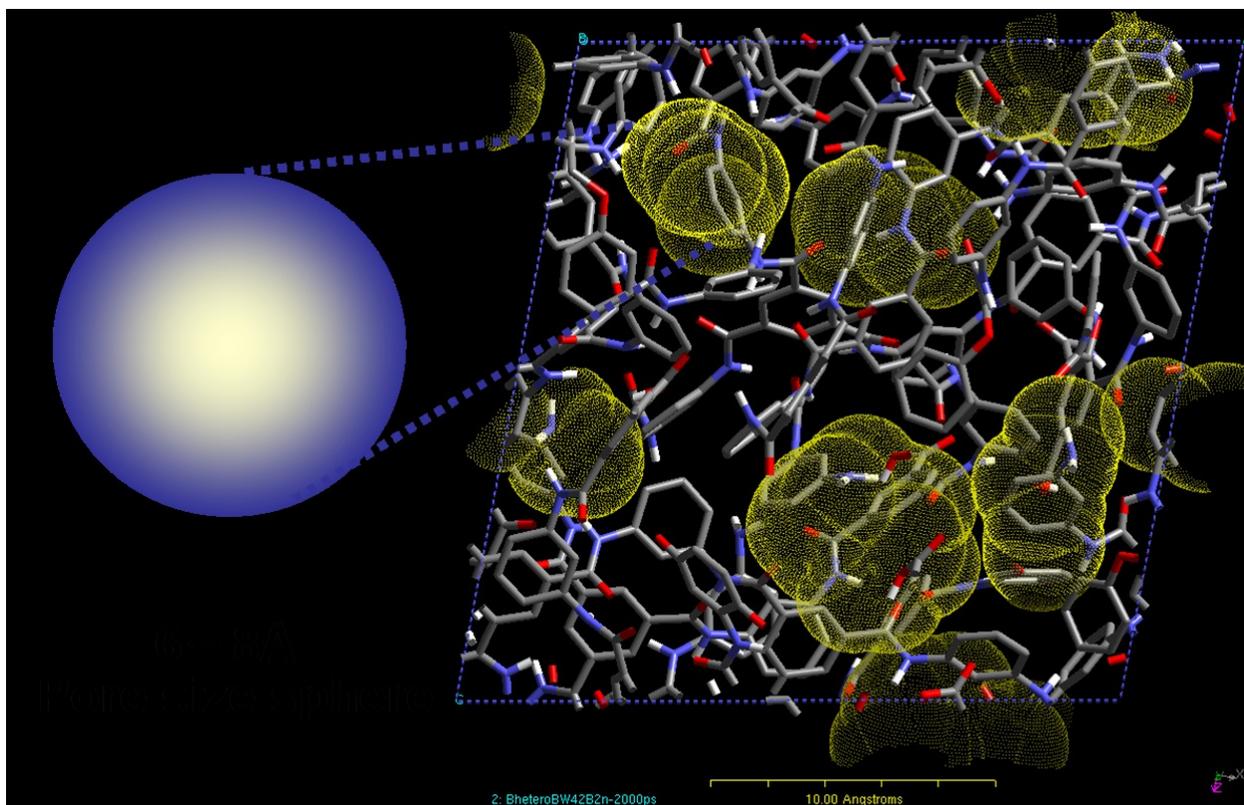


Figure 1 Investigation of RO membrane structure via MD simulations analyses

COLL 164

Foundational layer formation of metal-organic coordinated thin films

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This research explores layer-by-layer (LBL) assembly for two types of metal-organic coordinated thin films, multilayers (ML) and frameworks (MOF). Controlled step-wise assembly defines the resulting film structure, presenting an opportunity to design these materials for specific applications, such as sensing and gas storage. Towards this realization, both films are fabricated by alternating, sequential solution-phase deposition. Both systems were synthesized beginning with a 16-mercaptophexadecanoic acid (MHDA) self-assembled monolayer on gold. ML were composed of α,ω -mercaptopalkanoic acids and Cu (II) ions and MOF were composed of 1,3,5-benzenetricarboxylic acid and Cu (II) ions (HKUST-1). Both films were characterized using ellipsometry to measure film thickness and scanning probe microscopy (SPM) to map topographical morphology of film growth LBL. Using image analysis software, quantitative data regarding the growth of these thin films based on the images was procured. Ellipsometry suggests both ML and MOF form continuous, conformal layers that are each about 2 nm thick. However, SPM images elucidate two distinct systems,

one that forms a conformal film with distinct “islanding” during the first few layers of deposition (ML) and one that forms a rough surface of nucleating crystallites (MOF). Future work includes observing continued MOF growth to determine at what point it becomes continuous and to investigate how the film forms beyond the threshold of complete surface coverage. The effects of deposition conditions, such as temperature and solution concentration, have been investigated in order to tailor film morphology. Preliminary findings will be presented utilizing surface IR for gas absorption within the MOFs. Further studies will investigate other metal-organic coordinated thin film systems to understand the chemical and physical processes by which different film morphologies arise.

COLL 165

Investigation of the stability of Ag nanoparticles in solution by isothermal titration calorimetry (ITC) and zeta-potential measurements

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Results from the formation of Ag nanoparticles (AgNPs) via the borohydride reduction synthesis indicate a direct correlation between the temperature and the pH of the AgNPs solution, suggesting a products-related pH response. This products-related pH response, in addition to post-formation pH studies, have been investigated using isothermal titration calorimetry (ITC) in order to gain a more comprehensive understanding of the surface character of the Ag nanoparticles. Zeta-potential studies show the most stable Ag nanoparticle solutions at pH ranges from 6.5-8.5 and 9.5-10.0 pH units with aggregation occurring at extreme pH points. Scanning tunneling electron microscopy grids were prepared during Ag nanoparticle formation and post-formation to investigate the size and morphology of these AgNPs.

COLL 166

Study of fractal colloidal gels using DLS and SALS

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Suspensions of colloidal aggregates are important in various industrial and biomedical applications. These aggregates, which show fractal aggregation characteristics, can grow until they fill the entire volume and form a gel. Dynamic Light Scattering (DLS) and Small Angle Light Scattering (SALS) were used to study the gelation of 20nm polystyrene spheres destabilized by various concentrations of MgCl₂. The dynamic structure factor of the fractal colloidal gel exhibits stretched exponential behavior. The

aggregates show a fractal dimension of ~ 1.75 , which is in agreement with Diffusion Limited Cluster aggregation.

COLL 167

Effects of H₂O and H₂ plasma surface modification of SnO₂ nanowires and spiked nanowires

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As energy production has increased, emission of toxic gasses, such as NO_x, benzene, and formaldehyde, has also increased. Unfortunately, current gas sensors are unable to sense at or below the toxicity levels for many of these gasses. Tin(IV) oxide (SnO₂) nanomaterials have properties that may help address these current gas sensing limitations, including being inexpensive, having high surface area, and capacity for dual valency (Sn²⁺ and Sn⁴⁺), all properties leading to enhanced gas-surface interactions. One way to increase gas-surface interactions is via increasing adsorbed oxygen on the surface of SnO₂, which creates a charge exchange, ultimately leading to resistivity changes associated with the gas-specific sensitivity and selectivity of SnO₂. To create SnO₂ nanomaterial gas sensors, we began by growing SnO₂ nanowires. Chemical vapor deposition (CVD) was successfully used to grow SnO₂ nanowires at 700 °C and spiked nanowires with increased surface area were formed at 650 °C. Low temperature plasmas (H₂O_(g)) were used to etch the SnO₂ nanomaterial surfaces, thereby creating greater oxygen adsorption. Surface characterization of untreated and plasma treated SnO₂ nanowires and spiked nanowires is described by X-ray photoelectron spectroscopy (XPS). XPS analysis shows that low temperature H₂O plasma treatment effectively etches surface oxygen and reduces the Sn from Sn⁴⁺ to Sn⁰ in nanowires and spiked nanowires. Powder X-ray diffraction (PXRD) shows changes in crystallinity of nanowires and spike nanowires after H₂O plasma reduction. In conjunction with XPS and PXRD, scanning electron microscopy (SEM) reveals that with the reduction of Sn there is a change in the morphology of the nanowires. At ≥ 100 W, the nanowires and spiked nanowires agglomerate into micron-sized Sn particles. Collectively, our analyses show H₂O plasma treatments result in varied reduction and morphologies between nanowires and spiked nanowires. The extent of Sn reduction and resulting morphology changes are dependent on applied RF power and treatment time. Although H₂O is often known to be an oxidizing plasma, the reducing effect observed here may be a result of the presence of both oxidizing (O, O*, OH) and reducing (H, H*, H₂) species within the plasma. A comparison of the species present and their resulting surface modifications in H₂ plasma relative to H₂O plasmas will also be presented to help elucidate the mechanism for Sn reduction during plasma treatment of SnO₂ nanomaterials.

COLL 168

Molecular orientation studies of nematic liquid crystals using FTIR imaging technique

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Liquid crystal (LC) molecules possess long range orientation order and thus form a variety of molecular arrangements, such as planar, homeotropic, and random orientations. Since LC molecules on a polymer surface can be aligned along a certain direction through molecular interactions between LC and polymer molecules, it is necessary to orient the polymer chains along one direction in order to induce LC arrangements. Rubbing and photo-alignment techniques have been used to induce anisotropic distribution of chains in a polymer alignment layer. In this study, the alignments of LC molecules on a polymer alignment film were studied using a novel spectroscopic experimental method: Fourier Transform infrared (FTIR) imaging technique. This is a relatively new but powerful technique to directly obtain visual imaging information on molecular orientations. The analysis of local LC orientation with micron resolution is of prime importance in understanding the structure of LC phases. In order to visualize the complex spatial orientations of LC molecules, non-destructive and non-invasive FTIR imaging technique is necessary.

COLL 169

Analysis of polymeric phase separation within a thermoset polymer blend for applications in high performance low gloss coatings

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Several polymeric resins with differing polar and hydrogen bonding characteristics have been developed and blended together with commercially available fillers and pigments to generate a high performance low reflectance coating. Understanding the origins of low reflectance from the polymer blend has been approached through microscopy, thermal analysis and spectroscopic analysis of both pigmented and control clear coatings. Polymeric phase separation was thermally observed in the pigmented coating by the presence of two distinct glass transition temperatures. Microscopy revealed random surface features for the pigmented coating therefore, the pigments and fillers were removed to observe the polymer-polymer interactions within the blend under curing conditions. Upon removal of the pigment and filler materials the polymeric phase separation was readily observed with microscopy techniques. Identification of the polymeric domains was then performed using Raman spectroscopy mapping of cross-section samples embedded within a polyester resin. Cross-section samples of the blended polymeric resin film were utilized to isolate encapsulated polymer domains from the encapsulating continuous polymer network to minimize spectral averaging from both domains. Raman analysis was performed for the polymeric phases within the blend and compared to films consisting of the individual resins. The Raman analysis shows that

the encapsulated domains were generated from the polymer with the highest polar and hydrogen bonding characteristics and the continuous polymer matrix was formed from the polymer with the lowest polar and hydrogen bonding characteristics.

COLL 170

Controlling the unit cell lattice parameters in nanoscaled $\text{Cu}_x\text{Pd}_{1-x}\text{O}$ by composition and crystallite size

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Control of structural parameters for nanoscaled materials is important in their optimum use in catalysis and other materials applications. The effects of crystallite size on the lattice parameters of the $\text{Cu}_x\text{Pd}_{1-x}\text{O}$ system are explored through powder x-ray diffraction for crystallites ranging in size from approximately 3 nm to macroscopic dimensions. Nanoscale crystallites of $\text{Cu}_x\text{Pd}_{1-x}\text{O}$ demonstrate a lattice contraction in both the "a" and "c" unit cell dimensions when compared to macroscopic crystallites, and this effect can be correlated with crystallite size. For example, for the system $\text{Cu}_{0.2}\text{Pd}_{0.8}\text{O}$, "a" is about 98% and "c" is about 99% of the macroscaled values for crystallites of approximately 3 nm. The unit cell parameter also contracts with increased copper concentration (x value), and for a given particle size follows Vegard's law of linearly decreasing cell parameters with increase in x, indicative of the formation of a homogeneous solid solution across the crystallite. The nanoscale crystallites demonstrate lattice parameter trends consistent with the macro scale crystallites from $0 \leq x \leq 0.6$. The phase limit of Cu in a PdO host structure is also explored for nanocrystalline $\text{Cu}_x\text{Pd}_{1-x}\text{O}$, and is found to be between $x=0.6$ and $x=0.7$, similar to the macrocrystalline solid solution.

COLL 171

Synthesis, characterization, and imaging applications of various silver nanoparticles morphology

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Silver nanoparticles have been commonly used in the past decade in a wide range of applications. In medicine, these have been historically used as antibacterial agents but recently their properties for improvement of resolution in X-ray images and drug delivery have been studied. The study of X-ray absorption by nanoparticles in complex media has been placed on the spotlight, since plasmonic properties make them useful as tumor markers, photo-thermal ablation media or even for physical protection against such harmful rays. State of the art research has found gold suspensions to have high absorbance of X-rays[1] although other metals also exhibit such capability; this study

will compare silver with gold, since from an economic point of view it is more viable to use silver for large scale implementations.

The aim of this study is to provide a fundamental description of how the shape of silver nanoparticles can affect the X-rays attenuation behavior. Therefore, the profile evolution of X-rays attenuation versus the nanoparticle concentration as a function of morphology is determined experimentally. For this purpose, various shapes of silver particles are synthesized using a modified Turkevich method.

Particles are later characterized using transmission electron microscopy (TEM), Zeta potential and UV-VIS-NIR spectroscopy. Absorption of X-rays is made using a CCD Medipix detector; images are later processed using specialized image analysis software. We provide results on a preliminary study on diffusion profiles in complex media as well as X-ray attenuation caused by plasmon absorption using different nanoparticle shapes. Future directions on the application of silver nanoparticles for complex tissue imaging are discussed.

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COLL 172

Chemical synthesis and High temperature structural stability of monodisperse ruthenium nanostructures

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The catalytic performance of metallic nanoparticles is highly correlated with their structure and size, and an understanding of their various phases, transitions and stability – particularly at high temperatures – is essential to understanding high temperature catalytic reactions. Ruthenium nanostructures are well known as a model catalytic system due to their high catalytic performance such as CO oxidation, hydrogenation, and ammonia synthesis. Moreover, recently was discovered existence of a metastable fcc structure in Ru nanoparticles, which does not exist in the bulk phase diagram, and which apparently survives up to 450°C [1]. In this work we present studies regarding the stability of Ru phases in nanostructures at temperatures as high as 800°C. We synthesized uniformly spherical and monodisperse ruthenium nanoparticles with average size of 2.5nm via an acetate-assisted polyol route. By varying precursors and reaction solvents, we were able to vary the ratio of Ru nanoparticles that have either primarily hcp or fcc structures. A study of the structural stability of metastable fcc Ru and detailed quantification of the size variations of both fcc and hcp Ru

nanoparticles as determined environmental transmission electron microscopy (800°C in > 1Torr Ar/H₂ atmosphere) will be presented.

1. K.Kusada et. al., JACS 135, 5493 (2013)
2. "Research carried out in part at the Center for Functional Nanomaterials, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract No. DE-AC02-98CH10886."

COLL 173

Effect of doping density on current-voltage behavior and quantum yields of dye-sensitized single crystal TiO₂ electrodes

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Single crystal TiO₂ electrodes offer an ideal model for studying the fundamental processes that occur in the dye-sensitized solar cell system. Such simple and controlled model systems do not exist with nanocrystalline mesoporous scaffolds. Atomic force microscopy can be utilized with the single crystal system to ensure ideal electrode surfaces preparation, as well as insights into sensitizer coverage and structure. Photochemical and electrochemical investigations of one-dimensional photo-induced charge transfer from dye molecules at well-defined atomically flat crystallographic faces are presented. Charge collection as a function of doping density in single crystal electrodes with well-defined electric fields is investigated. A general mathematical model for electron transfer into the semiconductor conduction band in both light and dark is presented and applied to the experimental data. Experiments were performed using the ruthenium chromophore N3 and the trimethine cyanine dye G15 sensitizers, which have contrasting photoexcitation mechanisms.

COLL 174

Directed synthesis of bimetallic nanoparticles using poly(2-vinylpyridine) colloids

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Energy related catalysis will become increasingly more important as we transition toward sustainable energy systems. Devices such as direct alcohol fuel cells (DAFCs) will require optimized catalyst structures that improve the overall stability and efficiency of the device. Electrodes composed of pure platinum lack adequate electrocatalytic activity needed for oxidation and reduction reactions in DAFCs. Furthermore, a pure platinum anode is highly susceptible to CO poisoning which further decreases catalyst activity and lifetime. Alloy bimetallic platinum-based nanoparticles (Pt_xM_{100-x} NPs; where

M = Au, Ir, Pd, etc.) have shown excellent catalytic activities for both anodic and cathodic reactions as well as the ability to oxidize surface adsorbed carbonaceous poisons.

Synthetic methodologies that allow for intentionally designed structures Pt_xM_{100-x} with a specified size, composition, and inter-particle spacing are therefore key to advancing energy related catalysis. The synthesis of these catalyst nanostructures can be carried out using well-defined polymer frameworks that selectively retain catalyst precursors. Poly(2-vinylpyridine) (PVP) a polymer bearing pyridine residues is capable of metal-coordination or electrostatic association with metal anions in acidic media. In this work, we explore the synthesis of cross-linked PVP colloids capable of loading with catalyst precursors (ie: $PtCl_6^{2-}$, $AuCl_4^-$, $IrCl_6^{2-}$). Pt_xM_{100-x} NPs were produced in PVP frameworks by chemical reduction and were analyzed via scanning transmission electron microscopy energy dispersive x-ray spectroscopy (STEM-EDS). Elemental composition was determined by x-ray photoelectron spectroscopy (XPS) and laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) and electrochemical measurements for electrocatalytic oxidation of alcohols were examined using cyclic voltammetry (CV).

COLL 175

Modulating beta amyloid (A β) aggregation with metal ions and nanochelators

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Alzheimer's disease (AD), the most commonly diagnosed form of dementia, affects 37 million people with no known cure, cause or early diagnosis. While there are competing ideas over AD development, one potential idea is the "metal hypothesis", which states that metal ions (Cu^{II} , Zn^{II} and $Fe^{II/III}$, Al^{III}) play a crucial role in AD pathogenesis. These metallated-A β aggregates may cause reduced cell signaling and neuronal cell death by destabilization or oxidative damage to membranes. However, depending on experimental conditions and type of A β aggregate, inhibitory effects are observed. For example, Cu^{II} is known to inhibit fibrillation by Zn^{II} , while other studies show Zn^{II} attenuates non-toxic plaque formation and is neuroprotective. Recent research has shown that soluble A β oligomers display more neurotoxicity than larger forms of A β aggregates. Understanding the relative toxicity of metallated-A β oligomers can aid in the understanding of how they play a part in AD progression. Consequently, controlled studies are required to uncover the important mechanisms by which metals induce A β oligomerization that lead to their neurotoxic or neuroprotective roles. The most convincing piece of evidence supporting a link between metal homeostasis and the two pathological processes (A β_{1-42} aggregation and oxidative damage) comes from chelation studies showing resolubilization of A β deposits and clinical improvement of patients with AD. These studies suggest that chelation therapy is a powerful "disease modifying strategy". We will describe a new class of site-directed nanochelators to improve the limitations of traditional chelators, such as ability to cross the blood brain

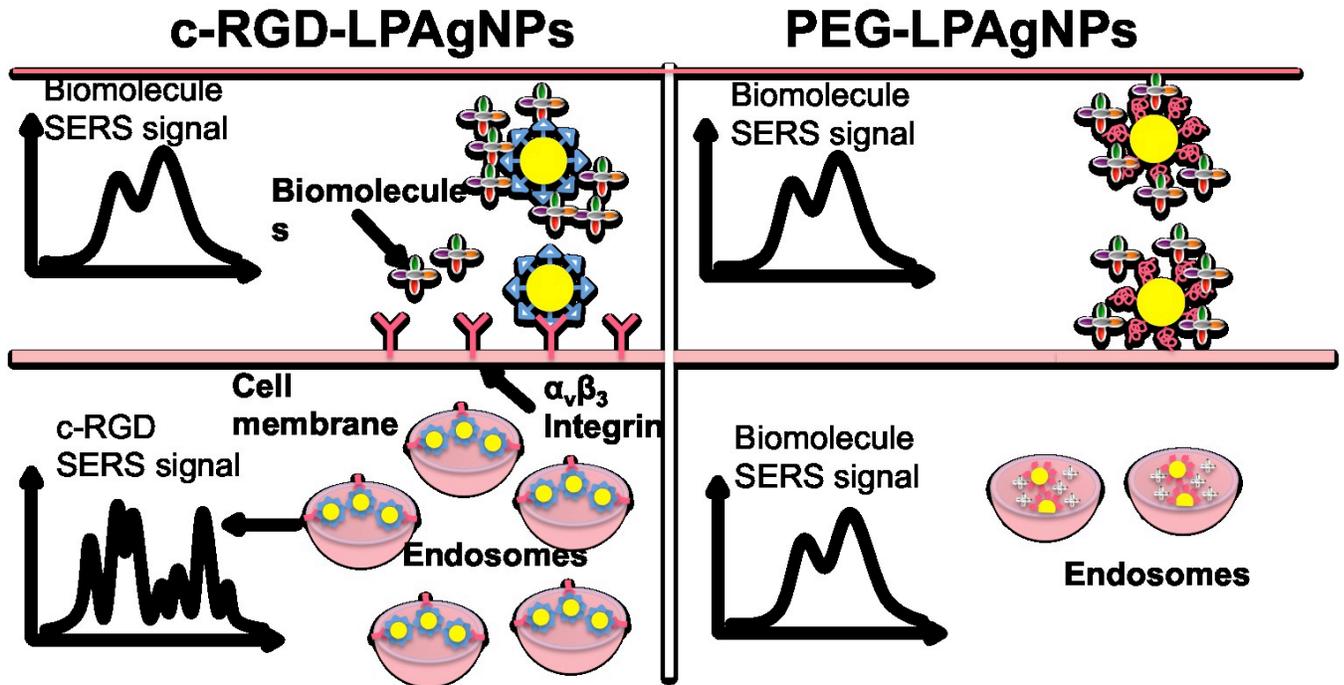
barrier and non-specific metal binding. The synthesis of these nanochelators and their metal binding affinities will be presented along with metal aggregation studies with A β using fluorescence spectroscopy.

COLL 176

Surface-chemistry effect on cellular response of luminescent plasmonic silver nanoparticles

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Cellular response of inorganic nanoparticles (NPs) is strongly dependent on their surface chemistries. By taking advantage of robust single-particle fluorescence and giant Raman enhancements of unique polycrystalline silver NPs (AgNPs), we quantitatively investigated effects of two well-known surface chemistries, passive PEGylation and active c-RGD peptide conjugation, on *in vitro* behaviors of AgNPs at high temporal and spatial resolution as well as chemical level using fluorescence and Raman microscopy. The results show that specific c-RGD peptide- $\alpha_v\beta_3$ integrin interactions not only induced endosome formation more rapidly, enhanced constrain diffusion but also minimized nonspecific chemical interactions between the NPs and intracellular biomolecules than passive PEGylation chemistry; as a result, surface enhanced Raman scattering (SERS) signals of c-RGD peptides were well resolved inside endosomes in the live cells while Raman signals of PEGylated AgNPs remained unresolvable due to interference of surrounding biomolecules, opening up an opportunity to investigate specific ligand-receptor interactions in real time at the chemical level.



COLL 177

Enhanced dispersion of cellulose nanocrystals for nanofibrilled cellulose nanocomposites

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Cellulose nanocrystals (CNC) are of interest as a very attractive material because of the relative low density ($\sim 1.6 \text{ g/cm}^3$), low cost, non-toxic character, high surface area and high modulus of elasticity ($\sim 130 \text{ GPa}$). They can be isolated from various cellulose sources, such as wood pulp, cotton, ramie, bacterial cellulose, algae and tunicates by acid hydrolysis. In this work, the CNCs were obtained by hydrolysis of cotton filter paper in a desiccator saturated with HCl vapor, which provides a simple and fast method for the production of CNCs. However, the resulting CNCs were still tightly packed in the filter paper and their colloidal stability was also very low. Therefore, mechanical disintegration of CNCs and improvement of their colloidal stability by non-covalent modification by additive molecules, such as cellulose binding proteins and carbohydrates were investigated in this work. Dynamic light scattering (DLS), high performance anion exchange chromatography (HPAEC) and TEM were used to characterize the dispersion of CNCs. The dispersed and functionalized CNCs can

further be used in high value-added application and as building blocks for nanocomposites.

COLL 178

Microscopy study of poly(3-hexylthiophene) films processed from binary mixtures of organic solvents

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Polymer assembly and organization into well-defined nanostructures is of great interest for organic electronic and organic photovoltaic applications. Recent experimental endeavors have shown that well-ordered P3HT assemblies formed in solution can improve the crystallinity and morphological uniformity of thin films and composites, thereby providing a promising route to more efficient polymeric optoelectronic materials. We have studied the aggregation behavior of poly(3-hexylthiophene) (P3HT) ($M_n \approx 28.2$ kDa, regioregularity > 96 %, PDI ≈ 1.3) in >100 binary solvent mixtures using UV-Vis absorption spectroscopy, and it is clear that the identity of the poor solvent used to drive aggregation has a significant impact on the structural order and crystallinity of the P3HT aggregates in solution. Our goal now is to study the impact that the solvent composition and the structural order of P3HT aggregates have on the assembly and organization of P3HT films. Here we report on our use of optical and atomic force microscopy techniques to investigate thin films of P3HT processed from different binary mixtures of organic solvents. Our results show that relatively small variations to the P3HT solutions can produce significant changes in the morphology and macromolecular structures of the P3HT films.

COLL 179

Distinct assembly and disassembly pathways of nanotube formed by drug amphiphile

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Supramolecular polymers offer us dynamic structures that could have great impact in areas ranging from energy to medicine. Sophisticated and multifunctional supramolecular polymers are of high interest for application, but requires elegant molecular design involving multiple types of intermolecular forces. It is therefore fundamentally important to explore the interplay of different forces that are involved in the assembly and disassembly process of supramolecular polymers. Peptides and their

derivatives are excellent building blocks to create such supramolecular polymers, since multiple intermolecular forces, in other words complex information of molecular packing, can be easily engineered into one short peptide. The hydrogen bond can be included in the system through the backbone of a peptide or the introduction of amino acids like glutamine, while the hydrophobic force, electrostatic interaction, π - π stacking or even covalent bond can be introduced through the usage of amino acids like valine, arginine, phenylalanine, and cysteine, respectively. And also, the terminuses of a peptide could be further modified with other functional groups including small molecular drugs. Here, we reported distinct assembly and disassembly pathways of nanotubes formed by drug amphiphiles, which two process are a collective result of π - π stacking, hydrophobic effect, electrostatic repulsion, hydrogen bonding and disulfide bond. During the assembly of nanotubes from monomers, nanofibers, nanotapes and twisted nanotapes were observed as intermediate structures, suggesting the sequential contribution of π - π stacking, hydrophobic interaction, hydrogen bonding and electrostatic repulsion in the process. Physical or chemical treatment of the formed nanotubes through mild sonication or glutathione, respectively, resulted in the section or kinks and unzipping of nanotubes, which were completely different from the pathway adopted during self-assembly. Our system offers a useful example to explore the fundamental mechanism of self-assembly and disassembly, and the results here unveiled the complexity and also the beauty of supramolecular polymers involving multiple forces.

COLL 180

Investigation of bone growth onto titanium rods investigated with model cell membranes

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Langmuir-Blodgett Monolayers of collagen and phospholipids on titanium substrates were used to investigate the capability of collagen to attach to titanium rods as a model system for examining the ability of osteoblasts to attach to titanium. The Langmuir Monolayer technique allows for the analysis of the organization of amphiphilic molecules at an air-water interface and is; therefore, a useful technique for the formation of model cell membranes. Collagen, Type I from calf skin, was used as a substitute for human bone and titanium nitride foil was used as the substrate due to its increased biocompatibility. Monolayers of collagen were found to have a higher degree of order (less fluidity) and to be more stable indicated by a higher surface pressure at low molecular areas when incorporated into a film with phospholipids such as dipalmitoylphosphatidylcholine (DPPC) and dipalmitoylphosphatidylethanolamine (DPPE). Similarly, preliminary transfer ratio data of collagen monolayers onto silicon (SiO_2) substrates increased in the presence of DPPC or DPPE indicating that this may be a good model system for this investigation. Future data will involve transferring the collagen/phospholipid monolayers to titanium nitride foil and using

dipalmitoylphosphatidylglycerol (DPPG) in our model because of its impact on bacterial resistance in the bone cell model membrane.

COLL 181

Exploring the desolvation of BSA–ligand complexes using the quartz-crystal microbalance and dual polarization interferometer

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Rational drug design requires understanding the properties of drug-like molecules, as well as the interaction between the ligand and its binding site. However, predicting interactions between drugs and binding sites is complicated by the involvement of water. Accounting for the movement of water within binding pockets can allow for a more complete understanding of binding interactions of ligands. Our methodology takes advantage of the different hydration sensitivities of two instrumental techniques — dual polarization interferometry (DPI) and quartz-crystal microbalance with dissipation monitoring (QCM-D) — in order to track the movement of water molecules upon drugs binding to immobilized bovine serum albumin (BSA), a common bloodstream protein. We employed this methodology to determine the approximate number of water molecules involved in desolvation of ligand–protein complexes upon binding. We examined eight drugs with different hydrophobicities in this manner in search for a relationship between the ligands' physicochemical properties and its desolvation behavior with BSA. We aim to use this data and quantitative structure activity relationship (QSAR) models to relate these desolvating properties to the structure of the drugs. If such a relationship exists, it would be of great importance in using rational drug design techniques to develop drugs with higher affinity for their targets.

COLL 182

Composite layer-by-layer films formed using functionalized carbon /nanoparticles and cationic *moringa oleifera* protein

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Electrostatic layer-by-layer (LbL) self-assembly of multilayer films has been the focus of recent research efforts and this technique has been used for development of multifunctional coatings, electronic devices, bioreactors, and unique drug delivery systems. In this work, novel thin film coatings were successfully formed on glass substrates using the layer-by-layer assembly of glycerol derived carbon nanoparticles and a positively charged *moringa oleifera* protein taken from a seed extract. Synthetic negatively charged carbon nanoparticles (< 50nm) were synthesized through a one-pot

dehydration of glycerol using sulfuric acid at 150°C and were multi-functional in nature with hydroxyl, carboxylic acid and sulfonic acid functional surface groups. LbL composite film growth, topography, composition and stability were analyzed using uv-vis spectroscopy, x-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and atomic force microscopy (AFM). In-situ attenuated total reflectance (ATR) infrared spectroscopy was also used to monitor the chemical composition and growth of individual layers. Results showed that films could be easily formed with a thickness and linear growth rate that depends on both ionic strength and pH. In-situ ATR-IR results showed that this technique could be used to easily monitor protein binding and film growth. Preliminary tests of the composite film to serve as an antimicrobial surface were conducted using E. Coli adsorption with analysis using the LIVE/DEAD™ bacterial viability kit. Fluorescent imaging indicated that the nano-carbon/moringa composite film (10 bi-layers) could indeed kill E. Coli (>80%) and the overall results showed that LbL films with novel properties could be formed from renewable starting materials.

COLL 183

Synthetic route for the growth of entirely I-III-VI semiconductor core/shell nanocrystals

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In this work, we demonstrate our method of using two compatible I-III-VI semiconductors for the colloidal synthesis of completely ternary core/shell nanocrystals. For this system we chose to shell copper indium sulfide (CIS) nanocrystals using silver gallium sulfide (AGS). The two materials share a chalcopyrite structure with comparable lattice constants, and a type I band-gap alignment. Due to the high mobility of both copper and silver ions, we propose the final structure is a highly alloyed material leading to a more stable graded shell. The nanocrystals have been characterized by TEM and XRD for shape and structure analysis, optical absorption and emission for band-gap behavior, as well as ICP for compositional analysis.

COLL 184

Synthesis of micrometer-sized CdSe nanosheet via cation exchange

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Cadmium Selenide (CdSe), a well-known direct band gap semiconductor which absorbs a whole range of the visible spectrum, is a promising material for applications in light-emitting diodes (LEDs), photodetectors, solar cells, biomedical imaging and field-effect transistors (FETs). In particular, two dimensional (2D) geometry such as nanoplatelets (NPLs) and nanosheets (NSs) has drawn extensively attention due to their unique

properties associated with its morphology. Ultrathin CdSe NSs and NPLs have been successfully synthesized using solution-based route; however, there are difficult to produce a large lateral size in the range of micrometer scale.

We present the use of cation exchange to synthesize micrometer-sized single-crystal thin CdSe (NSs) difficulty to produce directly through solution-based chemistry. Starting from hexagonal-phased CuSe NSs as a template, CdSe NSs are obtained by cation exchange of copper to cadmium. This exchange reaction preserves well the 2D morphology of the starting NSs and also retains their hexagonal crystal structure. Resulting CdSe NSs have a lateral size up to 6 μm and an average of thickness approximately 5 nm. Optical properties of NSs will be further investigated. Such a large lateral dimensional size of these NSs has advantages for single sheet optical properties studies suggested for applications in optical and electronic devices.

COLL 185

Zein nanoparticles as superhydrophobic coating: a simple and ecofriendly way to antiwetting textiles surfaces

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Robust, superhydrophobic, and self-cleaning textile fabrics were fabricated via nanoprecipitation of zein, a major protein of corn. Zein is an amphiphilic protein, possessing both hydrophobic and hydrophilic properties. Due to high content of nonpolar amino acid residues, zein is insoluble in water and alcohol but soluble in an aqueous alcohol solution in a certain concentration range (50%-80%). By adding water as anti-solvent into a zein aqueous alcohol solution under stirring, zein nanoparticles can be formed. Fabrics were coated with zein nanoparticles through a simple dipping process followed by oven curing at 130°. The produced superhydrophobic coating had high mechanical stability because of the crosslinking structure formed under high temperature. By controlling different parameters, such as zein concentration, water/alcohol volume ratio, and the amount of water added as anti-solvent, the wettability of the coated surface can be tuned.

COLL 186

Laser-induced copper deposition from solution with the addition of non-ionic surfactants: Influence of hydrophilic properties

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The interest in laser-induced chemical deposition of metal from solution (LCLD) stems from the prospects of its use in microelectronics due to the ability to create extended localized metal structures 5-100 μm wide on dielectric surfaces. Scanning a dielectric

surface with a focused laser beam in an electrolyte solution leads to locally initiated chemical reduction of copper. Composition of plating solution is organic complexing agent, usually sodium potassium tartrate or EDTA and reducing agent, copper salt and alkali. The spot of locally initiated reaction can be moved along substrate using computer-controlled motorized translation stage. LCLD is known to be a perspective method for manufacturing of metal interconnections for printed and flexible electronic devices. It is maskless technology, promising cost-effective environmentally friendly manufacturing process for prototyping and small-scale production of high precision PCBs and electrochemical sensors.

An unsolved technical problem that prevents the practical application of LCLD is intense gas evolution occurring around the laser beam focus point on the dielectric surface. The formation of gas bubbles in the laser beam path leads to its defocusing. As a result, metal deposition from solution is uncontrollably discontinued, or it occurs in a refracted or reflected irradiation zone. In such a case, diffuse edges, areas with unsatisfactory topology, ruptures, tails of the metal deposited in a non-localized way, and other flaws are formed on the metal deposited structure.

In order to solve the problem of gas evolution in direct copper deposition process our group has developed a number of metallization solutions, containing nonionic surfactants. The scanning speed of laser beam was 0.01-01mm/s, DPSS laser (532nm) working in continuous mode was used for irradiation of samples, power of laser beam was 200-1000mW, diameter of focal spot was 10-50 μm . These series of experiments were performed with oxide glass and glass-ceramics material «Sital» consisting of Al_2O_3 and SiO_2 . The effect of non-ionic surfactants on the structure of copper deposits was observed. Using of the surfactants with lower HLB but still soluble in water help lead to formation of electrical conductive copper microwires with narrow structure.

COLL 187

DFT study of the dissociative adsorption of chlorobenzene and 1,2-dichlorobenzene on Si(100)

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The dissociative adsorption of chlorobenzene and dichlorobenzene on Si(100) surface was modeled using density functional theory. A double and triple dimer cluster was used to represent the (100) face of silicon. Initial adsorption occurs by breaking one double bond on the phenyl ring and forming two new carbon-silicon bonds with the silicon dimer. For further dissociation to occur, the system must undergo a spin crossing process from the singlet electronic configuration to a higher energy triplet state. After this spin crossing event, the chlorine can then bond to the silicon surface. The possible mechanisms of dissociation are explored for both chlorobenzene and dichlorobenzene. The minimum energy crossing point for the spin crossing is found by minimizing the energy gradients between the two electronic states. The probability of spin crossing at the minimum energy crossing point is calculated, and the activation energy for the

process is determined. It is found that the activation energies for the spin crossings are small in comparison to the other steps in the proposed mechanisms.

COLL 188

Ultrastrong epoxy nanocomposites containing self-assembled synthetic clay in smectic order

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Epoxy films containing self-assembly of 2D colloidal α -zirconium phosphate nanoplatelets (ZrP) in smectic order have been prepared *via* a simple, energy-efficient film fabrication process favorable to industrial practices. The ZrP nanoplatelets in epoxy form a chiral smectic mesophase with simultaneous lamellar order and helical arrangements. These epoxy nanocomposite films are transparent and flexible, and exhibit exceptionally high tensile moduli and strengths values. Implication of the present finding for a vast variety of engineering applications is discussed.

COLL 189

Self-assembly of polymeric/inorganic nanoparticle magneto-plasmonic hybrid vesicles with controllable pattern as dual-mode imaging probes

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The inorganic/polymeric hybrid vesicles are promising nanomedicines because of their unique ability to encapsulate and deliver hydrophilic and/or hydrophobic compounds simultaneously as well as their potential applications in imaging, diagnostics, and therapy. How to integrate multiple types of inorganic materials into the hybrid vesicles and control the hybrid morphologies to enhance their performances in nanomedicine remains a challenge to be solved.

This paper describes a self-assembly method to integrate both gold NPs (AuNPs) and magnetic NPs into the hybrid vesicles' membranes. In addition, we are able to control the distribution of AuNPs and magnetic NPs, resulting in both segregation and mixing of AuNPs and magnetic NPs within the vesicular membranes. Thus, the optical and magnetic properties of the resulting hybrid vesicles can be controlled.

This work will help us to understand the fundamentals that how different types of NPs

would cooperatively influence the final assembly morphologies. Furthermore, this work will provide us the guidance to control the assembly morphologies in order to improve the properties. The magneto-plasmonic vesicles are simultaneously responsive to external magnetic field and light. These vesicles can be manipulated towards specific location with the assistance of magnetic field. We have demonstrated that the hybrid vesicles can be used as dual model imaging probes (*i.e.* photo acoustic imaging and magnetic resonance imaging). We envision that this method would be a general method to generate multifunctional vesicles with well-defined NP domains for various applications.

COLL 190

Synthesis and characterization of homogeneous $Zn_xCu_{1-x}O$ solid-solutions

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In order to utilize ZnO/CuO catalysts effectively, it is important control the structure, concentration and morphology of the material. $Zn_xCu_{1-x}O$ solid-solutions, which can form when copper and zinc hydroxides are heated, were synthesized at the copper-rich side via sol-gel synthesis utilizing microwave radiation. ZnO is only partially miscible in CuO, since the difference in crystal structures results in a less favorable energy for Zn^{2+} in the CuO, which can only be overcome by the entropy of mixing over a small part of compositional range. X-ray diffraction (XRD) revealed a tenorite structure (CuO) for $0 \leq x \leq 0.15$ and no apparent wurtzite (ZnO) phase until $x > 0.15$. Reitveld refinement was performed on the XRD patterns to determine the lattice parameters, which varied linearly with concentration to approximately $x = 0.1$ indicating a homogeneous solution over much of the range of miscibility. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) revealed that the particles were irregularly shaped flakes with average dimensions of $7.8\mu m \times 13.6\mu m$ in width and $0.2\mu m$ in thickness, with preferred growth in the [100] and [010] surface directions. As Zn^{2+} is substituted into the CuO lattice, the platelet gradually elongates along the [100] direction and narrows in the [010] direction into belt-like shapes with dimensions of $4.5\mu m \times 29.9\mu m$ in width, although the thickness remains constant at $0.2\mu m$. Preliminary data suggest that the driving force for the change in morphology involves preferential segregation of Zn^{2+} onto the (111) plane.

COLL 191

Size- and shape-controlled synthesis of Gold nanoparticles using chitosan as a stabilizer

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In recent years, gold nanoparticles (AuNPs) have been extensively studied due to their favorable colloid stability, good biocompatibility and tunable surface modification chemistry. Chitosan, an ideal material in the biomedical and biotechnologies fields, have been used as a polymeric stabilizer to synthesize zerovalent gold nanoparticles, which can be widely used in sensors, drug/DNA delivery and imaging. Herein, we report size- and shape-controlled synthesis of AuNPs functionalized with chitosan as polymer stabilizer in the presence of halide ions (F^- , Cl^- , Br^-) by controlling temperature, pH, reductive agent, and chitosan concentration. Considering the excellent conjugation of folic acid (FA) and chitosan, FA-chitosan functionalized AuNPs are further synthesized and can be extensively applied in target CT imaging, and even target bioimaging and drug delivery fields.

COLL 192

Influence of shelling temperature and time on the optical and structural properties of CuInS₂/ZnS quantum dots

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Copper indium sulfide/ zinc sulfide (CuInS₂/ZnS) core/shell quantum dots (QDs) are an important class of nanomaterials for optoelectronic, photovoltaic and photoluminescence applications. They consist of lower toxicity materials (than the prototypical Cd-based QDs) and show long fluorescence lifetimes, which opens up great potential in biological imaging applications. It is particularly important to develop reproducible synthetic methods for this new class of nanomaterials in order to maintain small sizes with high quantum yields. CuInS₂ core QDs have been shelled with ZnS at various temperatures from 90-210°C for reaction times ranging from a few minutes to a couple of hours to examine the role of both thermodynamics and kinetics on the shell growth. Temperature was found to have a larger effect on the photoluminescence intensity and lifetime than the reaction time indicating more thermodynamic than kinetic control. Using High Resolution TEM and ICP-MS, it was observed that shelling initially results from cation exchange, leading to negligible size increase upon shelling but a significant increase in fluorescence. Only after a second round of injection does a ZnS shell grow onto the particles, increasing the particle size. By analyzing the radiative and non-radiative contributions to the decay processes in the QDs, we related the changes in structural properties during shelling to their optical properties.

COLL 193

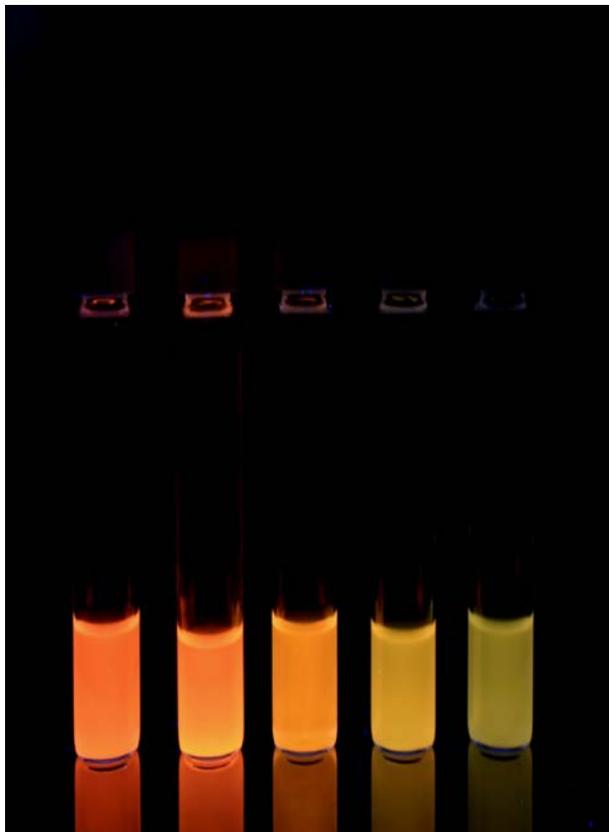
Bright tunable photoluminescence in colloidal amorphous porous silicon nanostructures

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Nano-silicon, a prime example of nanostructured materials where quantum or spatial confinement is the origin of its luminescence, comes either in an amorphous state or in a crystalline one. When broken into colloidal crystalline nanoparticles, the emission can be tuned across the visible spectrum only when their sizes vary via a painstaking filtration method that is hard to scale up and the yield is too low for technological applications. Bright tunable colloidal amorphous porous silicon nanostructures, however, have not been reported before.

In this work, we fabricated a novel material made of freestanding bright tunable colloidal amorphous porous silicon nanostructures. We achieved a 100 nm modulation of the emission, across the visible region, of the colloidal dispersions of amorphous silicon that have been fabricated from silicon wafers by stain etching followed by a controlled oxidation pathway, through band-gap engineering. We note here that while we achieved a blue shift by oxidizing our colloidal amorphous silicon nanostructures, oxidation of silicon nanoparticles was responsible for a red shift instead. HRTEM, EELS, Raman spectroscopy, Photoluminescence as well as UV-Vis absorbance were used in this work to characterize this bright tunable emission and its physical origin.

To our knowledge, this is the first time such a large blue-shift has been observed in colloidal amorphous porous silicon with a highly uniform emission. These colloidal nanostructures can be used in many applications such as liquid LEDs, liquid filters and solar energy harvesting as well as oxygen detection in solution and on surfaces.



Colloidal dispersions of Amorphous Porous Silicon Nanostructures under UV illumination (365 nm). The degree of oxidation increases from left to right.

COLL 194

Topical delivery of lipophilic carbonic anhydrase inhibitors with liposomal formulations

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The objective of this study was to optimize the topical delivery of a lipophilic fluorescent carbonic anhydrase inhibitor (CAI) using liposomes as biocompatible delivery vehicles.

Liposomes were prepared from lipids/lipid mixtures of DMPC, DMPE, DOPE & GS17 using the dried lipid film technique. A constant amount of CAI was added to each formulation and after hydration and sonication, the drug-loaded liposomes were gel-filtrated through a Sephadex G-10 column in PBS at room temperature in order to remove the unencapsulated CAI. The size of resulting liposomes was measured using a NanoZS Zetasizer and fluorescence spectroscopy was used to assess the encapsulation efficiency of the CAI. The maximum loading capacity was determined in a similar way for the best liposomal delivery systems, at different CAI/lipid molar ratios. These drug-loaded liposomal formulation in PBS (100 μ L) were incubated for 15 min- 1h at 37 $^{\circ}$ C with colon cancer cells and the amount of drug delivered was assessed via fluorescence microscopy/spectroscopy.

The main parameters governing the CAI encapsulation and delivery to the target cells will be discussed.

COLL 195

Model system development for urban films and environmental adsorption

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Urban films are ubiquitous coatings comprised of semi-volatile organic and inorganic compounds that accumulate on impervious surfaces as a result of natural and anthropogenic emissions. These chemically dynamic films amass significant amounts of persistent organic pollutants (PCBs, PAHs, pesticides), considerably affecting pollutant fate and transport in the environment. This work presents efforts to develop acceptable urban film model systems in a laboratory setting and assess film maturation under controlled exposure to UV radiation and oxygen/ozone. Films composed of stearic acid and eicosane were deposited onto silicon wafers and thermally evaporated silver on glass substrates via spin processing. Film composition and maturation, thickness,

topography, and wettability were analyzed using transmission infrared spectroscopy, ellipsometry, atomic force microscopy, and water contact angle, respectively. Our data show maturation of the film as a function of exposure time to UV/ozone, which is evidenced by the presence of oxidation products in infrared spectra and increased film wettability. Based on our analysis, we determine that these films are acceptable platforms for future studies to model persistent organic pollutant ab/adsorption and transformation within urban films.

COLL 196

Stretchable surface-chemical patterns

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Well-defined patterns of surface functional groups have been achieved using, for example, self-assembled monolayers (SAMs), polymer grafting, and micro-contact printing. These methods enable control over the surface chemistry and surface energy of a material, and thus surface properties (e.g. wettability or reactivity); however, because these methods use (or require) hard materials, additional processing is necessary to modify the surface chemistry. We demonstrate systems that use soft, elastomeric polymers as supports for surface-chemical patterns. Specifically, we have covalently modified elastomeric polymers (e.g., polydimethylsiloxane) to fabricate homogeneous or heterogeneous patterns of chemical functionality. We show that by mechanically straining these functionalized polymer films, we are able to reversibly control the density of surface-bound moieties and thus the surface energy and surface chemical properties of the material. These systems operate by coupling surface chemistry with the mechanical properties of the elastomer. We have initially focused on the attachment of small molecules and fluorescent molecules, which enable convenient quantification of the strain induced changes to the surface (e.g., molecular density and pattern), and are now exploring chiral and/or self-ordering molecules (e.g., liquid crystal mesogens). We illustrate the applicability of these materials in the control of surface-energy-dependent processes such as nucleation and wettability. Unlike surface-chemical patterns based on hard materials, the systems we describe can be reversibly modified using strain, and could potentially be used in applications where surface properties need to quickly adapt to the environment.

COLL 197

Oxidative decomposition of Au₂₅(SR)₁₈ clusters in a catalytic context

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Gold nanoparticle catalysis of chemical transformations has emerged as a subject of intense interest over the past decade. In particular, Au₂₅(SR)₁₈ has emerged as a model catalyst. In an effort to investigate their potential as intact, homogeneous, unsupported catalysts, we have discovered that Au₂₅(SR)₁₈ clusters are not stable in oxidizing conditions reported for catalytic styrene oxidation. Further investigation suggests that the active catalytic species is an Au(I) species resulting from oxidative decomposition of the starting gold cluster. This conclusion appears independent of R-group on thiolate-ligated Au₂₅(SR)₁₈ clusters.

COLL 198

Titania containing thin films for the detection of TATP and peroxide vapors

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Titania nanoparticles in a hydroxypropyl cellulose matrix produced using a sol-gel method were utilized to prepare coatings on cellulose paper, glass microfibers, and silica. The exposure of these materials to hydrogen peroxide gas and TATP vapor leads to the development of an intense yellow color. Using an inexpensive web camera and a tungsten lamp to measure the reflected light, first-order behavior in the color change was observed when exposed to peroxide vapor of less than 50 ppm. The coatings on the filter paper had a detection limit of 5.4 ppm peroxide for a 1-minute measurement and 0.09 ppm peroxide for a 1-hour integration. For coatings on silica, an extremely sensitive detector could be realized. This silica based material is capable of detecting TATP vapors in concentrations of a few parts per million (ppm) within minutes of exposure and are stable for extended periods in ambient air. The high sensitivity and rapid response of these films makes them a promising material for use as a sensitive detector for peroxide based materials.

COLL 199

Synthesis of large-pore SBA-15 silica at room temperature

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Over the last several years, reliable methods were developed for the synthesis of surfactant-micelle-templated SBA-15 silicas with a two-dimensional hexagonal (honeycomb) structure of cylindrical mesopores of diameter from 12 to as large as ~30 nm. However, initial self-assembly steps of these syntheses are performed below room

temperature, typically at 12-17 °C. Recently, we have developed room-temperature synthesis procedures for large-pore SBA-15 silicas with (100) interplanar spacings up to at least 15 nm and pore diameters from 12 to at least 15 nm. The resulting silicas are highly ordered and exhibit large pore volumes. One of these synthesis procedures can be completed in several hours instead of carrying it over a few days, as is typically done in SBA-15 synthesis.

COLL 200

Surface reactions of gas-phase atomic radicals with alkanethiolate monolayers

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Scanning tunneling microscopy (STM) is used to study the reaction between gas-phase atomic radicals and surface-adsorbed organic monolayers. The changes observed in surface structure depend on both the identity of the gas-phase reagent and the composition of the surface. For example, exposure to atomic chlorine results in a loss of order, accompanied by alkane-chain cross-linking and chlorination; reaction with atomic hydrogen, in contrast, is more likely to strip organics from the surface completely. The design and construction of a cryogenically cooled STM for gas-surface reaction studies in ultra-high vacuum allows for a more detailed investigation of these systems, including the potential trapping of reactive intermediates.

COLL 201

Stability and transport properties of magnetic nanoparticles under high temperature, high salinity aqueous conditions for oil reservoir imaging

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Superparamagnetic iron oxide nanoparticles (IO NPs) can be utilized as contrasting agents for electromagnetic imaging of subsurface formations for the purpose of enhanced imaging of the distribution of oil in the reservoir. However, bare IO NPs are unstable under working conditions for subsurface applications, namely high temperature and high salinity. Furthermore, minerals present in subsurface reservoirs will interact with these nanoparticles and cause particle adsorption during transport. This research is focused on addressing these issues by engineering functional nanoparticles that (1) remain dispersed under high temperature and high salinity conditions, and (2) minimally interact with the subsurface porous environment.

A novel coating method to efficiently synthesize polymer-grafted IO NPs was

developed. By using amine in concert with silica coating on IO NPs, one can modify the surface of synthesized IO NP cores with polyelectrolytes to provide electrostatic stabilization of the colloids and, at the same time, attain low adsorption on the anionic media in modeled subsurface environments. This platform coating strategy is demonstrated with highly magnetic IO NP cores synthesized by thermal decomposition in triethylene glycol. The effects of various parameters on IO core synthesis and particle stabilization was studied by an array of characterization techniques and static batch adsorption tests in concentrated brine. Specifically, the parameters for complete silica coating of IO NPs were studied and their effects on the amine functionalization of IO NPs were investigated. A complete coating on nanoparticles with controlled cluster size and surface amine density enabled the successful grafting of polymers. The compatibility of the grafting scheme across different systems was demonstrated. This result allows one to attach polyelectrolytes to any particles of interest with high magnetic susceptibility, colloidal stability and low adsorption in the subsurface environment.

COLL 202

Layer-by-layer assembly of polyelectrolytes and different size and shape gold nanoparticles

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Gold nanoparticles (GNPs) have a wide range of properties with potential applications in electronics, optics, catalysis, and sensing. In order 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 (LBL) techniques. Four polymers (poly(diallyldimethylammonium chloride) (pDADMAC), polyvinylpyrrolidone (PVP), polyethyleneimine (PEI), and poly(sodium 4-styrene sulfonate) (PSS)) with positive or negative charge and four different size and shape gold nanoparticle (spherical, rod, prism, and octahedral) were used. Citrate capped spherical gold nanoparticles were synthesized with a 19 nm diameter. Rod gold nanoparticles were synthesized using cetyltrimethyl ammonium bromide (CTAB) with a length of 100 nm. Triangular prismatic gold nanoparticles were synthesized with L-*alpha*-phosphatidylcholine (PC, from soybean, type IV-S, 30%) with a length of 90 nm. Octahedral gold nanoparticles were synthesized using pDADMAC and phosphoric acid with an edge length of 50 nm. Each polyelectrolyte was used to assemble LBLs with each gold nanoparticle shape. Gold nanoparticles and LBLs were characterized via dynamic light scattering (DLS), UV-vis spectroscopy, transmission and scanning electron microscopy (TEM and SEM), and atomic force microscopy (AFM). Binding and sensing applications were detected by measuring the localized surface plasmon resonance (LSPR) of the GNPs.

COLL 203

Multiwalled carbon nanotube incorporated “molecular fan” coatings for optimized thermal management applications

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Molecular fan technology is based on hybrid organic-inorganic emulsions, containing high emissivity and high thermal conductivity nanomaterials. The coatings are assembled to display active molecular vibrations and quantized lattice motions, which absorb energy from the heat source and release their excess energy by emitting IR radiation. These surface molecular motions act as miniature cooling fans and hence are termed “molecular fan” (MF). In this work, we investigate multi-walled carbon nanotube (MWCNT) based polymer composite coatings and possible factors that can affect the cooling efficiency. The multi-wall carbon nanotube (MWCNT) is selected in this study, because MWCNT displays a greater cooling performance as compared to carbon black and nano-diamond powder, due to its higher lattice quantization. The investigated factors include size, loading amount, film thickness, input power, surface modification and coating substrate. The results indicate that MF made of an 8 nm MWCNT can cool down 4 °C more of heat source temperature than that assembled with a 50-80 nm size of MWCNT. The activity of lattice motions for smaller size MWCNT is higher than that of larger size, where the radiative emission was monitored by an IR imaging camera. When a higher power input is applied to a heat source, a higher operation temperature (T) of a device is attended. The radiative cooling of MF is independent of environmental conditions, but dependent only to T^4 of the heat source temperature. The MF cooling of heat source temperature was measured to be 10 °C and 20 °C for an input power of 35V and 55 V on the same heat dissipation unit (HDU). Using the optimal factors to formulate and apply MF coating on commercial HDUs, and the results are compared to the similar system treated with powder coating, surface anodization, and uncoated bare devices. The advantages of using MF coating are illustrated and discussed.

Keywords: molecular fan, thermal management, lattice quantization, radiative cooling, surface emissivity

COLL 204

Size dependence of gold nanoparticle interactions with a supported lipid bilayer: A QCM-D study

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Nanoparticle-cell interactions are important to many critical applications, such as drug delivery and diagnostics, as well as relevant for determining the safety of nanoparticles to humans and the environment. This study focuses on a unique mechanism of cytotoxicity, namely, membrane destabilization, that is principally dependent on the nanoparticulate nature of the material rather than on the molecular properties. The interactions of 2, 5, 10, and 40 nm-diameter gold nanoparticles with supported lipid bilayers (SLB) of L- α -phosphatidylcholine (PC) were investigated with QCM-D technique. The nanoparticles were tested in their citric acid stabilized state as well as in the presence of polymethacrylic acid (PMA). The results show that 2, 5, 10 and 40 nm diameter citric acid stabilized gold nanoparticles caused only a small lipid loss from the bilayer. When the nanoparticles were coated with PMA, the smaller nanoparticles caused a mass increase on the bilayer. We proposed that the increased adhesion between the nanoparticle and the bilayer due to PMA is responsible for increased nanoparticle adsorption overcompensating for the loss of some lipid molecules. We observed significant mass loss in the case of the 40 nm PMA coated nanoparticle. We proposed that the bilayer engulfs the nanoparticle and its removal from the crystal surface is responsible for the observed significant mass loss. We propose a simple model to suggest that the competition between the particle-bilayer adhesion energy, the bilayer bending energy and the interfacial energy at bilayer defect edges allows the larger nanoparticles and more adhesive nanoparticles to be engulfed by the bilayer and leave the crystal surface causing mass loss. This large mass change can certainly be associated with membrane disruption and cytotoxicity. This suggests that even if gold nanoparticles are intrinsically not cytotoxic, they can become cytotoxic in the presence of other organic additives through manipulation of their adhesive interactions with the bilayer.

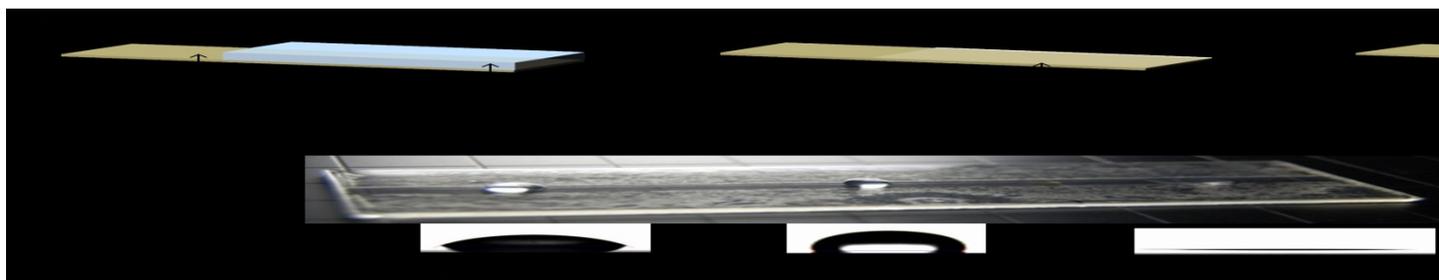
COLL 205

Extreme-wettable nanomolecular layer

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Here, we reported that only chemically induced super-hydrophilic state on the common polymer substrates can be occurred by introducing the photo-induced extremely-wetting nanomolecular layer. Utilizing the intrinsically transferable low-molecular weight siloxane oligomer by contact printing method with benefit from the sequentially easy modification into hydrophilic state *via* ultra-violet, we universally achieved the state in regardless of materials of polymer substrate. We confirmed that anomalous extremely-wetting nanomolecular layer is due to the numerous formations of hydrophilic groups, which is derived from the nano-roughness morphology of low-molecular weight siloxane oligomer. With ultra-thin thickness, the only things the resulting extremely-wetting nanomolecular layer can change the characteristics is the wetting properties, but any influence on the other properties, for example, decrease in transmittance as well as the superior mechanical flexible properties of own polymer substrate. In addition,

the chemical state is maintained for 15 days without any recovery phenomenon in comparison with those of directly photo-induced oxidation on the bare polymer surface. To demonstrate the capability of the extremely-wetting nanomolecular layer to serve as a highly versatile chemical surface modifier, indium tin oxide (ITO) layer was deposited by spin-coating method on the commercial polyimide substrate treated with extremely-wetting nanomolecular layer, in which the ITO precursor solution was not allowed to deposit without the layers. The electrical resistance of resulting ITO polyimide films was only increased to 20% under condition of bending radius 1.0mm, which was significantly superior flexibility compared to that of thick hydrophilic modifier.



COLL 206

Droplet size distributions of water-in-oil emulsions using low field NMR before and after gas hydrate formation

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The turbulence flow typically found in the oil and gas pipelines can often result in the formation of a water-in-oil (W/O) emulsion. Depending on the size of the dispersed water droplets, the formation of this emulsion may or may not be desirable for the operators. For example, the W/O characteristics, including droplet size distribution, can influence the gas hydrate formation/agglomeration processes, which depend on the available surface area for hydrate formation and the extent of hydrate conversion. Determining the DSD of W/O emulsions before and after gas hydrate formation can also provide insight into the extent of hydrate particle agglomeration, since the latter should result in significant coalescence of water droplets in oil after hydrate dissociation. Therefore, there is a need to determine the water droplet size distribution (DSD) in a W/O emulsion. One method for determining the accurate DSD of an emulsion is the use of Low Field (2 MHz) Nuclear Magnetic Resonance (NMR) spectroscopy. An advantage of using this NMR method is that the entire sample is analyzed, while at the same time maintaining the characteristics and properties of the emulsion. In this work, the DSDs of water-in-oil (W/O) emulsions with water volume fractions in oil ranging from 10 – 70 vol.

% were measured before and after gas hydrate formation using a low field NMR spectrometer. Different oils that result in different droplet sizes were used in this work. The use of different oils allows the determination of the limit of the DSD that could be measured using the proposed method. In addition, the DSDs of the W/O emulsions obtained from NMR were found to compare well with microscopy analysis.

COLL 207

Methane activation on ceria surfaces modified with metal nanoparticles

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Mild activation of methane is highly topical in catalysis. Breaking the C-H bond in CH₄ is generally discussed as descriptor for the ability of a catalyst to activate methane. We aim at virtual screening of metals on active supports using first principles density functional theory (DFT) simulations to study the energies involved in methane adsorption and the activation of the C-H bond on candidate catalyst materials. This contribution presents the results of DFT studies of methane activation on ceria (111) and (110) surfaces, which are modified by 1 nm diameter metal particles of Au, Ag, Cu, Ni and Pt. The ceria surfaces are described by the well-known DFT+U approach commonly used for this oxide. We present firstly results for adsorption structures of the metals on the (111) and (110) ceria surfaces and discuss their activity in terms of oxygen vacancy formation, in particular the importance of the metal-oxide interface in enhancing the formation of O vacancies. We then compare the energies of molecular and dissociative CH₄ adsorption at the metal-ceria structures and use nudged elastic band (NEB) calculations to compute a reaction barrier for the breaking of the C-H bond. The results are discussed in terms of the structure and the reducibility of the metal-ceria systems and we compare with previous work of methane activation on cation-doped ceria.

COLL 208

Surface properties of hydrocolloid-stabilized magnetite Murrh capped nanoparticles

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Here we provide a new method to synthesize stabilized colloidal of magnetic nanoparticles (MNPs). A new class of monodisperse water-soluble magnetite nanoparticles was prepared by a simple and inexpensive method based on a co-precipitation method. In this respect, the iron ions were prepared from reaction between ferric chloride and potassium iodide beside iodine. The ferrous and ferric ions were hydrolyzed at pH 9 in the presence of iodine to produce iron oxide nanoparticles at low

temperature. Murrh as natural product gum was used as capping agent to produce high dispersed coated magnetite nanoparticles. The structure and morphology of the magnetic nanogel were characterized by Fourier transform infrared spectroscopy (FTIR) and transmission electron microscopy (TEM). X-ray diffraction (XRD) used to examine the crystal structure of the produced magnetite nanoparticles.

COLL 209

Epoxy/clay nanocomposites containing clay layers in smectic long-range order

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Epoxy/clay nanocomposites based on alpha-zirconium phosphate layer structure were prepared by both spray coating and film applicator approaches. The clay layers in epoxy form a long-range smectic order aligned parallel to the substrate surface and span across the entire thickness of the coating and film. These coatings and films exhibit exceptional physical and mechanical properties, which include outstanding barrier properties against oxygen and moisture, superb mechanical rigidity and strength, good optical properties, great fire retardation and corrosion resistance properties, low viscosity under shear, and many others. The fundamental principles responsible for the formation of long-range smectic order of clay in epoxy are introduced. Implication of the present finding for a vast variety of engineering applications will also be discussed.

COLL 210

Isolation and investigation of distinct cytochrome c/cardiolipin interaction sites

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Recently, there has been great interest in understanding the role of cytochrome c (Cyt_c) as it pertains to the intrinsic apoptotic pathway. Positively charged domains on Cyt_c interact with the anionic phospholipid cardiolipin. Although the exact mechanism of this interaction is still under investigation, Cyt_c undergoes a conformational change upon association with cardiolipin. In the presence of superoxide radicals, these conformational changes lead to increased peroxidase activity of Cyt_c. Cyt_c is capable of oxidizing cardiolipin acyl chains leading to Cyt_c dissociation from the membrane, and downstream initiation of apoptosis through apoptosome formation. Using circular dichroism and UV-visible spectroscopy methods, we investigate the cytochrome c/cardiolipin interaction. To date, three potential cardiolipin interaction sites have been proposed on cytochrome c. Through environmental manipulation, we are able to isolate and study the cytochrome c/cardiolipin interaction at individual sites. Monitoring the binding of Cyt_c variants to cardiolipin vesicles allows us to investigate the role of

individual amino acids in the protein-lipid interaction and elucidate the mechanism for cardiolipin interaction at the different interaction sites on cytochrome *c*.

COLL 211

Role of lysine 72 in human cytochrome *c* alkaline conformational transition

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The role of human cytochrome *c*, HuCyt_c, lysine 72 in heme alkaline conformational transition has been poorly defined. It has also been thought to not act as a binding ligand as indicated by work with horse cytochrome *c*. Cyt_c has the ability to interact with cardiolipin containing vesicles. During this interaction, alternative lysine bound conformers are formed which are thought to inhibit peroxidase activity, thus making it important for understanding which residues act as alternate ligands in this transition. Here we present evidence that K72 in HuCyt_c may in fact act as an alternate heme ligand during the alkaline conformational transition. Using a Hu K72A mutant, we see only minor stabilization of the global structure, monitoring α -helical unfolding via circular dichroism (CD) and stepwise addition of guanidine denaturant. Shifts in stability of a global nature with a single amino acid mutation are uncommon so this is to be expected. However looking at the alkaline conformational transition with a stepwise pH titration, we see a shift in apparent pK_a from 9.54 ± 0.03 for WT to 10.00 ± 0.13 for K72A. Our current interpretation of this shift is native state (M80 bound) stabilization caused by K72 no longer being present to displace M80. We tested this further by stopped-flow pH Jumps monitored at 406 nm for changes in heme ligation, which clearly showed a distinct change in population of alkaline conformers between WT and K72A HuCyt_c over a range of pH values, indicative of K72-heme ligation for WT.

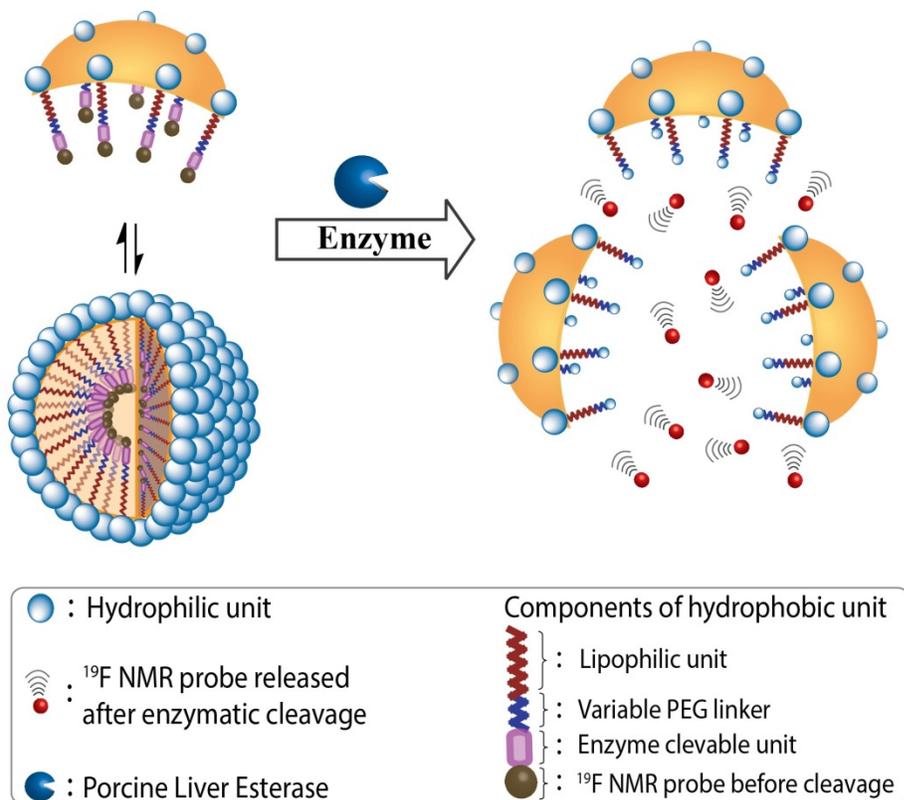
COLL 212

¹⁹F Dendron probes for specific detection of enzyme activity

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Magnetic resonance imaging (MRI) is one of the most powerful tools for *in vivo* detection and imaging of enzyme activity due to deep tissue penetration and high spatial resolution. Among all the MRI nuclides, ¹⁹F has emerged to be a promising alternative to Gd-based imaging in recent years. However, ¹⁹F MRI is still in its infancy. Despite its potential value in medical diagnostics, ¹⁹F magnetic resonance strategies for specific detection and imaging of enzyme activity *in vivo* are very limited. We describe a

novel ^{19}F NMR probe based on self-assembled facially-amphiphilic dendrons for detecting enzyme activity. The ^{19}F amphiphilic dendron probe self-assembles into large aggregates and is NMR-silent. In the presence of the target enzyme, the aggregates disassemble and give a sharp ^{19}F signal. The probe is capable of detecting enzyme concentration in the sub-nanomolar range. Response time of the probe was found to be affected by the hydrophilic-lipophilic balance of dendrons. The design principle should be applicable to detect other enzymes simply by changing the substrate on the dendrons.



Schematic representation of assemblies formed from enzyme cleavable dendrons and the release of ^{19}F reporter upon enzyme exposure

COLL 213

Biomolecular patterning via chemical lift-off lithography

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Soft lithography, e.g., microcontact printing (μ CP), has been used to generate chemical patterns on noble metal surfaces for biological applications including biosensing and protein-ligand interaction assays, and for studying cellular behavior on solid substrates. However, soft lithography suffers from lateral ink diffusion and gas-phase deposition of volatile inks during printing that can result in poor quality patterns. To overcome such limitations, we have devised a number of modified soft lithography methods, e.g., microdisplacement printing, microcontact insertion printing. Recently, we discovered chemical lift-off lithography (CLL), which utilizes contact-induced reactions between *activated* stamps and hydroxyl-terminated alkanethiol SAMs on gold surfaces to lift-off alkanethiols. Lift-off occurs only in the contact areas where surface chemistries of the stamp and the SAM are complementary avoiding commonly encountered problems in μ CP. Using CLL, patterns of surface-tethered neurotransmitters are fabricated with high pattern fidelity for the placement of bioactive molecules via backfilling. We found that patterning tether molecules pre-functionalized with neurotransmitters showed *consistent* antibody recognition and improved specific binding compared to previous post-patterning functionalization approaches. CLL does not remove all alkanethiols in the contact regions and the remaining alkanethiols act as spacers for controlling the density of the active backfilled molecules. We found that the SAM conformation of remaining alkanethiols modulates access to the gold substrate surfaces. Together, these advantages enable highly controlled biomolecule patterns to be created.

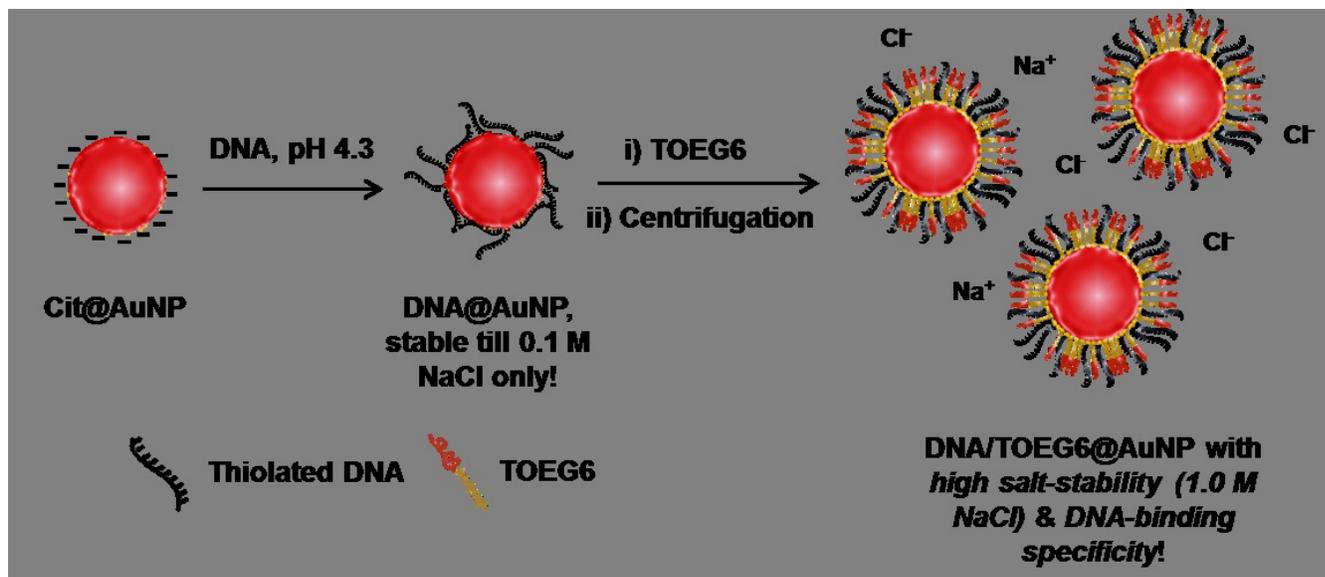
COLL 214

Surface passivation and acidic conditions allow for the rapid synthesis of DNA-conjugated gold nanoparticles with high salt stability and DNA-binding specificity

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We report a novel approach for the quick synthesis of highly stable single-stranded DNA (ssDNA) functionalized gold nanoparticles (AuNPs). The method is based on the combined effect of low pH conditions and surface passivation by (1-mercaptopundec-11-yl)hexa(ethylene glycol) ie TOEG6, does not require any salt nor high excess of ssDNA, and can be generalized for oligonucleotides of any length or base sequence. The synthesized ssDNA-coated AuNPs are stable at salt concentrations as high as 1.0 M and also functional and specific towards DNA-DNA hybridization, as shown from UV-vis spectrophotometric, Scanning Electron Microscope, Gel Electrophoresis, Fluorescence and Small Angle X-ray Scattering based analyses. The presented method is highly

flexible and holds the potential of modulating the total number of ssDNA per AuNP thereby addressing multiple pertinent issues related to the functionalization of DNA on AuNPs.



COLL 215

Sialic acid decorated polymer@goldNP as biofunctional hybrids: assembly, lectin and viral binding

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Sugars can be used as recognition signals to specifically deliver biological active components, since a number of mammalian cells express cell surface sugar-binding proteins. In nature, sialic acid residues on the surface of mammalian cells could initiate the infection cycle of influenza virus, based on the interaction with viral homotrimeric fusion protein hemagglutinin. In our work, the modification of gold nanoparticles with sialic acid containing polymer was performed via a combination of RAFT polymerization and reductive amination. Polymers with various ratios of N-(2-Hydroxypropyl)methacrylamide and N-(3-aminopropyl)methacrylamide (HPMA and APMA) were synthesized by reversible-addition fragment transfer (RAFT) polymerization, and the final ratio of APMA monomer was determined afterwards via ¹H-NMR measurement. RAFT yields polymers with a sulfur end group that can couple to metallic gold. The sialylation of the polymers was obtained via one-pot reductive amination of α-2,6-sialyllactose with the APMA monomeric repeating units. The extent of sugar modification was determined via ninhydrin assay. Surface modification of citrate-stabilized goldNP with the glycopolymers was achieved by spontaneous ligand

exchange in aqueous medium. After separation of free polymer from gold nanoparticles by centrifugation, sialic acid glycopolymer decorated gold nanoparticles were obtained. The presence of sialic acid group in the corona of the polymer coated gold nanoparticles was demonstrated by investigating goldNP aggregation by UV-Vis spectroscopy and dynamic light scattering (DLS) in presence of SNA (Sambucus Nigra Lectin). SNA induce aggregation of sialic acid engineered goldNP, leading to a shift in the surface plasmon peak from 529nm to 540nm and a strong decrease in absorbance due to macroscopic precipitation, which was also confirmed by the increase in size obtained by DLS measurement. Inactivated influenza virions were mixed with sialyllactose@goldNP, inducing agglutination as witnessed by the emergence of a double distribution of goldNP and agglutinated virus by DLS. TEM further confirmed selective binding of sialic acid engineered goldNP to influenza virions. In conclusion, sialic acid decorated goldNP was successfully achieved by a simple combination of RAFT polymerization and one-pot reductive amination, which maintained the specific binding property of the sialic acid group.

COLL 216

Using fluorescent-labeled nanodiscs to study lipid interactions with yeast Cytochrome C

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Cytochrome c (cyt c) is a positively charged protein (+8 at neutral pH) that interacts with the inner mitochondrial membrane, which is composed of a large fraction of negatively charged phospholipid, cardiolipin (CL) (-2 at neutral pH). The peroxidation of CL by cyt c initiates the intrinsic pathway of apoptosis. We are investigating the interaction between cyt c and CL and the cyt c-CL complex using nanodiscs (ND). ND are a discoidal phospholipid bilayer model system, for which size and shape are governed by two membrane scaffolding proteins (MSP) belt proteins. The lipid composition can be altered to represent native-like or other experimental conditions. ND preparations are more stable and consistent between preps when compared to liposomes. Fluorescent labeling of the MSP belt proteins provides an effective method to monitor cyt c-CL interactions without perturbing the formation of cyt c-CL complexes. The quenching of the emission from the fluorophore-labeled MSP belt protein by the cyt c heme group is used to measure the binding affinity of cyt c for cardiolipin. Quenching is also used to determine stoichiometry and higher order assembly of cyt c-CL complexes.

COLL 217

Plasmonic enhancement of dye-sensitized solar cells using SiO₂@AuNP thin films

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Dye-sensitized solar cells (DSCs) are economical photovoltaic devices, which provide a simple template to study optically addressable nanomaterials for the purpose of increasing solar cell efficiencies. In this research, plasmonic silica coated gold nanoparticles ($\text{SiO}_2\text{@AuNPs}$) are assembled into thin films that are integrated into the photoanode of DSCs in an effort to increase their efficiency using localized surface plasmon resonance. The extinction maximum of the $\text{SiO}_2\text{@AuNPs}$ employed is centered at 540 nm which corresponds to the frequency of light that is responsible for exciting ruthenium based dyes, such as Z-907; these dyes serve to photosensitize the titanium dioxide photoanode. For this reason, it is postulated that the thin film of $\text{SiO}_2\text{@AuNPs}$ will act to increase the effective absorbance of the dye because the oscillation of plasmons within a gold nanoparticle at its characteristic resonant frequency generates electromagnetic radiation of the same frequency that can, in turn, excite adsorbed dye molecules. Electrical characterization results will be presented for $\text{SiO}_2\text{@AuNP}$ -free control DSCs and DSCs incorporating $\text{SiO}_2\text{@AuNPs}$ thin films to test the validity of this hypothesis. Preliminary electrical measurements of voltage and current under a variable load under solar illumination show that power conversion efficiencies of DSCs doped with $\text{SiO}_2\text{@AuNPs}$ may be up to 17% greater than that of the controls.

COLL 218

Preparation of Fe(II)-impregnated granular activated carbon for arsenate removal from water

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In this study, granular activated carbon (GAC) was impregnated with ferrous sulfate using Fe(II)-H₂O₂ or Fe(II)-O₂(air), and considered in terms of the potential for improved removal of arsenic, in the form of arsenate ion, from drinking water. The equilibrium adsorption capacity (q_e) of Fe-GAC prepared in the same method increased linearly with the iron content in the GAC ($R^2 > 0.94$). The impregnated iron was used more efficiently for arsenate removal when applying the Fe(II)-H₂O₂ process, with nano-scale rod-like structures of FeOOH on the surface of the GAC being mainly responsible for the arsenate removal. The adsorption capacity (q) of Fe-GAC prepared in the different method increased linearly with the iron content in the GAC ($R^2 > 0.91$). The presence of Cl⁻, SO₄²⁻, NO₃⁻, ClO₄⁻, and PO₄³⁻ inhibited the adsorption of arsenate, but BrO₃⁻ promoted the adsorption of arsenate.

COLL 219

Enhanced photocurrent via plasmon excitation of ultrasmall PbS quantum dots on Au/TiO₂ electrode

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Plasmonic enhancement on the photoelectrochemical response was studied using PbS quantum dots (PbS-QDs) on titanium dioxide electrode with gold nanoparticles (Au-NPs). PbS has relatively small effective mass both of electrons and holes, showing metallic properties, such as large Bohr radius of 18 nm. Consequently, strong confinement could be expected because of the mode coupling PbS-QDs and Au-NPs. Enhanced photocurrent using size-controlled PbS QDs excited by localized surface plasmon resonance was observed at relatively wide wavelength region between visible and near infrared. The effect of plasmon modes on the enhancement discussed addition to the bandgap resonance of the quantized states of PbS-QDs in the present system. The observation proves the advantage of the QDs system to extend the wavelength region of plasmon photovoltaics.

COLL 220

Nucleation and growth of silver nanoparticles by AB and ABC-type atomic layer deposition

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We report synthesis strategies to produce Ag nanoparticles by AB-type and ABC-type atomic layer deposition (ALD). Recently, ALD has been used to synthesize supported metal nanoparticles such as Pd and Pt which have applications in heterogeneous catalysis (1, 2). Expanding the library of materials for catalytic applications that can be synthesized by ALD is highly desirable. Supported Ag nanoparticles were synthesized using trimethylphosphine(hexafluoroacetylacetonato)silver (I) (hfac)Ag(PMe₃) and formalin (AB-type) and (hfac)Ag(PMe₃), trimethylaluminum, and H₂O (ABC-type).(3) In situ quartz crystal microbalance (QCM) measurements reveal a Ag growth rate of 1-2 ng/cm²/cycle by ABC-type ALD at 110 °C and 2-10 ng/cm²/cycle for AB-type ALD at 170-200 °C. QCM measurements show that AB-type Ag ALD has a nucleation or incubation period before continuous linear growth that can be shortened by using a deposition temperature of 200 °C. Transmission electron microscopy reveals that AB-type Ag ALD particles have an average size of ~1.8 nm after 10 cycles. ABC-type Ag ALD particles have an average size of ~2.2 nm after 20 cycles. With increasing ALD cycles, ABC-type Ag ALD increases the metal loading while maintaining the particle size but AB-type Ag ALD results in the formation of bigger particles in addition to small particles. UV-visible diffuse reflectance spectroscopy shows that the localized surface plasmon resonance of the Ag nanoparticles redshifts with increasing ABC-type ALD cycles. X-ray photoelectron spectroscopy studies reveal that the as-prepared Ag nanoparticles are in the metallic state and that the silver atomic percent concentration

increases with the number of ALD cycles. The ability to synthesize supported metal nanoparticles with well-defined particle sizes and narrow size distributions makes ALD an attractive synthesis method compared to conventional wet chemistry techniques.

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COLL 221

Supramolecular polypeptide structures assembled from folded, globular proteins

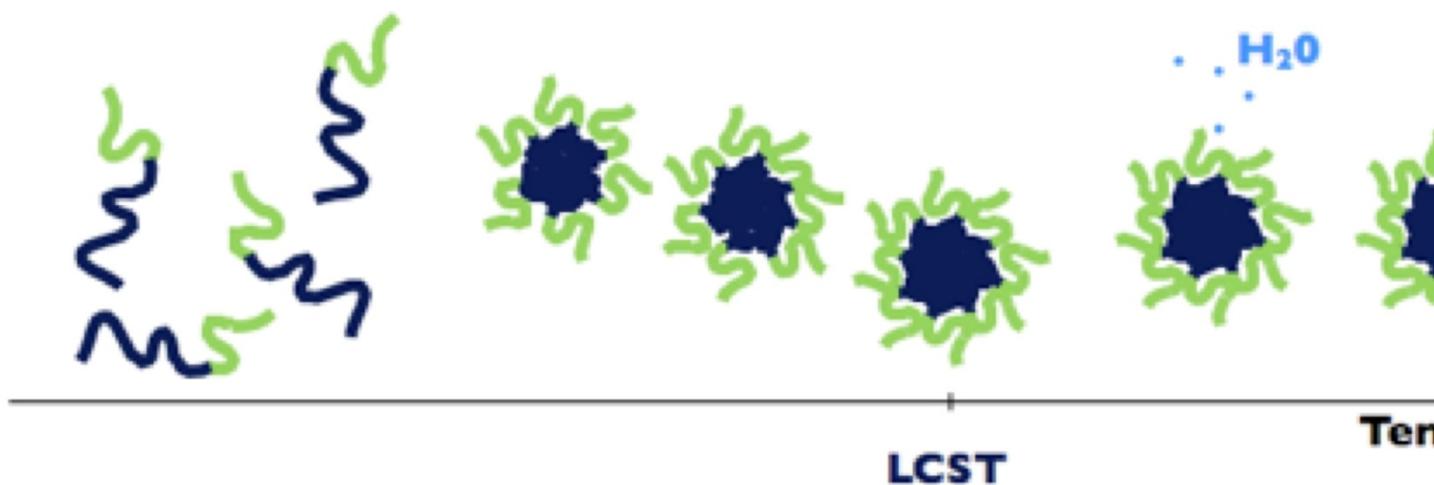
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Nature utilizes self-assembly to build functional structures from bio-macromolecules. In synthetic systems, self-assembly is an attractive tool to manipulate polypeptides into supramolecular structures at physiologically relevant conditions. Naturally derived protein motifs present useful self-assembling properties, and combination of multiple motifs can provide new opportunities to control the assembly processes. For example, elastin-like polypeptides (ELPs) are temperature-responsive self-assembling protein motifs, which have been extensively engineered to form various suprastructures upon inverse phase transition. Leucine zippers are coiled coil peptides that form dimeric or higher ordered complexes with engineered affinity. This work illustrates how engineered protein building blocks containing these domains can form different structures dictated by assembly conditions. More importantly, the protein building blocks also contain folded, globular proteins and these are incorporated into the structures without disruption of folding and activity. Two examples of such structures will be discussed, protein vesicles and protein nanosheets. Protein vesicles are formed when a globular protein and ELP are attached non-covalently via leucine zippers and warmed to room temperature in buffer. The vesicles are hollow or can encapsulate small molecules, protein coacervates, or nanoparticles. Their size and formation is salt dependent. Protein nanosheets are formed when random coil polypeptides capped with leucine zippers are dried on a surface. Rehydration of the sheets in the presence of globular proteins fused to leucine zippers integrates the proteins on the sheets. For both structures, these are the first examples of their kind that contain full-sized, folded globular proteins. Incorporation of various types of proteins including enzymes, therapeutic proteins, or binding ligands can lead to significant benefits in applications such as biocatalysis, drug delivery, and molecular imaging.

Elastin-based amphiphilic copolymers as precision building blocks for controlled self-assembly

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Protein-engineering techniques are powerful alternatives to traditional chemical polymerization methods to synthesize monodisperse polymers, as they offer exquisite control over molecular weight, sequence, architecture and functionality. Due to their intrinsic biocompatibility, these systems are highly attractive alternatives to traditional synthetic polymers for biomedical applications, especially drug-delivery where most recombinant polymers are based on the pentapeptide repeat [-Val-Pro-Gly-Val-Gly-] derived from the elastomeric domain of elastin. An essential property of elastin-based sequences is their temperature-triggered phase transition (LCST or Tt). This behavior has been exploited to create temperature-triggered self-assembly of protein block copolymers. Raising the solution temperature can selectively desolvate one block and drive the self-assembly above a critical micellization temperature (CMT) into micellar structures. Self-assembly can be controlled with hydrophilic-to-hydrophobic block ratio, copolymer MW, and distribution of polar and apolar regions along the polymer chain. We have recently designed a series of recombinant amphiphilic diblock copolymers wherein the hydrophobic block ($301 < 45^\circ\text{C}$) contains multiple repeats of hydrophobic (VPGVG) motifs and the hydrophilic block with a higher transition temperature ($T_{t2} > 60^\circ\text{C}$) contains repeats of 30 or 60 (VPGXG) motifs with where X is alanine or glycine at a 1:1 ratio. The hydrophilic mass fraction of the copolymer was tuned from 10 to 60%. Extensive analysis (DLS, SANS, TEM, AFM) of the self-assembly behavior of these diblock peptide polymers were performed and relationships between their chemical composition, sequence, and nanoscale structure will be discussed.



COLL 223

Growth factors engineered for super-affinity to the extracellular matrix enhance tissue healing

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In the 1950's, the discovery of growth factors (GFs) held great promise for tissue regeneration. Nevertheless, the translation of GFs into clinical therapies is far from having fulfilled the expectations, and is currently facing important limitations related to safety and cost-effectiveness. In fact, significant improvement of tissue healing is achieved by repeated delivery of high doses of GFs to the impaired tissue, which also dramatically increase the cancer risk of patients, as has been warned by the U.S. Food and Drug Administration. Interestingly, in physiological conditions, GFs are highly effective at very low doses, thanks to their optimal delivery by the local extracellular matrix (ECM). Thus, we reasoned that GFs with high affinity for ECM proteins would induce better tissue morphogenesis because of their longer-term release from the ECM and their subsequent prolonged receptor activation. We recently characterized the interactions between 25 GFs and 6 key ECM molecules, and discovered a peptidic domain from the Placental Growth Factor-2 (PIGF-2₁₂₃₋₁₄₄) that displays a super-affinity for ECM proteins. We used rational protein engineering to incorporate PIGF-2₁₂₃₋₁₄₄ into GFs that bear clinical translation limitations, particularly VEGF-A, PDGF-BB and BMP-2. We successfully showed that engineered GFs-PIGF-2₁₂₃₋₁₄₄ display super-affinity for ECM proteins and heparan sulfate proteoglycans, which allow them to be strongly retained into fibrin clots and endogenous ECMs. Furthermore, we demonstrated that the delivery of low doses of GF-PIGF-2₁₂₃₋₁₄₄ drastically enhance tissue healing in models of skin chronic wound in db/db mice and critical-size bone defect in rats, in comparison to wild-type GFs. Impressively, this acceleration in tissue healing has been observed when GF-PIGF-2₁₂₃₋₁₄₄ were delivered with fibrin matrices or by simple topical applications on the wounds. In conclusion, the super-affinity of GF-PIGF-2₁₂₃₋₁₄₄ for the ECM allows a precise spatio-temporal delivery and release of these engineered factors into wounds, what permits to significantly reduce their therapeutic doses and side effects. This broadly applicable growth factors engineering approach may overcome some of the important and current limitations of growth factor-based therapies in the clinic.

COLL 224

Effect of surfaces in modulating peptide assembly

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Peptide-surface interactions are at the heart of a number of emerging technologies, including protein micro-arrays, biosensors and biomaterials. The effect of surfaces on peptide structure and stability can vary substantially depending on the chemical composition of the surface. In this talk, I will present both coarse-grained and atomistic simulations of peptides folding and assembling on organic thin-films and graphite surfaces.

COLL 225

Materials with desired nanostructure through peptide design and solution assembly

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Self-assembly of molecules is an attractive materials construction strategy due to its simplicity in application. By considering peptidic molecules in the bottom-up materials self-assembly design process, one can take advantage of inherently biomolecular attributes; intramolecular folding events, secondary structure, and electrostatic interactions; in addition to more traditional self-assembling molecular attributes such as amphiphilicity, to define hierarchical material structure and consequent properties. These self-assembled materials range from hydrogels for biomaterials to nanostructures with defined morphology and chemistry display for inorganic materials templating. Both hydrogels and hybrid materials will both be discussed. With respect to hydrogels, the local nano- and overall network structure, and resultant viscoelastic and cell-level biological properties, of beta-hairpin self-assembled peptides will be presented. These peptide hydrogels are potentially excellent scaffolds for tissue repair and regeneration due to inherent cytocompatibility, porous morphology, and shear-thinning but instant recovery viscoelastic properties. The molecules fold and self-assemble into a rigid hydrogel based on environmental cues such as pH, salt, and temperature including physiological conditions. The hydrogel is composed of a network of fibrils that are 3 nm wide and heavily branched and entangled with no covalent crosslinking required for gel stiffness. Importantly, slight design variations of the MAX1 sequence allow for tunability of the self-assembly/hydrogelation kinetics as well as the tunability of the local peptide nanostructure and hierarchical network structure. New peptide designs that provide for specificity in hydrophobic packing and a severe limiting of fibril branching will be presented along with other new peptide designs that provide for post-assembly covalent chemistry to alter hydrogel physical properties. In addition, peptide nanostructures can be used to template the growth of inorganic materials as well as the assembly of inorganic nanoparticles. Fibrillar nanostructures as well as two-dimensional nanostructures are being explored for inorganic particle templated assembly.

COLL 226

Fibrillar protein and peptide co-assemblies: Design and applications in medicine

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Biomaterials based on the assembly of peptides and proteins are currently being developed for a wide range of biomedical applications, from cell encapsulation and 3D culture to vaccines and other immunotherapies. Each of these biological contexts is highly complex and multi-factorial, where specific phenotypes arise from a diversity of biomaterial-related inputs.

To interface this complexity, and to elicit highly specific phenotypes from biology, we have been developing modular materials based on the assembly of peptides and proteins, where specific factors can be mixed together with high degrees of control and delivered to biological systems. Here we will describe recently designed protein and peptide hybrid materials where combinations of expressed proteins or peptide epitopes can be induced to assemble into nanofibers and hydrogels with exact stoichiometries of the polypeptides. New applications of these materials will be described, towards 3D cell culture, vaccines, and immunomodulatory therapies for chronic inflammation.

Towards defined matrices for 3D cell culture, fibronectin domains were expressed in *E. coli* in tandem with the recently reported “ β -tail” tag, which allows insertion of whole folded proteins into β -sheet peptide nanofibers. Using Western blotting and pulldown assays, co-assembly of specific amounts of fibronectin domains into peptide nanofibers was observed, and self-assembled fibrils incorporating the proteins facilitated the culture of LNCaP cells, a prostate cancer cell line that is challenging to grow in more traditional matrices such as Matrigel. Towards immunomodulating materials, we expressed the cytokine interferon- γ (IFN- γ) in tandem with the β -tail tag. Using pull-down and macrophage stimulation assays, we found that active IFN- γ could be inserted into the nanofibers at titratable doses, enabling subsequent use in polarizing immune responses against the materials. In a third example, adjusting the phenotype of vaccine responses, we found that self-assembling peptide nanofibers allowed the precise adjustment of T cell epitopes and B cell epitopes in the materials, and that systematic variation of the epitope content could be used to optimize antibody responses in a vaccine against methicillin-resistant *S. aureus* (MRSA). Collectively, these 3 examples demonstrate the breadth of biomedical applications that can be served using supramolecular materials able to integrate precise combinations of different biological cues.

COLL 227

Formation of protein coronas on gold nanorods stabilized by amphiphilic ligands

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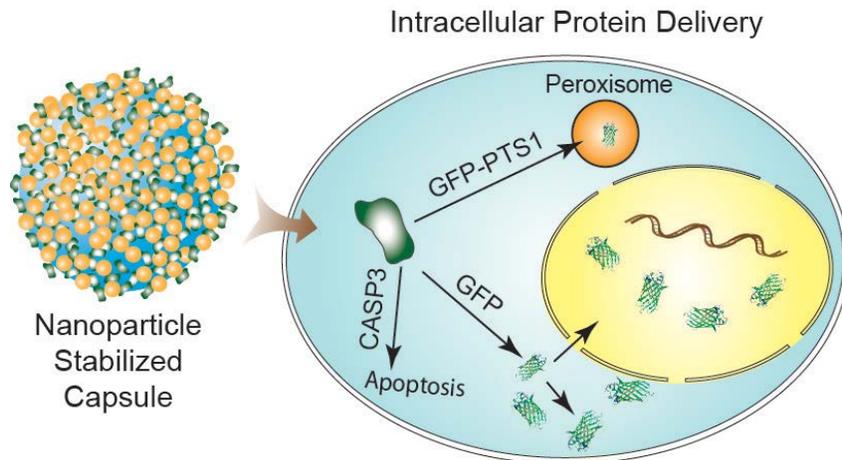
Gold nanorods (NRs) have been attractive for many applications in therapy, delivery, photothermal therapy. We studied the protein coronas that form around gold NRs coated with amphiphilic ligands (ALs). NRs coated with ALs can form large coronas of serum proteins, resulting in aggregates 100s of nm in diameter that contain multiple NRs. These coronas can greatly enhance the carrier properties of NRs because the corona has a much higher capacity for drug payloads such as DNA and small molecules than the NR itself. Furthermore, NR-coronas can be used for triggered delivery by exploiting the optical properties of the gold NR. We describe results in which we utilize the coronas around NRs for triggered release applications and show how we use it to switch on and off blood clotting with light. Laser excitation at the SPR can heat the NR, causing it to melt and disrupt its corona. We loaded two different NRs with thrombin binding aptamers and complementary DNA, and were able to halt and restore the blood clotting cascade by selective excitation of the NRs. In addition, we examined the effect the NR-AL coronas on cellular response. We studied the effect of changing the amphiphilic ligand on the properties of the corona that forms, and how that impacts the cytotoxicity and gene expression. Results also suggest that corona can influence small molecule behavior in cell culture. The cell media supplements penicillin/streptomycin had an effect on cell response in the presence of NR-coronas.

COLL 228

Direct delivery of proteins and nucleic acids to the cytosol using nanoparticle-stabilized capsules

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Therapeutic delivery of proteins and nucleic acids is a difficult goal. Of the many challenges in the delivery process, perhaps the most demanding is providing these biologics with access to the cytosol. Most delivery strategies employ endosomal uptake, requiring endosomal escape for the payload biologics to be effective. In our research, we have developed an alternative strategy that uses nanoparticle-stabilized nanocapsules (NPSCs) to deliver proteins and nucleic acids (siRNA and DNA) directly to the cytosol. These NPSCs use a membrane fusion process to bypass the endosomal pathway, providing highly effective payload delivery. Applications and mechanistic studies of these vehicles will be discussed.



Direct delivery of imaging and therapeutic proteins to the cytosol using NPSCs

COLL 229

In how far can we make nanoparticles mimic molecules?

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The past decades have witnessed remarkable success in the synthesis of inorganic nanoparticles with interesting optical, electronic, or magnetic properties. 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 functionalize nanoparticles by polymers for constructing novel building blocks that can mimic conventional molecules to assemble into hierarchical structures with programmable architectures. In one example, we produced supracolloids with well-defined surface patches by assembling block copolymer-tethered inorganic nanoparticles, and explored the further assembly of such supracolloids into superstructures with a high level of hierarchy. I will also present how the assembly of nanoparticles can benefit the application of nanoparticles in biomedical imaging and delivery.

COLL 230

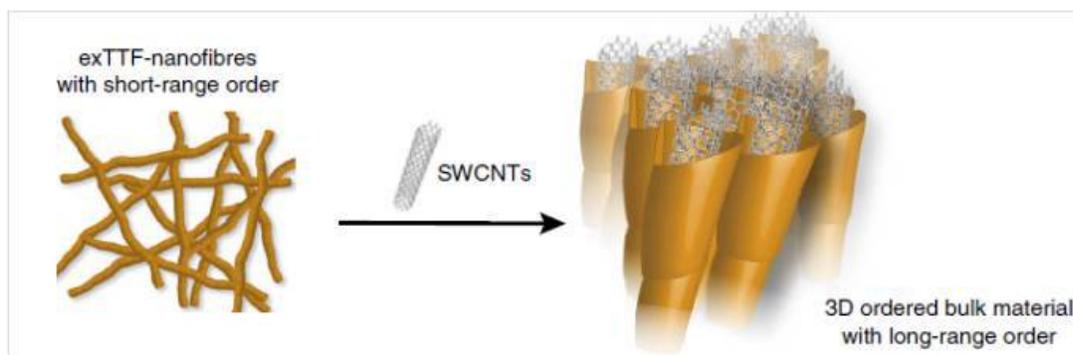
Hierarchical architectures from ordered electroactive small molecules

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Suitably modified 9,10-di(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (exTTF) has been used for the hierarchical growing of 1D p-nanostructures, 2D and 3D p-mesoarchitectures in which the efficient intermolecular p-p interactions between exTTF units ensure delocalization of both positive holes and excited states.^[1] This control has allowed the construction of new ordered p/n-nanohybrids, in which p- and n-nanostructures are organized in segregated domains converting them in suitable candidates for future uses in, for instance, photovoltaic systems.^[2] In this presentation our results on hierarchical molecular organization will be discussed.^[3]

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COLL 231

Modification of microgel surfaces with a self-assembling peptide

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Our group studies soft, colloidal particles, known as microgels, for biotechnology applications including drug delivery, coatings for implants, and tissue engineering scaffolds. Microgels are crosslinked polymer networks, highly solvated with water, ranging in size from 100-1000 nm in diameter. The surface of microgels can be modified through the polymerization of a shell or by adsorbing polymers, as in layer-by-layer deposition. Separately or in conjunction with these techniques direct conjugation of peptides, proteins, or fluorophores can be carried out to further add functionality. Here we demonstrate the modification of microgels with a (RADA)16-I peptide shell, which self-assembles onto the surface of anionic microgels as β -sheet fibrils. The peptide itself serves as a modular component as non-native amino acids can be added to the peptide during synthesis, granting access to a wider array of functional groups for bioconjugation. Modified RADA peptides co-assemble on the particle surface, permitting multiple functionalities to be added simultaneously. We are currently exploring this construct for orthogonal conjugation reactions, and as a modular biosynthetic building block in extracellular matrix mimetics.

COLL 232

Probing the dynamic and structure of nanoparticle protein corona by using single molecule spectroscopy

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The nanoparticle protein corona influences the interaction at the bio-nano interface, which ultimately affects the biological responses of the cells to nanoparticles. The composition of protein corona has been extensively studied, and their compositional change over time has also been reported. It has also suggested that protein unfolding at the nanoparticle interface can occur, but no in situ evidences have yet been reported. It is still not known how the protein absorption kinetics is related to the structural changes of the proteins. The structural changes of the adsorbed proteins could lead to adverse physiological effects because it is known that protein unfolding has a direct link to some neurodegenerative diseases. Thus it is imperative to study the dynamics and the heterogeneity of the protein corona at the level of single proteins. By combined analysis using fluorescence correlation spectroscopy, super resolution spectroscopy and CD spectroscopy, we demonstrate the relationship between the residence time and the probability of protein unfolding at the nanoparticle interface. This study also provides insight into competitive binding dynamics and conformational changes of protein in blood plasma.

COLL 233

Lipid coated gold nanoparticles as models of faceted and highly curved membranes

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Octahedral gold nanoparticles (GNP) provide a stable support for hybrid lipid membranes with defined facets and curvatures, which are useful as biosensors. Here, we synthesized octahedral and spherical GNPs and coated them with L- α -phosphatidylcholine (PC) and a hydrophobic anchor, propanethiol, to form a hybrid lipid membrane. An optimized concentration of PC and propanethiol were used to ensure that the GNPs were fully encapsulated within the membrane. Octahedral and spherical GNPs with similar surface areas required different concentrations of PC and propanethiol to achieve an ion-impermeable membrane as determined by a cyanide stability assay. The lipid coating process was monitored by measuring the localized surface plasmon resonance (LSPR) of the GNPs, which reports on small changes in refractive index near the GNP surface. Octahedral GNPs were found to be more sensitive than spherical GNPs to changes in refractive index. LSPR measurements were also used to obtain binding constants for an α -helical amphipathic peptide to the hybrid lipid membrane coated GNPs.

COLL 234

Role of ligands in the structure and properties of molecular silver nanoparticles and their assemblies

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Very small noble metal nanoparticles are in fact molecules with definite molecular formulae and structures, which have been determined by mass spectrometry and single-crystal x-ray diffraction, respectively. We have found that current models are far too simple to account for the chemical and physical properties of these complex and structurally diverse materials. Contemporary thinking is that molecular structures are determined by the details of the metal core, however we have found that the ligand can play a determinant role. For example, families of molecular silver nanoparticles are produced with aliphatic ligands, such as glutathione, captopril, or cysteine, as demonstrated by gel electrophoresis and mass spectrometry. In contrast, phenyl-containing ligands have been found to produce only a 44-atom Ag nanoparticle that is extremely stable and that is not observed with aliphatic ligands. The unprecedented stability of this nanoparticle resulted in (i) a truly single-sized molecular product, (ii) ~140 g of pure product from a single batch, and (iii) an opportunity to crystallize the nanoparticle and understand its protective ligand shell, atomic and electronic structure, and thereby its stability. Notably, this has provided key insights into the stability of silver nanoparticles, which has been a major obstacle. Further, the nanoparticle molecular crystal has a framework structure that is predicted to have very unusual mechanical

properties, with both structure and response being controlled by the ligands. From these results it is evident that ligands can have a very significant effect on the materials synthesized and in fact, with judicious choices, they be used as multiscale structure-directing synthons.

COLL 235

Theranostic gold nanorods for synergistic cancer treatment

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Gold nanomaterials have demonstrated their applications in cancer research due to established protocols for surface functionalization, optical properties and biocompatibility. We have developed a multifunctional gold nanorod (AuNR) complex for cancer cell imaging, drug delivery, photothermal therapy. This AuNR-based complex exploits the light-scattering properties of gold for dark-field imaging of cancer cells and the synergistic effects of ultraviolet (UV) light-triggered drug release and infrared (IR) light-induced hyperthermia causing cancer cell apoptosis. The AuNRs were functionalized with (2-hydroxypropyl)- β -cyclodextrin (CD-AuNR) to afford loading of doxorubicin (DOX) at the hydrophobic core of the CD. UV-active dextran-phenyl-azo-benzoate (DexAzo) was used to coat the CD-AuNR while folic acid-terminated ligand (FA) was incorporated as cancer cell targeting moiety. Intracellular delivery and DOX release was demonstrated by incubation of the DOX-loaded AuNR complex with HeLa cells followed by UV treatment, which resulted in less than 30% cell viability after 24 h. Photothermal therapy was demonstrated by IR treatment of HeLa cells with red laser at 800 nm at 5 W/cm² resulting in cell death as shown by trypan blue staining. Furthermore, the synergistic effects of UV and IR treatments using multifunctional AuNR complex in cancer cells were exhibited using live/dead cell assay. This AuNR-based complex offers a combined diagnostic and therapeutic tool for cancer treatment.

COLL 236

Determining drug efficacy using plasmonically enhanced imaging of the morphological changes of cells upon death

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We have recently utilized the optical properties of gold nanoparticles (AuNPs) for plasmonically enhanced Rayleigh scattering imaging spectroscopy (PERSIS), a new technique that enabled the direct observation of nanoparticle localization by monitoring the intensity and energy of light scattered by the AuNPs.¹ We now use PERSIS to compare the relative efficacy of three chemotherapeutic drugs on human oral squamous carcinoma cells by using AuNPs as light-scattering probes. Although the drugs induced

apoptotic cell death through differing mechanisms, morphological changes including cell membrane blebbing and shrinkage, accompanied by an increase in white light scattering, were visually evident. By utilizing the AuNPs to increase the cells' inherent Rayleigh scattering, we have obtained the time profile of cell death from the anticancer drugs using a single sample of cells in real time, using inexpensive equipment available in any lab. From these time profiles, we calculated cell death enhancement factors to compare the relative efficacies of the different drugs using our technique, which corresponded to those calculated from the commonly used XTT cell viability assay. Although this technique does not impart molecular insights into cell death, the ability to quantitatively correlate cell death to morphological changes suggests the potential use of this technique for the rapid screening of drug analogues to determine the most effective structure against a particular disease or cell line.²

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COLL 237

Functional DNA nanotechnology and its applications in environmental sensing and live cell imaging

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Recent progress in nanoscale science and technology has resulted in a number of nanomaterials with interesting optical, electrical, magnetic properties that can be ideal choices for signal transductions for analytical chemistry. However, most of these materials lack selectivity required for detection. Functional DNA, a new class of DNA with functions similar to either antibody (known as aptamers) or enzymes (called DNazymes) can provide high selectivity for a wide range of molecules, including small molecules such as metal ions and small organic molecules that antibodies do not bind with high selectivity. We have been able to use a combinatorial method called *in vitro* selection to obtain functional DNAs that can bind targets of choice strongly and specifically, and used negative selection strategy to improve the selectivity. By labeling the resulting functional DNA with gold nanoparticles, quantum dots, and supermagnetic iron oxide nanoparticles, we have developed new classes of colorimetric and fluorescent sensors, and smart MRI contrast agents for metal ions, organic and biomolecules.¹ A novel approach of using an inactive variant of functional DNA to tune the detection range of the sensors is also demonstrated. For even more straightforward field applications, these sensors have been converted into simple “dipstick” tests for qualitative detection. Recently, we have applied the method to functionalize lanthanide-doped upconversion nanoparticles for sensing and imaging applications.² Some of these functional DNA have been delivered into cells for imaging metal ions and other

molecules in living cells.³ These and other recent results will be presented.

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COLL 238

Role of the protein corona in mediating nanoparticle targeting

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Nanotechnology involves the engineering of structures, materials, and particle in the size range of 1 to 100 nm. These nanostructures have unique biological, optical, electronic and magnetic properties that are in direct to their size, shape, and surface chemistry. As a result of these properties, nanotechnology is currently exploited in medicine for diagnosing and treating diseases. In this presentation, the properties of nanomaterials and challenges associated with using them for cancer targeting will be discussed. Specifically, the discussion will focus on how biological fluids and serum proteins influence the morphology, surface chemistry, and targeting ability of the nanoparticles in cells outside and inside the body.

COLL 239

Prolonged hot electron dynamics in plasmonic-metal/semiconductor heterostructures with implications for solar photocatalysis

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Ideal solar-to-fuel photocatalysts must effectively harvest sunlight to generate significant quantities of long-lived charge carriers necessary for chemical reactions. Here we demonstrate the merits of augmenting traditional photoelectrochemical cells with plasmonic nanoparticles to satisfy these daunting photocatalytic requirements. Electrochemical techniques were employed to elucidate the mechanics of plasmon-mediated electron transfer within Au/TiO₂ heterostructures under visible-light (>515 nm) irradiation in solution. Significantly, we discovered that these transferred electrons displayed excited-state lifetimes two orders of magnitude longer than those of electrons photogenerated directly within TiO₂ via UV excitation. These long-lived

electrons further enable visible-light-driven H₂ evolution from water, heralding a new photocatalytic paradigm for solar energy conversion.

COLL 240

Enhanced light-matter interactions in nanoparticle arrays

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Metal nanostructures concentrate optical fields into highly confined, nanoscale volumes that can be exploited in a wide range of applications. This talk will describe new ways to design arrays of strongly coupled nanoparticles that can exhibit extraordinary properties and unconventional but powerful energy conversion pathways such as plasmon lasing. We will describe an unconventional nanocavity based on arrays of metal nanoparticles. These structures support lattice plasmon modes that can be amplified and that can result in room-temperature lasing with directional beam emission. We will discuss detailed modeling to understand the near-field coupling responsible for these amplified light-matter interactions.

COLL 241

Renal clearable metal nanoparticles for cancer imaging

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While metal nanoparticles with size-dependent material properties open up unprecedented opportunities for novel biomedical technologies, translation of these nanoparticles into clinical practices has been hampered by the potential toxicity resulted from their long-term nonspecific accumulation in healthy tissues. Emergence of renal clearable metal nanoparticles makes it possible to address this long-term challenge. In this talk, I will discuss how to use glutathione, a tri-amino-acid peptide to stable 2~3nm gold nanoparticles, which can give different colored luminescence upon their valence states of gold atoms. These glutathione coated gold nanoparticles (GS-AuNPs) have little interactions with serum proteins; and more impressively, they can be cleared from the body through kidneys with an efficiency of 10~100 times better than the same sized AuNPs and exhibit unique molecular-like pharmacokinetics. More recently, we found that they can passively target the MCF-7 breast cancer through enhanced permeability and retention (EPR) effect, which can be further enhanced through PEGylation. Finally, some material-chemistry challenges in the development of renal clearable metal nanoparticles are also discussed.

COLL 242

Functional reconstitution of integral membrane proteins in giant lipid vesicles by hydrogel swelling

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While giant unilamellar lipid vesicles (GUVs) are powerful tools for studying the properties of the cell membrane in a well-controlled experimental environment, their application to research in membrane protein biophysics has been limited by the challenges of reconstituting membrane proteins in GUVs. Traditional methods involving detergent exchange are time-consuming, low-yield, and require relatively large ($\sim\mu\text{mole}$) quantities of protein. We have recently developed a method for protein reconstitution into GUVs based on swelling a lipid film from the surface of a protein-loaded hydrogel. This method is rapid, producing large quantities of proteo-GUVs in less than twenty minutes. It requires only picomole quantities of protein, and all proteins so far investigated are functional upon reconstitution.

We have reconstituted detergent-solubilized preparations of spinach aquaporin SoPIP₂;1, bacterial aquaporin-Z, and bacteriorhodopsin in GUVs by adding these proteins to molten low-melting-temperature agarose such that the final mixture is below the critical micellar concentration (CMC) of the solubilizing detergent. The agarose was spread as a thin film on the surface of a glass coverslip, gelled, and partially dried before a lipid solution in chloroform was deposited on the surface and air-dried. Upon addition of buffer to the system, a close-packed layer of lipid bilayer-bounded compartments swelled from the surface of the hydrogel. Fluorescently labeled integral membrane proteins were colocalized with the bilayers. Individual GUVs could be separated from the film surface by pipetting. Detailed studies of SoPIP₂;1 in these GUVs showed that it was functional and that it co-segregated with the liquid disordered phase in phase-separating membrane compositions.

Membrane proteins can also be reconstituted directly from crude membrane fragments prepared from transformed cell lines. The protocol proceeded as for detergent-solubilized proteins, with membrane fragments dissolved in the agarose hydrogel prior to swelling the lipid film. This technique has been used for the functional reconstitution of G protein-coupled receptors, including the human serotonin receptor 5-HT_{1A} and human dopamine receptor D₂. Fluorescence microscopy of phase-separating GUVs with 5-HT_{1A} shows that this protein co-segregates with the liquid disordered phase rather than the liquid ordered phase, as some previous detergent-resistant membrane fraction studies had reported.

COLL 243

Membrane shape instabilities induced by BAR domain proteins

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Membrane curvature has developed into a forefront of membrane biophysics. Numerous proteins involved in membrane curvature sensing and membrane curvature generation have recently been discovered, including proteins containing the crescent-shaped BAR domain as membrane binding and shaping module. Accordingly, the structure of these proteins and their multimeric complexes is increasingly well-understood.

Substantially less understood, however, are thermodynamic and kinetic aspects and the detailed mechanisms of how these proteins interact with membranes in a curvature-dependent manner. New experimental approaches need to be combined with established techniques to be able to fill in these missing details. Here we use model membrane systems in combination with a variety of biophysical techniques to characterize mechanistic aspects of BAR domain protein function. This includes a characterization of membrane curvature sensing and membrane generation. We also establish kinetic and thermodynamic aspects of BAR protein dimerization in solution, and investigate kinetic aspects of membrane binding. We present two new approaches to investigate membrane shape instabilities and demonstrate that membrane shape instabilities can be controlled by protein binding and lateral membrane tension. Our findings are relevant to the mechanistic understanding of membrane trafficking phenomena, including endocytosis.

COLL 244

Nanoparticle-induced pore formation in lipid bilayers

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A number of studies have found that nanoparticles are able to disrupt biological membranes through lipid aggregation on nanoparticle surfaces or by creating pores in the membrane. Using artificial lipid bilayers as model membranes, we have electrically studied the ability of polymer, carbonaceous, metal, and metal oxide nanoparticles to disrupt and form pores in artificial lipid bilayers. We have made preliminary observations of pores formed by different particles with different conductance magnitude and kinetic properties, potentially indicating different pore morphologies and formation mechanisms. Using our bilayer array platform (Lu, *Biotechnology Journal* 9, 446-451 (2014)), we have also examined the pore conductance in over 1000 lipid bilayers while varying particle type, applied voltage, lipid composition, membrane charge, and solution ionic strength. I will report on these results as well as our current work with additional conditions and particle types.

COLL 245

Nanolipoprotein particles entrapped within nanoporous silica gel

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Entrapment of integral membrane proteins (IMPs) in transparent, nanoporous silica gels has proven to be a challenge, as current and previous techniques utilize liposomes as biological membrane hosts. The instability of liposomes in nanoporous gels is attributed to their size (~100 nm) and altered structure and lipid dynamics upon entrapment within the nanometer scale pores (5-50 nm) of silica gel. This ultimately results in disruption of protein activity. We intend to overcome these barriers by using nanolipoprotein particles (NLPs) as biomembrane hosts. NLPs are discoidal patches of lipid bilayer that are belted by amphiphilic scaffold proteins and have an average thickness of 5 nm, with diameters ranging from 10-15 nm. The IMP-NLP complexes are synthesized in a cell-free environment, which circumvents traditional protein reconstitution in membranes. Bacteriorhodopsin - a robust IMP that indicates its proper conformation via distinct purple coloration – will serve as a model IMP for this system. To ensure proper functioning of the system, we have investigated the phase behavior of the lipids and the secondary structure and environmental polarity of the scaffold proteins in gel-entrapped NLPs. In addition, we will present preliminary data on the physical and spectral properties of entrapped and non-entrapped bacteriorhodopsin-NLPs.

COLL 246

Multiple faces of cholesterol in membrane fusion

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Cholesterol modulates membrane structure in multiple ways. Depending on circumstances it orders or disorders lipid bilayers. It induces phase separations in multi-component lipid mixtures and partitions selectively between different coexisting lipid phases. It changes membrane curvature and it alters membrane tension. It alters the lateral distribution and diffusion of membrane proteins and changes the structure of water at the membrane interface. But, which of these properties are important for membrane fusion? – In this talk, I will review recent experiments that elucidate the multiple roles that cholesterol plays in HIV gp41-mediated and SNARE-mediated membrane fusion.

COLL 247

Designing biotinylated lipids for selective partitioning to liquid ordered phase

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Designing lipids to partition into specific membrane domains (e.g., lipid rafts) could provide routes towards labeling and characterizing assemblies involved with pathogen entry, signaling, and trafficking in cells. Commercially available lipids provide an array of functionality to label membranes but their partitioning behavior to ordered (Lo), the membrane phase associated with lipid rafts, or disordered (Ld) phases do not follow defined rules based on their molecular structure. We present work that lends insight into designing functionalized lipids for selective partitioning to the Lo phase. For this study, we focused on biotinylated lipids, which are useful for attaching ligands (e.g., antibodies) to the membrane surface. It is known that biotinylation of DPPE directly on the headgroup or with a caproyl spacer generate lipids that partition strongly towards the Ld phase, whereas using PEG2000 as the spacer enables partitioning to the Lo phase. However, because of PEG2000's considerable steric bulk and potentially unfavorable effects on membrane structure/stability we prepared and examined a series of shorter PEG spacers to determine if an optimal spacer length exists for Lo partitioning. Using FITC labeled streptavidin we found that as the length of the ethylene glycol chain increased from trimer to decamer selectivity of the lipids for the Lo phase improved reaching partitioning coefficients that exceeded DPPE-PEG2000-biotin by several fold.

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COLL 248

Photoinduced dynamics at metallic and semiconducting nanoparticles: time-domain ab initio studies

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Photo-catalysis with plasmonic and excitonic nanoparticles involves ultrafast non-equilibrium processes that require time-domain modeling, preferably at the atomistic level. The talk will describe the simulation methodology we have been developing for this purpose by combining time-domain density functional theory with nonadiabatic molecular dynamics. The application of the approach will focus on our recent studies of metallic and semiconducting nanocrystals involving a variety of competing processes: charge and energy transfer, elastic and inelastic electron-phonon scattering, and Auger-type processes. The emphasis will be placed on the chemical aspects of the photoinduced dynamics, including the role of adsorbants, defects, dopants and unsaturated chemical bonds.

COLL 249

Plasmons, hot electrons, and artificial photosynthesis

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Surface plasmons – collective conduction electron excitations in nanostructured metals and other good conductors – live for a few femtoseconds. On dephasing, they produce a shower of energetic electrons and holes that equilibrate adiabatically over 10-100 femtoseconds to form a Fermi distribution with electron temperatures of several thousand K. Most of the energy of this hot electron gas is subsequently thermalized over a few picoseconds primarily through electron-phonon interactions. By fabricating appropriately nanostructured devices a fraction of these hot carriers can be harvested before they thermalize, and used to carry out light-enabled redox chemistry. To do this efficiently one needs to design and construct materials and systems with appropriate dielectric properties, interfacial architectures and catalytic properties. Although the challenges that need to be overcome are many, remarkable progress has recently been achieved by multiple research labs across the globe in using plasmons in applications that were previously the sole purview of semiconductors. Our focus has been artificial photosynthesis, some examples of which will be presented.

COLL 250

Ligand effects on the aqueous plasmonic catalysis by alloyed gold-copper nanorods

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Alloyed materials are particularly appealing candidates for new aqueous catalysts because of the synergistic effects that arise from being alloys. Noble metals are particularly appealing because the localized surface plasmon resonance (LSPR) of these particles can be tuned in the visible and near infrared region of the spectrum. Organic phase synthesis has demonstrated extraordinary versatility in the generation of highly uniform, morphologically-controlled metal nanoparticles, but a phase transfer is necessary to produce aqueous catalysts. As such, metal nanoparticles were synthesized via alkylamine reduction and transferred to aqueous phase via ligand exchange. A variety of ligands and anchoring groups were used to generate distinct samples. The ligand's effects on the nanorods' catalytic activity and stability were investigated using gold-catalyzed and copper-catalyzed model reactions in the absence of irradiation. Photocatalysis by irradiation of these particles at their LSPR was also demonstrated using the same model reactions. The underlying mechanisms were further investigated.

COLL 251

Surprisingly efficient plasmon-induced hot electron transfer and photochemistry in semiconductor-Au nanoheterostructures

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Surface plasmon resonance in metal nanostructures has long been a subject of intense research interests. Plasmonic nanostructures have been used to enhance the efficiency of semiconductors and/or molecular chromophore based solar energy conversion devices by increasing the absorption or energy transfer rate through the enhanced local field strength. In more recent years, it has been shown that excitation of plasmons in metal nanostructures can lead to the injection of hot electrons into semiconductors and enhanced photochemistry. This novel plasmon-exciton interaction mechanism suggests that plasmonic nanostructures can potentially function as a new class of widely tunable and robust light harvesting materials for photo-detection or solar energy conversion. However, plasmon-induced hot electron injections from metal to semiconductor or molecules are still inefficient because of the competing ultrafast hot electron relaxation (via ultrafast electron-electron and electron-phonon scattering) processes within the metallic domain.

In this paper we discuss a recent study on the plasmon-exciton interaction mechanisms in colloidal quantum-confined epitaxially-grown semiconductor-gold plexcitonic nanorod heterostructures. Using transient absorption spectroscopy, we show that optical excitation of plasmons in the Au tip leads to surprisingly efficient hot electron injection into the semiconductor nanorod. In the presence of sacrificial electron donors, this plasmon induced hot electron transfer process can be utilized to drive photoreduction reactions under continuous illumination. Ongoing studies are examining the mechanism of such efficient plasmon-induced hot electron transfer processes and approaches for improving the plasmon induced hot electron injection efficiency through controlling the size and shape of the plasmonic and excitonic domains.

COLL 252

Characteristics of reaction intermediates at plasmon-induced water oxidation processes

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Excitation of localized surface plasmon resonance (LSPR) at Au metal nanoparticle on TiO₂ enable efficient water oxidation even under near-infrared light illumination. In this work, we observed plasmon-induced water oxidation process using in-situ surface enhanced Raman scattering (SERS) measurement. Size-controlled Au nanodimer arrays was fabricated on titanium dioxide single crystalline by angle-resolved nanosphere lithography. The Au - O stretching vibrations of Au oxide was observed from the intermediate of water oxidation. The formation of the intermediate at relatively negative potential is attributed to the water oxidation process via holes generated by

LSPR. We concluded that different mechanisms exist for water oxidation on plasmonic electrode, compared with that at bulk Au electrode.

COLL 253

Surface-enhanced spectroscopies by rational nanoantenna design

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Advances in our understanding of nanoantennas is enabling us to develop new substrates for surface-enhanced spectroscopies that extend beyond SERS to other modalities. Surface-enhanced coherent anti-Stokes Raman spectroscopy (SECARS) and surface-enhanced infrared absorption spectroscopy (SEIRA) each have their own specific requirements for detecting specific chemical moieties. We exploit coherent effects in coupled plasmonic clusters to enhance SECARS to achieve single-molecule sensitivity. For SEIRA, where lightning rod effects provide enhancement in the mid-IR region of the spectrum, we examine how to achieve few-molecule sensitivity using design strategies adopted partially from SERS nanoantenna design development, adapted to this region of the spectrum.

COLL 254

Synthesis of hybrid dumbbells with combined compositional and interfacial asymmetries

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Colloidal dumbbells with compositional asymmetries can possess distinct physical properties between two lobes such as the refractive index, electrical polarizability, or photoactivity. They have great potentials in self assembly, autonomous micro-robots, targeted drug delivery, and colloidal emulsifiers. However, it is challenging to synthesize them with well-controlled size, morphology, and compositions. Previous efforts mainly focused on making particles that are made of two different types of polymers. Although they possess some degree of compositional asymmetry, the particles overall are still polymeric. In this talk, we describe a versatile approach to synthesize organic-inorganic hybrid dimers whose chemical compositions (hence the bulk physical properties) are different. We swell the polystyrene seeds with a liquid silicon alkoxide precursor - tetraethyl orthosilicate (TEOS). Because of their immiscibility, a second lobe primarily composed of TEOS can be grown on the seeds. Although it is a liquid, TEOS can undergo sol-gel type hydrolysis and condensation to form solid silica in the presence of a weak base catalyst such as dodecylamine. Analyses based on the scanning electron microscopy, the fluorescent microscopy, and the energy-dispersive X-ray spectroscopy (EDX) confirm both monodisperse morphology and distinctive compositional asymmetry on our particles. Intriguingly, the particle morphology can be conveniently tuned by the

adjusting the concentration of base, the amount of TEOS, and the crosslinking density of the seeds. Because the surfaces of polystyrene and silica are very different, we can modify each lobe independently based on the well-established silane and polymer chemistries. Therefore, both interfacial and compositional asymmetries can be present simultaneously on these dimers, which further enable us to study the synergic effects of both asymmetries on particle propulsion and emulsifying properties of the hybrid dumbbells.

COLL 255

Synthesis and characterization of chemically and physically bonded Janus particles

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Structures with non-centrosymmetric distributions such as Janus particles have been shown to have interesting properties. The anisotropic nature of such particles modifies their properties at the micro and the macro scale. Bulk properties of suspensions of these materials are studied to gain insight as to how the bonding configuration of the surface modification can affect the macro-scale properties of interest (e.g., surface tension, boiling point, etc).

Silica particles of various sizes are synthesized using the conventional Stober and Fink method [1]. Subsequently, the silica particles are modified using two distinct surface modification methods for gold, namely Physical Vapor Deposition (PVD) and Direct Chemical Functionalization (DCF). The two methods result in Janus particles with two different metal-particle configurations. Although the two modifications use different routes, the shape and size of the particles is maintained nearly spherical for both sets of particles.

We will present data on the behavior of these particles at the air-water interface and contrast their behavior with that of silica particles without any modification. Further, we will report on the interfacial behavior of these particles modelled with the SE-FIT surface evolver fluid interfacial tool. The results show that the structure of the two Janus particles has a significant effect on the experimentally observed properties of the fluid. One structure shows strong surfactant properties in suspension tests, whereas the other shows no significant effect.

[1] W. Stöber, A. Fink, and E. Bohn, "Controlled growth of monodisperse silica spheres in the micron size range," *J. Colloid Interface Sci.*, vol. 26, no. 1, pp. 62–69, 1968.

COLL 256

Salt-induced detachment of non-touching colloidal particles from oil-water interfaces

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Solid particles at liquid interfaces provide interesting opportunities for the stabilization of liquid-liquid interfaces, for self-assembly on liquid interfaces, for the formation of colloidosomes and for studies on the 2D phase behavior. All these systems have in common that the particles are wetted both by oil and water, by penetrating the interface. Here, addition of salt to one of the phases can result into 2D (in plane) melting of a colloidal solid. In this presentation, we will discuss a surprising, new result: our particles could be detached from the interface by addition of salt only. This indicates that the micron-sized particles are not irreversibly trapped at the interface and suggests that particles are non-touching, meaning that they are completely immersed in the oil phase. In principle, the entrapment of non-touching colloids near an oil-water interface could be theoretically explained by a balance between image charge attractions [1,2] and Van der Waals repulsions [3]. In this presentation, we will discuss these new experimental findings and the salt-effects.

[1] Leunissen et al., PNAS (2007).

[2] Zwanikken et al., Phys. Rev. Lett. (2007).

[3] Oettel, Phys. Rev. E (2007).

COLL 257

Direct view of the nanobio interface

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Interfacial charge densities and potentials are determined for silica-supported phospholipid bilayers formed from lipids having zwitterionic, negatively charged, and positively charged headgroups. Quartz crystal microbalance with dissipation monitoring, fluorescence recovery after photobleaching, and atomic force microscopy demonstrate the presence of well-formed supported lipid bilayers, which, as probed by vibrational sum frequency generation, undergo negligible structural changes along their alkyl chains when NaCl concentration is raised from 0.001 to 0.1 M. Second harmonic generation measurements indicate each zwitterionic headgroup of the bilayer formed from pure DOPC is associated with an apparent charge corresponding to 1.8 ± 0.5 % of an elementary negative charge. Supported lipid bilayers interact with positively and negatively charged 4-nm diameter gold metal nanoparticles. Charge-charge repulsion is likely overcome by multivalent interactions that are estimated to involve three to five hydrogen-bond equivalents, or, alternatively, van der Waals interactions between, for instance, 30 to 35 methylene groups of the bilayer lipids and the particle ligands. SHG charge screening experiments are consistent with a charge density ranging between -0.06 and +0.02 C/m² when positively charged gold nanoparticles attach to a supported lipid bilayer, and -0.05 and -0.01 C/m² when negatively charged gold nanoparticles attach to the same bilayer, which includes the interfacial charge density of the bilayer of

-0.015 ± 0.007 C/m² that we estimate from our experimental data. The positively charged PAH-coated particles were shown by QCM-D to be present at surface coverages of roughly 1 × 10¹¹ particles attached per cm², from which the total charge density per attached PAH-coated particle. The surface coverage of the MPA-coated particles was too small to be detected by QCM-D and XPS while AFM and ToF-SIMS clearly show their presence. SHG adsorption isotherm measurements on this system result in apparent free binding energies of approximately -80 kJ/mol, and the attachment energetics appear to be invariant with salt concentration over the conditions surveyed. The importance of considering not just the surface charge but all charges within the hydrodynamic volume of attached particles is discussed. The quantitative thermodynamic, spectroscopic, and electrostatic data presented here serve to benchmark experimental and computational studies of the nano-bio interface.

COLL 258

Carbon dioxide-in-water foams stabilized with interfacially active nanoparticles and surfactants

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Whereas surfactants have been utilized to stabilize CO₂-in-water (C/W) foams, only recently have they been combined with nanoparticle amphiphiles to offer improved foam viscosity and stability. Highly viscous C/W foams are of interest in a variety of applications including enhanced oil recovery (EOR) and hydraulic fracturing. In this work, nanoparticles were added to surfactants to increase the foam stability, given the essentially irreversible adsorption of the nanoparticles at the CO₂-water interface. The role of nanoparticles and surfactants in formation and stabilization of viscous foams was investigated in a porous beadpack using a mixture of surface-modified silica nanoparticles with zwitterionic or anionic surfactants. Surfactant structure and formulation variables including temperature, pressure, and salinity were varied to quantify their effect on foam properties. Interfacial properties were measured to design and interpret foam formation and stabilization mechanisms. In some cases, strong synergy was observed where the mixture of nanoparticles and surfactant produced significantly more viscous and stable foams than either nanoparticles or surfactant alone. CO₂-in-water foams with viscosities of over 100 cP in a 1.2 darcy beadpack were generated, more than double the values when only surfactant was present. The nanoparticles alone stabilized weak or no foam. The surfactant lowers the CO₂/water interfacial tension to facilitate the formation of CO₂-in-water foams composed of small CO₂ bubbles (<100 micron diameter), while the adsorption of nanoparticles at the oil/water interface enhances emulsion stability by providing a large barrier to droplet coalescence and contributing to the disjoining pressure to slow film drainage. Weak interactions between silica nanoparticles and surfactant minimizes competition for surfactant molecules by nanoparticle surfaces and the CO₂/water interface.

COLL 259

Studying the molecular orientation and behavior of ionic liquid films at solid-liquid interface

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Ionic liquids (ILs) exhibit low vapor pressure, high thermal stability and electrical conductivity. They are of interest for applications in electrochemistry, catalysis, lubrication and other areas. The orientation and behavior of ILs at the solid surface governs their macroscopic properties and is therefore critical in assessing their viability for the aforementioned applications. Our work investigates the solid-IL interface using a dynamic wetting technique to create thin films of imidazolium based ILs on reflective silver substrates. Contact angle, ellipsometry and reflection infrared measurements were performed to study the wettability, thickness, structure, and of the IL films respectively. We found that the IL film matures over time, evidenced by shifting profiles of anion peaks in infrared spectra. Interestingly, the cation peak frequencies remain constant. As many IL application environments will inherently have appreciable levels of moisture, a parallel study was carried out for IL films in the presence of water. Major effects on film behavior as a function of water concentration are discussed.

COLL 260

Interactions and ordering of soft microgels at oil-water interfaces

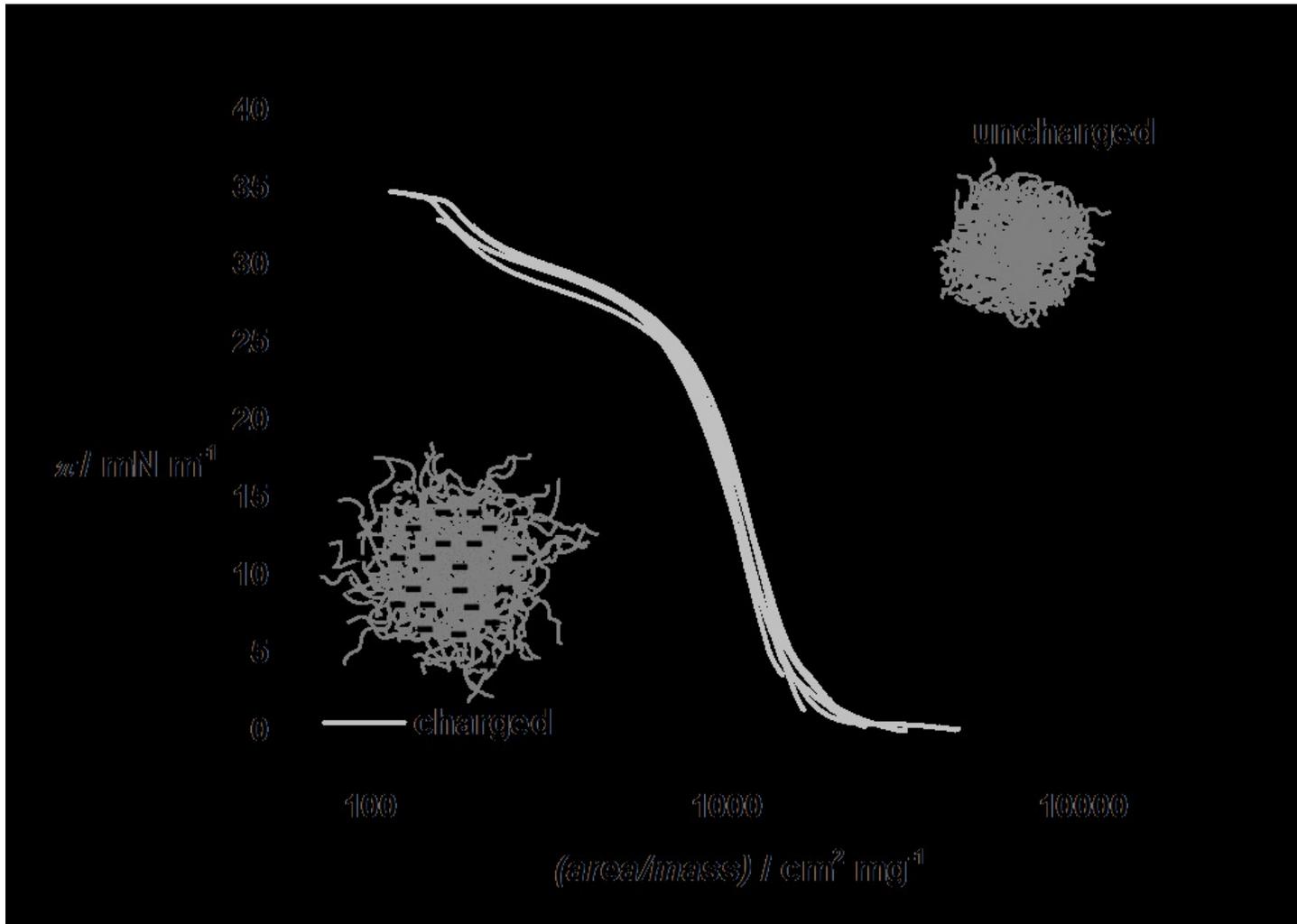
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Monolayers of soft microgels attract increasing attention due to their potential in the fabrication of tailored and responsive assemblies. Due to the fact that microgels are soft, deformable and partially penetrable makes them characteristically different from rigid colloidal particles.

The interaction of pH-sensitive Poly (N-isopropylacrylamide-co-methacrylic acid) microgels at oil water interfaces was investigated by means of compression isotherms in a Langmuir trough. Master curves were obtained at different pH-values. Surprisingly the microgels are easier to compress when they are in the charged as compared to the uncharged state. Thus the microgel-microgel interaction is not governed by direct Coulomb repulsion. This demonstrates the distinct differences of soft microgels as compared to rigid colloids.

The formation of ordered microgel structures on solid substrates is also of great interest. While the arrangement at the solid surface cannot be easily controlled after adsorption and self-assembly from the bulk phase, specific structures can be achieved by compressing a fluid interfacial microgel monolayer spread in a Langmuir trough and by transferring it onto substrates at distinct compression states. The degree of ordering

after compression surpasses the one that is reached after self-assembly from the bulk and is, in general, independent from the presence of charges and different microgel morphologies. As a consequence, by monitoring the surface pressure during compression it is possible to produce highly ordered microgel arrays where the interparticle distance can be systematically and externally controlled.



COLL 261

Synthesis of monodisperse, colloidal microcapsules, and their use in controlled encapsulation and release studies

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Monodisperse emulsion droplets are useful for many applications, for example in food science, cosmetics, microreaction technology and as delivery vehicles in pharmacy. In addition, such monodisperse droplets are ideal sacrificial particles for the synthesis of microcapsules based on a templating technique. However, a combination of bulk scale synthesis and monodispersity is scarce when working with emulsions. Conventional methods typically result in polydisperse systems whereas the production rate is too low for the monodisperse droplets formed with microfluidics. Here we describe the bulk scale synthesis of monodisperse polydimethylsiloxane (PDMS) droplets above 3 μm and their encapsulation in elastic, permeable shells. This is an extension of the synthesis method that was already developed in our group [1]. In addition, we show that these shells can be used in controlled release and encapsulation studies when working with various types of materials, including oils, fluorescent molecules and liquid surfactants. The amount of released oil can be highly tuned by adjusting the concentration of surfactant micelles that dissolve the oil, which also dictates the depth of the remaining, buckled microbowl. Release of liquid surfactant from the shells is found to occur spontaneously near the oil-water interface, which is most likely driven by the preferred partitioning of the released material in the oil.

[1] Carmen Zoldesi, Arnout Imhof, *Advanced Materials* (2005)

COLL 262

Nanoparticle induced charge redistribution of the air-water interface and its role in regulating nanoparticle spatial distributions

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The most abundant liquid interface on earth, that of air and water, is believed to carry a negative potential that is non-trivial to invert through changes in pH, electrolyte, or electrolyte strength. Here, through a combined experimental and theoretical study, we show that the close approach of a negatively charged nanoparticle induces a charge redistribution of the air-water interface. Using different electrolytes to control the interfacial potential of the nanoparticles, in situ X-ray photoelectron spectroscopy results establish that nanoparticles with a more negative zeta potential adsorb closer to the air-water interface than do the same particles with less negative zeta potential. The attractive force between two (nominally) negative surfaces is caused solely because of a charge redistribution of the air-water interface under the strong electric field of the nanoparticle. This induced positive charge density will subsequently influence, and could be used to control reactivity, stability and nanoparticle self-assembly at air-water interfaces. These insights will create new opportunities for applications in chemistry, nanotechnology, and nanomedicine.

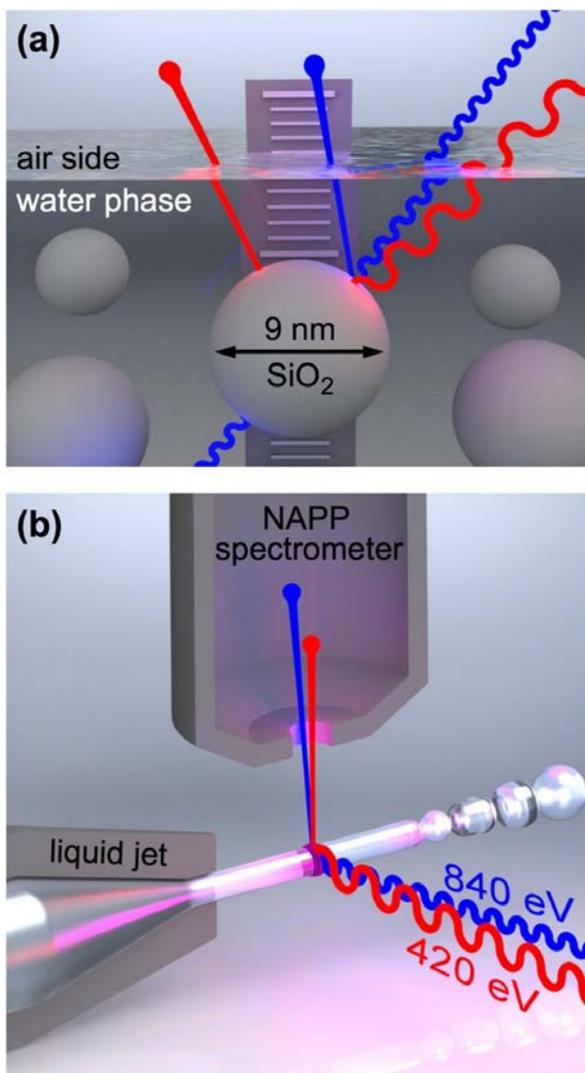


Figure 1. Experimental setup for XPS measurements from a liquid microjet of colloidal silica. **a**, The spatial distributions of nanoparticles at the air-water interface as a function of electrolyte are determined using X-ray photoelectron spectroscopy. **b**, Colloidal suspensions are injected into the vacuum measurement chamber using a fused quartz nozzle of 32 μm diameter. The photon energy of the synchrotron beam is set at 420 eV to ionize the Si 2p orbital. Second order radiation, 840 eV, is used to simultaneously measure O 1s photoemission. Measuring the Si 2p and O 1s orbitals within 10 eV pKE ensures a constant probe depth of the experiment.

COLL 263

Inverted pendant drop set-up for X-ray absorption spectroscopy of electrolyte solutions and their surfaces

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X-ray absorption spectroscopy is an invaluable tool in probing co-ordination environment of targeted elements in all forms of matter. Due to low penetration depths of few nanometers for electrons compared to hundreds of microns for X-ray photons, X-ray absorption measurements done by measuring total electron yield (TEY) and X-ray fluorescence (XRF) together can provide both interfacial and bulk co-ordination environments. We report on a simple and inexpensive set-up for collecting simultaneously TEY and XRF signals from an inverted pendant drop of electrolyte solutions. The set-up is tested with an aqueous solution of rare-earth element-europium. The X-ray absorption near edge structure (XANES) and the extended X-ray absorption fine structure (EXAFS) data obtained from the solution show remarkable differences in their TEY and XRF signals. The differences directly indicate variations in Eu^{3+} coordination environments near air-water interfaces compared to the bulk solutions. Simultaneous surface and bulk sensitivities, low volume requirements (less than 1 ml) of solutions, straight forward and quick alignment procedures of the set-up make it attractive and distinct from conventional way of collecting X-ray absorption measurements from solutions. This work and the use of the Advanced Photon Source, a U. S. Department of Energy (DOE) Office of Science User Facility at Argonne National Laboratory, is based upon work supported by the U. S. DOE, Office of Science, Office of Basic Energy Science, Division of Chemical Sciences, Biosciences and Geosciences, under contract No DE-AC02-06CH11357.

COLL 264

Plasmonic gold nanoparticles in the cancer cell: Following cell cycle, cell death, drug delivery dynamics and efficacy

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Conjugating small concentrations of gold nanoparticles to the nucleus membrane of the cancer cells we were able to record its SERS and/or its Rayleigh scattering images in the different phases of its full cycle (Ben Kang, Lauren Austen) , or as it dies if given cancer drugs(Austin and Kang), and enabled us to follow the dynamics of drug delivery (Kang, Marwa Ahmed and Austin) and measure the relative efficacy of different cancer drugs (using either Rayleigh (Aioub, Austin) or SERS method of detection (Kang and Austin). Finally, SERS technique was used in developing a technique that enabled us to follow the time profile of the different processes involved in the death mechanism (Austin, Kang) of a cancer cell caused by use of a cancer drug.

COLL 265

Chemically modified 2D nanoelectronic heterostructures

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The outstanding properties of graphene have been established on pristine samples in idealized conditions. However, for most applications, graphene needs to be chemically functionalized in a manner that either preserves its intrinsic properties or modifies its properties in a manner that enhances functionality. Towards these ends, several noncovalent chemistries have been demonstrated and characterized at the molecular scale with ultra-high vacuum scanning tunneling microscopy including 3,4,9,10-perylenetetracarboxylic dianhydride and 10,12-pentacosadiynoic acid. These self-assembled monolayers are shown to be effective atomic layer deposition seeding layers for dielectrics (e.g., Al₂O₃, HfO₂, and ZnO), which allows for substantial improvements in the uniformity and reliability of metal-oxide-graphene electronic devices. On the other hand, covalent modification schemes based on free radical chemistries allow for more fundamental changes to the electronic and chemical properties of graphene. In particular, atomic oxygen has been established as an effective method for homogeneously and reversibly functionalizing graphene with epoxide groups. In addition to chemically doping graphene, epoxidation yields local modification of the graphene bandstructure and provides pathways for further chemical functionalization, thereby expanding the suite of chemically modified graphene heterostructures. Finally, this talk will conclude with ongoing work in our laboratory to extend the chemical modification strategies for graphene to other two-dimensional materials including ultrathin silicon, black phosphorus, and transition metal dichalcogenides.

COLL 266

Surface chemistry and interface engineering for high performance perovskite solar cells

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In this talk, an integrated approach of combining material design, interface, and process engineering will be discussed to demonstrate significantly improved power conversion efficiencies (PCE >17%) of hybrid perovskite photovoltaic cells. Advances in controlled synthesis, processing, and tuning of the properties of perovskites have enabled significantly enhanced performance of organic-inorganic hybrid solar cells. The performance of these hybrid solar cells is strongly dependent on their efficiency in harvesting light, charge dissociation, transport, and collection at the metal/organic/metal oxide or the metal/perovskite/metal oxide interfaces. Therefore, it is very critical to tailor the molecular compositions of perovskite precursors and the interfaces with charge-transporting layers or device substrate to control the crystallization kinetics of perovskites and improve their quality and surface coverage. In addition, the stability of these hybrid devices can also be dramatically improved through simple surface functionalization to reduce device hysteresis during operation.

COLL 267

Adaptive wavelet approach for signal/image processing

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These last years, several adaptive methods were developed to analyze signals or images.

In this talk I will present a wavelet transform, called Empirical Wavelet Transform (EWT) to perform such adaptive analysis.

The EWT is based on wavelet filters built over frequency ranges obtained from the segmentation of the signal/image spectrum.

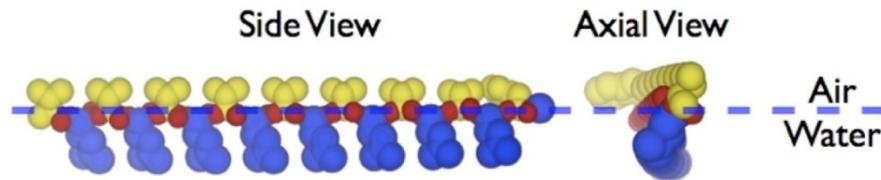
I will show that this approach provides very accurate time-frequency or scale-space representations. We will illustrate the strength of the proposed transform in the analysis of Electroencephalogram in Neuroscience and Microscopy imaging.

COLL 268

Periodically sequenced peptides: A new tool for nanoscale materials synthesis

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Periodically sequenced peptides can be confined to interfaces and assembled into patterns that present chemical functionalities with exceptional spatial precision. These rationally designed peptides and polypeptides are rapidly becoming useful components in nanostructured materials for applications ranging from drug delivery to energy storage. This presentation will examine several fundamental aspects of self-assembly and pattern formation of well-defined sheet forming peptides confined at interfaces (see figure). Our approach involves three steps. (1) We design and synthesize simple periodic peptide sequences, yielding surface-active β -strands that self-organize into aggregates to form patterns as a function of the peptide sequence. Rational peptide design allows us to systematically explore the role of hydrophobicity, electrostatics and molecular size on materials properties. (2) We use a set of interfacial characterization tools to examine in intermolecular assembly and supramolecular mechanics of the self-assembled structures. (3) We apply two-dimensional equations of state that define both the phase behavior and the critical surface concentrations of nascent aggregates at the interface. Subsequently, we can apply these parameters to predict the dimensions of pattern formation and to determine the potential of the peptide assemblies as biomimetic materials.



A periodically sequenced peptide confines a b-strand structure to the air-water interface, hydrophobic (yellow) and hydrophilic (blue) amino acids.

COLL 269

Design of 3-helix micelles as viable nanocarriers

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Nanocarriers, 10-30 nm in size, have unique advantages to improve therapeutic efficacy for drug delivery and vaccine formulation due to their ability to cross different biological barriers and undergo deep tissue penetration. However, micelles in this size range have limited *in vivo* stability, serious cargo leakage and rapid disassembly mainly due to their poor kinetic stability. We have developed 15 nm nanocarriers called “3-helix micelle” (3HM) based on amphiphilic peptide-PEG conjugates. The 3HM has a long blood circulation ($t_{1/2} \approx 29$ hours), reasonable drug loading efficiency (8% with DOX) with minimal cargo leakage, selective accumulation of in tumors and reduced accumulation in the liver and the spleen. More importantly, it was confirmed that the 3HM has deep tumor penetration in several tumor models. I will report our recent studies to understand the design principle to obtain micelles with tunable dynamic stability and with controlled cargo release profile.

COLL 270

Molecular design of peptide nucleic acid amphiphiles as self-assembled probes for electrophoretic miRNA detection

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Peptide nucleic acids (PNAs) are synthetic DNA analogs with superior DNA and RNA binding properties. PNAs have the phosphodiester backbone of natural nucleic acids replaced by a N-(2-amino-ethyl)-glycine version, which aids in binding stability but also leads to poor solubility and a tendency to aggregate in aqueous buffers. Maintaining the activity of PNAs in biosensing platforms has been a challenge in their wider implementation. One means to control the presentation of these powerful but poorly

soluble probes is to end-alkylate them for their organized assembly into surfactant microstructures, including micelles of nonionic surfactant, liposomes, or supported lipid bilayers, depending on the mode of detection desired.

Here we present the molecular design of a self-assembled PNA amphiphile system designed to detect sub-femtomolar amounts of miRNA in capillary electrophoresis.[1] A sandwich-type binding scheme is utilized that links a surfactant micelle with a long, dye infused length of DNA when a specific miRNA target is present. The electrophoretic mobility of the complex is set by the length of DNA attached to it, and multiple targets are detected in the same run by employing distinct lengths of DNA for each target. Additionally, use of long DNA tags provides ultra-high levels of fluorescence when infused with intercalating dyes such as YOYO-1 or PicoGreen. We demonstrate the stability and single-base-mismatch sensitivity of the sandwich hybridization assay in capillary electrophoresis, where 10-20 different targets are resolved in a 5-minute separation window. We also discuss implementation of a next-generation PNA design (γ PNA) which has a mini-PEG substitution at the γ position of the PNA backbone, leading to very high binding stability and an ability to specifically bind 5-6 base sequences at room temperature. We will also discuss efforts to improve detection limits by field-focusing methods and micelle-based separations compatible with kilobase-length DNA.

[1]Goldman et. al. *Biomacromolecules*, 2013, 14(7):2253-61.

COLL 271

Multistimuli responsive polypeptides and stimuli responsive hydrogels

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We have developed synthetic methods that allow incorporation of unprecedented levels of functionality into polypeptide materials. We report on the design and properties of stimuli responsive polypeptide motifs that are able to respond differently to different individual stimuli, such as redox, temperature, or enzymes. These materials allow multimodal switching of polypeptide properties to obtain desirable features, such as coupled responses to multiple external inputs. The reversible, multiresponsive nature of these polypeptides makes them particularly attractive as components in molecular devices or nanoscale assemblies capable of sequential, or triggered, responses to different stimuli, akin to switches capable of performing Boolean-like operations. We will describe how these motifs can be incorporated into self-assembled materials such as hydrogels.

COLL 272

Molecular engineering of peptide and protein therapeutics

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Through molecular engineering, it is possible to address complexities associated with the deficiencies and dynamics of diseases, such as ischemia and diabetes, in order to engineer improved therapies. The biological relevance of peptides, and the ability to precisely engineer supramolecular interactions through directional assembly and organized hydrogen bonding, enables the generation of platforms that can be utilized as new therapeutic materials. These bio-inspired materials interface with biology and physiology in a mimetic and active way. Self-assembling peptides can be used to present potent bioactive signals at high density to mimic the effects of angiogenic growth factors, or to prepare favorable niches for stem and progenitor cell therapeutics. This facilitates injectable strategies to regenerate blood vessels in models of peripheral ischemia, with improvements in microcirculation, limb necrosis, and motor function. Molecular interactions can additionally be leveraged to alter therapeutic dynamics and afford aspects of biologically relevant sensing in molecularly engineered protein therapies. Diabetes, and the complexities associated with glycemic control, present a significant engineering constraint in the design of therapies to recapitulate and replace the dynamics of native insulin signaling. Through covalent modification of insulin with molecular recognition motifs and aliphatic groups, the kinetics of insulin activity can be modulated by glucose-mediated intermolecular interactions, resulting in biomimetic insulin therapy. Specifically, this approach facilitates glucose-triggered insulin activity and responsiveness to glucose challenge mirroring that of a healthy functioning pancreas. In sum, these findings point to a new era of rationally engineered therapies rooted in predictable, biomimetic, tunable, and dynamic intermolecular and supramolecular interactions.

COLL 273

Biomimetic silica formation probed at the molecular level using SFG spectroscopy and MD simulation

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Specialized proteins can control the growth of biogenic mineralized tissue. Using specific recognition motifs, proteins bind and control the formation of mineral facets and can thereby grow the intricate mineral morphologies found in Nature. Particularly fascinating is the mineralization of high fidelity silica nanostructures in the frustules of diatoms. Within these unicellular algae, proteins called silaffins play a crucial role in the molecular biomineralization machinery. Material scientists are trying to harness the

concepts used by diatoms and other species to more efficiently fabricate mineral nanostructures and aim to formulate design rules for material precipitation to understand the mechanisms of protein–silica interactions. We found that designed peptides containing lysine and leucine side chains (LK peptides) can mimic silaffin’s role in the formation of diverse biosilica nanomaterials. By choosing the periodicity of L and K sites, these peptides were designed to fold into helical or beta-sheet structures and represent simplified model systems to study the effect of protein folding on mineralization (1,2). Using surface sensitive sum frequency generation (SFG) vibrational spectroscopy we have studied the interactions of LK peptides with biosilica surfaces. We determined how LK peptides fold at the silica–water interface and found that interfacial folding and solution aggregation is crucial for the silica morphology: spheres, rods and wire-type structures were produced – depending on LK folding. Side chains also actively participate in the mineralization process. We probed the side chain structure of LKs in contact with silicic acid solution and observed increased ordering of charged lysine side chains during the formation of biosilica, indicating their involvement in silica nucleation. Combined with TEM measurements and MD simulations the SFG studies provide important new details of peptide-driven silica formation.

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(2) A. Zane, C. Michelet, A. Roehrich, P.S. Emani, G.P.Drobny, *Silica Morphogenesis by Lysine-Leucine Peptides with Hydrophobic Periodicity*, *Langmuir*, **2014**, 30 (24), pp 7152–7161.

COLL 274

Engineering mitochondria-penetrating peptides

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The mitochondrion plays a major role in a variety of critical processes involved in cell survival and cell death. In particular, the elucidation of the mitochondrion’s function in various human diseases has generated an appreciable amount of interest in exploring this organelle as a potential drug target. As a result, a number of strategies to probe and combat mitochondria-associated diseases have emerged. We recently developed a set of peptide-based agents that are able to carry drug molecules into mitochondria, and have studied the effects of delivering clinically used anticancer and antibacterial agents to mitochondrial targets. Our work on using this approach to combat drug resistance and the structure-function relationships that define the requirements for mitochondrial transport will be presented.

COLL 275

Charge shuttling across membranes by functionalized gold nanoparticles

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Although it is still debated whether nanoparticles can transfer spontaneously across cell membranes without the need for endocytosis, there are numerous examples of nanoparticles penetrating various types of model membranes. Here we report the design, preparation and properties of functionalized gold nanoparticles that are not only capable of transferring across phospholipid bilayer membranes of vesicles, but also carry across both electronic or ionic charge. This is manifested in membrane polarisation and depolarisation, which is measured by fluorescence spectroscopy. The proposed function of the nanoparticles as electron and ion shuttles is contrasted against their potential ability to reside permanently inside the membrane and thus act as ion channels and electron wires, respectively. Cryo-TEM images are used to attempt to distinguish between these two fundamentally different mechanisms of charge transfer. Preliminary experiments with live cells instead of vesicles also show effects that indicate charge transfer and hence suggest that the nanoparticles can indeed penetrate also real cell membranes. Finally, the possibility of coupled ion and electron transfer mimicking aspects of biological energy conversion mechanisms is discussed.

COLL 276

Hyaluronic acid-modified Fe₃O₄@Au core/shell nanostars for multimodal imaging and photothermal therapy of tumors

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Development of multifunctional theranostic nanoplatforms for diagnosis and therapy of cancer still remains a great challenge. In this work, we report the use of hyaluronic acid-modified Fe₃O₄@Au core/shell nanostars (Fe₃O₄@Au-HA NSs) for tri-mode magnetic resonance (MR), computed tomography (CT), and thermal imaging and photothermal therapy of tumors. In our approach, hydrothermally synthesized Fe₃O₄@Ag nanoparticles (NPs) were used as seeds to form Fe₃O₄@Au NSs in the growth solution. Further sequential modification of polyethyleneimine (PEI) and HA affords the NSs with excellent colloidal stability, good biocompatibility, and targeting specificity to CD44 receptor-overexpressing cancer cells. With the Fe₃O₄ core NPs and the star-shaped Au shell, the formed Fe₃O₄@Au-HA NSs are able to be used as a nanoprobe for efficient MR and CT imaging of cancer cells in vitro and the xenografted tumor model in vivo. Likewise, the NIR absorption property enables the developed Fe₃O₄@Au-HA NSs to be

used as a nanoprobe for thermal imaging of tumors in vivo and photothermal ablation of cancer cells in vitro and xenografted tumor model in vivo. This study demonstrates a unique multifunctional theranostic nanoplatform for multi-mode imaging and photothermal therapy of tumors, which may find applications in theranostics of different types of cancer.

COLL 277

Nanostructured gold model catalysts on thin film substrates

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Nanostructured gold model catalysts on thin film substrates

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Au nanoparticles exhibit remarkable catalytic properties, particularly for low-temperature and selective reactions.¹⁻³ The precise role of Au, however, remains a subject of research even in simple reactions such as CO oxidation because of the potential involvement of the support material and reaction environment.^{4,5} We demonstrate that a monolayer hexagonal boron nitride (BN) film provides periodic sites for nucleation of monodisperse Au nanoparticles because it forms a long-range pore-wire superstructure when supported on Rh(111).⁶ Although the BN film is chemically inert, the resulting dense arrays of Au nanoparticles remain confined to the pore regions even at multi-layer Au coverages and on warming to room temperature. The system is characterized using a variety of methods, including scanning tunneling microscopy, X-ray photoelectron spectroscopy, electron energy loss spectroscopy, and chemisorption of probe molecules such as CO, as well as density functional theory based modeling. The DFT calculations and experiments are in close agreement regarding the adsorption properties of CO on the Au nanoparticles. Evidence is found for charge transfer resulting in negatively charged Au nanoparticles, with the charge localized at periphery Au sites that are highly reactive toward CO chemisorption, causing the C-O stretching frequency to red-shift considerably. The Au/BN/Rh(111) system represents a potentially

attractive model catalytic platform on which to study Au catalysis in the isolated Au limit.

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COLL 278

Nonwetable, oxidation stable, brightly-luminescent silicon nanocrystal film

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Silicon nanocrystals, which are considered as greener alternatives to traditional nanocrystals like CdSe and PbS, offer the benefits of being earth abundant, inexpensive, purportedly less toxic and compatible with silicon electronics. Compared to bulk Si crystal, nanoscale silicon crystals have new properties and functionalities and are expected to have new and exciting applications in microelectronic, photonic, photovoltaic and nanobiotech industries. A significant rise can be seen in the number of publications on silicon nanocrystals recent years, which witnesses a rising interest in this material.

We report for the first time the synthesis of colloidally-stable, brightly-luminescent silicon nanocrystals passivated by perfluorocarbon chains and compare the properties of solutions and films with the perhydrocarbon chain passivated relative. The superior hydrophobicity of the perfluorocarbon chain yields higher contact angle films, the enhanced electron withdrawing character induces blue shifts in the wavelength of photoluminescence and the lower frequency carbon-fluorine stretching modes disfavor non-radiative relaxation pathways and boost the absolute photoluminescence quantum yield.

COLL 279

Enzyme multilayer coatings prevent bacterial biofilm formation on urinary catheters

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Formation of antibiotic-resistant bacterial biofilms on indwelling medical devices poses a critical problem in healthcare settings, being responsible for the majority of hospital-acquired infections. Despite the recent advances in antimicrobial research, efficient

antibiofilm strategies to control the adhesion and proliferation of bacteria on medical devices are still needed. Herein, hybrid coatings comprising acylase and α -amylase built on silicone urinary catheters using a layer-by-layer technique were investigated as alternatives to the conventional antibiotic treatments for prevention of bacterial biofilm formation and further emergence of resistance. The assembling of multilayer coatings on the catheter surface was achieved by alternate deposition of negatively charged enzymes and positively charged polyethylenimine. These hybrid enzyme coatings were able to quench quorum sensing process and degrade biofilm adhesive components, thereby synergistically inhibiting biofilm formation by *Pseudomonas aeruginosa*. Furthermore, the dual-species biofilm occurrence (*Pseudomonas aeruginosa* and *Escherichia coli*) on urinary catheter was significantly reduced under dynamic conditions in an *in vitro* catheterized bladder model, when compared to the non-modified specimen. These antibiofilm active coatings that integrate anti-quorum sensing and anti-adhesive strategies did not affect the viability of the human fibroblasts (BJ-5ta) over seven days and could be a viable alternative to control pathogenic bacterial biofilms on indwelling medical devices.

COLL 280

Chemical and structural transformations in colloidal inorganic nanocrystals

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Colloidal inorganic nanocrystals (NCs) are among the most exploited nanomaterials to date due to their extreme versatility. Research on NCs went through much advancement in the last fifteen years, for example in the synthesis, which opened up the possibility to control their size, shape and topology in chemical composition. An additional step forward was the creation of a wide range of superstructures from the assembly of such NCs, which can be thought of as new types of artificial solids. This, coupled with the possibility to replace the native ligands on the surface of the NCs with shorter molecules, down to single atom ligands, has conferred unique electrical features to films of NCs that make them attractive for low cost alternatives to many technologies. Progress also came from the study of chemical transformations in nanostructures, most notably via cation exchange, which involves replacement of the sublattice of cations in a crystal with a new sublattice of different cations, while the sublattice of anions remains in place. Also, a new field of study has emerged recently, aiming at investigating the transformations in colloidal synthesized nanomaterials under conditions like thermal annealing and/or irradiation. In part this research is boosted by the recent availability of microscopy tools by which one can follow the transformations on individual NCs *in-situ*, *i.e.* when such perturbations are actually applied to the sample. The present lecture will highlight the recent progress (with emphasis on the contributions from our group) in the study of chemical and structural transformations in NCs.

COLL 281

Dithiocarbamate-anchored ligands on smooth and nanostructured gold surfaces

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Dithiocarbamates (DTCs) are a practical alternative to thiols for the functionalization of metal surfaces and nanostructures. In addition to their ease of preparation (often spontaneously formed by the addition of amines to CS₂), DTCs are strongly coordinating ligands and can be more resistant to surface desorption than thiols under various conditions. The adsorption kinetics of DTCs is rather different from that of thiols, and presents opportunities to deposit organic ligands onto nanostructured surfaces with kinetic control. Examples include using DTCs for the surface-selective passivation of metal nanoclusters and nanoporous gold, insertion of DTC ligands for surface-enhanced Raman scattering (SERS) with heightened sensitivity, the photopatterning of binary DTC and alkanethiol monolayers, and the DTC-mediated attachment of biomolecular recognition elements for applications in nanomedicine.

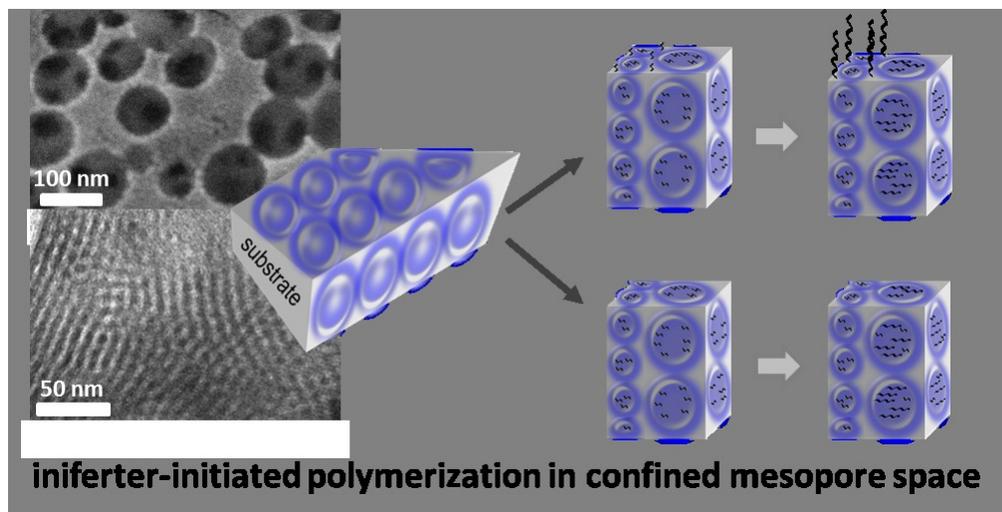
COLL 282

Mesoporous membranes, zwitterionic monomers, and iniferter-initiated polymerization: Where does the polymerization proceed?

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Functionalized mesoporous materials are relevant for applications from sensing to drug delivery. These materials, with a pore size below 10 nm, are characterized by a dominating inner surface area as compared to the external surface area. Furthermore, polymer surface modification is influenced by the spatial confinement. The knowledge on the location of the polymer modification should be crucial for the mesoporous film properties such as ionic permselectivity. Mesopore accessibility is limited by a number of factors like pore size, pore connectivity, porosity and pore wall charge. Here, we investigate potential control on polymer modification of mesoporous membranes by using an iniferter-initiated polymerization of the zwitterionic monomer carboxybetaine methacrylate (CBMA) in mesoporous silica thin films. Among other parameters we examined the effect of pore size and monomer concentration on the generated polymer amount. We not only investigated the potentially controlled character due to iniferter-initiation. We were as well able to specifically address polymer location in this grafting from approach and by this to synthetically discriminate between inner mesopore and external film surface. Characterization was carried out using infrared spectroscopy, ellipsometry, X-ray photoelectron spectroscopy, and X-ray reflectometry. Our results clearly indicate potential bottlenecks of iniferter-initiated polymerization in mesopores and conditions under which the external film surface clearly dominates the generated polymer amount. This is highly important for the understanding of polymerization in mesoporous materials but as well for applications in which functionalized mesoporous materials are used such as drug delivery or separation.

Because the CBMA polymer can be converted from a cationic to a zwitterionic state, ionic permselectivity can be modulated depending on pore size, polymer functionalization and pH.



COLL 283

Spectroelectrochemistry and electrochemiluminescence of mixed-thiolate protected Au₁₃₀ clusters

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Metal clusters have attracted tremendous research interest due to their rich optical and electrochemical properties for catalysis, charge and energy storage, sensing and other applications. Thiolate stabilized Au clusters are unique in that molecular composition and atomic bond structures can be elucidated. The information enables possible structure-functions correlations. Albeit exciting progresses have been made recently, strong resonance coupling between the metal core energy states and ligand molecular orbitals has not been achieved. In this talk, a mixture of monothiolate (phenylethylthiol) and dithiolate (1, 4-durene-dithiol) is used as ligands to stabilize Au₁₃₀ clusters. The molecular orbitals of durene-dithiolate ligands are found responsible for several electrochemical and optical transitions. The coupling of degenerated energy states on Au core and individual non-interacting molecular orbitals is studied by a variety of electrochemical and optical techniques. Selective oxidation and reduction of the Au core and ligands by electrochemistry is monitored by UV visible absorption and photoluminescence. The overall energy diagram of the Au₁₃₀ clusters is established based on those spectroelectrochemistry and electrochemiluminescence features.

COLL 284

Imaging nanoscale energy transfer at the limits of temporal resolution and spatial accuracy

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Plasmonic nanoparticle assemblies offer unique opportunities for controlling energy transfer at the nanoscale. Here, we demonstrate the ability of deterministic plasmonic arrays to control energy transfer in three key areas: 1) non-linear wave mixing of incident light; 2) structure-dependent circular dichroism; and 3) spatial localization of electromagnetic energy to nanoscale volumes. Single-particle second harmonic generation (SHG) imaging techniques developed in our lab provide high spatial accuracy and precision along with femtosecond time resolution for examining plasmonic assemblies. Femtosecond time-resolution is achieved by employing a sequence of phase-locked laser pulses to examine the nanostructures. Phase-stabilized laser pulse replicas are generated collinearly and used for nonlinear optical imaging by controlling the inter-pulse delay with attosecond accuracy. The phase stability of the pulse replicas persists for several hours, greatly exceeding the requirements for single-particle pump-probe measurements. These phase-stable pulse sequences have been employed to study a series of linear plasmonic nanostructures formed by surface-directed assembly. The results indicate that the position of the electromagnetic hot spot can be determined with an error as small as one nanometer, while simultaneously quantifying the polarization state of harmonic waves. The new experimental imaging capabilities are expected to impact significantly the development of structural nanophotonics, including controlling nanoscale energy transfer.

COLL 285

Tailoring optical and plasmon resonances in core-shell and core-multishell nanowires for plasmonic light harvesting

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Semiconductor nanowires are sub-wavelength structures exhibit strong optical (Mie) resonances in the visible range. In addition to such optical resonances, the localized surface plasmon resonances (LSPR) in metal-semiconductor core-shell (CS) and core-multishell (CMS) NWs can be tailored to achieve novel negative-index metamaterials (NIM), extreme absorbers, invisibility cloaks and sensors. Particularly, we present our recent progresses on semiconductor-metal-semiconductor core-multishell nanowires as photoelectrodes for enhanced visible light absorption and high efficiency water splitting.

By tuning the LSPR in the TE polarization and the optical resonance in the transverse magnetic (TM) polarization of metal-photocatalyst CS and semiconductor-metal-photocatalyst CMS NWs, the absorption within ultrathin (sub-50 nm) photocatalyst layers can be substantially enhanced. We theoretically demonstrated a specific core-multishell structure designed can reach photocurrent densities of $\sim 11.81 \text{ mA/cm}^2$, corresponding to a solar to hydrogen efficiency of 14.5%, 93% of the theoretical maximum. Notably, aluminum and copper based CMS NWs provide absorption enhancement remarkably close to silver and gold based CMS NWs respectively. Further, such absorption is polarization independent and remains high over a large range of incidence angles and permittivity of the medium. Therefore, due to the tunability of their optical properties, CS and CMS NWs are expected to be vital components for the design of nanophotonic devices.

COLL 286

Single-particle photoelectrocatalysis

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This talk will present our recent results in using single-molecule fluorescence microscopy to image photoelectrochemical reactions on single semiconductor nanostructures. We separately image hole and electron induced reactions, driven by light and electrochemical potential, and map the reactions at single reaction temporal resolution and nanometer spatial resolution. We also correlate the surface reactivity with the overall performance of each nanostructure in photoelectrochemical splitting of water.

COLL 287

Aqueous growth of fluorescence-tunable gold nanoclusters capped with lipoic acid-polyethylene glycol ligands

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We have developed a one pot aqueous synthesis to grow gold nanoclusters (AuNCs) that exhibit tunable fluorescence emission. The clusters are stabilized with poly-(ethylene glycol)-modified lipoic acid (LA-PEG) ligands. The synthesis is carried in borohydride-free conditions and involves the reaction between gold precursor (HAuCl_4^-) and photo-chemically transformed LA-PEG ligand in alkaline conditions and under reflux conditions. We found that the time of reaction and nature of the ligand terminal functional group strongly influence the fluorescent behavior of the prepared AuNCs. For instance, yellow-emitting AuNCs (emission at 560-570 nm) are prepared early in the reaction. Further heating gradually shifts the emission to either the blue (emission at

440 nm) or red (emission at 670 nm) region of the visible spectrum, depending on the exact nature of the terminal functional group used. The AuNCs offer a prolonged colloidal stability in PBS buffer media (pH 2-12) and saline medium.

COLL 288

Vivid, full-color plasmonic pixels

Stephan Link, *slink@rice.edu*. Dept of Chem MS 60, Rice University, Houston, Texas, United States

Here we show how vivid, highly polarized, and broadly tunable color pixels can be produced from periodic patterns of oriented gold aluminum nanorods. While the nanorod longitudinal plasmon resonance is largely responsible for pixel color, far-field diffractive coupling is employed to narrow the plasmon linewidth, enabling monochromatic coloration and significantly enhancing the far-field scattering intensity of the individual nanorod elements. The bright coloration can be observed with p-polarized white light excitation, consistent with the use of this approach in display devices. The resulting color pixels are constructed with a simple design, are compatible with scalable fabrication methods, and provide contrast ratios of at least 100:1. Compared to gold, aluminum is earth abundant, low in cost, compatible with complementary metal-oxide semiconductor manufacturing methods, and capable of supporting tunable plasmon resonance structures that span the entire visible spectrum.

COLL 289

Substrate specificity of the plasma membrane phosphatidylserine flippase

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Eukaryotic cell plasma membranes possess an asymmetric transbilayer distribution of phospholipids. The choline-containing phospholipids, phosphatidylcholine and sphingomyelin are enriched in the outer monolayer, while the aminophospholipids, particularly phosphatidylserine (PS), are enriched on the cytoplasmic surface. The dissipation of this gradient and exposure of PS on the surface of the cell, induces the recognition and destruction of the cell by macrophages and, in blood cells, the activation of plasma clotting factors. The action of several lipid-specific transporters, including an inwardly-directed, aminophospholipid-specific, ATPase or "flippase," outwardly-directed "floppases," and a bi-directional, non-specific "scramblase", play important roles in the generation, maintenance and regulated dissipation of plasma membrane phospholipid asymmetry.

The aminophospholipid flippase is highly selective for its lipid substrate. In the human erythrocyte, PS is the preferred substrate, requires energy in the form of ATP to catalyze lipid translocation, and is sensitive to inhibition by sulfhydryl reagents. Although

phosphatidylethanolamine, and other PS analogs, are transported by the flippase, transport is much slower, but is also ATP dependent and sulfhydryl reagent sensitive. Perhaps the most distinguishing characteristic, however, is an absolute specificity for the *sn*-1,2 configuration of the glycerol moiety of PS, but a lack of stereochemical specificity for the serine headgroup.

We, and others, have purified and characterized two candidate flippases: a PS-stimulated ATPase from human erythrocytes and a P₄-ATPase (ATP8A1). These enzymes share the same exquisite structural specificity for PS transport observed in intact cells, which is distinct from other PS-binding proteins. Our current studies focus on using the characteristic lipid specificity of the PS flippase to determine the substrate binding site of ATP8A1 and elucidate the transport pathway through the protein, using molecular modeling and selective mutagenesis. Several models recently proposed by others for the mechanisms of lipid transport by P₄-ATPases will be discussed and compared to our modeling and experimental data.

COLL 290

Anionic phospholipid asymmetry and translocation in lipid membranes

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Our current understanding of the structure and dynamics of cellular membranes emerged in the early 1970 's. However, there is still much we do not know about the underlying lipid dynamics in cellular membranes, specifically the process of lipid translocation or flip-flop. The flip-flop rates of only a few lipid species, principally phosphatidylcholines (PCs), have been measured. Anionic lipids, such as phosphatidylserine (PS), phosphatidylinositol (PI), and phosphatidylglycerol (PG), are known to play active roles in membrane function, but almost nothing is known of the rates of translocation of these species. While PS and PI are the major anionic lipids of eukaryotic cellular membranes, PG is mainly found in prokaryotic membranes and comprises about 10% of the phospholipid content of the mitochondria membrane in eukaryotes. In the work presented here, the native flip-flop rates of 1,2-diasterol-*sn*-glycero-3-[phospho-(1'-*rac*-glycerol)] (DSPG) and 1,2-distearoyl-*sn*-glycero-3-phospho-L-serine (DSPL) in 1,2-distearoyl-*sn*-glycero-3-phosphocholine (DSPC) bilayers have been investigated. Using methods of classical surface chemistry coupled with nonlinear optical methods, we have developed a novel analytical approach, using sum-frequency vibrational spectroscopy (SFVS), to selectively probe lipid compositional asymmetry in a planar supported lipid bilayer. This new method allows for the detection of lipid flip-flop kinetics and compositional asymmetry without the need for a fluorescent or spin-labeled lipid species by exploiting the coherent nature of SFVS. Using SFVS, the rates of DSPG and DSPL flip-flop in a DSPC matrix have been examined for the first time. Analysis of the dynamics provides an assessment of the underlying energetic barrier to PG and PS translocation. The results will be discussed in the framework of the protein-free energetic barriers to PG and PS flip-flop and the role of electrostatics in this process.

COLL 291

Infrared study of membranes and membrane proteins

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In this talk, we will show how linear and nonlinear infrared spectroscopic techniques can be used to quantify various physical properties of membranes and to reveal functionally relevant structural and dynamic information of membrane proteins. Specifically, we will discuss how site-specific infrared probes can be used to determine the local electrostatics and hydration status of membranes and how two-dimensional infrared spectroscopy can be used to provide a better understanding of the proton conducting mechanism of the M2 channel of influenza A virus.

COLL 292

Molecular transport through living cell membranes: Effects of molecular structure, membrane structure, and electrolyte composition

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Transport of medium size molecules through the membrane of living biological cells has been studied in real-time by a combination of Bright-Field Microscopy and the surface sensitive technique Second Harmonic Light Scattering. The effects of molecular structural factors such as polarity and charge, membrane structural factors such as packing of the lipid bilayer and membrane proteins, and the composition of the electrolyte in which the cells live in, on the transport rate are characterized through examining the adsorption/transport of malachite-green (MG), crystal-violet (CV), and bromocresol purple (BCP), charged or neutral hydrophobic molecules, at membranes of Gram-negative and Gram-positive bacteria, and the Murine erythroleukemia (MEL) cells in BPS or aqueous solutions with various salt concentrations.

COLL 293

Molecular interactions at model cell membranes

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In this research, we applied sum frequency generation (SFG) vibrational spectroscopy to study molecular interactions at model cell membranes. We used solid substrate supported lipid bilayers as model cell membranes. Interactions between model cell membranes and different molecules, such as drug molecules amantadine and chlorpromazine, transfection agent for gene delivery polyethylenimine (PEI) as well as Au nanoparticles, have been examined. It was found that amantadine and chlorpromazine interact with model cell membranes differently. Linear and branched

PEI molecules exhibit varied interaction mechanisms with model cell membranes, and such interactions have strong temperature dependence. We found that Au nanoparticles caused flip-flop in the model cell membrane. The effect of Au nanoparticle size on the membrane flip-flop has been elucidated.

COLL 294

Plasmonic hetero-oligomer nanoparticle arrays for hydrogen sensing

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The ability to arrange plasmonic nanoparticles (NPs) into well-ordered assemblies is a powerful strategy to produce new near-field and far-field optical properties. Bottom-up assembly methods using molecular recognition such as DNA linkers are effective, but the yield and purity of the NP oligomers is low. Top-down tools such as electron-beam lithography can create assemblies with good control over NP shape and separation; however, throughput is limited, especially for NP assemblies made from more than one metal. This talk will describe a new approach, Reconstructable Mask Lithography, to situate plasmonic NPs within a subwavelength footprint that can also be scaled over in^2 -areas. We will discuss the versatility of this method to create Au-Pd NP dimers and NP trimers for hydrogen gas sensing. We carried out FDTD modeling to explain blue and red resonance wavelength shifts of the plasmonic hetero-oligomers after hydrogen adsorption.

COLL 295

Optical gas sensors based on localized surface plasmon resonance

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Gas species recognition through fully optical devices is currently a raising trend over the well-established conductometric approach, as it opens new possibilities especially for *in situ* recognition of flammable and/or toxic species such as CO, H₂, NO₂ or volatile organic compounds (VOC).

Au nanoparticles (NPs) dispersed in an oxide matrix represent an effective design for a gas sensor's active material owing to their catalytic and localized surface plasmon resonance (LSPR) properties. Noble metal NPs can exhibit catalytic properties and hence modify the chemical interactions between the oxide surface and the target analyte, thereby improving the sensing process. Moreover, if the metal NPs show a LSPR peak in the visible range (like Au), the nanocomposites can be used as selective optical gas sensors. The variation in the dielectric constant around the LSPR peaks will differ for different gas species, leading to a diverse variation in the optical properties at different wavelengths.

TiO₂ thin films with embedded Au and/or Pt NPs have been obtained by synthesizing

high-quality metal and metal oxide colloids and directly spinning a nanocrystalline ink made of colloidal solutions on glass substrates. These TiO₂-Au samples showed fast and reversible changes in optical absorption when exposed to H₂ and CO species at 200°-350°C, with high sensitivities. More impressively, TiO₂-Au-Pt films showed room-temperature response to H₂ and VOC.

Thin films composed of Au NPs dispersed inside a TiO₂-NiO mixed oxide matrix were obtained spin coating a sol-gel solution on a glass substrate and subsequently thermal annealing. These samples show high response to H₂S down to few ppm and almost no interference in response is observed during simultaneous exposure to CO or H₂. For mechanistic studies, experimental evidence using reaction product analysis and thin film surface characterization suggests a direct catalytic oxidation of H₂S over the Au-TiO₂-NiO nanocomposite film.

More recently Dark Field Microscopy (DFM) has been used for the direct observation of the kinetics of H₂ gas interaction with single gold nanorods (NRs) coupled with Pt NPs and/or with metal oxide matrices. The longitudinal Au LSPR band shift has been monitored by DFM looking at the variation of the scattering spectrum of a single Au NRs in the presence of H₂ and the gas interaction mechanisms for the different samples with distinct oxide supports have been studied.

COLL 296

Localized surface plasmon resonance (LSPR) optical detection of hydrogen

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Hydrogen, H₂, is an asphyxiant and an explosive gas and is extremely difficult to detect due to its colorless and odorless properties. Therefore, fast, reusable and reliable sensors are needed to limit accidental deaths and injuries caused by H₂ leaks. Much attention has been given to Pd for H₂ sensing due to its ability to absorb approximately 900 times its own volume of H₂ by forming a reversible PdH_x phase. We report a rapid optical detection of gaseous hydrogen using Au nanostructures. It is hypothesized that the hot electrons generated from resonantly optically excited substrate-based gold nanohemispheres (Au NHs) induce the H₂ dissociation on Au NHs. It is speculated that the subsequent formation of a metastable gold hydride (AuH_x) causes a change in optical transmission due to modification of the nanostructure dielectric constants which revert back once the gas is removed. Numerical simulations, using the discrete dipole approximation, were carried out to explain the optical changes associated with the formation of metastable AuH_x.

COLL 297

Thermal energy harvesting plasmonic based chemical sensors

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The surface plasmon resonance band of gold nanomaterials embedded in metal oxide heterostructure films is used both as an energy harvesting device structure as well as an optical beacon for the detection of emission gases, CO, NO₂ and H₂, at temperatures ranging between 500 and 800°C. A summary of previous experiments detailing the sensing characteristics will be provided. Challenges for their detection include high levels of sensitivity, the selective detection of the gas of interest within a catalytically active environment as well as surmounting future integration challenges. Recent work will be detailed which shows the implementation of plasmonic based sensing arrays for the detection of emission gases. Variations in nanoparticle size, shape, geometric arrangement as well as the metal oxide matrix chemistry are being varied to produce next generation sensing arrays with enhanced selective sensing properties. Coupled with these recent studies is the novel design of plasmonic arrays that are being developed for their energy harvesting capabilities. Studies will be detailed on these next generation plasmonic structures that include their energy harvesting characteristics and subsequent detection of emission gases without the need of an external white light excitation source.

COLL 298

Plasmonic spectroscopy and photochemistry on highly damping platinum group metals

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In the field of plasmonics, noble metals such as Au or Ag have been frequently utilized due to their strong plasmon resonances arising from the Drude-like property of free electrons. On the other hand, transition metals such as platinum group metals (PGMs) are not considered as a plasmonic material because of their weak plasmon resonances damped by localized d-electrons. It is, however, known that transition metals exhibit various unique functionalities such as due to the d-electrons. For example, Pt can be a good electrocatalyst for various reactions. Pd can be a hydrogen storage material due to its ability to absorb and release large quantities of hydrogen gas. Therefore, if such functionalities are combined with plasmonic nano-systems, plasmonic applications may be extended to various fields.

Surface enhanced Raman scattering (SERS) is recognized as a powerful vibrational spectroscopic method for studying molecular adsorbates on a metal surface despite the technical limitation for PGMs. Recently, we have reported that SERS spectra of molecular adsorbates can be obtained even on PGM surfaces using a sphere-plane type nanogap structure. Importantly, this technique enables us to observe SERS on atomically defined metal surfaces, meaning that atomic surface structure dependence of

metal-molecule interactions can be studied using SERS.

Pd can absorb hydrogen into the crystal lattice, resulting in formation of palladium hydride, PdH. Since optical constants of PdH are different from those of Pd, one can expect that plasmon resonance energy can be tuned by hydrogen uptake. Based on this system, we have demonstrated photo-induced variation of plasmon resonances.

J. Hu, M. Tanabe, J. Sato, K. Uosaki, K. Ikeda, *J. Am. Chem. Soc.*, 136, 10299 (2014)

COLL 299

Nanocomposite fiber optic pH sensor for high temperature applications

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Optical pH sensing can enable minimally invasive, remote, real time and continuous distributed pH monitoring. Despite the availability of various technologies for pH sensing under ambient conditions, measurement of pH in extremely harsh environments remains a significant challenge, yet it is of increasing importance for applications in oil and gas production, geological carbon sequestration, industrial chemical manufacturing, and nuclear power generation, among others. This talk describes a nanocomposite fiber optic pH sensor, which is comprised of plasmonic and metallic nanoparticles embedded in a silica matrix, with a wide pH response range and capability of operation under elevated temperature conditions as well as in saturated salt solutions. Unlike previously reported optical pH sensors that invariably rely on pH sensitive, but delicate, organic materials, the nanocomposite optical fiber pH sensor reported here is based on materials that are expected to be robust and stable at extreme temperatures (up to at least 600 °C) and pressures. Results from our experiments are suggestive that the sensing mechanism is related to the change of the surface charge density at different pH's of the silica-based matrix. To the best of our knowledge, this optical effect has not been reported before and it opens a pathway towards possible future development of robust optical pH sensors for the most demanding environmental conditions. The effect also offers the potential for control of the optical properties of plasmonic materials for a range of other applications such as electrochromic devices.

COLL 300

Advances in targeted multifunctional inhalation aerosols with nanotechnology and solid-state particle engineering design

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The fundamental and applied aspects of surface chemistry, nanotechnology, and advanced particle engineering technologies are employed in the design and optimization of multifunctional microparticles and nanoparticles in the solid-state for targeted pulmonary delivery as high-performing dry powder inhalation aerosols. Biodegradable and biocompatible “stealth” nanomaterials enable high aerosol dispersion performance of model drugs representing different therapeutic classes of importance in the treatment of several lung diseases. A systematic approach is used and includes comprehensive solid-state physicochemical characterization, thermotropic phase behavior, design of experiments (DOEs), controlled drug release studies, aerosol dispersion characterization and predictive modeling. The solid-state physicochemical properties correlate with dry powder aerosol dispersion profiles. Controlled-release of drug followed mathematical controlled-release mechanistic models with high correlation. Aerosol dispersion performance parameters were correlated and modeled with solid-state phase transition temperatures, nanomaterial properties, and advanced spray drying particle engineering parameters

COLL 301

Effects of formulation on the affinity of an SPD peptide fragment toward hair keratin: Experimental and molecular dynamics data

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The affinity of SPD peptide fragment (QAAF₂SQ) in compositions based in benzyl alcohol and ethanol towards hair keratin was studied by molecular dynamics simulations and fluorescence microscopy. A computational model of hair protofibril was built for coarse grained simulations with the MARTINI force field. Benzyl alcohol showed to promote the disorganization of the keratin chains, expanding the fiber and improving the peptide linkage. The fluorescence results showed that the absorption of the SPD peptide by hair was related to the increase of benzyl alcohol content. The work present in this paper show that the coarse grained model is detailed enough to evaluate the effects of organic solvents and active agents that interact with the hair shaft.

COLL 302

Design of thermal gelling polymer formulations for spray applications

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Many applications exist where there is a need for a solution to remain adhered to a surface after application. The fundamental challenge is that solutions with properties

that result in ideal spray performance, such as low viscosity, may also easily flow from the surface soon after application. A route to overcome this challenge is the design of solutions that gel upon contact with the surface. For example the use of a temperature change as a trigger for a thermal responsive solution containing polymers such as methylcellulose derivatives. The gelling properties of these polymer solutions are driven by polymer variables including molecular weight, concentration, and distribution of substituents on the cellulose backbone, as well as interactions with other formulation components. Tailoring these variables can adjust the temperature at which gelation occurs, the magnitude of the viscosity change upon gelling, and the relationship between polymer chain collapse and gelation. For example, simply adjusting the methoxy substitution level of a hypromellose polymer in an 8% aqueous solution from 0.08 to 0.36 while keeping all other properties the same results in an increase in gelation temperature from 26 to 49°C. The impact of other solution components can drastically affect gelation as well; the addition of 3% salt to the 8% polymer solution previously mentioned decreases the gelation temperature from 49 to 36°C. Understanding the impact of polymer and solution variables on the gelation process allows for the design of formulations to meet the needs of specific applications and active ingredients.

COLL 303

Novel parameter to replace HLB

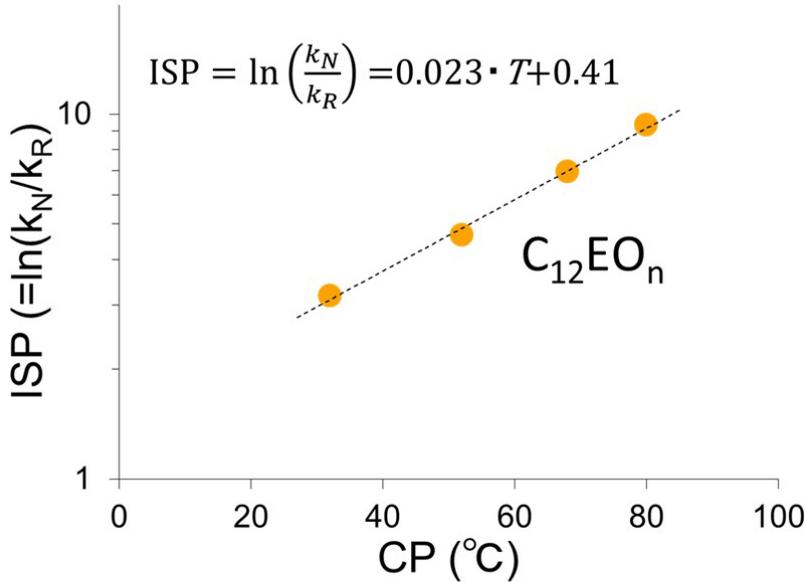
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HLB is a very practical concept to identify the properties of surfactant as an emulsifier. Many methods to calculate HLB had been proposed, but some are not opt for general molecules and others are too complicated. Furthermore, such calculated HLB would not represent emulsifier's intrinsic prpperties in practice other than polyoxyethylene (POE) type non-ionic surfactants. This is because HLB was established for and by POE nonionics.

It is noteworthy that thin layer chromatography (TLC) gives hydrophilic and hydrophobic character of the molecule by using normal phase or reversed phase method, respectively. We have originally investigated the empirical method for the characterization of amino acid-based surfactants in comparison with POE alkyl ethers based on this TLC analysis. [1]

With reviewing our previous procedure, the present study shows the novel method to evaluate potency not only for CmEOn but also for general molecules to propose a practical index of surfactant characteristics as integrated surfactant potency (ISP). [2] By using ISP expressed as the ratio of two capacity constants empirically obtained through TLC measurements, the real nature of a surfactant can be well-defined. In addition, it is shown that ISP was linearly correlated to the surfactant properties such as cloud temperature, which is inconsistent with HLB. In the presentation, we will look back to the basics of HLB and renovate it to ISP as practical parameter longed by industry with theoretical back ground.

- [1] Sakamoto K.; *Society of Cosmetic Chemists, Annual Scientific Meeting*, 1986.
 [2] Yamashita Y., Sakamoto K.; *The Bulletin of Chiba Instit. of Sci.*, 2013, 6, 89-92.



ISP v.s. Cloud Temperature (CP)

(1wt.% $C_{12}EO_n$ aq. soln.)

COLL 304

Watching paint age

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The Dow Chemical Company has been conducting exposure tests on waterborne architectural paints for over 50 years, since its development of acrylic polymer dispersions. Dow scientists employ its exposure stations as outdoor laboratories all over the world to evaluate performance of exterior paints, coatings and caulks as well as the components employed in such formulations. The data gained from exposure testing have played and continue to play a vital role in the company's effort to provide the latex architectural coating industry with technologically advanced products for exterior paints. Through this research there has been in-depth analysis of varying failures observed in waterborne latex paints exposed outdoors. These failures include gloss and color retention loss, efflorescence, adhesion failures to varying substrates, cracking, flaking, soiling, and blistering, to name but a few. This presentation will provide an overview of

the composition of water-borne acrylic paints, the exposure testing approach, analytical analysis of paint performance, and finally a structure/ property correlations between paint formulation composition and exterior paint performance

COLL 305

Development of multifunctional nano carrier platforms for cancer treatment

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I will introduce our multifunctional mesoporous silica nanoparticle (MSNP) platform to show how discovery at the nano/bio interface and iterative design can be used to provide improved nanocarriers for cancer treatment. One example is overcoming multidrug resistance by designing MSNP surfaces that allows co-delivery of synergistic anticancer drugs or drugs plus siRNA into drug-resistant cancer cells. The functionalization of the particle surface allows electrostatic binding of the chemotherapeutic agent, doxorubicin (Dox), to the porous interior. Phosphonate modification allows exterior coating with polyethyleneimine (PEI), which endows the carrier with the ability to bind and deliver P-glycoprotein (Pgp) siRNA that silences the expression of the efflux protein. Following the establishment of a Dox-resistant MCF-7 breast cancer xenograft model in nude mice, we demonstrated that a 50 nm MSNP functionalized by a PEI-polyethylene glycol (PEI-PEG) copolymer provides protected delivery of Dox and Pgp siRNA to the tumor site. This design was chosen for its effective biodistribution properties, reduced reticuloendothelial uptake, and the ability to have 8% of the injected dose retained at the tumor site. Compared to free Dox or the carrier loaded with drug alone, dual delivery resulted in synergistic inhibition of tumor growth. Dox encapsulation by the carrier was associated with reduced systemic side effects, including cardiotoxicity. However, analysis of the tumor biopsies demonstrated heterogeneous Pgp knockdown, resulting in effective Dox killing only at where the drug resistance gene was knocked down. The variable distribution of the carrier is due, in part, to heterogeneous vascular access across the tumor matrix and stroma. Since one of the major factors leading to heterogeneous carrier distribution is interference in vascular access due to pericyte coverage, we turned our attention to pancreatic ductal adenocarcinoma (PDAC), in which pericytes in the dysplastic stroma exerts a major effect on drug uptake and carrier availability. In order to deal with this challenge, we developed a dual wave therapeutic approach in which one MSNP carrier delivers a small molecule that interferes in pericyte coverage in the vasculature, while a 2nd nanocarrier (liposomes) introduced gemcitabine, resulting in a synergistic treatment effect.

COLL 306

Enabling biomolecule selection by small molecule-functionalized substrates: A decade of collaborative progress

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Identifying selective molecular recognition elements from large combinatorial pools of biomolecules is key to advancing small-molecule sensing. However, uncontrolled small-molecule functionalization of substrates, e.g., Sepharose[®] beads, to produce biomolecule selection materials leads to high degrees of nonselective recognition and thus, poorly optimized pools of candidate biomolecule “receptors”. We developed a number of methods for controlled placement and ligation of small molecules on self-assembled monolayer substrates. Moreover, we discovered various methods of patterning small-molecule substrates to create negative and positive areas of functionalization with features as small as tens of nanometers and patterns over millimeters. Our findings have enabled a set of design rules that achieve high degrees of specific and selective biomolecule recognition of immobilized small molecules mimicking free solution interactions. Recent advances include identification of surface-bound small molecules by nucleic acid binding partners, and patterning and characterization of pre-functionalized small-molecule tethers. Ongoing efforts are directed at developing substrate-based approaches for determining affinity constants with high throughput.

COLL 307

Nanoparticle-mediated sorting of circulating tumor cell subpopulations

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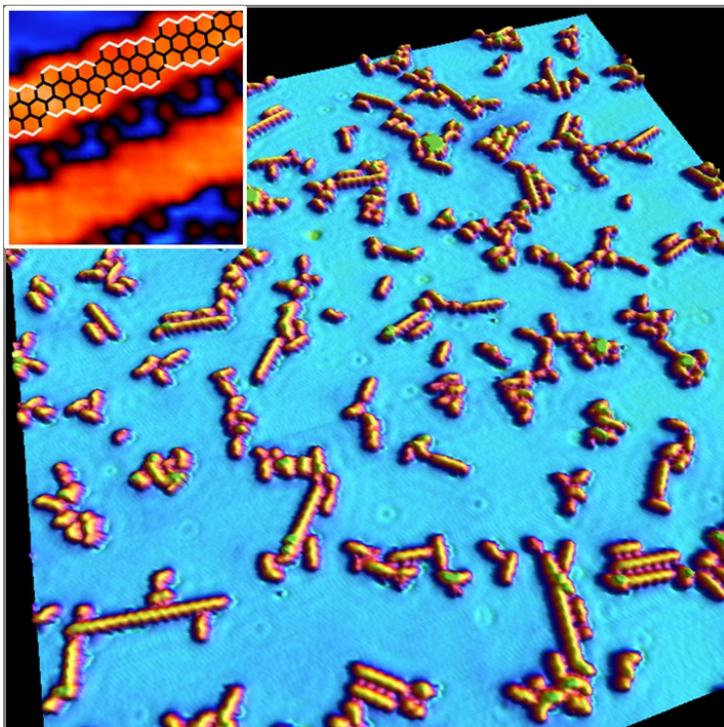
The analysis of circulating tumor cells (CTCs) is an important capability that may lead to new approaches for cancer management. CTC capture devices developed to date isolate a bulk population of CTCs and do not differentiate subpopulations that may have varying phenotypes with different levels of clinical relevance. Here, we present a new device for CTC spatial sorting and profiling that sequesters blood-borne tumor cells with different phenotypes into discrete spatial bins. Antibody-functionalized magnetic nanoparticles facilitate CTC sorting, and permit deconvolution of phenotypic subpopulations. Working with patient blood samples, we obtain profiles that elucidate the heterogeneity of CTC populations present in cancer patients.

COLL 308

Graphene integration by molecular assembly

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Graphene is an extraordinary material because of its low dimensions, high stability, high strength, and high charge-carrier mobility. Further, theory predicts that extraordinary electronic and magnetic properties can be tailored into graphene by controlling its atomic structure alone. These findings promise graphene to revolutionize the next-generation electronics and spintronics, but only if graphene nanodevices can be fabricated: 1) without defect, and 2) at locations where they are needed. Here, we discuss our recent work that uses molecular assembly to target both requirements. We demonstrate that molecular assembly may be a key strategy toward graphene integration into future electronics.



Graphene nanoribbons fabricated by self-assembly on Cu{111}. Inset highlights the edge configuration of individual ribbons.

Reactions and functionalizations of graphene and surfaces

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Paul Weiss lured me and my group into the studies of reactions on surfaces and of surfaces. Several fruitful collaborations ensued!

After a brief review of these collaborative efforts with the Weiss group, I will discuss quantum mechanical studies of reactions of dienes, 1,3-dipoles, and various other reactive intermediates with graphene and Si surfaces.

COLL 310

Artificial light harvesting system composed of organic dyes and clay minerals

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We have been investigating complexes composed of anionic nanolayered materials such as clay nanosheets and cationic dye molecules. It was found that the structure of dye assembly on the layered materials can be effectively controlled by the use of electrostatic host-guest interaction called as "Size-matching Effect" or "Intercharge Distance Matching Effect". The intermolecular distance, the molecular orientation angle, the segregation/ integration behavior, and the immobilization strength of the dyes can be controlled in the clay-dye complexes (Fig. 1). Unique photochemical reactions such as energy transfer through the use of this methodology have been examined. Almost 100% efficiency of the energy-transfer reaction was achieved in the clay-porphyrin complexes as a typical example for an artificial light-harvesting system. Control of the molecular orientation angle is found to be useful in regulating the energy-transfer efficiency and in preparing photofunctional materials exhibiting solvatochromic behavior. In this paper, we will talk on the enhancement of photochemical properties of dyes on the clay surface such as fluorescence enhancement and efficient energy transfer systems in clay-dye complexes. A unique phenomenon of the strong enhancement in the fluorescence quantum yield (ϕ_f) and the excited lifetime (τ) of tetra-cationic porphyrine dye (Pz) upon a complexation with inorganic nanosheets were observed. Although Pz does not strongly fluoresce in a bulk solution ($\phi_f = 0.01$, $\tau = 0.1$ ns), ϕ_f and τ increased up to 19 and 34 times by an intercalation into stacked clay nanosheets. Steady-state and time-resolved fluorescence measurements revealed that this strong enhancement in ϕ_f and τ is derived from the suppression of nonradiative deactivation pathways of Pz by a complexation with clay nanosheets. We here name this phenomenon a "Surface-Fixation Induced Emission (S-FIE)". By using such favorable photochemical character, light harvesting system where the efficiency was almost 100% even under the ratio of donor/acceptor = 1/1-6/1 was achieved.

Ref. S. Takagi *et al. Langmuir* (Invited Feature Article) **2013**, *29*, 2108-2119; *Langmuir*

2013, 29, 1748–1753; *J. Phys. Chem. C* 2013, 117, 9154–9163; *J. Phys. Chem. C* 2014, 118, 10198–10203; *J. Phys. Chem. C* 2014, 118, 20466–20471.

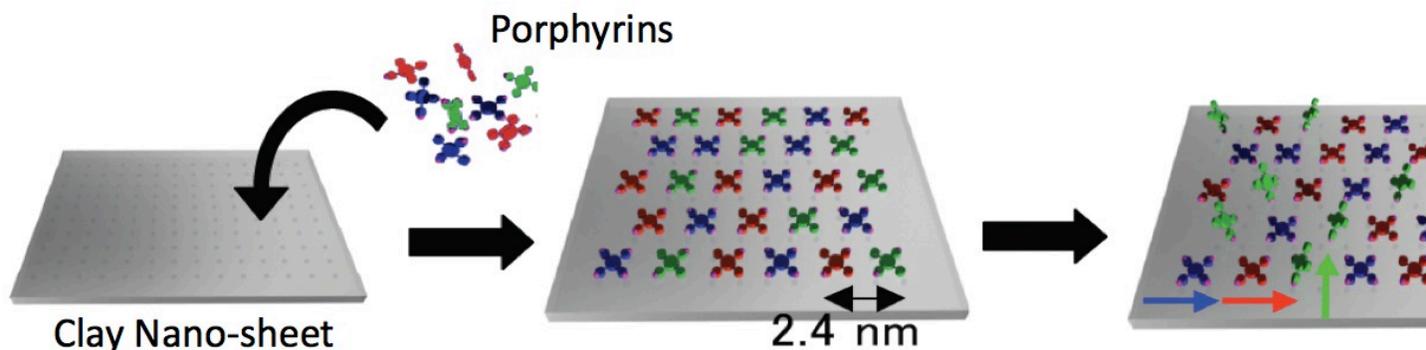


Figure 1. The molecular alignment control of porphyrin molecules on the clay nano-sheet.

COLL 311

Protein analogous micelles: Versatile, modular nanoparticles

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Peptides are functional modules of protein macromolecules that can be displayed apart from the whole protein to create biofunctional surfaces and interfaces, or can be re-assembled in new ways to create synthetic mimics of protein structures. Each of these routes are being employed to gain new insight into protein folding and to develop new, functional, biomolecular materials. Conjugation of a peptide to a synthetic or natural lipid or fatty acid confers on the conjugate self-assembly capabilities not present in peptides alone. Examples of work from our laboratory in this area using peptide-lipid conjugate molecules (peptide amphiphiles) will be discussed with applications to peptide secondary structures and its relationship to function, DNA-binding peptide assemblies, synthetic vaccines, and particles that home to cancer and atherosclerotic plaques. *In vivo* testing shows efficacy of these self-assembled nanoparticles in stimulating both T-cell and B-cell immunity, as well as targeting early stage atherosclerosis. Work done in collaboration with Eunji Chung, Bret Ulery, Lorraine Leon, and Matthew Kade.

COLL 312

Enzymatic transformation and self-assembly of peptides for future cancer therapy

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While molecular-targeted therapeutics, which mostly are based on ligand-receptor interaction or enzyme inhibition, have been a key strategy for developing anticancer therapeutics, recent advances in cancer biology have revealed the great complexity of cancers, such as redundant signaling pathways, adaptive drug resistance, genomic instability, intratumoral heterogeneity, and tumor microenvironment. These insights not only elucidate the limitation of the current cancer therapy that aims to only one or two molecular targets (e.g., enzymes, receptors, or transcription factors), but also underscore an urgent need of new approaches for future cancer therapy. In this talk, we highlight two related approaches, enzymatic transformation (ET) and self-assembly (SA), for the development of molecular medicines for future cancer therapy. Enzymatic transformation allows one to develop approaches to target “undruggable” targets or “untargetable” features of cancer cells; self-assembly provides the opportunity for simultaneously interacting with multiple targets. Using the phosphatase catalysis and the self-assembly of small peptides as examples, we will discuss the integration of ET and SA to inhibit multidrug resistance (MDR) cancers *in vitro* and *in vivo*, and illustrate a potential paradigm shift for developing anticancer medicines for targeting multiple hallmarks of cancer that are the major challenges in current cancer therapy.

COLL 313

Designability of peptide-based materials

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Structurally defined materials on the nanometer length-scale have been historically the most challenging to rationally construct and the most difficult to structurally analyze. Sequence-specific biomolecules, i.e., proteins and nucleic acids, have advantages as design elements for construction of these types of nano-scale materials in that correlations can be drawn between sequence and higher order structure, potentially affording ordered assemblies in which functional properties can be controlled through the progression of structural hierarchy encoded at the molecular level. However, the predictable design of self-assembled structures requires precise structural control of the interfaces between peptide subunits (protomers). In contrast to the robustness of protein tertiary structure, quaternary structure has been postulated to be labile with respect to mutagenesis of residues located at the protein-protein interface. We have employed simple self-assembling peptide systems to interrogate the concept of designability of interfaces within the structural context of nanotubes and nanosheets. These peptide systems provide a framework for understanding how minor sequence changes in evolution can translate into very large changes in supramolecular structure, which provides significant evidence that the designability of protein interfaces is a critical consideration for control of supramolecular structure in self-assembling systems.

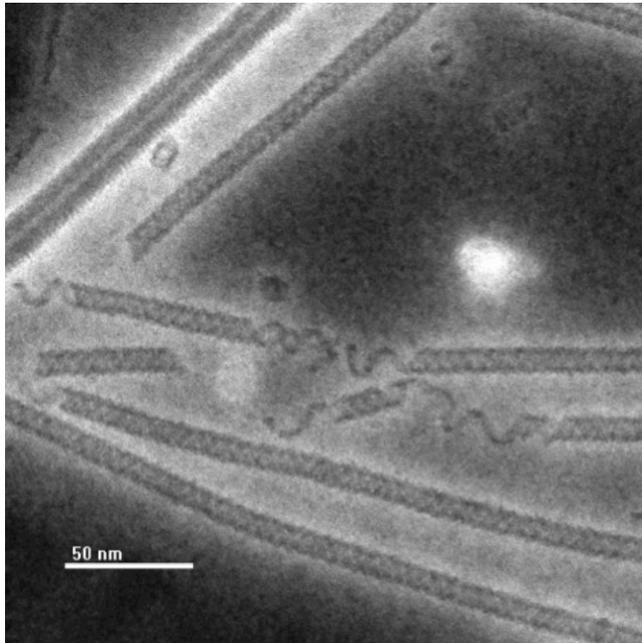


Figure 1. STEM image of nanotubes derived from self-assembly of a *de novo* designed, bi-faceted coiled-coil peptide.

COLL 314

Tumor-penetrating peptides in the targeting of drugs and theranostic nanoparticles

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This laboratory studies tissue-specific vascular markers, “vascular zip codes”, and their use in selective targeting of drugs and nanoparticles to diseased tissues. Screening of phage libraries in live mice identifies peptides that direct phage homing to a specific target in the body. When the libraries are injected into the circulation, tissue-specific or tumor-specific differences in endothelial cells are primarily targeted. The homing peptides from these screens have revealed a zip code system of molecular changes in the blood vessels of normal tissues and the vessels of various diseased tissues, such as tumors. The power of *in vivo* phage screening is illustrated by the recent discovery of peptides with unique tumor-penetrating properties. These peptides, through a complex mechanism that involves a proteolytic cleavage and binding to a second receptor, activate an endocytic transport pathway related to but distinct from macropinocytosis. This trans-tissue pathway, dubbed the CendR pathway, mediates the exit of payloads ranging from small molecule drugs to nanoparticles from the blood vessels and transport through extravascular tumor tissue. The CendR technology provides a solution to a major problem in tumor therapy, poor penetration of drugs into tumors. The tumor-penetrating peptides are capable of taking a payload deep into tumor tissue in mice,

and they also penetrate into human tumors *ex vivo*. Targeting with these peptides specifically increases the accumulation in tumors of a variety of drugs, such as doxorubicin, antibodies and nanoparticles, as well as imaging agents. Remarkably the drug or nanoparticle to be targeted does not have to be coupled to the peptide; the peptide activates a bulk transport system that sweeps along any compound that is present in the blood. Treatment studies in mice show improved anti-tumor efficacy and less damage to normal tissues. Recent results suggest applications for this technology beyond cancer, to fields such as cardiovascular and neurodegenerative diseases.

COLL 315

Peptide-guided drug assembly

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Directly assembling therapeutic drugs into supramolecular nanostructures offers an innovative strategy to create self-delivering nanomedicine containing a high and fixed drug content. However, since only a limited number of drugs are capable of forming stable, discrete assemblies suitable for systemic delivery, it is often necessary to incorporate an auxiliary segment to guide the drug assembly process. Here I discuss our recent progress in the use of oligopeptides to fine-tune the size, shape, stability, and dissociation kinetics of anticancer drug assemblies, with the goal of obtaining desired physicochemical and stimuli-responsive properties for targeted cancer chemotherapy.

COLL 316

Engineering underwater adhesives: Leveraging cation- π interactions to govern peptide cohesion

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The amino acid 3,4-dihydroxyphenylalanine (Dopa) is a principle component of the adhesive plaques of marine mussels. However, the susceptibility of Dopa to autoxidize to a non-adhesive quinone form at neutral-to-basic pH conditions remains a major challenge to the implementation of Dopa in synthetic underwater adhesives. In this work, we used a surface forces apparatus to characterize the adhesive properties of a series of short, synthetic peptides (36 amino acids in length) that are inspired by a Dopa- and lysine-rich segment from the sequence of a key mussel foot adhesive protein, mfp-5. By comparing the Dopa, tyrosine, phenylalanine, and leucine

(hydrophobic control) analogues of the same model peptide sequence, we show that the interfacial cohesion of these nanoscale peptide films depends critically on cation- π interactions when confined between two mica surfaces. Notably, the cohesive strength increases with increasing π -electron density of the aromatic groups, F_{ad} : leucine \ll Dopa \sim tyrosine \ll phenylalanine. Thus, while Dopa remains an important functional group for applications involving specific coordination chemistry, the incorporation of redox resistant aromatic residues in lysine-rich peptides may provide an attractive general platform for designing robust underwater adhesives that resist autoxidation over a wide range of aqueous conditions.

COLL 317

Peptide-polymer amphiphiles as programmable synthons for biologically-responsive nanomaterials

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We describe a strategy for rendering peptide-based polymeric materials and nanostructures responsive, or resistant to proteolysis by formulating them as high-density brush polymers and particles assembled from peptide-polymer amphiphiles (PPAs). The utility of this approach is demonstrated by polymerizing well-established cell-penetrating peptides (CPPs) or substrates for disease-associated proteases, and showing that the resulting materials exhibit unusual properties both in tissues *in vivo*, and within cellular assays *in vitro*. We contend that resistant materials offer a plausible method of preparing peptides for *in vivo* use, where rapid digestion by proteases has traditionally restricted their utility. Similarly, enzyme-responsive materials open doors for the directed assembly of structures within tissues. This second application will be described in terms of their potential in drug delivery, and in guided surgery.

COLL 318

Interaction of colloidal nanoparticles with mammalian cells: Correlation of uptake and toxicity with physicochemical properties, such as surface coating

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Investigations of the interaction of functionalized inorganic colloidal nanoparticles with mammalian cells are now performed within the context of nanotechnology since two decades, and even some earlier examples exist. We will highlight some generally-accepted concepts about this research. While details of these complex interactions strongly depend, amongst others, upon the specific properties of the nanoparticles used, cell type, and their environmental conditions, a number of fundamental principles

exist, which are outlined in this review. We will correlate interaction of the nanoparticles with cells with the physicochemical properties of the nanoparticles. The problem of entanglement of different physicochemical properties will be discussed. A special focus will be given on potential cytotoxicity associated with nanoparticle uptake by cells.

Colloidal particles with fluorescence read-out are commonly used as sensors for the quantitative detection of ions. Regardless the sensing mechanism the particles act as carriers. Surface chemistry of the particles thus determines their interaction with cells, in particular pathway of uptake, intracellular location, as toxicity. Different surface chemistry for particle functionalization will be compared, which can be applied to different particle geometries such as spheres, rods, etc. It also will be explained how surface chemistry can interfere with read-out. Besides delivery and intracellular location of particle-based fluorophores also other experimental difficulties such as crosstalk of the fluorescence read-out with pH, and spectral overlap of the emission spectra of different fluorophores will be discussed.

COLL 319

Impact of gold nanoparticles on cells: PEGylation's type matters

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Functionalization of colloidal nanoparticles (NPs) with polyethylene glycol (PEG), i.e. PEGylation, is among the most widely employed surface modification methods to provide NPs with enhanced colloidal stability in physiological media, as well as to reduce unspecific adsorption of proteins (i.e. the formation of the protein corona). Indeed, PEGylation has been demonstrated to increase the blood circulation time of colloids in animal models. Although the word PEGylation is often used to describe NP grafting with PEG, as it was a universal type of coating, the molecular weight and end-terminal groups of PEG can significantly change the physicochemical properties of the colloids. In this work, we have investigated the impact of different PEGylations *in vitro*. Gold colloids of increasing sizes were modified with thiolated PEG chains of decreasing sizes, respectively, which allowed us to produce different types of PEGylated gold NPs with the ca. same hydrodynamic size and similar stiffness, different size of inorganic core and organic shell thickness. Moreover, the net charge of the NPs was modified to investigate the effect of the charge. The *in vitro* results reveal distinct cellular effects which can be correlated with the physicochemical properties of the PEGylated NPs.

COLL 320

Silanization of layer-by-layer assemblies: Mechanisms and application for the fabrication of superhydrophobic surfaces

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Layer-by-layer assembly (LbL) which is the stepwise adsorption of polyelectrolytes in multilayers, and silanization, which is the assembly of silanes on hydroxylated surfaces such as silicon oxide, are two well-known methods of surface functionalization. The combination of these two complementary techniques offers interesting opportunities to fabricate complex functional films. However, exploiting fully the potential of this combination requires to understand in depth the phenomena occurring when silanizing LbL assemblies. Therefore, we focus here on improving our understanding of the gas phase silanization of typical polyelectrolyte multilayers based on poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA), and use this knowledge to fabricate sturdy superhydrophobic surfaces containing these polyelectrolytes and silica nanoparticles.

The silanization process is first studied by Secondary Ion Mass Spectrometry, Atomic force Microscopy, contact angle and X-ray reflectometry, depending on reaction time and temperature, pH of multilayer assembly, and nature of the reacting silane group. Whereas monochlorosilanes only diffuse in the multilayer and graft in limited amount, trichloro- and triethoxy-silanes form rapidly a continuous gel layer on the surface of the multilayer, with a thickness of ca. 10-20 nm. The reactivity is lower in the strongly-paired regime of the multilayers (neutral assembly conditions), but otherwise not affected by the pH of multilayer assembly.

Then, robust thin superhydrophobic and self-cleaning films are prepared by assembling silica nanoparticles of various nature over a PAH/PAA cushion layer, followed by fluorosilanization, giving rise to systems of varying transparency and hydrophobicity. Characterization of the surface roughness by power spectral analysis confirms the Wenzel roughness to be a useful criterion to predict superhydrophobicity, whereas the components of the roughness of wavelength above a few hundred nanometers are responsible for the loss of transparency. Based on this analysis, an optimized design is proposed, leading to superhydrophobic transparent layers with contact angles as high as 155°, 0° roll-off angle and strong rebound of water droplets, demonstrating the potential for applications of the technology.

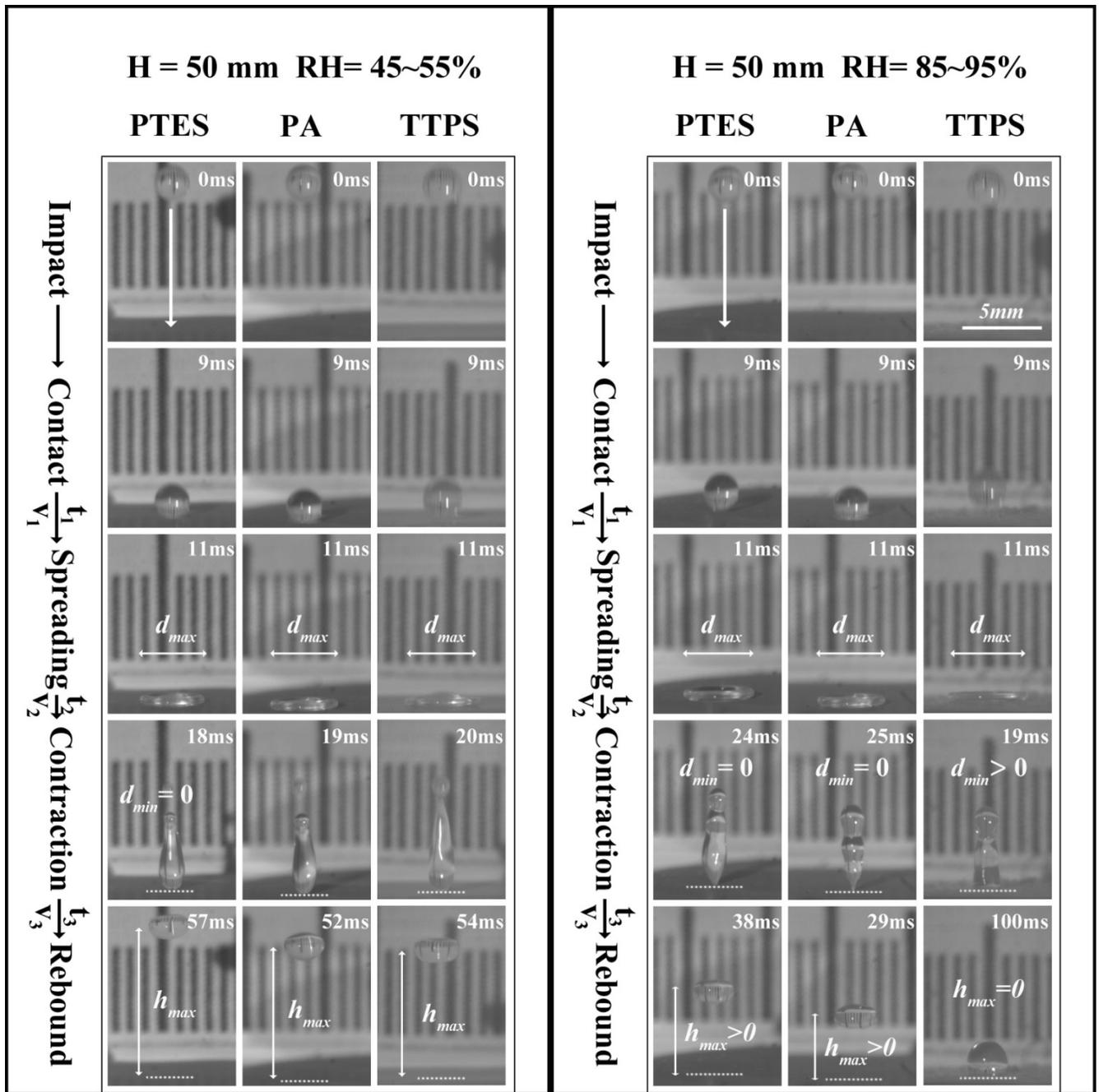
COLL 321

Verification of anti-icing/icephobic properties of different chemical modified superhydrophobic surfaces

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Inspired by the animals and plants in the nature, superhydrophobic surfaces received increasing attention as the most attractive strategy for preparing anti-icing materials. In order to investigate the wettability transition of superhydrophobic surface under

condensate condition especially the influence of chemical modification to this shift, three superhydrophobic surfaces with different chemical modification [1H,1H,2H,2H-perfluorodecyltriethoxysilane (PTES), triethoxysilylethyl-terminated polydimethylsiloxane (TTPS) and palmitic acid (PA)] on similar nano-/micro-topological structure were prepared. Their surface wettability in terms of water contact angle and sliding angle and the anti-icing property of these surfaces were studied under different humidity at -10 °C. The icephobic property (reduction of ice adhesion) investigation was carried out on both regular and condensed samples. The results indicated that the anti-icing/icephobic properties were varied wildly of these three superhydrophobic surfaces at subzero environment, droplet rollability and rebounding ability only reserved on PTES surface under extremely condensate situation. It is worth stressing that, the ice adhesion increased obviously on condensed samples but none of them presented penetrated anchoring effect. In addition, distinctive self-propelled combining and jumping of condensed micro- water droplets behavior like Leidenfrost phenomenon was discovered on all three superhydrophobic surfaces while the highest jumping frequency was found on PTES surface. The excellent positive ice-repellent and icephobic property of PTES surface may be attributed to the PTES modification with the synergistic effect of low surface energy and stable rod rigid structure.



Sequential images of the dynamic behavior of 7.25 μ L overcooled water droplet impact three horizontal superhydrophobic surfaces from a height of 50 mm at -10°C under RH of 45-55% and 85-95%.

COLL 322

Super-high resolution of control assembled fluorescent-TMV using microlens

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Abstract

Controlled assembly of nanoparticles with high precision and high levels of integration has great applications in electronics and optics industry. Bio-nanoparticle namely tobacco mosaic virus (TMV) has a high aspect ratio that can be engineered to facilitate self-assembling on various substrates and also serve as a template for synthesis of nano-structured materials. TMV is a rod-like plant virus consisting of 2130 identical protein subunits arranged helically around a single stranded RNA, where tyrosine residues present on the exterior surface of 300nm long TMV particle was modified using click chemistry for efficient attachment of fluorescent beads through biotin-streptavidin complex. These fluorescent TMV were patterned within digital versatile disc (DVD) and Blu-Ray grooves thereby produced a linearly assembled TMV substrate. Furthermore, super high resolution of these patterned nanoparticles was performed using our reported Microlens based optical microscope technique, which has the ability to spatially resolve hard/soft nanoparticles separated by a distance of 100nm under a visible light source. UV-Visible and fluorescence spectroscopy, mass spectrometry, and dynamic light scattering were used to characterize the attachment of fluorophores on TMV, whereas fluorescence and scanning electron microscope were used for imaging the assembled fluorescent-TMV in Blu-Ray and DVD grooves. We demonstrate super-high resolution of fluorescence on these assembled TMVs utilizing Microlens based optical microscope.

Keywords: Optical Microscope, Microlens, Tobacco mosaic virus, Fluorescence and DVD

COLL 323

Surface-enhanced Raman scattering nanoparticles as optical labels for imaging cell surface proteins

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Assaying the expression of cell surface proteins has widespread application for characterizing cell type, developmental stage, and monitoring disease transformation. We report on the use of narrow band width surface-enhanced Raman scattering (SERS) nanoparticles as optical labels for multiplexed immunophenotyping. Two types of surface coatings were investigated to passivate the gold nanoparticles, incorporate SERS functionality, and to facilitate attachment of targeting antibodies. Thiolated poly(ethylene glycol) forms dative bonds with the gold surface and is compatible with multiple physisorbed Raman-active reporter molecules. Ternary lipid bilayers are used to encapsulate the gold nanoparticles particles, and incorporate three different classes of Raman reporters. TEM, UV-Visible absorbance spectroscopy, DLS, and electrophoretic

light scattering were used to characterize the particle coating. Colourimetric protein assay, and secondary antibody labelling were used to quantify the antibody conjugation. Three different *in vitro* models were used to investigate the binding efficacy and specificity of SERS labels for their biomarker targets. Primary human CLL cells, LY10 B lymphoma, and A549 adenocarcinoma lines were targeted. Dark field imaging was used to visualize the colocalization of SERS labels with cells, and evidence of receptor clustering was obtained based on colour shifts of the particles' Rayleigh scattering. Widefield, and spatially-resolved Raman spectra were used to detect labels singly, and in combination from labelled cells. Fluorescence flow cytometry was used to test the particles' binding specificity, and SERS from labelled cells was also detected using a modified flow cytometer. The work reported herein demonstrates SERS immunophenotyping using multiple cancer models, and adaptability to clinical instrumentation.

COLL 324

Surface modification of inorganic nanoparticles for biomedical applications

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Inorganic nanoparticles are widely used as research tools in life science, including therapy and diagnosis. It is well known that the nanoparticle surface is one of the most important parameters to define their biological fate. In this talk we will present a general method to polymer coat noble metal nanoparticles (NPs). One of the most widely used approach to stabilize NPs in aqueous solution involves wrapping NPs with amphiphilic polymers. This methodology has been extensively employed for coating of NPs capped with aliphatic chains, thereby enabling phase transfer of NPs from an organic solvent to aqueous solution. The polymer coating approach is herein extended to NPs originally synthesized in aqueous solution by a two-step method. Firstly, NPs are subjected to aqueous-to-organic phase transfer. The phase transfer protocol was demonstrated for NPs made of different materials (Au and Ag), sizes (up to 100nm) and shapes (spheres, rods and flat-triangular prisms). In a second step NPs are coated with an amphiphilic polymer. The colloidal stability of surface modified colloids was assayed against different media of biological relevance. The biocompatibility of polymer coated NPs was studied in cancer and non-cancer cells.

COLL 325

Engineering the optical properties of gold nanoparticles by assembling into highly packed 2D arrays of different structure

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The proper assembly of nanoparticles can enhance their properties and improve their applicability. Likewise, imprudent assembly can damage the unique properties of the nanomaterials. Accordingly, finding robust techniques for making ordered assemblies of nanoparticles is a hot topic in materials science research. Langmuir-Blodgett (LB) technique was used to assemble polymer-functionalized gold particles (AuNPs) into highly packed 2D arrays with different structures. This technique is based on creating polymeric micelles within the AuNPs monolayer, which drives the nanoparticles to assemble into a highly packed structure even at low LB surface pressures. Interestingly, the micelles could be made more diffuse by changing the LB trough surface pressure, which allowed for tuning the width and the structure of the AuNP 2D arrays. The areas occupied by the micelles appeared as voids that separated the AuNP arrays and prevented the formation of a uniform monolayer of AuNPs.

COLL 326

Protein resistant nanoparticle surfaces designed for the assembly of biodegradable plasmonic gold nanoclusters

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A significant challenge within the field of nano-diagnostics and therapy is the design of sub-100 nm gold nanoclusters to target cancer cells with strong NIR extinction. We have assembled clusters from 5 nm gold primary particles by mixing a dispersion of Au nanospheres with a polymer solution to manipulate the various colloidal interactions. The weakly adsorbed polymer quenches the cluster growth and provides steric stabilization. The size of the clusters was tuned from 20 to 100 nm by varying the Au concentration, particle surface charge (by varying the ligand ratio, pH, salinity), polymer/Au ratio and degree of solvent evaporation. Upon polymer degradation in cellular pH 5 environments, the nanoclusters undergo biodegradation all the way back to the original particles to allow clearance through the kidneys. However, the adsorption of even a single protein molecule can increase the particle size beyond this 5 nm threshold. Therefore, we have designed by place exchange ~5 nm gold nanoparticles with primary and secondary ligands on the surface, which completely resist protein adsorption in undiluted fetal bovine serum (FBS). The moderately-charged particles are comprised of an uneven ratio of anionic citrate and one of two naturally-occurring amino acids, either cationic lysine or zwitterionic cysteine. The ligands contain buried charges that are below zwitterionic tips, which are known to interact weakly with protein molecules. Dynamic light scattering measurements of the particles shows no size increase after particle incubation in 100% FBS indicating the lack of any protein adsorption. Therefore the surface functionalization of the Au nanospheres plays a

central role in achieving controlled nanocluster assembly, high NIR extinction, and nanocluster dissociation to primary particles which resist protein adsorption.

COLL 327

Metallic nanocomposites of carbon nanotube and their bioconjugates: effective antimicrobials?

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Recent advances in nanotechnology have shown remarkable promise towards biomedical applications. In particular, metallic nanocomposites of carbon nanotubes such as silver coated carbon nanotubes (AgCNTs) have various biomedical applications from engineering to nanomedicine. One of the most exciting areas of development is the use of AgCNTs as effective and resistance free antimicrobials. Due to their unique physico-chemical properties, AgCNTs have emerged as strong antimicrobial agents. Despite this, the toxicity of these nanoparticles to eukaryotic cells of human origin limits their use as antimicrobials. However, the toxicity issue can be addressed by the process of bio-conjugation, a method wherein nanoparticles are conjugated with a suitable biological entity such as DNA, RNA or antibacterial peptide (AP). This synergistic relationship between AgCNTs and APs will have therapeutic benefit as nanoparticles are already well known for their application as effective drug carriers. Strategies such as modification or functionalization of AgCNTs will reduce their toxicity and improve the biocompatibility of these molecules. Herein, we will focus on how the toxicity of AgCNTs can be reduced using functionalization strategies and the potential use of these metallic nanocomposites and their bioconjugates as effective antimicrobials.

COLL 328

Au/CdS plasmonic photocatalytic nanostructures constructed using P22 virus-like particles for enhanced photoactivity

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Plasmonic photocatalytic nanostructures have been fabricated under mild synthetic conditions using genetically engineered bacteriophage P22 virus-like particles (VLP) as a nanoplatform. The unique P22 VLP nano-architecture, composed of a shell assembled from 420 copies of coat protein (CP) and an interior cavity containing approximately 300 copies of scaffolding protein (SP), offers tremendous opportunities for materials design and synthesis. The confined synthesis of photocatalytic CdS inside P22 VLP is realized by genetically engineering CdS binding peptides onto the SP.

Subsequently, plasmonic gold nanoparticles that are symmetrically positioned on the shell of VLP are synthesized. The size of gold nanoparticles can be suitably tuned by adjusting the relative ratio of gold precursor and VLP template. The controlled formation of gold nanoparticles on the outer shell of VLP-CdS dramatically enhances the photoactivity of CdS confined inside the VLP, as tested by studying the photodegradation kinetics of methylene blue (MB) using a solar simulator. In contrast, the gold nanoparticles by themselves exhibit no significant effect on the photodegradation of MB. These findings are relevant for the synthesis of a wide range of alternative plasmonic photocatalytic materials with desired components, architectures, and performance.

COLL 329

Scalable metal-semiconductor nanostructure integration for multimode gas sensing at high temperature

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Three-dimensional (3-D) integration of nanostructures or nanostructure arrays into applicable platforms or devices represents the need for meeting ever-increasing demands of human beings for cost-effectiveness, structure sophistication, multi-function enabling, while simplified and efficient practical operations. Such an integration process generally involves a diverse array of nanostructured entities that include various dissimilar nanoscale building blocks such as nanoparticles, nanowires, and nanofilms made of metals, ceramics, or polymers in the nanoscale form. In this talk, I will highlight our latest research progress on the 2-D and 3-D metal and semiconducting metal oxide based nanostructure integrations toward applicable ultrahigh efficiency, robustness, and improved functionality. Specifically, examples through design in scalable nanomanufacturing, and gaseous species sensing utilizing electrical, electrochemical and optical modes will be used as the connecting dots to display a nanomaterials roadmap linking from scalable 2-D toward 3-D integration.

COLL 330

Plasmonic enhancement characteristics of multilayered metallic nanostructures

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Metal nanostructures are of considerable interest due to the unique mechanism by which these structures interact with light. Extensive work has been reported on the synthesis, modeling, and utilization of various morphologies of plasmonic structures. Recently, the synthesis of highly crystalline Ag:SiO₂:Ag core:spacer:shell particles of varying geometries by the hydrogen reduction method was reported. Herein, we report

the effect of spacer thickness and shell morphology on the coupling of plasmon modes and thus the relative ratio of plasmon relaxation pathways. Likewise, the relationship between CSS particle geometry, analyte molecule placement, SERS and SEF enhancement factors, and analyte emission lifetimes is explored.

COLL 331

Exotic Au nanostructures: structure solution, properties, and applications

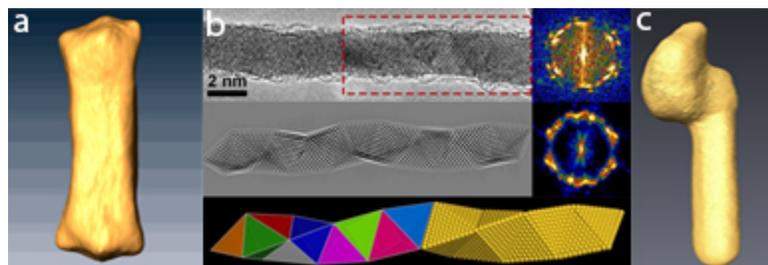
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In this presentation, I will give three examples of exotic Au nanostructures that we recently fabricated, including (i) a Au-Pd bimetallic nanostructure through site-specific epitaxial growth of Au-Pd alloy horns at the ends of Au nanorods (Figure a);^[1] (ii) Chiral Gold Nanowires with Boerdijk-Coxeter-Bernal Structure (Figure b);^[2] and (iii) an asymmetric Au nanorod-Au nanoparticle dimer structure (Figure c).^[3] Their synthetic strategies, structural characterization, and applications in heterogeneous catalysis, surface-enhanced Raman spectroscopy, and nanophotonics, will be elaborated.

[1] Jianfeng Huang, Yihan Zhu, Ming Lin, Qingxiao Wang, Lan Zhao, Yang Yang, Kexin Yao, and Yu Han, "Site-specific Growth of Au-Pd Alloy Horns on Au Nanorods: a Platform for Highly Sensitive Monitoring of Catalytic Reactions by Surface Enhancement Raman Spectroscopy" *J. Am. Chem. Soc.*, 135 (2013), 8552-8561

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[3] Jianfeng Huang, Yihan Zhu, Yu Han, "An Asymmetric Monometallic Au Nanorod-Au Nanoparticle Dimer with Extraordinary Broadband Optical Extinction: Synthesis, Growth Mechanism, and Applications", submitted.



COLL 332

Ultrasensitive detection using SERS and SEHRs: From nonlinear optical properties to nuclear forensics

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The intersection of higher-order spectroscopies with the field of plasmonics is an unexplored frontier; therefore, we are exploring the ability of plasmonic nanostructures to drive nonlinear spectroscopies, such as hyper-Raman. In this talk we discuss recent progress in surface enhanced hyper-Raman scattering (SEHRS). In particular we highlight its ability to detect single molecules, explore the nonlinear properties of nonlinear chromophores and enhance short-wave IR sensing. New SERS based detection schemes for environmental pollutants and nuclear forensics are also discussed.

COLL 333

Conformation and dynamics of endogenous cannabinoid ligand 2-AG in a lipid matrix and its interaction with cannabinoid type II receptor

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The endogenous cannabinoid ligand, 2-arachidonoylglycerol (2-AG), is a lipid-derived signaling molecule that activates cannabinoid receptors in brain and peripheral tissue. Because of its high lipophilicity, 2-AG readily partitions into lipid bilayers. We had reported earlier, based on unbiased molecular dynamics simulations, that a lipid pathway for binding of 2-AG to cannabinoid type II (CB₂) receptor is necessary¹. Here we studied location, structure, dynamics of 2-AG, kinetics of acyl-chain migration (2-AG→1-AG), and the binding of 2-AG to CB₂ in lipid bilayers by solid-state NMR, neutron diffraction, and MD simulations. Neutron diffraction data and ¹H NOESY cross-relaxation rates revealed that the glycerol group of 2-AG resides in the lipid/water interface of bilayers, while the double bonds of the arachidonyl chain show a wide distribution with highest density in the hydrophobic core of lipid hydrocarbon chains of the bilayer. The arachidonyl chain retains a high level of flexibility in bilayers as determined by order parameter and relaxation time measurements. The exponential-decay constant of 2-AG→1-AG conversion in bilayers at the physiological temperature of 37°C is 43 min. Binding of 2-AG to purified CB₂ receptor that was functionally reconstituted into liposomes was probed by ²H magic-angle-spinning NMR on glycerol-deuterated 2-AG (2-AG-d₅). In the presence of CB₂, the ²H resonances of 2-AG-d₅ shifted upfield and broadened. The upfield shift was absent when the binding pocket was blocked with a high affinity agonist like CP-55,940, demonstrating specificity of 2-AG interaction with CB₂. The data are in agreement with a rapid exchange of 2-AG between a membrane location and bound to CB₂. It is proposed that preferred location of 2-AG in lipid bilayers and the conformational flexibility of 2-AG are critical for an efficient interaction with the ligand binding pocket of the receptor.

1. Hurst, D.P. et al, J. Biol. Chem. 285 (2010) 17954-17964.

COLL 334

Studying the mechanism of coiled coil mediated membrane fusion

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Fusion of lipid bilayers, or membranes, is a ubiquitous process. It occurs in the cells of our body during cargo exchange by membrane vesicles and during viral infection, but also in industrial processes such as yeast production. While many proteins like SNAREs have been identified that play crucial roles in membrane fusion, the molecular mechanism of fusion remains unclear. This fascinating process is unexpectedly complex and our aim is to understand the details of this process using a biomimetic model system which has all the characteristics of natural membrane fusion; targeted docking, followed by lipid and content mixing in the absence of leakage.

We developed a model system composed of a complementary pair of lipidated peptides able to form a heterodimeric coiled coil motif at the membrane interface similar to natural SNARE subunits. The different steps of membrane fusion are currently studied using biophysical and biochemical techniques with a special focus on peptide-peptide and peptide-lipid interactions. Unravelling of the molecular mechanism of membrane fusion using a multi-faceted approach of complementary techniques will result in a unique, in depth view of the process of membrane fusion.

COLL 335

Exploring the interactions of ions with supported lipid membranes

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Lipid bilayers contain of a variety of functional groups such as phosphates, carboxylate, amine and choline moieties that can interact with ions from the adjacent aqueous solution and in turn affect the physical properties of the membrane. Herein we will describe the use of fluorescence measurements using supported bilayers inside microfluidic channels to explore the interaction of metal ions with these model membranes as a function of lipid chemistry, pH, ionic strength, and temperature. Complementary spectroscopic experiments to observe the molecular level details of these interactions will also be reported as well as the implications for the associated water structure. These results suggest that metal ion affinity can vary quite widely depending upon the specific conditions of the system and the binding affinities can be quite strong.

COLL 336

Dynamic reorganization and correlation among lipid raft components probed by imaging mass spectrometry

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While the structural biology of proteins and nucleic acids have advanced enormously, the *organization* of components in cells, in particular in cell and organelle membranes, remains relatively poorly understood. We use imaging mass spectrometry to characterize model and native membranes using a NanoSIMS [*Ann. Rev. of Biophysics*, **38**, 53 (2009)], and this has been applied to obtain quantitative information on the dynamic reorganization of components to characterize the association state of raft lipids. The concept exploits supported membrane patterning and membrane electrophoresis [*Acc. Chem. Res.*, **35**, 149. (2002)], and the unique single negative charge on the raft marker G_{M1} . When subjected to an electric field, G_{M1} moves towards the positive electrode forming a gradient due the competition between the electrophoretic force and diffusion. The question we address is whether cholesterol and sphingomyelin, both neutral molecules that do not move by themselves by application of an electric field, co-migrate with G_{M1} ? Using recently developed methods for isotopically enriching cholesterol (^{13}C or D) and addition of a single fluorine label at the end of G_{M1} , we analyze the lateral composition of these membranes following electrophoresis using the NanoSIMS. The analysis demonstrates that cholesterol and sphingomyelin only move in an electric field when G_{M1} moves, demonstrating that these molecules are intimately associated in these model membranes. Further analysis provides information on the stoichiometry of these transient extended complexes, a long-sought quantity in membrane biophysics. Extensions of this approach to other membrane-anchored components relevant to signaling and raft localization will be described.

COLL 337

Functionalized lipid–nucleic acid nanoparticles for delivery applications

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Cationic liposomes (CLs) are studied worldwide as carriers of DNA and short interfering RNA for gene delivery and gene silencing, and related clinical trials are ongoing. Optimization of transfection efficiency and silencing efficiency requires elucidation of the interactions of CL–nucleic acid nanoparticles (NPs) with cell membranes including events leading to release of active nucleic acids within the cytoplasm. Synchrotron x-ray scattering has revealed the distinct liquid crystalline phases of CL–nucleic acid complexes including the lamellar, inverse hexagonal, hexagonal, and gyroid cubic phases. The talk will describe experiments with surface-functionalized PEGylated CL–DNA nanoparticles (NPs) (Majzoub et al., *Biomaterials* 2014), including fluorescence

microscopy colocalization with members of the Rab GTPases, which has revealed CL–DNA pathways and interactions with cells (Majzoub et al. submitted paper). The functionalization, achieved through custom synthesis, is intended to address and overcome cell targeting and endosomal escape barriers to nucleic acid delivery faced by NPs designed for in vivo applications. Funded by NIH R01 GM 59288.

COLL 338

Nanometric gap structure between substrate-supported model membrane and silicone elastomer

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We developed a nanometric gap structure between substrate-supported model membrane and silicone elastomer (polydimethylsiloxan; PDMS) as a novel biosensing platform. A micropatterned membrane comprising polymeric and fluid lipid bilayers was generated on a glass substrate by the lithographic polymerization of diacetylene phospholipid and subsequent incorporation of natural (fluid) lipid bilayers. We chemically functionalized the surface of the polymeric bilayer with biotin moiety and bonded a flat PDMS slab onto it by using the biotin-streptavidin linkage. We employed lipid vesicles having biotin moiety as a bonding agent between the polymeric bilayer and PDMS. Due to the finite size of lipid vesicles, a very thin gap was formed between the fluid lipid bilayer and PDMS. The thickness of the gap was estimated to be less than 100 nm. Proteins that could bind onto the fluid bilayer by molecular recognition was selectively transported into the gap structure by the lateral diffusion within the bilayer. The combination of nanogap structure and selective transport by the lipid bilayer offers a novel platform for selective and sensitive detection of biological molecules.

COLL 339

Super-resolution imaging of plasmonic nanostructures

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Noble metal nanostructures are well-known for their ability to support localized surface plasmons, which lead to enhanced local electromagnetic fields at the nanoparticle surface, local heating, and hot electron generation. As a result, it has become increasingly important to characterize these structures at both the single particle and single molecule length scales, in order to understand how plasmon excitation can increase spectroscopic signals and/or promote reactions on the nanoparticle surface. Unfortunately, when we try and image these processes using visible light, we run into the fundamental resolution limit defined by the Rayleigh criteria and known colloquially as the diffraction limit of light. This talk will discuss how super-resolution optical imaging

techniques can help us overcome this fundamental resolution limit and allow us to probe metal-molecule interactions with <5 nm resolution.

COLL 340

Plasmonic efficiency enhancement for up-hill photocurrent generation at gold electrode modified with self-assembled monolayer

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We have reported highly efficient photoinduced up-hill electron transfer at gold electrode modified with self-assembled monolayer (SAM) of porphyrin-ferrocene coupling thiol molecule. Although this system shows very high quantum efficiency, only small fraction of solar energy can be utilized because main absorption peak of porphyrin, an absorber, is around 420 nm and absorbs not much photons in higher frequency region. Optical antennas, which interface between free-propagating light and localized electromagnetic energy, are indispensable to construct efficient solar-energy conversion system. Here a metal nano-gap system was introduced as a photon antenna in order to improve the photo-energy conversion efficiency. Theoretical calculation shows that particle plasmon and surface plasmon strongly hybridize in the Au-NP/SAM/Au substrate system. Since such hybridized plasmon is accompanied with extraordinarily enhanced electric field, *i.e.*, photon energy is concentrated in the gap region with the volume of $\sim \text{nm}^3$, one can expect that various optical events would occur more efficiently in the gap. Photocurrent action spectra of the porphyrin-ferrocene SAM clearly shows that photocurrent is significantly increased by the presence of adsorbed Au-NPs, as expected. The wavelength dependence of the enhancement factor is similar to the calculated extinction spectrum, confirming the enhancement of effective photo-energy conversion efficiency by plasmonic resonances in the nano-gap systems. The present result opens up a new possibility for design of photofunctionalized molecular devices with plasmonic photon antennas.

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COLL 341

Localized surface plasmon (LSPR) based optical detection of ions in aqueous solution

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The role of halide adsorption on the localized surface plasmon resonance (LSPR) of thermally assembled surfactant-free Au nanostructures is investigated. Previously, it was shown that the exposure of surfactant stabilized, solution dispersed, metallic nanostructures to ions results in a red shift and a dramatic dampening of the LSPR. A major drawback of such studies is that solution phase templates, upon exposure to ions, are (i) susceptible to aggregation and (ii) provide a surface which is much different from that of the intrinsic interface formed between halides and a Au nanostructure. The use of thermally assembled Au nanostructures circumvents these problems and provides access to the interaction of Au nanoparticles with the ions exclusively. Our results show that the adsorption of halogen ions (e.g. F⁻, Cl⁻, Br⁻, I⁻) on surfactant-free Au nanostructures induces the expected dampening of the LSPR, but where, in contrast to surfactant coated nanoparticles, the resonance is blue shifted. We attribute these observations to an increase in the electron density of the nanostructure upon exposure to halogen ions. Scanning electron micrographs confirmed that the morphology of these nanostructures were conserved before and after the exposure to ions.

COLL 342

Nanogap plasmonic structures for Raman studies of single molecules and heating

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Over the last few years we have developed nanogap structures between extended electrodes that support localized plasmon modes with very large field enhancements in the near-infrared. These structures enable us to perform *in situ* surface-enhanced Raman spectroscopy on single- or few-molecule systems while driving these molecules out of equilibrium via the flow of current and the application of large dc electric fields. I will discuss recent results in which we have been able to observe vibrational and electronic heating as a function of bias. I will also present data showing bias-driven charge transfer and resultant electronic tuning of vibrational energies in C60 molecules, and recent evidence of the vibrational Stark effect in C60 derivatives possessing permanent dipole moments. Time permitting, I will conclude by showing progress on simultaneous measurement of Raman and inelastic electron tunneling spectroscopy on individual molecules.

COLL 343

Ultrabright luminescent Metallic nanoparticles

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It is found that by curing the surface defects that quench photo excited carriers and fluorescence, luminescence efficiency of metallic nanoparticle can be dramatically increased. For Ag nanoparticles, as much as 300 times increase in photo-excitation induced luminescence is observed upon surface adsorption of ethanethiol. The same treatment increases Au nanoparticle luminescence efficiency by a factor of three. A model based on the elimination of surface defects by the S-metal bond formed upon thiol adsorption can quantitatively account the observations. These observations also indicate that nanoparticles without proper surface treatment typically have low luminescence quantum yields.

COLL 344

Hybrid core-shell and coupled nanostructures: Design and applications

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We report a class of hybrid nanostructures that can be used as efficient surface-enhancement Raman scattering (SERS) substrates. The metallic core consists of either silver nanowires or gold nanorods, prepared through a chemical reduction process, that are used to capture a model analyte. The silica or titania shell was prepared through a modified Stöber method and consists of patchy or full silica/titania coats. These configurations were used to quantitate/explore (a) the effect of the electromagnetic field at the tips of the nanowire (“hot spots”) in the Raman scattering experiment and (b) their sorption and photocatalytic capabilities.

COLL 345

Nanoparticle assembly and gelatin binding mediated by collagen mimetic peptide hybridization

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Since elevated collagen remodeling activity is associated with numerous pathologic conditions, the ability to target denatured collagens could lead to new diagnostics and therapeutics, as well as applications in regenerative medicine. In this talk, I will present a new strategy for targeting denatured collagens that is based on triple helical hybridization between collagen strands (of diseased tissues) and synthetic collagen mimetic peptide (CMP). The talk will also include controlled assembly and gelatin binding behaviors of CMP conjugated nanoparticles in the context of selective removal of gelatin from protein mixtures, triggered release of CMP conjugates, and targeted imaging of denatured collagens in diseased tissues. Due to the high loading capacity and multi-ligand platform, the CMP conjugated nanoparticles offer a variety of delivery and imaging modalities to be utilized in the management of diseases associated with high level of collagen remodeling.

COLL 346

Supercritical angle fluorescence (SAF) microscopy with nanometer resolution investigating the interaction and aggregation of proteins at lipid bilayer

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The adsorption of proteins at interfaces is known to be an important step in cellular and molecular biology. Supercritical Angle Fluorescence (SAF) Microscopy is a simple to use, low cost and highly sensitive method for real time monitoring which can also be used in the Foerster Resonance Energy Transfer mode. Based on SAF we have investigated recently the adsorption and aggregation of α -synuclein supposed to be the key player in Parkinson disease.

In the presentation we show the two distinguished adsorption processes, a non-aggregative adsorption of proteins molecules along the lipid bilayer and the aggregate forming adsorption resulting in micrometre sized plaques. The disruption of the membrane as a consequence of the adsorption is discussed. The results obtained by SAF are complemented by X-ray reflectometry measurements showing the penetration of protein molecules and the disturbance of the lipid bilayer.

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COLL 347

Fibrinectin conformation and integrin binding on crowded surfaces

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The ability of proteins to participate in specific biorecognition events on surfaces is a critical issue in technologies like implanted prosthetics and medical devices, nanoparticles for disease diagnosis and therapy, and scaffolds for regenerative medicine. Surface properties can alter the structure and orientation of proteins in addition to biasing the number and type of proteins that adsorb from solution. To study such effects at a molecular level, this work used FRET microscopy and single-molecule tracking to connect surface chemistry to protein conformation and subsequently to specific biorecognition events for the extracellular matrix protein, fibronectin, binding to different types of model integrin receptors.

An engineered fibronectin construct, Fn₈₋₁₀, containing domains 8-10 of the native protein, was site specifically labeled with different FRET-capable dyes near RGD and PHSRN peptide sequences that support specific integrin binding events. FRET between these two dyes indicated protein structure while FRET between the dyes on Fn₈₋₁₀ and a third FRET-capable dye on soluble integrins indicated Fn₈₋₁₀-integrin binding. Model hydrophobic, hydrophilic, cationic, and anionic surfaces demonstrated differences in their ability to maintain native-like spacing between RGD and PHSRN and this correlated directly with the duration of integrin binding events on an uncrowded surface. These experiments, in which proteins adsorbed to the surface from dilute buffer solutions, were compared to experiments done in plasma, where the surface was laden with serum proteins in addition to the labeled FRET constructs. These results indicated the degree to which crowding, as mediated by surface chemistry, affects Fn₈₋₁₀-integrin binding.

COLL 348

Docking model of synaptotagmin 7 C2A via electron paramagnetic resonance

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Synaptotagmins (syt) are a class of proteins that are ubiquitous within animals and play a role in membrane trafficking. Syt is composed of two C2 domains, C2A and C2B, and several of its isoforms act as Ca²⁺ sensors involved in membrane docking and fusion. While Syt1 has been extensively studied due to its role in extremely fast neurotransmitter release, other Syt1 isoforms such as Syt7 function in other secretory pathways. In particular, Syt7 is known to bind and release from membranes much more slowly than Syt1, due, at least in part, to tighter membrane binding by its C2A domain. However, the structural origins of this tighter binding are unknown. In this study, electron paramagnetic resonance (EPR) spectroscopy was used to model the singular domain Syt7 C2A and its location within a membrane. Spin-labelled singular cysteine mutants of Syt7 C2A were created at key positions in the Ca²⁺ binding loop. Mutant functionality and similarity to wild type was verified through stopped flow experiments. From EPR readings, depth parameters for each mutant were combined with a publically available structure of Syt7 C2A to create a model of the docking geometry of the membrane-bound state. Additional models were also created based on simulations of the Syt7 C2A domain bound to 3 Ca²⁺ ions. The resulting models consistently show binding loops 1 and 3 penetrating the membrane. Binding loop 1 of Syt7 C2A is somewhat more deeply inserted than the corresponding loop of Syt1, suggesting a partial explanation for the slower membrane dissociation kinetics of Syt7 relative to Syt1.

COLL 349

Lateral diffusion of synaptotagmin 1 and 7 on supported lipid bilayers: Assessing the frictional additivity of C2A-C2B tandem domains

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The synaptotagmin (Syt) family of proteins contains tandem C2 domains, C2A and C2B, which bind membranes in the presence of Ca^{2+} triggering vesicle fusion during exocytosis. While it has been suggested Syt1 C2A and C2B bind membranes cooperatively, the roles and extent of interdomain interactions for both Syt1 and Syt7 in membrane binding remain unclear. We have demonstrated frictional additivity to lateral diffusion on a planar lipid bilayer by fluorescent-tagged C2A, C2B, and C2AB domains from human Syt7. These findings suggest that C2A and C2B are well separated when membrane bound to a planar supported lipid bilayer. Analogous measurements were not previously performed with Syt1, as Syt1 C2A dissociates too rapidly to measure lateral diffusion under the conditions used. Here, we identify membrane lipid compositions to which each Syt1 C2 domain binds stably enough to measure diffusion on the seconds timescale. These studies measure diffusion of fluorescent-tagged C2A, C2B, and C2AB domains from human Syt1 using total internal reflection fluorescence microscopy with single-particle tracking. Our goal is to discover whether the C2 domains of Syt1 interact with each other on supported lipid bilayers or bind these membranes independently like those of Syt7. The results may shed light on general molecular mechanisms of cooperative membrane binding and function of synaptotagmin C2 domains.

COLL 350

Molecular dynamics simulations of PEGylated dendron-based micelles adsorption on biological membranes

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We study the effect of PEG chain length distribution on the interactions of PEGylated dendron-based copolymers (PDCs) micelle with cell. First, we use classical molecular dynamics simulations to model the interactions of PDCs with PEG chains, having positively charged ammonium groups at their tips, with negatively charged lipid bilayer. We show that PDCs micelles (3rd generation of Dendron and 8 PEG chains per monomer) with shorter PEG chains have significantly stronger Coulombic coupling with the membrane, due to cooperative behavior of their charged groups (polyion). These PDCs are observed to pass the cell membranes in the experiments. Second, we investigate the target based interactions of mixed PDCs micelles (ratio of monomers with different PEG chain length is different in the micelles) containing folic acid as a

targeting group, with membrane receptor. We calculate solvent accessible surface area of the folic acid, local PEG density surrounding the folic acid and the probability of the folic acid to be extended from the corona surface. We show that the extension of the folic acid from the corona surface is the main controlling factor for the interactions. We also show that clustering of the folic acids on the surface can reduce the interactions. The simulation results are in good agreement with the experimental observations.

H.-J. Hsu, S. Sen, R. M. Pearson, S. Uddin, P. Král, and S. Hong, **Poly(ethylene glycol) Corona Chain Length Controls End-Group-Dependent Cell Interactions of Dendron Micelles**, ACS Macromolecules(2014)

COLL 351

Xanthan/magnetite scaffolds for neuronal adhesion, proliferation and differentiation of embryonic stem cells

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In this work, neat xanthan (XCA) hydrogels and hybrid scaffolds made of XCA and magnetite nanoparticles (XCA/mag) were used as matrix for *in vitro* neuronal differentiation of embryonic stem cells (ESC). ESC showed similar differentiation rates on scaffolds with magnetization of 0.25 and 0.60 emu/g, but did not survive on scaffolds with 1.80 emu/g. Adhesion rates were more pronounced when cells were seeded on XCA/mag than on neat XCA or plastic dishes; however, proliferation levels were independent from the scaffold type. Differentiation rates, expressed as the number of neurons obtained on the chosen scaffolds, were the largest with neat XCA, which has a high density of negative charge, and the smallest with commercial plastic dishes. The local magnetic field inherent of magnetite particles present on the surface of XCA/mag facilitates synapse formation, since electrical transmission was increased when compared to the other scaffolds used in our study. Our results demonstrate that XCA and XCA/mag hydrogels are scaffolds with superior performance for adhesion and differentiation of ESC into neurons.

COLL 352

Programmable atom equivalents from nucleic-acid modified nanostructures: constructing a new "Table of Elements"

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The crystallographic parameters of atomic and ionic solids are fixed by the size and coordination number of their elemental building blocks, thus restricting the types of structures that can be formed. We have demonstrated that these limitations can be

overcome using spherical nucleic acid (SNA) nanoparticle conjugates as “artificial atoms” in superlattice assemblies. These three-dimensional conjugates consist of densely functionalized, highly oriented nucleic acids covalently attached to the surface of inorganic nanoparticles. The strength and length of the programmable DNA “bonds” between these structures can be adjusted by varying DNA sequence and length, and the properties of the “atoms” can be adjusted by varying nanoparticle size, shape, and composition. We have developed design rules for this assembly process, analogous to Pauling’s Rules for ionic solids but ultimately more powerful. These rules can be used as a guide for the rational construction of functional nanoparticle-based materials for plasmonic, photonic, and catalytic applications

COLL 353

Colloidal nanocrystal building blocks for large-area optical metamaterials

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Colloidal gold and silver nanocrystals (NCs) are widely explored for their size- and shape-dependent localized surface plasmon resonances. However they are largely unstudied as building blocks for mesoscale, plasmonic superstructures since the ligands used in synthesis introduce a large spacing between NCs in solids that gives rise to dielectric materials properties. Here, we will show that by chemical exchange of the NC surface with more compact ligand chemistries, we realize a dielectric-to-metal transition seen by a 10^{10} range in DC conductivity and a dielectric permittivity ranging from everywhere positive to everywhere negative across the whole range of optical frequencies. The compact ligand exchange allows us to realize a "diluted metal" with optical properties not found in the bulk metal analog, presenting a new axis in plasmonic material design and allowing the realization of optical properties akin to next-generation metamaterials. We harness the properties of metal NCs by using nanoimprint lithography to print large-area metamaterials on glass and plastics with widely tailorable optical properties that are used to fabricate near-infrared devices.

COLL 354

Surface chemistry of DNA at the single molecule level: Plenty of room at the bottom?

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DNA molecules attached to solid surfaces are a vital component in many biotechnological platforms. Yet, our ability to understand and control the properties of the DNA molecules at the relevant length scales remains in its infancy. Little is known

about the spatial distribution and conformation of these molecules on biofunctional surfaces, which may profoundly impact interfacial molecular recognition. Nor can we control the spatial distribution of the DNA probes. My research group has been developing new capabilities in probing and manipulating single DNA molecules on biofunctional surfaces. We have developed atomic force microscopy techniques to image the DNA probes with substantially improved spatial resolution. Our in situ AFM has provided novel insight into the conformational changes and hybridization of single molecules and is informing new strategies to engineer more robust and reproducible DNA sensors. Additionally, our single molecule nanografting method has patterned individual DNA molecules in well-defined chemical environment through precision nanoscale assembly. The ability to pattern single molecules is enabling new opportunities in single molecule biophysical measurements and self-assembly of more complex structures of biomolecules.

COLL 355

Molecular photonics for materials science, Energy and healthcare

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Molecular photonics explores and exploits the light-molecule interactions, which underpin many important processes and applications such as photosynthesis, vision, and molecular spectroscopy. Progress in nanoscience and nanotechnology has enabled design, measurements and control of light and molecules at an unprecedented level, opening up a window of new opportunities for both scientific discoveries and engineering applications in molecular photonics. In this talk, I present our advances in this emerging field in three categories: (1) directed assembly and engineering of photoresponsive molecules and supramolecules; (2) plasmon-enhanced optical spectroscopy and sensors; and (3) transparent organic solar cells and fuels. The talk is concluded with a discussion on the challenges and future opportunities for molecular photonics.

COLL 356

Surface chemistry in solar energy harvesting materials

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Solar materials must absorb light, separate charges, and extract electrons and holes with a minimum of current loss and voltage loss. The latest generations of solar cells are based on nanostructured materials, and thus consist of abundant surfaces that must be carefully understood and managed. I will discuss advances in, and insights from, surface studies that have enabled progress in solution-processed solar cells and that illuminate the path forward.

COLL 357

Anomalous nanocolloids defying the likes dissolves likes rule

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Particles are known to disperse best in solvents of similar hydrophobicity. This is commonly known as the similarity rule or “*Likes dissolve Likes*”. In this study, it was demonstrated that in addition to surfactants and surface derivatization other methods of dispersing particles in media of dissimilar polarity are possible. It was achieved using nanostructured surface interface of dispersed particles. Realization of unconventional surfactant-less dispersion has broad fundamentals and technological impact due to wide-spread use of particle dispersions and environmental problems associated with surfactants.

COLL 358

Dimensional control of chemical interfaces using polymerizable amphiphiles

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Precise dimensional control of surface chemistry at the nanoscale has important implications for applications ranging from biosensing to solar devices. Here we discuss a surface templating strategy based on the use of polymerizable amphiphiles that produces a surface with a repeating hydrophilic-hydrophobic pattern similar to the cross-section of a lipid bilayer. Structure formation is assessed using scanning probe and other interface-sensitive techniques, and large scale semi-empirical molecular models are correlated with image features at the nanometer scale. Strategies for further elaboration of the surface based on the amphiphilic template pattern will be discussed.

COLL 359

Award Address (ACS Award in Colloid and Surface Chemistry sponsored by Colgate-Palmolive Company). Assembly and measurements of isolated and coupled functional molecules

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Through combinations of self-assembly and measurements, we have learned to place individual, pairs, lines, and two-dimensional clusters of molecules together in controlled environments on surfaces. We simultaneously developed the means to record tens and hundreds of thousands of structural, functional, spectroscopic, and dynamic measurements with submolecular resolution. These capabilities and extraordinary

students, postdocs, and collaborators have enabled us to elucidate the mechanisms of function in these molecular and supramolecular systems and to control the chemical, physical, and biological interactions of materials with the surrounding world.

COLL 360

Light-activated multicomponent materials for tandem catalysis

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The global energy condition calls for the transition of energy-intensive catalytic methods toward green and sustainable approaches. Photocatalytic reactions initiated by sunlight are considered one of the top approaches to fulfill this need, yet only minimal methods are driven by sunlight to meet an ever-increasing energy demand. By transitioning catalytic reactions towards light-activated systems, sustainable processes could be developed that could persist for extensive future use. Towards this end, Pd-decorated Cu₂O (Cu₂O/Pd) materials were fabricated for sustainable tandem catalytic activity to achieve these goals. For this, Pd nanoparticles were deposited onto Cu₂O structures of selected morphologies to generate the composite structure. *In situ* generated H₂ was observed at the Cu₂O surface *via* proton reduction for catalytic use at the Pd surface. To study this catalytic activity, the reductive dechlorination of polychlorinated biphenyls was examined, where the Cu₂O/Pd materials exhibited significant catalytic functionality. To demonstrate the versatility of this integrated light-activated system, the shape and morphology of the Cu₂O material has been varied to determine structural effects on catalysis. In this regard, Cu₂O octahedra of various sizes have been synthesized to incorporate into the system. Their photocatalytic reactivities have been initially evaluated *via* the photodegradation of model pollutants. By constructing multicomponent and multifunctional materials that can harness visible light, tandem catalytic capabilities were achieved, where innovative sustainable technologies could be created from this unique system.

COLL 361

Zn-MOFs with pyridine-based organic linkers and their carburized, N-doped carbons analogues as CO₂ capture adsorbents

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With the continuously increasing global energy demand, selective capture of anthropogenic CO₂ from fossil fuel-fired power plants is needed to mitigate the negative effects of CO₂ on the environment. This triggers the use of metal-organic frameworks (MOF) as CO₂ adsorbents due to their tunable structure through the variation of MOF components (i.e., metal center source and organic linker source) prior to MOF synthesis. This can lead to the introduction of functionalities beneficial to CO₂ capture into MOF structure that can also provide polarity, acidity/basicity, and flexibility. In this study, Zn-based MOFs (ZnMOFs) have been synthesized using pyridine-based organic linkers to provide free pyridine functionalities with Lewis basicity. Surprisingly, instead of incorporating free pyridine functionalities, these ZnMOFs were demonstrated to have unique pore geometries with the presence of Lewis acidic open Zn²⁺ sites. These sites were shown to be accessible to CO₂, as evidenced by *in-situ* DRIFT studies using acetic acid as a probe molecule.¹

Structural investigation of ZnMOFs also suggests their use as templates/precursors for the formation of hierarchical nanoporous carbons (NC) with N dopants via carbonization. The use of ZnMOFs as templates was shown to direct macroscopic morphology and porosity of the resulting NC materials.^{2,3} In addition, the properties of the NC materials can be tuned via the alteration of organic linker (MOF precursor) prior to ZnMOF synthesis. Using the ZnMOFs described here, the surface area and final amount of N species in the NC materials were controlled through the variation of molar ratios of Zn/C and N/C inherent to the parent ZnMOF. The presence of N dopants in the NC materials led to their use as CO₂ adsorbents. Furthermore, these NC materials exhibited high recyclability during thirty CO₂ adsorption/desorption cycles.

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COLL 362

Synthesis of VTMS(X)-HMS-3 mesoporous ordered silica for hydrogen storage

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Vinyl trimethoxysilane (VTMS)-modified hexagonal mesoporous silica (HMS-3) has been synthesized at varied loading concentrations of VTMS to determine the effect of VTMS loading on hydrogen adsorption capacity. Materials were synthesized with 0, 10, 20, and 31.5 mole percent starting VTMS with respect to total silica precursor. In the modified VTMS(X)-HMS-3 silica submicron particles (X = 0%, 10%, 20%, and 31.5%) hydrogen adsorption capacity increased, with a maximum of 0.72 wt % adsorbed by VTMS(31.5)-HMS-3. This adsorption surpasses the adsorption capacity of the unmodified

VTMS(0)-HMS-3, which attained 0.50 wt% adsorption. The correlative increasing trend in adsorption capacity following increased organic modification provides inspiration for similar modifications to periodic mesoporous organosilicas (PMO), which exhibit higher adsorption capacity than traditionally modified particles.

COLL 363

Insights in sol-gel matrix diffusion methodology in the synthesis of soft materials from second group (Ca^{2+} , Ba^{2+} , Mg^{2+}) earth alkaline metals

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The idea behind the sol-gel synthesis methodology is to “dissolve” a compound in a liquid in order to bring it back as a solid in a controlled manner. Though this method, multi component compounds can be prepared in a controlled stoichiometry leading to the formation of an oxide network through polycondensation reactions from a molecular precursor dissolved in a solution. Thus, the sol-gel method for inorganic synthesis prevents problems such as (a) co-precipitation, which may be inhomogeneous and caused gelation reaction, and (b) it enables mixing at an atomic level, which results in small particles that are easily sinterable.

In addition, the method allows prepare materials with a variety of shapes, such as porous structures, thin fibers, dense powders and thin films. The explosion and interest in hybrid inorganic/organic framework materials containing carboxylates and phosphonate ligands, has been driven by both the diversity of structural and chemical types and the possible applications of these hybrid framework materials in areas such as catalysis, separations, hydrogen storage, and electrical conductivity.

An attractive strategy for the synthesis of these networks is through the reaction of main group metal salts such as *magnesium*, *calcium*, and *barium* under the presence of di topic carboxylate and phosphate ligands. We have sought to extend our work in this area towards an ease formation of sol gel matrix to growth homochiral inorganic frameworks, which can be used in enantio selective separations as well in homogeneous or heterogeneous asymmetric syntheses. Long ago, we have choice to study the use of dicarboxylate *L*-tartrate (*L*-tart = $\text{C}_4\text{H}_4\text{O}_6$) and HPO_4^{2-} ligands towards a feasible sol gel framework synthesis.

COLL 364

Synthesis of Pt-based catalysts for DMFCs by microfluidic reactors

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Microfluidic reactor technology has been developed in chemical synthesis due to their unique characteristics, such as enhanced mixing for reactants, rapid reactions, rapid heat transfer, precise control, and safe operational environment. Ordered intermetallic nanomaterials are of great interest for fuel cells due to their unique electronic and structural properties. Traditionally, synthesis of intermetallic compounds requires high-temperature and long time processes. Developing rapid, phase- and size- controlled synthesis techniques is still a great challenging issue. The performance of electrocatalysts remarkably depends on their physical and chemical properties relative to particle structures, morphologies and surface effects, and therefore their synthesis requires superior control of reactions. Fortunately microfluidics reactors can cater to the requirement for size-, shape-, and structure-controlled syntheses. In this study we explore the approach of microfluidic systems to synthesize intermetallic nanoparticles (NPs) utilizing its feature of superior control of reactions. PtBi₂ intermetallic compound is one of the promising candidates of direct methanol fuel cell catalysts because of its high catalytic activity and excellent methanol tolerance property. Here we proposed a one-step, facile and ultrafast, phase- and size- controlled process for synthesizing ordered Pt-Bi intermetallic NPs in microfluidic reactors in seconds. Single-phase PtBi and PtBi₂ intermetallic NPs were prepared by tuning the reaction temperature and size-controlling was achieved through the changing of solvents. The as-prepared Pt₁Bi₂ intermetallic NPs from PEG600 were selected and loaded on the XC-72 carbon support to act as an electrocatalyst for DMFCs, and the electrochemistry performance showed the mass current densities of PtBi/XC-72 is 185.6 mA/mg_{Pt} at 300 mV, which is 1.7 times higher than that of commercial Pt/C (110.9 mA/mg_{Pt}) although this value is lower than nanotubed supported Pt catalyst. The results show Pt₁Bi₂/XC-72 catalysts possess significant enhancement of the ORR electrocatalytic activity and excellent methanol tolerance capacity compared to those of commercial Pt/C.

COLL 365

Design of polymeric solid acid catalyst for efficient biofuel production

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A novel polymeric solid acid catalyst consisting of dual polymer chains for biomass hydrolysis and subsequent dehydration was successfully synthesized. A poly (styrene sulfonic acid) (PSSA) polymer chain is immobilized on a substrate and used to catalyze biomass hydrolysis and its subsequent dehydration reactions. A neighboring poly (vinyl imidazolium chloride) ionic liquid (PIL) polymer chain is grafted to help solubilize lignocellulosic biomass and enhance the catalytic activity. The immobilized polymeric catalyst demonstrates over 97% total reducing sugar (TRS) and 70% 5-hydroxymethylfurfural (HMF) yields for cellulose hydrolysis and dehydration in [EMIM]Cl respectively. This solid acid catalyst is highly efficient, stable, reusable and

environmentally friendly. In order to understand its catalytic activity and further optimize its performance, the interactions among the PSSA, PIL polymer chains and cellulose were investigated using classical Molecular Dynamics (MD) simulations. In addition, the free energies associated with polymer chain interactions were determined using metadynamics (MTD) simulations. Our results demonstrate that the properties of polymer chains and their interactions play a crucial role in their catalytic activities. Additional improvement for catalytic activity by substitution or copolymerization is suggested. This solid acid catalyst can be tuned and potentially be used for many other acid catalyzed reactions and conversions.

COLL 366

Metal-organic frameworks for on-board storage of hydrogen and natural gas

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Materials exhibiting reversible hydrogen adsorption with high gravimetric and volumetric capacities are sought for use in on-board storage systems of hydrogen fuel cell-powered vehicles. Microporous metal-organic frameworks with high internal surface areas have been shown to display excellent storage properties, but only at cryogenic temperatures. Methods for synthesizing frameworks containing coordinatively-unsaturated metal centers are therefore being developed as a means of increasing the H₂ adsorption enthalpy. In particular, we seek to synthesize thermally-robust, high-surface area materials with a high concentration of open metal coordination sites. By adjusting the electronic structure of the metal ions, it is expected that an optimal H₂ adsorption enthalpy in the range -15 to -20 kJ/mol can be achieved, leading to a high storage capacity at room temperature and pressures of up to 100 bar. Such materials could similarly be of utility in boosting the methane storage capacity in the tanks of natural gas-powered cars operating at reduced pressures of 35 or 65 bar. Particular attention will be devoted to recent results involving efforts to achieve new materials in which multiple H₂ or CH₄ molecules can adsorb at a single metal site, and in which the thermal management requirements associated with gas adsorption/desorption can be reduced.

COLL 367

Detecting biomolecular interactions and photodynamics in solution by suppression of Brownian motion

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The capacity of single-molecule fluorescence measurements to allow study of asynchronous dynamics and to expose molecule-to-molecule photophysical and behavioral diversity continues to make rich contributions to the understanding of biological macromolecules. Exploration of dynamical processes in the solution phase is particularly appealing since it conducts the measurement in the biomolecule's close-to-native environment. However, diffusion of single nm-sized biomolecules typically limits the observation time to around a millisecond in many solution-phase single-molecule assays. Although surface immobilization is widely used to address this problem, such measures might perturb the system being studied, thus contributing to the observed heterogeneity. We utilize a combination of high-sensitivity single-molecule fluorescence microscopy, real-time feedback control and electrokinetic forces in a microfluidic geometry, specifically a device called the Anti-Brownian Electrokinetic (ABEL) trap, to significantly prolong the observation time of single biomolecules in solution and thus record diverse dynamical changes. By extracting multiple parameters from each molecule, this device has been used to explore the detailed dynamics of single pigment-protein complexes involved in photosynthesis, multisubunit enzymes, redox enzymes, and even single fluorophores. With advanced analysis of the motion in the trap, even the diffusion coefficient and electrokinetic mobility of the trapped molecule can be estimated in real time, thus providing new variables for single-molecule studies that enable sensing of protein-protein associations and other binding events.

COLL 368

Super-resolution imaging and reaction mapping of P450 3A4 and P450 reductase in heterogeneous biomimetics: Starry night

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The dynamics of P450 and P450 reductase (POR) as they move through lipid bilayers, associate with one another, and how they are partitioned within the membrane are all essential elements of how they function. We have undertaken several super resolution fluorescence imaging and single particle tracking studies (1) to understand the nano-scale heterogeneity of a standard P450 lipid membrane composed of DOPC:DLPC:DLPS (1:1:1 wt), (2) to directly observed how P450 and POR are partitioned within and around the lipid "raft-like" structures that compose the membrane, and (3) how P450 and POR move and interact with one another in this heterogeneous environment. Moreover, we have conducted super resolution reaction mapping studies using resorufin benzyl ether as a substrate to directly observed single molecule

metabolism at individual P450 enzymes. These studies have been used to develop a multiphasic discrete state model(s) for protein-protein interactions and give tantalizing insights into the relationships between these interaction and substrate turnover.

COLL 369

Stimuli-responsive chymotrypsin conjugates synthesized using polymer-based protein engineering

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The attachment of inert polymers, such as polyethylene glycol (PEG), to proteins has driven the emergence of a multibillion dollar biotechnology industry. In all cases, proteins have been stabilized or altered by covalently coupling the pre-existing polymer to the surface of the protein. This approach is inherently limited by a lack of exquisite control of polymer architecture, site and density of attachment. In this work, polymer-based protein engineering (PBPE) with a novel water-soluble atom transfer radical polymerization (ATRP) initiator was used to design several stimuli responsive enzyme-polymer conjugates using the model enzyme chymotrypsin. By using a “grafting from” approach, we synthesized homogenous enzyme-polymer conjugates by first covalently coupling the ATRP initiator to over 85% of accessible surface lysines followed by polymerization outward from the enzyme surface. The growth of temperature-responsive polymers, poly(*N*-isopropyl acrylamide) (pNIPAm), poly(sulfobetaine methacrylate) (pSBMA), poly(sulfobetaine methacrylamide) (pSBAm), and the pH-responsive polymer poly(2-(dimethylamino)ethyl methacrylate) (pDMAEMA), from the surface of chymotrypsin made it possible to predictably alter chymotrypsin-polymer conjugate activity, productivity, stability, substrate affinity, and structural conformation. Specifically, chymotrypsin-pSBAm-*block*-pNIPAm conjugates showed temperature dependent changes in substrate affinity and productivity when cycled above or below their critical solution temperatures. Similarly, chymotrypsin-pDMAEMA conjugates showed predictably altered kinetics and stability that were dependent on pH. Furthermore, by growing the charged polymer, (poly(quaternary ammonium methacrylate)) (pQA), from the surface of chymotrypsin, we showed that it is possible to use polymers to rationally tailor protein-protein interactions, specifically the chymotrypsin binding of two oppositely charged protease inhibitors. Most interestingly, each of the chymotrypsin conjugates showed dramatically increased stability in low pH conditions when compared to native chymotrypsin. Our work with chymotrypsin has provided the groundwork to synthesize functional conjugates with other proteins such as (strep)avidin, glucose oxidase, and galactosidase for a variety of applications that are currently being explored in our lab.

COLL 370

Cytochrome c: An electrostatically bound peripheral membrane protein

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Early biomembrane studies recognized cytochrome c as a peripheral protein, attaching to acidic phospholipids. A more elaborate view has since emerged, with a plethora of new features. Accordingly, cyt c was demonstrated to sequester acidic phospholipids, corresponding to the cluster of cationic charges in cyt c. In a bilayer of DPPC and unsaturated phosphatidic acid, undergoing the main transition upon cooling, the clustering of the acidic phospholipid results in the formation of a highly negatively charged lipid domain capable of scavenging cyt c from the solution to the membrane. More intriguing was the formation of superlattices of cyt c bound to liposomes, most likely reflecting bending rigidity and repulsive potential between the membrane deformations as a driving force.

Along with basic biophysical studies on cyt c came the unprecedented realization, that in addition to the shuttling of electrons to cytochrome c oxidase in the mitochondrial respiratory chain, its functions include a key role in apoptosis, release from mitochondria resulting in the activation of the caspase cascade. Studies on the microperoxidase activity of the heme moiety contained in fragments of cyt c were later complemented by the demonstration of peroxidase activity of intact cyt c, capable of oxidizing unsaturated acyl chains. Taking into account that phospholipids with oxidatively truncated acyl chains cause lipid bilayers to lose their permeability barrier function, it is likely that part of the proapoptotic activity of cyt c results from this activity. Two phospholipid binding sites (A and C) were initially described in cyt c, with third L-site added later. A novel lipid-protein interaction, extended phospholipid anchorage, was deciphered, with one acyl chain flipping out and becoming accommodated within a hydrophobic cavity in cyt c, establishing hydrophobic interaction without intercalation into the bilayer. This mechanism has been suggested also for Orf-9b, bet3, as well as Hsp-70. Redefined this mechanism includes the flipping of two cardiolipin acyl chains into cyt c. The double bond between carbon atoms 9 and 10 of the acyl chain contacts the heme, in keeping with the peroxidase activity of cyt c.

Attachment of cyt c to acidic phospholipids was shown by DSC to destabilize its structure and induce the molten globule state, a likely prerequisite for the formation of amyloid type fibers in the presence of liposomes, leading to enhanced cardiolipin peroxidase activity.

COLL 371

Interfacial exposure, recognition, and signaling by mitochondrial cardiolipins

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Cardiolipins are ancient mitochondria-specific anionic phospholipids normally confined

almost exclusively to the inner mitochondrial membrane. In this talk, I will present new concepts and data on the emerging role of cardiolipins in the interfacial signaling by dis-regulated mitochondria resulting from the collapse of the asymmetry, trans-membrane re-distribution, and externalization of cardiolipins to the organelle's surface. I will describe two major pathways through which cardiolipins may accomplish the signaling function via their: i) recognition by an executionary protein of the autophageal machinery, LC3, causing mitophagy, and ii) oxidation catalyzed by an intermembrane space hemoprotein, cytochrome c, leading to apoptosis. Finally, I will discuss a new concept that interfacial cardiolipins and their oxidation/hydrolysis products constitute a rich communication language utilized by mitochondria of eukaryotic cells for diversified regulation of cell physiology and metabolism as well as for inter-cellular interactions.

COLL 372

Conformational diversity of cytochrome c on cardiolipin containing liposomes probed by fluorescence and circular dichroism spectroscopy

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Cytochrome c is a multifaceted protein which adopts it multiple conformations with different degrees of folding to perform different functions. In order to serve as an electron transfer carrier the protein has to be intact with M80 as its sixth ligand. In addition to this canonical function cytochrome c can acquire peroxidase activity in order to trigger its release from the inner membrane of mitochondria. This process requires a partial unfolding of the protein. Over the last years cardiolipin containing liposomes have emerged as an ideal model system for studying the interactions between cytochrome c and the inner membrane. We measured the W59 fluorescence, its steady state anisotropy and visible circular dichroism to probe the binding and subsequent unfolding of ferricytochrome c to liposomes with different CL/DOPC ratios with and without the presence of NaCl. A comprehensive global analysis of the data revealed three different binding processes assignable to different binding sites of the protein. These sites are distinct from the so-called A- and C-sites proposed by the Kinnunen group. Proteins bound via these three sites differ significantly in terms of the unfolding of their tertiary structure. Only the binding process with the lowest affinity was found to be inhibited by the addition of NaCl, suggesting that the remaining two processes are at least in part governed by hydrophobic interactions. Our findings suggest that the different binding steps produce different equilibria for the coexisting conformers C and E proposed by the Pletneva group. We are in the process of characterizing the proteins in the obtained conformations with resonance Raman spectroscopy.

COLL 373

Template free fabrication of vertically aligned Ag nanorods for surface plasmon enhanced photocatalytic reactions and Raman spectroscopy

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A template and surfactant free method is developed for the fabrication of vertically aligned Ag nanorod (NR) arrays. The diameter and length of Ag NRs could be tuned through adjusting the electrodeposition time. The growth mechanism of Ag NR arrays is explored through monitoring the morphology of Ag NRs with various electrodeposition time. Because of their large specific surface area and strong surface Plasmon coupling, these Ag NR arrays are able to enhance photocatalytic reaction as well as to serve as sensitive and reproducible substrates for Raman scattering. This method could be potentially applied to prepare other metal NR arrays in a large scale which would have broad applications.

COLL 374

Copper plasmonics and catalysis: Role of electron-phonon interactions in dephasing localized surface plasmon

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Copper metal can provide an important alternative for the development of efficient, low-cost and low-loss plasmonic nanoparticles, and selective nanocatalysts. However, poor chemical stability and lack of insight into photophysics and plasmon decay mechanisms has impeded study. Here, we use smooth conformal ALD coating on copper nanoparticles to prevent surface oxidation, and study dephasing time for localized surface plasmons on different sized copper nanoparticles. Using dephasing time as a figure of merit, we elucidate the role of electron–electron, electron–phonon, impurity, surface and grain boundary scattering on the decay of localized surface plasmon waves. Using our quantitative analysis and different temperature dependent measurements, we show that electron–phonon interactions dominate over other scattering mechanisms in dephasing plasmon waves. While interband transitions in copper metal contributes substantially to plasmon losses, tuning surface plasmon modes to infrared frequencies leads to a five-fold enhancement in the quality factor. These findings demonstrate that conformal ALD coatings can improve the chemical stability for copper nanoparticles, even at high temperatures (>300 °C) in ambient atmosphere.. These findings demonstrate that nanoscaled copper is a good alternative

material for many potential applications in nanophotonics, plasmonics, catalysis and nanoscale electronics.

COLL 375

Electrodeposited alloy thin films for catalysis applications

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Porous metals are of interest for their high surface area and potential for enhanced catalytic behavior. Electrodeposited NiCu thin films with a range of compositions were electrochemically dealloyed to selectively remove the Cu component. The structure, composition, and reactivity of these samples were characterized both before and after the dealloying step using scanning electron microscopy, energy-dispersive x-ray spectroscopy, and electrochemical measurements. The hydrogen evolution reaction and methanol oxidation reaction were measured on dealloyed samples and compared to similar measurements on as-deposited samples. Complementing the reactivity measurements, the surface area of electrodeposited thin films was evaluated using electrochemical double-layer capacitance, electrochemical area measurements using a redox couple, and topographic atomic force microscope imaging. Nanostructured materials fabricated by electrochemical dealloying are a promising area of catalysis research. Double-layer capacitance measurements are a practical technique for estimating the accessible surface area of a sample to determine intrinsic catalytic reactivity.

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COLL 376

block copolymer template-directed synthesis of mono- and bimetallic nanoparticle catalysts

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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 acted as the benchmark 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 high performance PEMFCs 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 and/or cations.

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/Pd, 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 direct metallurgy 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 (Pt/Au, Pt/Ir, Pt/Pd) is presented. Details for the methanol and formic acid oxidation reactions and oxygen reduction reaction and tolerance to catalyst poisoning are discussed. Preliminary details on a structure–activity relationship between nanocatalysts and their self-assembled block copolymer templates is also discussed.

COLL 377

Rational design of nanocatalysts for oxygen reduction reaction

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Engineering nanocrystals with size, shape, composition and structure control for enhancing oxygen reduction reaction (ORR) and small molecule oxidation reactions is highly desirable for promoting the development of fuel cell devices. In this presentation, I will focus on my recent advances in rational design and controlled synthesis of high-quality multicomponent nanocrystals for enhancing ORR and small molecules oxidation reactions. I will start with three examples on how to engineer FePt NWs, FePtPd/FePt core/shell nanowires (NWs) and graphene-FePt nanoparticles (NPs) composite for getting advanced Pt-based catalysts for ORR with extremely high activity and stability. After that, I will move to non-Pt catalysts such as graphene-Co/CoO NPs and M/CuPd NPs (M=Ag, Au), which exhibit comparable and even higher ORR activity and stability than commercial Pt catalyst.

COLL 378

Tunable plasmonic nanoparticles for enhancing photocatalytic reactions

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Hollow gold-silver nanoshells were prepared for plasmonically enhanced solar-to-fuel energy conversion. These nanostructures were designed to absorb light at wavelengths from the visible to the near-infrared, covering a large portion of the solar spectrum that reaches the surface of the earth. The bulk of our studies focused on coating these particles with silica, a protective layer that reduces aggregation and insulates the photocatalyst from the metal, leading to a doubling of the energy output of our photocatalytic system. This research has provided us a template for further investigations with alternative core-shell structures. This presentation describes the utilization of various strategies for improving the performance of our nanoshells in solar energy collection and conversion systems. Specifically, our studies seek (1) to extend the active wavelength further into the visible and the near-infrared range, thus enhancing the coverage of the solar spectrum, and (2) to optimize the dielectric environment to enhance the activity of the photocatalyst in the composite material. In addition, we have synthesized unique tin oxide-coated gold-silver nanorattle structures. The nanorattle structures offer the potential for boosting hydrogen production due to the strong localization of plasmonic enhancement between the metal and metal oxide interfaces. The targeted nanoparticles were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDX), and UV-visible (UV-vis) spectroscopy.

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Enhanced photocatalytic activities of chemical vapor deposited hematite films for solar water splitting by Au NPs in embedded configuration

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The photoactivity of n-type nanostructured hematite is limited by its poor absorptivity and a limited carrier diffusion length. Plasmonic metal nanostructures of Au, Ag, and Cu are known to concentrate and scatter broad range wavelengths of incident light and hold the promise on enhancing the light absorption cross-section of a semiconducting material. We present photoelectrochemical (PEC) characteristics of a smooth hematite photocatalytic layer embedded with Au nanoparticles (NPs). The plasmonic enhancement increases with the amount of Au NPs considering the same thickness of

hematite. Thickness dependent plasmonic activity studies indicate that a maximum enhancement in 107nm hematite films as compared 630nm hematite films where the plasmonic activity of Au NPs is least shielded.

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Electrochemical investigation of nanoparticles modified glassy carbon electrode and its application for ketoconazole determination

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This work reported on ketoconazole determination using nanoparticles modified glassy electrodes. The electrodes have been successfully modified and the related experimental parameters such as concentration of ketoconazole, scan rate, pretreatment time, pretreatment potential, different electrodes were optimized. Ketoconazole behavior at GC electrode and modified GC electrodes was investigated. Cyclic voltammeter was used to examine the electrochemical behavior of ketoconazole at glassy carbon, platinum and gold electrodes as well. Potential range from (-0.2 to +1.4) V was applied for cyclic voltammeter. PH value of the solution buffer on the signal was also studied in a range of 2-9 and the PH of four showed the highest peak. The dynamic range was obtained with correlation coefficient of 0.9989.

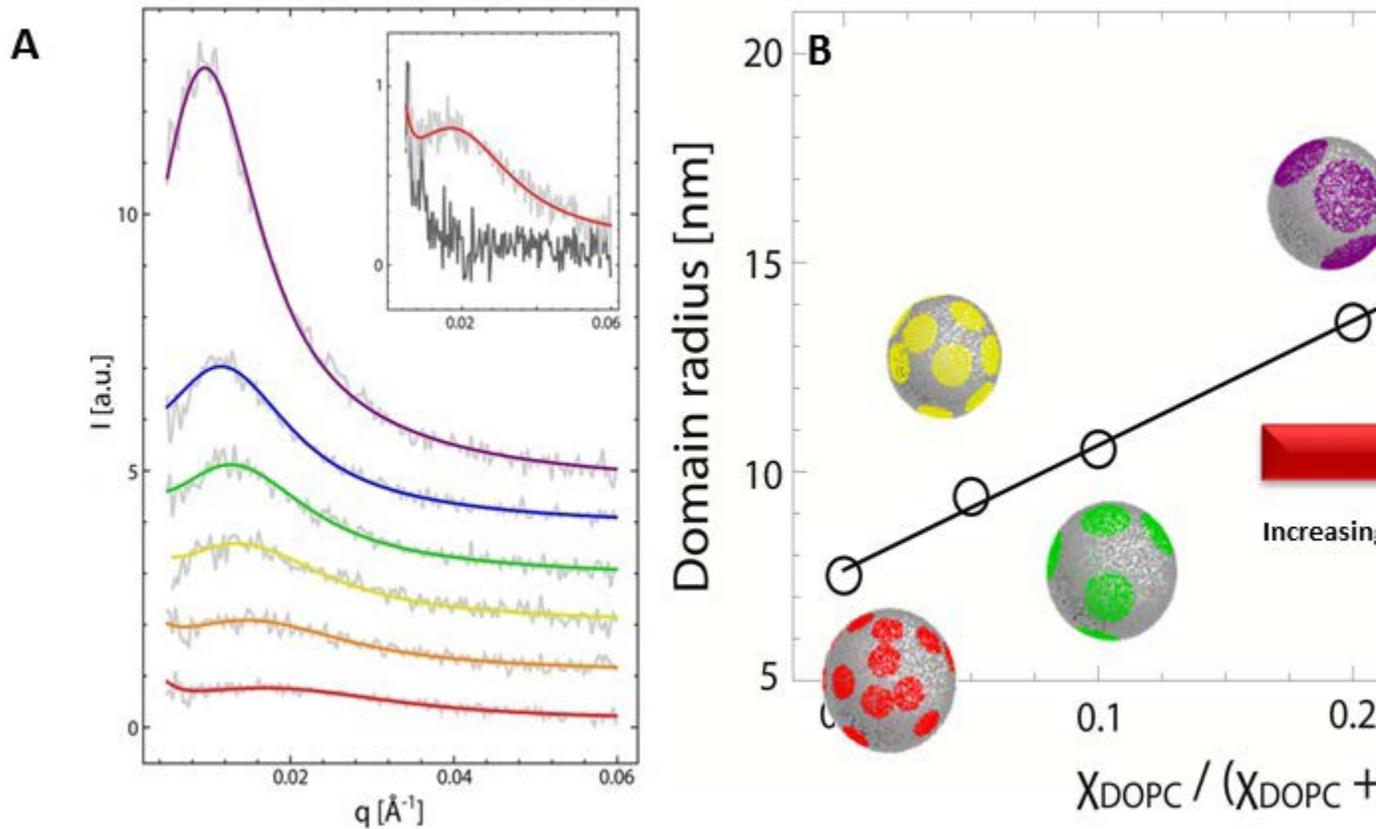
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Biomembrane structure using neutron scattering and molecular labeling

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Biomembranes provide the interface between cells and their surroundings. More than just protective barriers, they are sophisticated, dynamic machines that perform a diverse array of functions, including selective transport, localization, communication, recognition and synthesis of complex materials. It is also widely accepted that lateral heterogeneity in the plasma membrane (PM) plays a role in signaling, transport, and the pathogenesis of some viruses and bacteria. It is believed that the separated lipid regions have different physical properties from the surrounding lipids and are believed to be the basis for functional lipid domains ("rafts") in cells. So-called rafts are implicated in a wide range of cellular functions, including signal transduction, drug uptake and interactions with pathogens. Using small angle neutron scattering and molecular labeling we have

studied nanoscopic lipid rafts in model membrane systems and recently, in the Gram-positive bacterium *Bacillus subtilis*.



A) Monte Carlo fits to small angle neutron scattering data at 20 °C. **B)** Domain size as a function of increasing amounts of the non-biologically relevant lipid DOPC to POPC/DSPC/cholesterol lipid mixtures [Heberle et al., J. Am. Chem. Soc. **135**, 6853 (2013)].

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Experiment and simulation reveal the bending properties of nanoscopic lipid domains

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There has been a great deal of interest in studying the mechanisms that give rise to nanoscopic lipid domains in model mixtures. To this end, experimental studies have focused, in large part, on membrane structural parameters, such as bilayer thickness

mismatch, but not on the membrane's mechanical properties. This apathy regarding the mechanical properties of lipids domains can be attributed to the fact that most techniques look at the membrane's bulk properties. Neutron Spin Echo is a technique that can directly measure the bending modulus of phase separated bilayer systems through the use of neutron contrast matching, where domains can be highlighted. We will present results detailing, for the first time, the bending modulus of nanoscopic lipid domain. We have also measured both the structural and mechanical properties of pure phase composition bilayers. Not surprisingly, our results confirm that the liquid-ordered phase is more rigid than the liquid disordered phase. Interestingly, the value of the bulk bending modulus in phase separated vesicles with nanoscopic domains, approaches that of the liquid ordered-phase. However, when the same sample is contrast matched, so that only the nanoscopic liquid disordered domains are visible, their mechanical properties seem to maintain their liquid disordered identity. We analyzed our results with the aid of all atom MD simulations which accurately reproduce the structural properties of our experimental system, and agree with the trend in mechanical properties that we observe. These results have implications for determining important domain forming properties such as the line tension.

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Shear flow-induced de-registration of compositional domains in supported lipid bilayer membranes

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Formation of overlapping compositional lipid domains embedded within opposing leaflets of a bilayer membrane has been observed experimentally in a wide range of multicomponent lipid systems. The emergence of such correlated domains can be attributed to the presence of a thermodynamic coupling between the leaflets, and while the existence of such a coupling is generally accepted, neither the detailed physical mechanisms responsible for the coupling nor its magnitude for specific lipid systems are well-understood. In fact, existing experiments only provide a very weak lower bound based on the observation that excursions of the domains away from perfect overlap due to thermal fluctuations have not been discerned using standard optical microscopy techniques.

In this work, a quantitative framework is developed to understand and analyze the flow-induced de-registration behavior of compositional domains (either liquid or gel) embedded within opposing leaflets of multicomponent lipid bilayers spreading over a solid substrate under external shear. In particular, closed-form analytical formulas are derived to predict the threshold membrane flow velocity associated with such de-registration processes. Our predictions for the threshold velocity in case of gel or liquid domains are amenable to direct experimental verification, and facilitate an experimental measurement of the strength of the thermodynamic coupling term.

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Determination of membrane bending moduli from fully atomistic simulations

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The bilayer bending modulus, K_c , is one of the most important physical constants characterizing lipid bilayer membranes, but determination of K_c from atomically detailed simulations has proven difficult. A practical methodology for extracting K_c from simulations will be presented along with a theoretical motivation behind the analysis and results for DPPC, DOPC and DOPE lipids.

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Nanoscale structure of sphingolipid containing liquid-ordered phases

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Sphingomyelin is found in the outerleaflet of the mammalian plasma membrane, where, in concert with cholesterol, it is thought to play a crucial role in the lateral organization of membrane proteins. Published NMR data reveals average chain structure in mixtures containing sphingomyelin and cholesterol; phase diagrams and lateral organization on 100 nm lengthscales based on fluorescence microscopy have also been published. Here we present detailed results on the nanoscale organization of sphingomyelin and cholesterol with either POPC or DOPC as the unsaturated lipid. As in our previously published work on mixtures of DPPC/DOPC/CHOL, we observe hexagonally ordered substructure within the liquid-ordered phase. Differences are observed, however, including tighter packing and persistent hydrogen bonds, which likely have significance for partitioning of membrane proteins in sphingomyelin liquid-ordered phases.

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Self assembly and kinetic pathways of pore forming toxins in supported lipid bilayers

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Pore forming toxins are protein molecules that have evolved to form unregulated pores on the cell membrane leading to osmotic stress and lysis. These water soluble proteins bind to lipid membranes and following a process of self assembly at the membrane interface form nanometer sized pores. Although pore forming toxins have been extensively studied, the molecular mechanisms of the oligomerization pathways and the fate of lipids during the final stages of pore formation are incompletely understood. Using a combination of experimental and molecular dynamics simulations we study the pore forming mechanism for the Cytolysin-A pore forming toxin. Using supported lipid bilayer platforms and atomic force microscopy, several intermediate states of pore formation are captured. All atom molecular dynamics simulations are used to comment on the stability of these partially formed intermediates as well the manner in which membrane lipids reorganize during the pore formation process.

COLL 387

Enhancing catalytic efficiency of hollow palladium nanoparticles by photothermal heating of added gold nanoparticles to their cavity: palladium-gold nanorattles

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Hollow nanocatalysts such as palladium nanoshells have high catalytic efficiency. Gold nanospheres, which generate photothermal heat when photo-excited, are synthesized inside the palladium nanoshells to form the gold-palladium nanorattles (PdAuNRTs). Upon optical excitation of the gold nanospheres while using the PdAuNRTs in the catalysis of the reduction of 4-nitrophenol by borohydride as a model reaction, the efficiency of the catalytic process was enhanced by amounts that are sensitive to the relative size of gold nanosphere to that of the hollow palladium nanocage. Since measuring the temperature inside the cavity is not possible, the value of activation energy determined for this reaction was used to estimate the increase in the temperature resulting from the plasmon excitation which suggested to be ~ 20 °C.

COLL 388

Plasmon resonant enhancement of photocatalytic processes

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Over the past few years, we have demonstrated plasmon resonant enhancement of several photocatalytic processes (e.g., water splitting¹, methyl orange decomposition², CO oxidation³, and chemical vapor deposition⁴) by integrating plasmon resonant nanoparticles with strongly photocatalytic semiconductors. When the incident photon energy matches the plasmon resonance of the Au nanoparticles, we observe a significant enhancement in the photocatalytic activity due to the intense local

electromagnetic fields created by the surface plasmons of the Au nanoparticles. Here, the Au nanoparticles improve the photocatalytic performance by coupling light very effectively from the far field to the near field, right at the surface of the photocatalyst. We model the plasmon excitation at the Au nanoparticle-photocatalytic semiconductor interface using finite difference time domain (FDTD) simulations, which provide a rigorous analysis of the electric fields and charge at the interface. We have also demonstrated plasmonic enhancement of dye sensitized solar cells, which also benefit from the focusing of light to the near field regime at a very thin layer of adsorbed dye molecule.⁵ While most of our earlier work utilized TiO₂ as the photocatalytic semiconductor, we have recently demonstrated plasmon-enhanced water splitting on TiO₂-passivated GaP photocatalysts, which makes more efficient use of the solar spectrum than bare TiO₂.⁶ Furthermore, the TiO₂ passivation layer makes the actively absorbing GaP photochemically stable and robust to corrosion.

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COLL 389

Visible-light, plasmonic, heating for catalytic CO₂ conversion applications

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Managing carbon emissions is one of the most pressing issues currently faced by the energy sector. One interesting approach for dealing with these emissions is to catalytically convert CO₂ into liquid fuels, olefins, aromatics, and industrial chemicals that can be sold to offset carbon management costs. This approach requires the development of novel catalysts capable of utilizing carbon-friendly forms of energy to activate CO₂ and drive a chemical reaction. My talk will focus on a very simple Au-ZnO heterostructure where visible-light plasmonic excitation of the Au generates heat to drive chemical reactions on the ZnO substrate. In this system, CO₂ and H₂ can be converted to CH₄, CO, and H₂O through a chemical pathway that experiments and thermodynamic simulations show is entirely thermal. The instantaneous and localized

nature of plasmonic heating offers many advantages and challenges for reactor design and heat management in catalytic processes. These aspects of plasmon-based reaction engineering will also be highlighted.

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Photochemical reactions on plasmonic metal nanostructures

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We will show that composite photo-catalysts combining plasmonic metallic nanoparticles of noble metals and semiconductor nanostructures exhibit improved photo-chemical activity compared to conventional photo-catalytic materials.^{1,2} We will also show that plasmonic silver nanoparticles, optically excited with low intensity visible light, exhibit direct photo-catalytic activity. We will discuss underlying mechanisms associated with these phenomena.^{2,3,4} We propose that this new family of photo-catalysts could prove useful for many heterogeneous catalytic processes that cannot be activated using conventional thermal processes on metals or photo-catalytic processes on semiconductors. I will show an example of such a process.⁵

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COLL 391

Active control of surface chemistry on plasmonic nanomaterials

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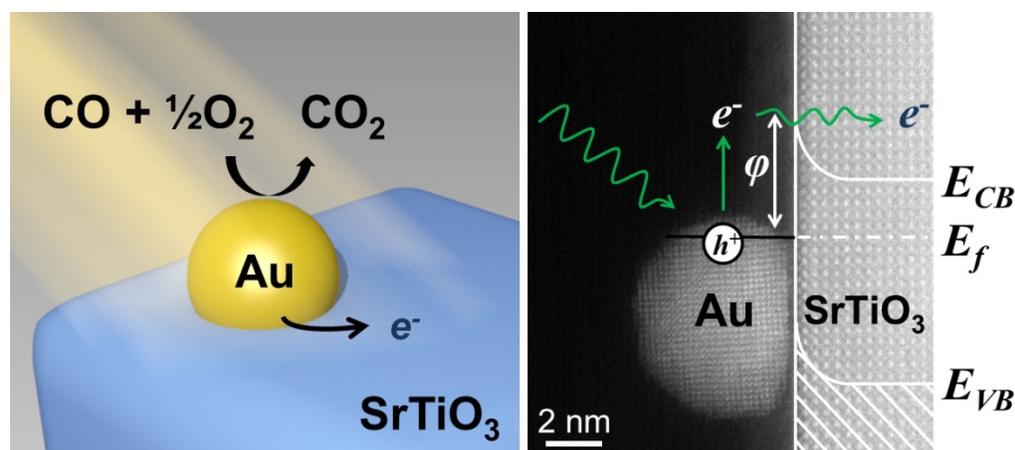
Novel chemical and physical processes occur at nanoparticle surfaces, both aided and reported by the broad tunability of their plasmonic properties. Active control is one way to relate plasmon resonance shifts to underlying changes in morphology, composition, and surface chemistry. We approach this challenge with electrochemical redox tuning of bimetallic nanoparticles and assembled structures. Our method allows us to deposit silver and/or its salts on the surface of gold nanostructures and selectively grow silver metal on the surface of these structures. We demonstrate repeatable spectro-electrochemical tuning of single nanoparticles and dimers. Potential applications include novel heterogeneous catalysis routes, experimental tests of charge transfer plasmonics, and nanoscopic plasmonic switches.

COLL 392

Plasmon-driven CO oxidation in Au-SrTiO₃ nanostructures at room temperature

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Gold (Au) nanoparticles (NPs) exhibit unique catalytic activity for a variety of aerobic oxidation reactions, but this activity is intimately linked to their electronic structure. Here, we demonstrate a method that leverages the inherent optical properties of Au nanoparticles (NPs) to controllably alter their electronic structure in order to improve carbon monoxide (CO) oxidation activity. We determine that the electronic structure and resulting carbon dioxide (CO₂) yield are closely tied to the surface plasmon resonance of the Au NPs. By employing a molecular approach to monitor CO adsorption in situ, we demonstrate that plasmon-mediated electron transfer (PMET) from the Au NPs to the strontium titanate (SrTiO₃) support reduces the electron density at the Au-CO interface, launching a new paradigm through which optimization of industrial catalysts can be more sustainably realized.



Plasmon-mediated electron transfer enables improved aerobic oxidation activity through the controlled manipulation of the Au NP electronic structure.

COLL 393

Elucidation of reaction mechanisms in complex catalytic networks

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We present an approach to analyze complex reaction networks for over solid heterogeneous catalysts. The approach effectively solves in polynomial time a number of reaction path problems that were thought to formally be NP-complete. This is done through the extensive use of the reaction matrix sparsity. The methodology is

implemented as a restful tool allowing anybody to utilize it on their own data over the web. The coupling of the tool to large databases of transition metal surface reactions is discussed, and the application to complex hydrocarbon synthesis reactions is discussed as an example application.

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Isolated metal active site concentration controls catalytic CO₂ reduction selectivity

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Developing relationships between catalyst active site geometry and performance is necessary for the design of optimal catalysts. Model single crystal catalysts, under ultra-high vacuum conditions, as well as more realistic size or shape controlled metal nanoparticle systems have been utilized to elucidate these insights in the past. However, it has also been shown that difficult to detect isolated metal atoms on oxide supports can play an unexpected role in governing the reactivity of heterogeneous metal catalysts. Significant effort has recently been dedicated to understanding atomic scale catalyst characteristics that control selectivity in the reduction of CO₂ by H₂ to produce higher valued carbon-based products. Studies examining reactivity and selectivity trends for CO₂ reduction by H₂ over transition metal catalysts have identified particle size as a main characteristic controlling catalytic performance. In addition, it has been shown that larger particle sizes are less stable under CO₂ reduction reaction conditions than small particles, in opposition to typically observed instability associated with smaller metal catalytic particles. Direct evidence relating these particle size dependent phenomena in CO₂ reduction catalysis to the nature of active sites controlling catalytic functionality is still lacking.

Here we explore catalytic CO₂ reduction by H₂ at stoichiometric methanation and H₂-lean CO₂:H₂ feed ratios over various weight loadings of Rh on TiO₂ supports. We observe a strong correlation between the reverse water gas shift turn over frequency (TOF) and the concentration of isolated Rh atomic sites on the TiO₂ support (Rh_{iso}) and a concurrent correlation between the methanation TOF and the concentration of Rh sites on the surface of Rh nanoparticles (Rh_{NP}). We also found that larger particles disperse under reaction conditions to form Rh_{iso} sites and that the dispersion process controls the instability of catalytic selectivity. The results strongly suggest that Rh_{iso} sites on the TiO₂ support are active sites almost exclusively for CO₂ reduction to CO, whereas Rh_{NP} sites are active sites almost exclusively for CO₂ reduction to methane. This study provides critical information for the design of selective CO₂ reduction catalysts and highlights the importance of thorough analysis of particle geometry dependent catalytic reactivity, where other factors, such as isolated site concentration, may actually be affecting catalytic performance.

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Mechanism and kinetics of surface limitations in MFI zeolite catalysts

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Zeolites are widely used in the conversion and upgrading during traditional petrochemical processes as well as biomass to renewable fuels and chemical pathways [1]. Combined high surface areas, shape selectivity, and catalytic functionality of zeolites have made them ideal for high temperature reactions. To maximize catalytic turnover, microporous and mesoporous materials are now being synthesized with length scales approaching that of a single lattice (pillared, nanosheets, membranes, etc.) in an attempt to reduce transport time. However, new MFI zeolite materials with small length scales are dominated by their surfaces. In small particles, surface permeation becomes dominant and the apparent diffusivity appears to be orders of magnitude smaller than through large particles [2, 3]. Two independent experimental systems are utilized to measure the contributions of the bulk and surface to desorption through desorption profiles (Zero Length Chromatography), and sinusoidal steady state of the uptake/desorption system (Frequency Response) [2,4]. Kinetic Monte Carlo simulations were used to mechanistically probe the effect of physical surface structures on overall transport timescales, including regular surface restrictions and total pore blockages. Comparison of experimental surface kinetics with predicted 2D surface structures in MFI zeolites indicate that approximately 99.9% of surface pores are impermeable to six-carbon-ring compounds.

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COLL 396

Hydrogenation of butadiene on Pt in realistic hydrogen pressure : mechanistic insights from DFT

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The selective hydrogenation of butadiene into butene is of great interest for the butene purification process. Platinum and tin-platinum surface alloy are known to be among the best metal catalysts for this application. The reactivity of butadiene on Pt(111) surface and Pt/Sn-Pt(111) surface alloy was already studied by our group at low coverage of hydrogen[1-3] within the periodic DFT framework. However, the practical reaction is done under a pressure of H₂ of ca 1 bar and at a temperature close to room temperature. In this study, our aim is to take into account the effect of those two factors. For that purpose, a thermodynamic model was coupled to the DFT calculations. We show that the mechanism of hydrogenation is changed. At low pressure, and low coverage of hydrogen, butadiene is chemisorbed and hydrogenation occurs following a Langmuir-Hinshelwood mechanism. At high pressure of hydrogen (1 bar), the most stable co-adsorption structure consists of 1 ML of chemisorbed hydrogen with butadiene chemisorbed on top of this layer. First hydrogenation occurs between H on the surface and butadiene from the gas phase, i.e. following a Eley-Rideal mechanism. Such a mechanism appears general for olefins at high pressure of hydrogen, in contrast with the picture emerging from the UHV surface science studies.

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COLL 397

Kinetics and mechanisms of oxidation reactions on metal oxide surfaces

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Both simple oxides (e.g., PdO/Al₂O₃) and complex oxides (e.g., LnBaPdO₅, where Ln = a lanthanide) catalyze the oxidations of CO, NO and H₂, however, the rate laws vary depending on both the catalyst and reactant. In turn, the form of the rate law influences both the shape and position of the conversion-temperature profile recorded in a packed-bed reactor. Thus catalyst comparisons in terms of "light-off temperatures" can be highly misleading. Instead, we will describe how to extract accurate kinetic information by curve-fitting the profiles using non-isothermal models for the reaction kinetics. It is necessary to minimize temperature gradients for the highly exothermic oxidation reactions by using inert diluents for both the catalyst and the reactants. Variation of the volumetric flow rate establishes the range of conversions for which mass transport can be neglected, assuring purely kinetic observations. The method allows the simultaneous measurement of kinetic parameters (activation energy, pre-exponential factor) and reaction orders (providing mechanistic insight about the rate-controlling steps). This

analysis shows that changes in the number and/or nature of the active sites as a function of conversion are observed for the more reducible simple oxides, but not for the more robust complex oxides. While curve-fitting analysis fails for the former, it is nevertheless possible to extract information about the timing of these changes and to link them to the dynamic behavior of the catalyst.

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Differences in the reaction mechanisms of hydrodeoxygenation (HDO) of m-cresol on platinum and ruthenium catalysts

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We have conducted experimental and theoretical studies for the HDO of m-cresol on Pt and Ru catalysts. Our experimental results show that the previously proposed hydrogenation/dehydration mechanism does not occur in the absence of support acidity. Toluene is generated directly from m-cresol. The direct hydrogenolysis mechanism proposed previously in the literature is also ruled out as our DFT calculations show the energy barrier for the direct hydrogenolysis of m-cresol on Pt(111) surface is as high as 260 kJ/mol. Thus, based on the experimental results and the DFT calculations, we propose a mechanism that a ketone intermediate is firstly formed by enol-keto tautomerization of m-cresol. The following hydrogenation of the C=O bond of this ketone intermediate followed by the dehydration leads to toluene, while the following the C=C bonds at the ring forms 3-methyl-cyclohexanone and 3-methyl-cyclohexanol. Our DFT calculations show that the overall energy barrier for the tautomerization, C=O hydrogenation and dehydration path towards toluene is about 60 kJ/mol lower than the direct hydrogenolysis path. It also shows that the overall energy barrier for the hydrogenation of the ketone intermediate at the C=C bonds towards 3-methyl-cyclohexanone is also lower than the barrier for the hydrogenation at the C=O bonds towards toluene. This agrees with our experimental observations that the selectivity over 3-methyl-cyclohexanone is higher than toluene. In contrast, the HDO of m-cresol on the more oxophilic Ru/SiO₂ catalyst shows enhanced selectivity of toluene than Pt/SiO₂. In addition, significant amounts of C₅-C₆ hydrocarbons were formed on the Ru/SiO₂ catalysts. This different reaction patterns on the Ru/SiO₂ and Pt/SiO₂ catalysts indicate different reaction mechanisms on these two metal catalysts. Our DFT calculations show that as the oxophilicity of the metal increases, the energy barrier for the direct C-O bond breaking on the metal decreases. The energy barrier for the direct C-O bond breaking of m-cresol to form toluene on Ru(0001) surface is calculated to be 103 kJ/mol, which is much lower than on the Pt(111) surface. Thus on the Ru catalyst, the direct C-O bond breaking pathway for the HDO of m-cresol is more favorable. After the direct C-O bond activation reaction, the formed carbon-bound intermediate can readily break the C-C bond to form C₅-C₆ hydrocarbon products, which is in agreement with the experimental observations.

COLL 399

Theoretical studies of oxygenates derivatives by metallic heterogeneous catalysts. A micro-solvation approach

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The shift from petroleum to biomass feedstock triggers the search for efficient catalysts working in aqueous environment. Water is necessary to solubilise reactants and products. However, it can also strongly modify the kinetics and the selectivity of a reaction compared with gas phase conditions. Thus, we need a reliable and simple strategy to probe this effect. Based on the well-established periodic slab model, we proposed to use a micro-solvation approach within the DFT framework. At a minimal cost, we showed recently that a single water molecule can strongly affect the dehydrogenation of alcohols on Rh(111)^{1,3} and Pt(111).^{2,3} In presence of a chemisorbed water molecule, an alcohol is preferentially H-bonded to this water molecule, its oxygen being far from the metallic surface. This co-adsorption process is synergetic leading to stronger adsorption energies. Despite the unusual distance, the OH bond scission is strongly activated on Rh, much less Pt. On the other hand, the CH scission is barely affected. We will show that this water assistance is even stronger for the reverse reaction, the catalytic hydrogenation of ketones.⁴ Oxophilic metals (Ru, Rh, etc.) are more active with a drop of the energetic span of ~0.40 eV while less oxophilic metals such as Pd or Pt are barely affected. Thus, in presence of water, platinum is not anymore the metal of choice to reduce ketones into alcohols and should be replaced by iridium or ruthenium for instance. This water assistance effect may explain why Ruthenium is widely used in biomass conversion.

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COLL 400

Thermodynamics and kinetics of oxygen induced chain-like reconstructions on the Pt(111) surface

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Late-transition-metal-catalyzed oxidations are fundamental to many applications of heterogeneous catalysis, including fuel cells, selective oxidation of organic compounds, chemicals synthesis, and environmental protection. Detailed understanding of surface

structures and changes caused by the adsorption of reactants is needed to improve catalytic oxidation on transition metal surfaces. Several metal oxygen surface states (e.g. chemisorbed adsorbed oxygen, surface oxides, and bulk metal oxides) exhibit different oxidation catalytic properties. To understand the nature of experimentally observed surface oxygen structures we investigated oxygen adsorption on unreconstructed and various reconstructed Pt(111) surfaces. The stability of clean and oxygen covered surfaces were evaluated energetically by density functional theory (DFT). We found several new ground state structures at oxygen coverages from 0.4-0.9ML showing oxygen induced reconstruction of surface platinum is energetically favorable. At these coverages oxygen induces surface buckling of the Pt rather than previously thought place-exchange surface oxide formation. The barrier for oxygen diffusion on buckled surface structures are compared to the barrier for oxygen diffusion on a clean and chemisorbed Pt(111) surfaces. Nudge Elastic Band (NEB) calculations are suitable for describing surface oxide structure formation by saddle points corresponding to reaction barriers of oxygen diffusion. These NEB calculations also provide a smooth potential energy surface for physically meaningful molecular dynamic simulations of oxygen diffusion on platinum. Further details relating kinetics and the atomistic mechanism of oxide formation involved in forming oxygen covered surfaces is addressed and the initial states of Pt(111) surface oxide formation is suggested.

COLL 401

Adsorbate-adsorbate interaction model for microkinetic trend studies and catalyst screening

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Presence of steps and edges has been proven to be important for catalytic reactions and in many cases these sites are the active sites transforming the reactants to products. The strong adsorption at the under coordinated step and edge sites leads to rather high coverages of the adsorbates. Hence the inclusion of adsorbate-adsorbate interactions can become important for catalytic activity descriptions. Here we propose a model to describe the interaction between the adsorbates adsorbed at two different sites of a same surface, since the metal nanoparticles in general consist of many different surface sites, such as terrace, steps, edges, kink and corners. For this study we have chosen the stepped (211) surface as our model surface. This surface consists of three different sites: steps, four-fold and terrace. The adsorbate-adsorbate interaction model is parameterized for the (211) surface to find the correct parameters to describe the interaction between different adsorbates on a single surface consisting multiple sites. Three model reactions are selected, namely steam reforming and dry reforming of methane and CO methanation, in order to verify the 'multi-site model'. The volcanoes shown in Figure 1 are obtained for CO methanation. The difference in the formulation

between the previous one-site interaction model and this newly proposed multi-site interaction model, along with the difference in predicted catalytic activities are discussed in detail.

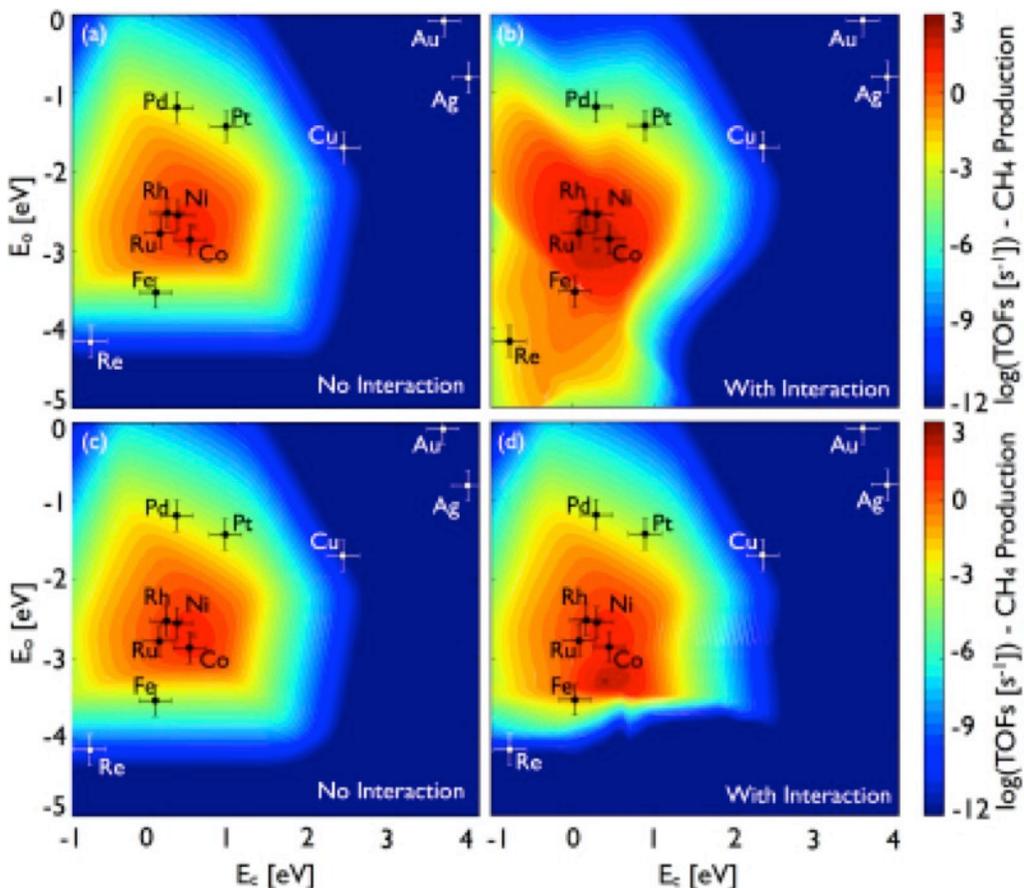


Figure 1. CH_4 formation rate in CO methanation as a function of the carbon (E_c) and oxygen (E_o) binding energies.

COLL 402

Long chain alkylimidazole switchable surfactants

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Surfactant with switching performance can realize switch between emulsification and demulsification so that oil and water are separated. It not only eliminates the need for the use of demulsifier, but also recycles surfactant. CO_2 switch surfactant shows no pollution, low cost, easy operation and excellent performance. A large number of CO_2 used in industrial production can reduce the greenhouse effect and enhance low carbon

environmental protection.

A series of long-chain N-alkylimidazole intermediates and switchable surfactants were designed and synthesized. The efficient surface activity was shown that surface tension could reach to 24.1 mNm^{-1} when the long carbon chain increased to 16. We studied the relationships between molecular structures and emulsifiability, switchable function, interfacial properties of synthesized surfactants. The optimum emulsification conditions were confirmed as 3% concentration of surfactant, 1:1 ratio (v/v) of alkane/water, 30 min of ultrasonic treatment. The stable switchability was proved by 5 cycles of conductivity and emulsification-demulsification used CO_2/N_2 as a trigger.

On this basis, N-decylimidazole switchable surfactant was applied to emulsion polymerization to study the switching performance. We researched the effect of different concentrations of surfactant and initiator on the particle sizes and ζ -potential of polystyrene. The cycle changes of particle sizes of emulsion show that N-decylimidazole switchable surfactant possesses switchable and controlling function.

COLL 403

Interfacial characterization of chemically modified sophorolipid derivatives

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Sophorolipids are natural biosurfactants that are made from renewable feedstocks. There has been considerable interest in using sophorolipids as a safe alternative to conventional surfactants currently found in food, cosmetic, and personal care applications. Compared to many other surfactants, sophorolipids show significant reduction in surface tension and a low critical micelle concentration.

Natural sophorolipids, however, have limitations as a surfactant with respect to their solubility and emulsification. Simple chemical modification of the lactonic form of the sophorolipid results in dramatically improved surface and interfacial properties. Transesterification of the lactonic sophorolipid with alkyl alcohols has resulted in surfactants with improved surface tension reduction, solubility, and critical micelle concentration.

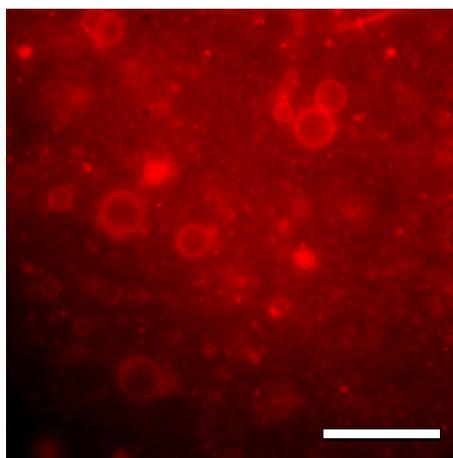
To better understand the structure-property relationship of the modified sophorolipids, emulsification and oil-water interfacial tension were investigated. Lemon oil, almond oil, and paraffin oil were chosen as the hydrophobic phases of interest in order to probe the sophorolipid interaction with fatty acid, alkane, and terpene based oils. Surfactant concentration was varied to determine relative surfactant potency against oils of interest based on structure. Interfacial tension was measured using a drop shape analyzer. Emulsions were analyzed with laser diffraction particle size analysis, dynamic light scattering, and zeta potential analysis.

COLL 404

Bilayer self-assembly from single-chain amphiphiles during the origins of life

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The origins of life required the assembly of three key components: a metabolic system, an information system, and a membrane that protected the other components and controlled diffusion of essential components. Before the modern lipids evolved, these membranes were likely composed of simple surfactants that follow basic aggregation behaviors, leading to the first cell membrane. Unfortunately, most membrane research is done with complex phospholipids, that have very different properties than single chain amphiphiles proposed for the origins of life. In this research, bilayer structures were made from short fatty acids, amines, alcohols, and sulfates, which self-assemble under different environmental conditions (see figure). The energetic contribution of hydrophobicity and headgroup interactions to aggregation behaviors were compared showing that the major contribution to aggregation behavior (measured by critical vesicle concentration) were the headgroup interactions with water. This is significantly different that phospholipid bilayers which have much larger hydrophobic contributions to aggregation. Additionally mixtures of these surfactants were found to have emergent properties that allow the bilayer structures formed to persist through large changes in the environment, including changes in temperature, pH and ionic strength. This research helps to define the environmental conditions that were most suitable for self-assembly leading to the formation of life on Earth.



Membranes formed from 20mM decanoic acid and 20 mM decylamine at pH 2, in 100 mM CaCl_2 . Visualized using fluorescence microscopy; membranes stained with Nile Red.

COLL 405

Monitoring the effect of surfactant type and process condition on sebum removal from CNF/PET surfaces in an aqueous solution using QCM/SPR technique

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The detergency effect of nonionic and ionic surfactants to remove the sebum from hard surface of cellulose nanofibrils (CNF) and polyethylene terephthalate (PET) in aqueous solution under various conditions was investigated using quartz crystal microbalance (QCM) and surface plasmon resonance (SPR) techniques. We have employed different temperatures, surfactant concentrations (below and above the critical micelle concentration), rinsing steps and shear to monitor the soil removal efficiency. The results of our study indicate that there is a higher affinity between sebum to cellulose as compared to PET. The use of surfactants at concentrations below the CMC caused its deposition on the film. In contrast, concentrations above the respective CMC produced significant soil depletion. Increasing the shear also led to a higher removal rate of the soil from the surface. The increase in temperature adversely reduced the surfactant efficiency. We used the Sauerbrey equation to calculate the effective mass change on the substrates. As a result the optimal parameters for each type of surfactant can be identified and therefore it is possible to obtain heuristic rules useful in detergency.

COLL 406

Study of surfactant influence on the low-pH stability of polyolefin dispersions

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Surfactant-free polyolefin dispersions containing ethylene-octene and ethylene-(sodium) acrylate copolymers were created using a mechanical dispersion process. This dispersion has a pH of 10.5 and is stable at room-temperature storage. However, it becomes un-stable with significantly increased viscosity when the pH is lower than 9.5, limiting its applications where a low pH environment is required. The goal of this study was to improve the low-pH dispersion stability through formulation approaches by addition of surfactants. Zeta potential was employed to systematically study the charge densities of different dispersion/surfactant combinations and to predict the colloidal stability. The stability of the polyolefin/surfactant mixtures depends on the surfactant type and concentration. Polyolefin dispersions with the addition of 10 wt% of the identified surfactants were stable even at the pH of 3.5 without agglomeration and the mixtures have low viscosity. These results suggest that zeta potential measurement is a useful tool to study polyolefin dispersion stability.

COLL 407

Solutes stabilized by brush amphiphiles: A study of solutes induced morphological transitions of brush amphiphile micelles

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Polymeric micelle systems, generated by self-assembly of amphiphilic polymers attract great interests and have been widely studied as nano-carrier for therapeutic molecules. Architecture of molecules plays an important role in determining properties of polymeric micelles system. Particularly, brush polymers or molecular brushes are a group of graft polymers with densely grafted side-chain, resulting in an extended backbone conformation. More complex asymmetric (bivalent) brush polymers with hetero side-chains attached to each repeating unit were created. Compared with tradition brush amphiphiles, branched structures have greater microstructural homogeneity, and the “pseudo-alternating” microstructure provided more steric shielding of the core from external reagents. However, little previous work has studied the physical entrapment of solute by more complex asymmetric brush amphiphiles.

Our recent work has successfully prepared an amphiphilic asymmetric brushes constructed on poly(glycidyl methacrylate) (PGMA) backbone with two polymer side-chains attached to each repeating unit. Poly(D,L-lactide) (PLA) and poly(ethylene glycol) (PEG) were selected to build hydrophobic and hydrophilic side chains respectively. We are interested to explore fundamental solute loading behavior of our amphiphilic brush amphiphile system with tunable bivalent brush architecture and versatile assembly morphologies. Herein, it is reported the solute entrapment study of brush amphiphiles by using b-carotene and polystyrene oligomer as model drugs. Different brush amphiphiles and their linear analog were compared in terms of solute stabilization properties by evaluating their morphologies, loading capabilities. A rare worm-to-spheres/ellipsoids transition induced by solute loading was observed in this study. And it is further compared the effects of different molecular and process parameters on assembly morphologies as well as solute-amphiphile interaction to understand unusual ellipsoids formation and mechanism of morphological transition.

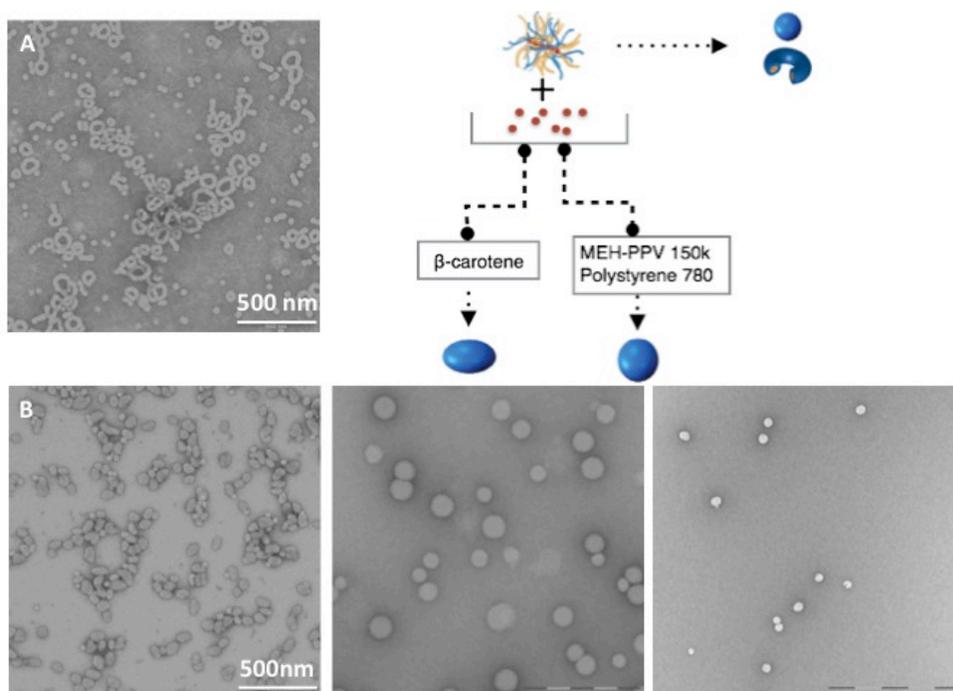


Figure. TEMs of micelles formed by asymmetric brush amphiphiles, with or without solutes loading, (A) empty micelles (B) loaded with b-carotene (C) loaded with Polystyrene 780 Da (D) loaded with semiconducting polymer MEH-PPV 150 KDa.

COLL 408

Aqueous delivery of π - π conjugated polymer solutions through a network formed by a fungal Janus-like surfactant

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Current interest in electronics, sensors and sources of alternate energy has driven important efforts directed towards identification of π -conjugated polymers as low-cost conducting/semiconducting organic materials. Poly (3-hexylthiophene), P3HT is perhaps the most popular conjugated polymer, widely investigated for device applications due to its hole transport properties, solubility in a range of organic solvents

and good film-forming characteristic. Present device manufacturing involves the use of hazardous and environmentally unfriendly solvents. Future solution roll-to-roll processing of polymers will require nonhazardous solvents.

This work describes an approach to deliver P3HT polymer solutions into an aqueous environment intermediated by Cerato ulmin, CU, an amphipathic fungal protein from the class II hydrophobin. CU has been implicated in Dutch elm disease. The efficient encapsulation of P3HT solution by CU biomembranes serves two purposes. First it ensures a benign delivery of essentially solvent-free P3HT films. Second, the CU-stabilized capsules seem to contain a well-aligned polymer with a long-range order, as demonstrated by polarized light optical microscopy, Raman and UV-Vis spectroscopy. This feature enables a better charge carrier mobility by electron hopping which is desired in improving polymeric materials for device manufacturing.

This work was supported by the NSF grant (DMR 1306262, PR) and AFOSR (FA9550-12-1-0248, ER).



Combined fluorescence and differential interference contrast image showing dendritic structure formed by Cerato ulmin biomembranes encapsulating poly(3-hexylthiophene).

COLL 409

Self-assembly of novel fluorosurfactants with polyoxometalates (POMs) as polar component in acetonitrile/water solution

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Presently, the self-assembly behavior and aggregate structures of normal surfactants like fluorosurfactants, polyoxometaltes (POMs)-containing hydrocarbon surfactants in different solvents are fairly well understood. In comparison, to our best knowledge, POM-containing fluorosurfactants by integrating more hydrophobic fluorinated “tail” and hydrophilic huge, adjustable polar part POMs “head” into one molecule unit, has not been reported in literature, rather little is known about the self-assembly of such unique

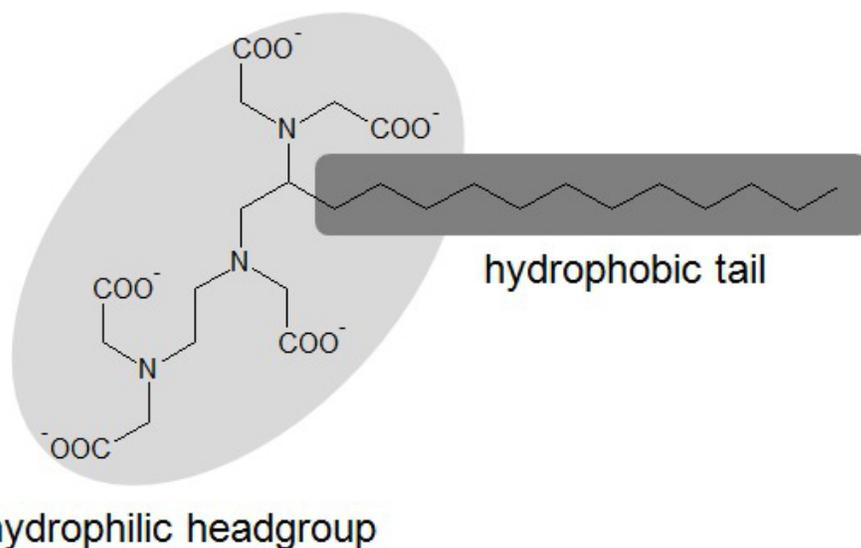
surfactants. The aim of this work is to study the self-assembly behaviors of POM-containing fluorosurfactant in mixed acetonitrile/water solvent by using laser light scattering (LLS) and electron microscopy techniques to explore the possibility of self-assembly behavior of such POM-containing fluorosurfactant. This type of fluorosurfactant can self-assemble in acetonitrile/water mixture solvent. It is found that the length of the fluorinated tails do not make obvious effect on the self-assembly, but the counterions play a significant role during the self-assembly process. When the counterions are TBAs, they can self-assemble into spherical vesicular structures, which may be interesting to catalysis scientists due to the large surface area; when the TBAs counterions are replaced by protons, nanobelts are observed under the same conditions. The nanobelts are interesting to photoelectronic scientists due to superior abilities to transfer electrons and photos.

COLL 410

Characterization of a chelating surfactant: Solution behavior and application prospects in ion flotation

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Chelating surfactants are functional molecules with both chelating and surface active properties. This dual functionality enables efficient recovery of metal ions from water system by for instance ion flotation. Furthermore, chelating surfactants are interesting from a fundamental point of view due to their characteristic molecular structure. The investigated chelating surfactant 4-C₁₂-DTPA (2-dodecyldiethylenetriaminepentaacetic acid) was designed and synthesized at Mid Sweden University. In the absence of metal ions, all eight donor atoms in the headgroup are titrating and the charge can be tuned from +3 to -5 by altering the pH. Because of the large, multiply charged and amphoteric headgroup 4-C₁₂-DTPA exhibits interesting solution properties such as pH dependent solution behavior, decreasing surface excess concentration (measured by neutron reflectivity) after micelle formation, slow adsorption to the air/liquid interface and pronounced pH changes at the formation of micelles. Interaction parameters for mixed systems of 4-C₁₂-DTPA and different foaming agents were calculated following the approach of Rubingh's regular solution theory, and the correlation between the interaction parameter and the ion flotation efficiency was examined. To our knowledge, no attempts to outline this properly have been presented previously. Strong correlation was found between the interaction parameter and the phase transfer efficiency of Ni²⁺ ions during flotations. Conditional stability constants (log *K*) were determined by competition measurements. From the small differences in log *K* between coordination complexes of DTPA and 4-C₁₂-DTPA it was clear that the hydrocarbon tail only affected the chelating ability of the headgroup to a limited extent. A significant difference in log *K* between different metal complexes with 4-C₁₂-DTPA enabled selective ion flotation recovery of the metal ion with the highest log *K*.



Molecular structure of 4-C₁₂-DTPA at high pH, with eight potential donor atoms, i.e., the five carboxylate oxygen atoms and the three nitrogen atoms.

COLL 411

Properties of novel bioinspired glycolipid surfactants: Tailoring function by disaccharide headgroup and alkyl tail length

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Glycolipid surfactants, comprised of sugar headgroups and lipid tails, offer high biodegradability and low toxicity while maintaining excellent surfactant performance. Their potential as greener alternatives to commonly used surfactants requires systematic study of the structure-function relationship of various glycolipid surfactants. This type of study has been precluded previously by costly and difficult synthesis; however, recent advancements in facile synthesis of highly pure glycolipid surfactants enable the analysis of a diverse set of glycolipids. This paper investigates the solution phase properties of two suites of glycolipid surfactants, O-n-alkylmelibiosides and O-n-alkylcellobiosides, which are composed of melibiose or cellobiose headgroups and varying straight-chain alkyl tails of 8-12 carbons. Surface tensiometry shows CMC values of 0.1-40 mM and molecular areas of 48-70 Å²/molecule. Dynamic light scattering documents multiple aggregate populations with a predominant micelle population of $R_h \sim 2$ nm with an aggregation number of 50-100 molecules/micelle determined by fluorescence spectroscopy. The comparatively larger headgroup size of melibiose and greater hydrophobicity and tail length of longer alkyl chains greatly affect the principal surfactant properties.

COLL 412

CO₂-reactive surfactant ionic liquids for reversible control of colloidal morphology and DNA compaction

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Surfactants are employed in materials and biological science to generate self-assembly structures to stabilize interfaces, affect solubilisation, morphology, biological and physicochemical properties. Conventionally, surfactant properties are manipulated by varying pH, temperature, and ionic strength, often leading to irreversible changes in system composition and phase stability. However, a more sophisticated approach is to use external stimuli to activate changes in molecular architecture, manifesting itself in changes in the overall system. CO₂-switchable surfactants based on the reaction of CO₂ with built in functional groups such as amines and amidines to form amidinium bicarbonates, zwitterionic adducts or ammonium carbamates have recently received much interest as CO₂ exhibits good biocompatibility and is non-toxic and abundant. However, on the molecular level all the mechanisms rely on switching “on” and “off” of the surfactant. Here, we show a new class of CO₂-reactive ionic liquid surfactants where the counterion is the responsive species, allowing for fine tunability of surfactant properties. We report how alteration in the surfactant architecture and electrostatics after reaction with CO₂ feeds through to significant changes in micellar structure as well as surface tension in a way not seen by any other surfactants. In turn, we demonstrate how this can be put into effect in various colloidal systems ranging from microemulsions to polymers suitable for applications in enhanced oil recovery, catalysis, CO₂-capture and novel ionic liquid separations. In particular relevance to gene therapy and targeted drug delivery, we demonstrate surfactant binding to DNA (and other biomolecules) and reversible compaction on bubbling with CO₂ and N₂.

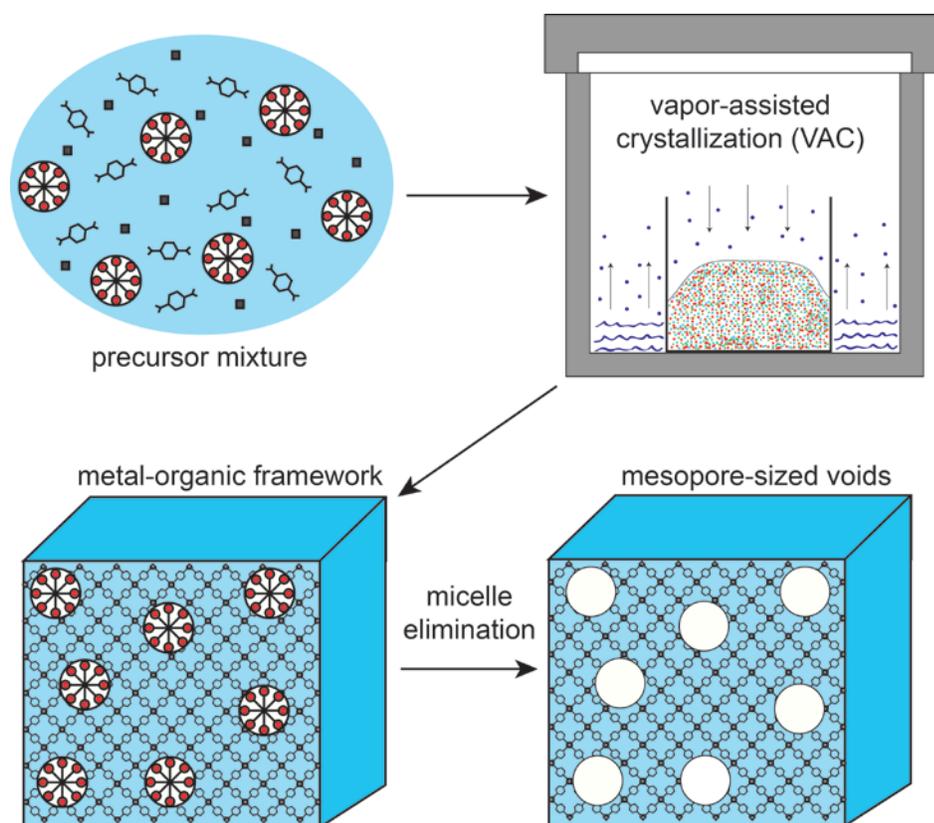
COLL 413

Vapor-assisted crystallization synthesis of a microporous (Ti) MIL-125 exhibiting significant mesoporosity

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Titanium materials are excellent catalysts for a multitude of chemical and photochemical reactions. Specifically, Ti materials exhibit beneficial semiconductor properties making them ideal photocatalysts, and they can be easily activated by peroxides, thus making them versatile oxidation catalysts. When designing solid Ti-based catalysts, high

surface area and accessible active sites are required for an active material. Metal-organic frameworks (MOFs) typically exhibit the former of these parameters due to their high crystallinity resulting in a microporous material. As a relevant example, the Ti-based MOFs MIL-125 and NH₂-MIL-125 have been shown to be active catalysts for photocatalytic H₂ production via water splitting, various photocatalytic reductions, and various chemical oxidations. Due to their molecular dimensions however, the use of MOFs as catalysts has been limited to small reactants. In this work, through the utilization of a vapor-assisted crystallization technique in conjunction with a soft template, microporous MIL-125 exhibiting significant mesoporosity was synthesized (Scheme 1). The mesoporous MIL-125 was then shown as an active catalyst for oxidative desulfurization applications (of a substrate too large to fit into micropores), outperforming a strictly microporous MIL-125 material. The source of this activity was linked to an increase in accessible active sites.



Scheme 1. Schematic representation for the synthesis of hierarchically porous MIL-125 through a vapor-assisted crystallization method using a soft template.

COLL 414

Synthesis and electromagnetic absorption properties of core-multishell MWCNT/Fe₃O₄/PANI/Au hybrids

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It is highly demanded to fabricate efficient EM absorbers with superior absorption qualities to address the growing electromagnetic pollution. In present research, core-multishell MWCNT/Fe₃O₄/PANI/Au hybrids were controllably synthesized and used as high efficiency electromagnetic absorbers, in which dielectric loss component (MWCNT and PANI), magnetic loss (Fe₃O₄) and Au nanoparticles were combined together. The hybrid is characterized by techniques including TEM, SEM, XRD, IR, Raman, UV-vis, and vector network analysis. It is found that charges are redistributed within the components of the hybrids. Multiple electronic phases at the interfaces are emerged. These redistributions lead to the complementarity between the dielectric loss and magnetic loss. The spawned interfacial polarization and synergetic interaction between magnetic and dielectric components extensively attenuate microwaves when exposed to an altering electromagnetic field. The excellent electromagnetic absorption ability of the prepared hybrids endows them attractive candidate as electromagnetic absorbers.

COLL 415

Computational discovery of metal-organic frameworks gas capture and storage

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Because of their high surface areas, crystallinity, and tunable properties, metal-organic frameworks (MOFs) have attracted intense interest as next-generation materials for gas capture and storage. An often-cited benefit of MOFs is their large number of possible structures and compositions. Nevertheless, this design flexibility also has drawbacks, as pinpointing optimal compounds from thousands of candidates can be time consuming and costly using conventional experimental approaches. As a consequence, computational approaches are garnering increasing importance as a means to accelerate the discovery of high-performing MOFs. Here we demonstrate a range of computational techniques that have been applied to predict the performance of MOFs for CO₂ capture and the storage of gaseous fuels (methane and hydrogen). The techniques include: (i) high-throughput screening based on data-mining and empirical correlations [1]; (ii) Monte Carlo simulations based on quantum-mechanically-informed interatomic potentials [2,3]; and (iii) first-principles calculations of thermodynamics and electronic structure [4,5]. For CO₂ capture and CH₄ storage, these techniques are illustrated on metal-substituted MOFs based on M-DOBDC and M-HKUST-1, which have demonstrated amongst the highest capture/storage capacities at moderate pressures and temperatures. In the case of H₂, we identify trends and promising adsorbents from amongst 4,000 known metal-organic compounds mined from the Cambridge Structure Database.

[1] Goldsmith et al., Chem. Mater. 25, 3373 (2013).

[2] Rana et al., J. Phys. Chem. C 118, 2929 (2014)

[3] Koh et al., submitted

[4] Koh et al., Phys. Chem. Chem. Phys. 15, 4573 (2013)

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COLL 416

Enhancement of optical absorptions in oxide nanostructures: Insight from a TDDFT study

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The current understanding of photo-excitement of electrons at the “nano” level is not very clear, and may mislead in making assumptions to the photocatalytic chemistry for these nano-crystals. Several key issues remain challenging in metal-oxide nano-crystals, such as identification of the fundamental gap and the actual optical gap, the nature of energy levels (“band”) in the nano-crystals, etc. Apart from these challenging issues, metal-oxide nano-crystals can show unpredictable electronic behavior due to their unsaturated and charge uncompensated surface bonds. These charge unpassivated ionic bonds may attract different chemical species to passivate themselves, and hence the electronic properties of the nano-crystals may change significantly. The first principle theories, such as density functional theory (DFT) and time-dependent-DFT (TDDFT), are state of the art theoretical methods to shed light in these aspects. To demonstrate how theoretical studies can guide the path, a unique class of highly stable, self-saturated and self-charge-compensated delafossite nanocrystals has been identified. The DFT study of structural and electronic properties of these nano-crystalline materials will be presented. To have a better estimate of the electronic excitation energies, and consequently the optical gap, time dependent DFT has been employed as well. The goal here is to study whether the nano-phases can enhance the optical absorption near band gap energies of these nano-structures compared to its bulk state for its application as a photocatalyst.

COLL 417

Selective reduction of CO₂ to formate by a homogeneous Iron electrocatalyst in water between pH 5 and 13

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This talk will discuss reduction of CO₂ to formate mediated by a homogeneous iron electrocatalyst in aqueous solution (pH 5 - 13). Iron carbonyl clusters, in particular [Fe₄N(CO)₁₂], can mediate the selective reduction of CO₂ to formate in buffered aqueous solution at -1.2 V vs. SCE with Faradaic efficiency of 95 %. The intermediates in the catalytic reaction have been studied using infra-red spectroelectrochemistry and this shows the formation of a reduced hydride which reacts with CO₂ to selectively produce formate. The pK_a and acidity values for these intermediates was measured

and a discussion of their relative values in MeCN and aqueous solution, and the influence on the products of the reaction will be explained. These values were also measured for a related cluster, $[\text{Fe}_4\text{C}(\text{CO})_{12}]^{2-}$, that does not reduce CO_2 to formate. Comparison of the two clusters provides insight into the design of CO_2 reduction electrocatalysts. Methods for the covalent immobilization of molecular electrocatalysts on conductive, high surface area carbon materials will also be discussed.

COLL 418

Nanoparticles and nanomaterials for electrochemical conversion of oxygen and carbon dioxide

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In this talk, we discuss aspects of our work related to the structure and reactivity of electrode surfaces. We report on our efforts directed at establishing the mechanism of oxygen and peroxide reduction on many different metal surfaces. By using a combination of spectroscopic, imaging, electrochemical stress, and x-ray scattering techniques combined with detailed calculations, we show that a crucial step involves the spontaneous cleavage of the O-O bond to form a mixed metal-hydroxide complex. This hydroxide complex is reduced during the electron transfer event, leading to the product water. The understanding derived from the mechanistic work provides directions for synthesis of advanced catalysts for oxygen reduction. In particular, we have synthesized a series of bio-inspired metal coordination polymers exhibiting oxygen reduction activity. The synthetic platform utilized for the ORR work also is shown to have utility in other reactions. Specifically, we show by using electrochemical stress measurements and electrochemical testing that Ni or Ni/Fe surfaces modified with N-containing molecules exhibit substantially higher Oxygen Evolution Reaction activity relative to unmodified surfaces. Similarly, Ag surfaces modified with the same N-containing molecules exhibit higher currents for carbon dioxide reduction to form CO. The origins of this behavior relate to modifications in the stability of products on the surface.

Finally, we use this synthetic work to construct a reversible switch that gates proton transport to a molecular oxygen reduction reaction (ORR) catalyst, a strategy which gives unique mechanistic insight not only to the ORR, but to all proton-coupled electron transfer (PCET) reactions.

COLL 419

Optical response of molecule — semiconducting nanoparticle hybrids

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We will present theoretical results we have recently obtained concerning the Enhanced Raman Scattering (ERS) of a Dopamine molecule adsorbed on a TiO₂ nano-particle. Raman enhanced response for molecules adsorbed on metallic nano-particle is mainly due to plasmon resonance excitation. In the case of TiO₂ semi-conducting nano-particles, the enhancement can not be explained in term of plasmons. We will explore the mechanisms responsible for ERS with semi-conducting nano-particle, and how to model them. We have developed an efficient method for calculating resonance Raman spectrum for such systems, which posses the peculiar property that their excited electronic states decay in a short time. Numerical implementation of this method along time TD-DFT calculations will be presented.

We will also present a model for these hybrid systems which is a Fano-Friedrichs-Anderson model but including a relaxation process described in terms of a Liouville-Lindblad equation. The complete optical response: fluorescence emission, Rayleigh and Raman scattering, calculated in the framework of this model, will be presented. In particular, the conditions for the observation of Fano interferences profile in the emission line shape of such hybrids will be investigated.

COLL 420

Cytochrome c unfolding at cardiolipin-rich membrane surfaces

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Interactions of cytochrome *c* (cyt *c*) with cardiolipin(CL)-rich mitochondrial membranes play an important role in early stages of apoptosis. Induced by these interactions, conformational changes in cyt *c* promote the peroxidase function of the protein, the activity that targets CL itself. Our fluorescence studies of multiple dye-labeled cyt *c* variants have revealed that the CL-bound species vary in degree of the polypeptide compactness and the heme exposure. Binding to the CL-rich membrane triggers loosening of the cyt *c* structure, protein anchoring to the membrane, and ultimately the large-scale polypeptide unfolding on the membrane surface. Within these extended structures, heme misligation inhibits the cyt *c* peroxidase activity. When the membrane surface area is limited, the protein ensemble is more compact. Several mutants of cyt *c* were engineered to probe the effects of perturbation of the heme environment without the large-scale protein unfolding. Disruption of the intraprotein hydrogen-bonding network in cyt *c* opens the heme crevice to stimulate the intrinsic peroxidase activity but also globally destabilizes the protein yielding a higher fraction of extended structures in the CL-bound ensemble. The fluorescence studies are being extended to biological membranes where many of the same phenomena are observed.

COLL 421

Conformational dynamics of cytochrome c related to peroxidase activity during apoptosis

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Cytochrome c (Cyt_c) binding to membranes containing cardiolipin (CL) leads to a conformational change that causes loss of Met80 ligation to the heme. This conformational change provides an open coordination site on the heme resulting in a gain of peroxidase function. The peroxidase activity of Cyt_c is known to oxygenate CL, which is believed to be the earliest signal in the intrinsic pathway of apoptosis. We are investigating which residues in the highly conserved sequence of Ω-loop D (residues 70 to 85) are particularly important for modulating the peroxidase activity of Cyt_c. We have solved the structure of a K72A variant of yeast iso-1-Cyt_c in which Met80 has been replaced by a water molecule. The conformational change that occurs is small, but would clearly be sterically hindered by the presence of the trimethyllysine at position 72 in wild type iso-1-Cyt_c. We have also shown that K72A iso-1-Cyt_c has enhanced peroxidase activity relative to wild type. The K72A iso-1-Cyt_c structure indicates that steric size also could be a factor at position 81, which has evolved from alanine in yeast to large aliphatic residues in higher eukaryotes. We have studied the dynamics of loss of Met80-heme ligation by replacing Ala81 of iso-1-Cyt_c with the more sterically bulky amino acid, histidine. Gated electron transfer and pH jump kinetic experiments show that this mutation slows the loss of the Met80 ligand and decreases the time that the heme coordination site is vacant. Thermodynamic measurements indicate that the change in dynamics results primarily from stabilization of the Met80-bound state of the heme by the A81H mutation. The results suggest that position 81 has evolved to more sterically bulky amino acids in higher eukaryotes to increase the stringency of the onset of peroxidase activity early in the intrinsic pathway of apoptosis.

COLL 422

Artificial virus nanoparticles to control cellular processes at the virus-host interface

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The monosialodihexosylganglioside GM3 is a host-derived glycosphingolipid incorporated in the lipid bilayer of human immunodeficiency virus type-1 (HIV-1) particles that can elicit glycoprotein-independent interactions between HIV-1 and Siglec1/CD169 expressed on dendritic cells (DCs). A selective characterization of GM3 mediated virus binding to CD169 and uptake calls for model systems that are free of viral envelope glycoproteins or host-derived glycolipids. In response to this need we

have reverse-engineered GM3-dependent but envelope glycoprotein-independent viral binding with self-assembled artificial virus nanoparticles (AVNs). These biomimetic nanosystems contain a membrane of defined composition wrapped around a solid metal core. We demonstrate that GM3 containing AVNs induce a spatial sequestration in CD169-expressing HeLa cells and mature DCs that results in an enrichment of AVNs in peripheral, tetraspanin-associated compartments. This spatial distribution is reminiscent of CD169-dependent HIV-1 sequestration in DCs and highlights GM3-CD169 binding as an envelope glycoprotein-independent signal for virion sequestration.

COLL 423

Tracking amyloids with fluorescent oligo(*p*-phenyleneethynylene) electrolytes

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Abnormal deposition of protein aggregates with "amyloid" β -sheet enriched fibrillar structure is a pathological hallmark of a plethora of important diseases, among them Alzheimer's, Parkinson's and Huntington's diseases, type II diabetes, and the prion-transmitted spongiform encephalopathies. Understanding these diseases' pathology and progress, as well as developing treatments, requires us to find new ways of tracking destructive protein assemblies. We propose that oligo(*p*-phenyleneethynylene) electrolytes (OPEs) represent a new class of promising, protein-conformation-sensitive optical probes with multiple sensing modalities. Here we report a thorough characterization of four OPEs with varying chain lengths and charged groups as fluorescent stains for amyloid fibrils formed *in vitro* from hen egg white lysozyme. The OPEs tested perform as well as Thioflavin T, the current gold standard dye. Preliminary data indicates that OPEs are also capable of distinguishing between amyloid aggregates formed from different protein monomers. The OPE backbone also has potential as a scaffold for rational design of superior fluorescent ligands for amyloid; we present design principles that can be used to synthesize OPEs with highly desirable properties for three-dimensional *in vivo* tracking of amyloid aggregates.

COLL 424

Super-resolving the dynamics of a membrane-bound virulence regulator in *Vibrio cholerae*

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Single-molecule super-resolution methods are ideally suited to the small size of bacterial cells, and hold particular promise for understanding processes in microbiology that have important impact on human health and disease. In bacteria, two-component signaling systems are responsible for much of the interaction between the bacterium and the outside world. These systems can sense a wide variety of stimuli and respond, often by altering gene expression. In the pathogenic *Vibrio cholerae*, agent of the human cholera disease, a two-component signaling system regulates the toxin synthesis pathway at the ToxR regulon. Interestingly, the integral inner-membrane protein TcpP remains membrane-bound while binding DNA to upregulate toxin expression. The mechanism of such membrane-bound transcription has yet to be elucidated in live cells.

By measuring TcpP mobility from the trajectories of single molecules of this DNA transcription regulator, and by using genetic knockouts to examine the effects on TcpP motion of the TcpP interaction partner ToxR and of the *toxT* DNA promoter binding site, our live-cell super-resolution imaging has provided mechanistic insight into the *V. cholerae* virulence pathway (Haas et al., *Molecular Microbiology* 2014). Based on single-molecule trajectory analyses, including cumulative probability distributions, our observations support a mechanistic model in which ToxR recruits TcpP to the *toxT* promoter for transcription activation. This work, which informs on the mechanism by which *V. cholerae* regulates cholera toxin production, is timely because cholera remains a threat to health in the developing world.

COLL 425

Proximity energies and their consequences in living systems

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Cell cytosol, cell organelles, serum and interstitial fluids all may be considered complex, concentrated chemical systems. The colloidal properties of complex, concentrated mixtures may result in preferential solvation of macromolecules by other macromolecules. Charge-charge interactions between molecules provide the longest-range interaction. However, what governs the charge on biomolecules, particularly proteins, is still being examined. This talk will focus on the molecular features that contribute to their proximity energy, and how these features may lead to order in a complex system.

COLL 426

Molecular basis of high-affinity membrane binding by the C2A domain of granuphilin

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Membrane-binding proteins are key components of many signaling pathways in eukaryotic cells. Granuphilin, also known as synaptotagmin-like protein 4 (Slp-4), functions in tethering insulin secretory vesicles to the plasma membrane prior to exocytosis. Granuphilin contains two membrane-targeting C2 domains, C2A and C2B, which interact with plasma membrane lipids including phosphatidylinositol-(4,5)-bisphosphate [PI(4,5)P₂]. Both C2A and C2B bind anionic lipids such as PI(4,5)P₂ in a Ca²⁺-independent manner. In particular, the C2A domain binds with strong affinity to liposomes containing a physiological mixture of lipids including 24% phosphatidylserine (PS) and 2% PI(4,5)P₂ (apparent K_d of 2-5 nM). The same domain binds with much weaker affinity to anionic liposomes containing either 24% PS or 2% PI(4,5)P₂, but not both target lipids. Affinity is ~100-fold tighter in the presence of both target lipids, suggesting a multivalent and/or cooperative membrane binding mechanism. Here, the roles of cationic residues in two putative lipid binding pockets on the C2A domain are probed using a combination of molecular biological and biophysical approaches. Overall, granuphilin possesses several separate interactions with plasma membrane lipids and proteins, suggesting it may serve as a coincidence detector for targeting secretory vesicles to specialized regions of the plasma membrane.

COLL 427

Gold nanoparticle assembly for selective two photon scattering imaging of cancer cell

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Two Photon Scattering (TPS) or Second harmonic imaging using near infrared laser light is the key to improve the penetration depth. Unfortunately currently used TPS imaging techniques using organic dyes have limited capability due to the poor signal-to-noise ratio. Targeted tumor imaging over non-targeted organ is also challenging that need to be overcome. Here we will discuss our recent report on the synthesis and characterization of gold nanoparticle assembly and its use for selective TPS imaging of cancer cell. Experimental data indicate that two photon scattering intensity can be increased by few orders of magnitude by just developing nanoparticles self assembly. FDTD simulation modeling also indicate huge enhance of electric field in self-assembly structure. Experimental result shows that the bio conjugated gold nanocage assembly can be used for targeted TPS imaging of the breast cancer cell.

COLL 428

Size selective SERS analysis using nanorattles with porous polymer shell and entrapped gold nanoparticles

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Nanorattles or yolk-shell structures use here are made of metal nanoparticles entrapped within hollow polymer nanocapsules. Porous polymer shell of nanocapsules shows size-selective permeability, which allows unhindered transport of small molecules across the wall while blocking out molecules larger than the pore size. Here we report the feasibility of using newly formed nanorattles in analysis of complex mixtures using surface enhanced Raman scattering (SERS). Small molecules enter the nanocapsules through size-selective nanopores and interact with encapsulated gold nanoparticles to produce SERS signals. In contrast, molecules larger than the pore size cannot enter the capsules and do not show SERS signal enhancement.

COLL 429

Ultrafast laser induced synthesis of narrowly distributed sub-5 nm surfactant-free Au-Pd nanoparticles

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Bimetallic nanoparticles are known to possess enhanced optical, magnetic, and catalytic properties in comparison to their pure metallic counterparts. As these novel properties arise from synergistic effects between the components of the nanoalloy it should be possible to engineer the physical and chemical properties of the nanoparticle by controlling its shape, size, and composition.

Au-Pd nanoparticles are one of the most studied systems because they exhibit some of the properties mentioned above, which has motivated the development of synthetic methods for generating narrowly distributed, < 10 nm Au-Pd nanostructures. In the present study, surfactant-free Au-Pd bimetallic nanoparticles, as small as 2.4 ± 0.9 nm, are generated using intense femtosecond laser pulses to co-reduce aqueous solutions of $[\text{AuCl}_4]^-$ and $[\text{PdCl}_4]^{2-}$. High-resolution scanning transmission electron microscopy (STEM), selected area electron diffraction (SAED), and energy dispersive x-ray (EDX) measurements show the Au-Pd nanoparticles to be heterogeneously mixed Au-Pd alloys.

COLL 430

Fabrication of plasmonic nanoantenna arrays on flexible substrates via colloidal lithography for biosensing

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Metallic nanostructures have garnered a great deal of attention due to their fascinating optical properties, which have been resulted in wide variety of applications ranging from chemical and biological sensors to metamaterials with negative refractive index. Exploiting the unique properties of metallic nanostructures on flexible substrates can open the routes for new generation of plasmonic substrates. In our colloidal lithography approach, two-dimensional hexagonal closed packed (2DHCP) monolayer of polystyrene nanospheres was transferred from silicon substrate to Polydimethylsiloxane (PDMS). The size of polystyrene nanospheres was reduced by oxygen plasma treatment followed by evaporative deposition of nickel layer as a sacrificial layer. Next, gold was deposited and filled the area between nanospheres and nickel pits. Finally, by removing nickel layer, gold nanostructures were left and form fabricated substrate. Nanorings, nanodisks, nanocrescents, and crescent-dimers were obtained readily by making some modifications in fabrication steps. Substrates were characterized by scanning electron, atomic force and infrared microscopes as well as UV/VIS spectrometer. Samples were highly uniform, densely packed (around $7 \times 10^8 \text{ cm}^{-2}$) and exhibited tunable plasmon resonance. These characterizations made the substrates ideal for refractive index biosensing. Finally, we used the fabricated substrates for local refractive index sensing by studying the localized surface plasmon resonance shift.

COLL 431

DFT investigation of the speciation and vibrational frequencies of the uranyl cation on the surface of oxidized silver nanoparticles

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Uranium remains an important metal to society largely due to its use in nuclear power applications. However, mining operations for nuclear power and nuclear weapons development, along with the storage of spent nuclear fuel can leave populations at risk for exposure, which warrants fundamental investigations into its chemistry.

Noble metals such as silver and gold are well-established in their use for surface enhanced Raman spectroscopy (SERS) to gain orders of magnitude signal enhancement. This is particularly true for the uranyl cation (UO_2^{2+}), the predominant form of uranium in the environment, which in of itself has a large Raman cross-section. Several studies have established that silver in the forms of bulk surface, as well as colloids, has been used for SERS enhancement of the uranyl cation. The signal enhancement is accompanied by the uranyl symmetric stretch decreasing by over 100 cm^{-1} , suggesting both an interaction between the silver surface and uranyl cation, and a resultant decrease in the bond strength of the uranyl moiety (between the uranium and oxygen atoms). Less understood, however, is what kind of species are adsorbed to the silver surfaces, and the underlying interactions giving rise to the vibrational frequencies observed.

Here we present the use of Density Functional Theory (DFT) modeling to investigate questions about how uranyl adsorption onto silver gives rise to SERS enhancement and shifts the vibrational frequencies of the cation. Nanoparticles are first modeled as bulk silver metal surfaces cleaved in the (111) plane and terminated with an oxide layer. The adsorption of various species of the uranyl cation (monomeric aqua complexes as well as oligomers) is modeled. For each adsorbed geometry, the vibrational frequencies are calculated for comparison to the SERS results, and the normal modes are also determined.

COLL 432

Enhancement of enzymatic colorimetric response by silver island films on high throughput screening microplates

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In this study, we describe the use of an enzyme-based hybrid platform, which is comprised of silver island films (SIFs), enzymes, i.e., horseradish peroxidase (HRP) and alkaline phosphatase (AP) and high-throughput screening (HTS) microplates, to enhance the colorimetric response of enzymatic reactions. The hybrid platform was designed in a two-step process: (i) deposition of SIFs onto HTS microplates with low, medium, and high loading using Tollen's reaction scheme; and (ii) attachment of biotin-avidin protein (b-BSA) and biotin-poly (ethylene-glycol)-amine (BEA) as linkers for the immobilization of enzymes. Control experiments, where SIFs were omitted from the surfaces were carried out to confirm the effect of SIFs on the enzymatic colorimetric response. Significant colorimetric signal enhancement was observed for HRP or AP on SIFs (high loading) deposited HTS microplates using b-BSA (up to ~3-fold for AP and ~6-fold for HRP) or BEA (up to ~7-fold for both HRP and AP), as compared to our control samples. The observed increase in colorimetric response can be attributed to the nature of BEA, which exposes surface-bound enzymes to the substrate present in bulk more efficiently than b-BSA. This study proves that SIFs can serve as a valuable tool to improve the signal output of existing bioassays carried out in HTS microplates, which can be applicable to the field biosensors and plasmonics.

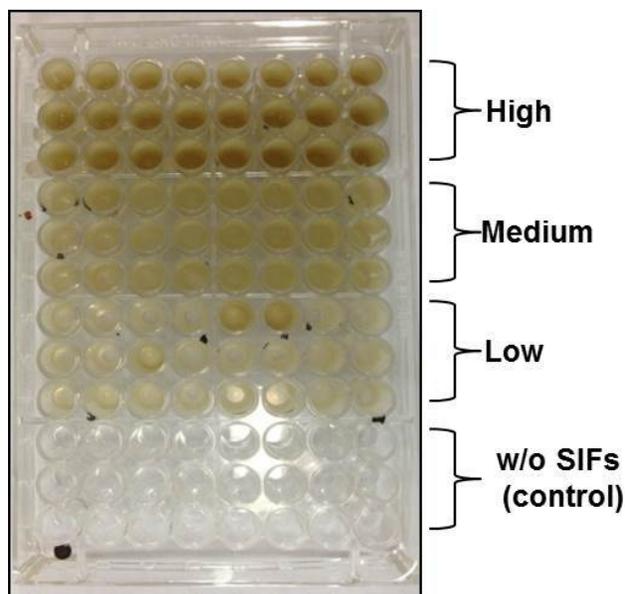
COLL 433

Development of polymer-metal colloid hybrid platforms for bioassays with improved dynamic range

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In this work, we report the use of chemical methods for the surface modification of poly(methyl methacrylate) (PMMA) based circular bioassay platforms and high throughput screening (HTS) wells with metal colloids to create hybrid bioassay

platforms. We also demonstrate that the use of hybrid platforms in conjunction with magnetic nanoparticles improve the detectability of target analytes in complex biological media (whole blood and serum). In this regard, hybrid platforms were created by coating the chemically treated PMMA and HTS wells with a colloidal film of silver, gold, copper or titanium oxide using a sputter coater. Model colorimetric direct bioassays based on the interactions of biotin and with streptavidin were carried out, where magnetic nanoparticles were decorated streptavidin-labeled with horseradish peroxidase were used to separate the target analytes (biotinylated human serum albumin) from complex biological media. With this method, all target analytes present in the samples conjugate with their binding partners present on the magnetic nanoparticles and are completely separated by the magnetic separator from the sample medium, which prevents the loss of the target analytes during washing steps. Subsequently, an increased detectability of target analyte from complex biological media can be achieved, as compared to traditional colorimetric bioassays that can give false negatives at the low concentrations of target analytes. Using our hybrid platforms, we observed up to ~8-fold increase in the colorimetric response (with a 4-log dynamic range and a lower detection limit of 10 pg/ml) for the detection of the target analytes as compared to those without the metal colloidal films.



Hybrid bioassay platform comprised of a standard HTS plate and silver island films

COLL 434

Surface plasmon enhanced photoelectrochemical performance of core-shell Ag@Ag₂S nanoparticles decorated Ti@TiO₂ nanowire electrodes

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Ti@TiO₂ nanowires decorated with plasmonic active Ag@Ag₂S core-shell nanoparticles is fabricated for visible light driven photoelectrochemistry studies. The Ti@TiO₂ nanowires provide a high surface area for efficient light absorption and efficient charge collection from the Ag@Ag₂S NPs. The local field enhancement of Ag surface plasmon is found to be able to significantly increase the visible light response of the Ag₂S shell photocatalyst. The shell thickness and core size of the Ag@Ag₂S core-shell structure can be controlled to achieve optimal photoelectrochemical performance. The optimal core-shell structure has been identified to show an ideal surface enhanced photoelectrochemical performance

COLL 435

Probing cellular mechano-sensitivity using biomembrane-mimicking cell substrates of adjustable stiffness

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Physisorbed polymer-tethered lipid bilayers consisting of phospholipids and lipopolymers show remarkable materials properties. In these planar membrane systems, lipopolymers act as crowding agents with profound influence on membrane organization, lipid dynamics, and membrane elasticity. Such biomembrane-mimicking supramolecular assemblies are well suited as cell substrates for the analysis of cellular mechano-sensing because individual linkers are free to assemble into immobilized linker clusters underneath focal adhesions, thus allowing cell spreading. Furthermore, substrate stiffness of polymer-tethered membranes can be systematically adjusted either by altering the degree of stacking in a polymer-tethered multi-bilayer stack or by varying the lipopolymer molar concentration in a single polymer-tethered lipid bilayer. Experiments on different mechano-sensitive cell lines are presented, which demonstrate the functionality of these cell substrates in the presence of ECM-cell-mimicking and cell-cell-mimicking linkages.

COLL 436

Evaluation of drug mediated changes in rhythmic contractile activity of cardiomyocytes

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The human pluripotent stem cell-derived cardiomyocytes have been used for safety pharmacology testing to obtain proarrhythmia assessment. The potential of Ca²⁺ channel antagonists, particularly nifedipine, to cause apoptotic cell death has been controversial and is of considerable importance for cardiomyocytes as loss of these cells is an important component of the pathophysiology leading to heart failure. Here we use AFM measurements to precisely monitor the arrhythmic contraction of cardiomyocytes with the treatments of Ca²⁺ channel agonists. The quantitative rhythmic and arrhythmic beating profiles of functional cardiomyocyte cells exposed to a series of concentrations of nifedipine. Cell death was evaluated by using the MTT(3-[4,5-dimethyl-thiazol-2-yl]-2,5-diphenyl tetrazolium bromide) assay. Influence and dosage responses of other types of pharmacological drugs were also tested and cell viabilities were determined. This has represented that AFM is a sensible tool to select and determine the effect of ion channels agonists on cardiomyocytes, thus can be used as an *in vitro* testing tool for toxicity of new drugs and proteins in cardiac diseases.

COLL 437

Changes in the cell surface during progression to cancer of human cervical epithelial cells

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Despite considerable advances in understanding the molecular nature of cancer, many biophysical aspects of malignant development are still unclear. Here we study physical alterations of the surface of membrane of human cervical epithelial cells during stepwise *in vitro* development of cancer (from normal to immortal (pre-malignant), to malignant). Atomic force microscopy (AFM) was used to measure adhesion between the AFM probe and membrane surface. The obtained maps of adhesion were analyzed by using more than 30 surface parameters. We found that there was a particular correlation between one parameter, which characterizes emergence of fractal structure, and the stage of cancer progression. Contrary to the previously expected correlation between cancer and fractals, we find that fractal occurs only at a limited period of development when immortal cells become cancerous; further cancer progression demonstrates deviation from fractal. Because of the connection between fractal behaviour and chaos (or far from equilibrium behaviour), these results suggest that chaotic behaviour of cell membrane coincides with the cancer transformation of the immortalization stage of cancer development, whereas further cancer progression recovers determinism of processes responsible for cell surface formation. The reported method of analysis can be directly applied to cells collected in liquid cytology screening tests. Thus, the fractal parameters could be treated as a new "physical marker" for identification of individual cervical cancer cells without tissue biopsy.

COLL 438

Probing the coupling between polybasic peptides and PIP₂ lipids in asymmetric supported lipid bilayers

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Electrostatic interactions are an important factor in the spatiotemporal organization of biological membranes. Probing these interactions in model membranes allows for experimental variables to be modulated while observing system features like mobility and clustering. Phosphatidylinositol phosphate (PIP) lipids are of particular interest in these experiments because of their central role in cell signaling and membrane structural modelling. However, incorporating PIP lipids into supported bilayers has been experimentally challenging, presumably because of interactions between the bottom leaflet lipids and the glass substrate. Here we report on a method to make asymmetric supported lipid bilayers with fluorescently labeled PI(4,5)P₂ lipids in the upper leaflet, for which the lipids display high mobility and no apparent clustering or aggregation. We then bind polybasic peptides to the bilayer and probe the lipids and peptides with time-resolved fluorescence spectroscopy. Pulsed interleaved excitation and time-correlated single photon counting is used to measure the mobility of the lipids and peptides as well as the degree to which their motion is correlated. This allows us to investigate the role of electrostatics in the organization of biological membranes.

COLL 439

Oncogene induced stiffening of living cells

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The mechanical properties of cells govern cell proliferation and motility; cellular functions that, when deregulated can cause tumour diseases. However, the role of cellular mechanical properties during cancer progression needs further elucidation. Our analysis indicate that the SV40T oncogene induces a reorganization of the vimentin intermediate filament network. To determine whether the observed oncogene-induced vimentin reorganization can control the stiffness of cells, colloidal probe AFM was used to measure the stiffness of normal cells with and without expression of SV40T. The data indicate that the SV40T expressing cells are stiffer than normal cells and that the specific inhibition of HDAC6 by tubacin revert this SV40T-induced stiffness back to normal. These findings are consistent with the possibility that oncogenes can increase the capacity of cells to resist mechanical deformation by a mechanism that depends upon HDAC6.

COLL 440

Electronic structure models of plasmon-enhanced processes

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This talk will focus on the use of electronic structure methods in combination with electrodynamics to describe plasmons and plasmon-enhanced optical processes. We begin by showing what one means by a plasmon from the perspective of quantum mechanics. Then we show that classical electrodynamics needs to be coupled to quantum mechanics for a quantitative description of SERS, including the chemical mechanism. Finally we discuss the interaction of ligand electrons with plasmons, and the influence of this on extinction spectra and plasmon enhanced chemical processes.

COLL 441

Ultrafast size-dependent electronic interactions in metal clusters

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Reduction of the size of a material to a few nanometer scale leads to drastic modifications of its physical and catalytic properties. In the case of metal nano-objects with sizes larger than a few nanometers, these modifications are mostly due to classical effects, as dielectric confinement which is at the origin of the presence of localized surface plasmon resonances in their optical response. In contrast, for smaller clusters with sizes below about 2 nm (less than about 250 atoms), quantization play an important role, leading to an evolution from a bulk-like behavior of the electronic properties (i.e., ruled by quasi-continuum of electronic states in the conduction band) to a molecular one (discrete energy states). Though the impact of quantization on static properties (ionization threshold, melting temperature, optical absorption, ...) of free clusters has been extensively investigated, the induced changes on the electronic interactions have been much less studied. This is due both to the difficulty in the synthesis of clusters with a well controlled size and environment, and in the experiments.

Using high-sensitivity femtosecond pump-probe spectroscopy, we measured the optical response of silver nanoparticles in the 3 to 1 nm size range. Investigations have been performed in surfactant-free glass-embedded clusters, to limit surface effects. Using different probe wavelengths, the relaxation of photoexcited nonequilibrium electrons was followed in the time-domain, yielding information on the electron-electron and electron-vibration energy exchange processes. The efficiency of the electronic interactions is shown to increase with size reduction down to about 2 nm (consistently with previous results in larger size particles). It is then shown to further decrease at smaller sizes, with a non monotonic behaviour. This effect is ascribed to quantization of

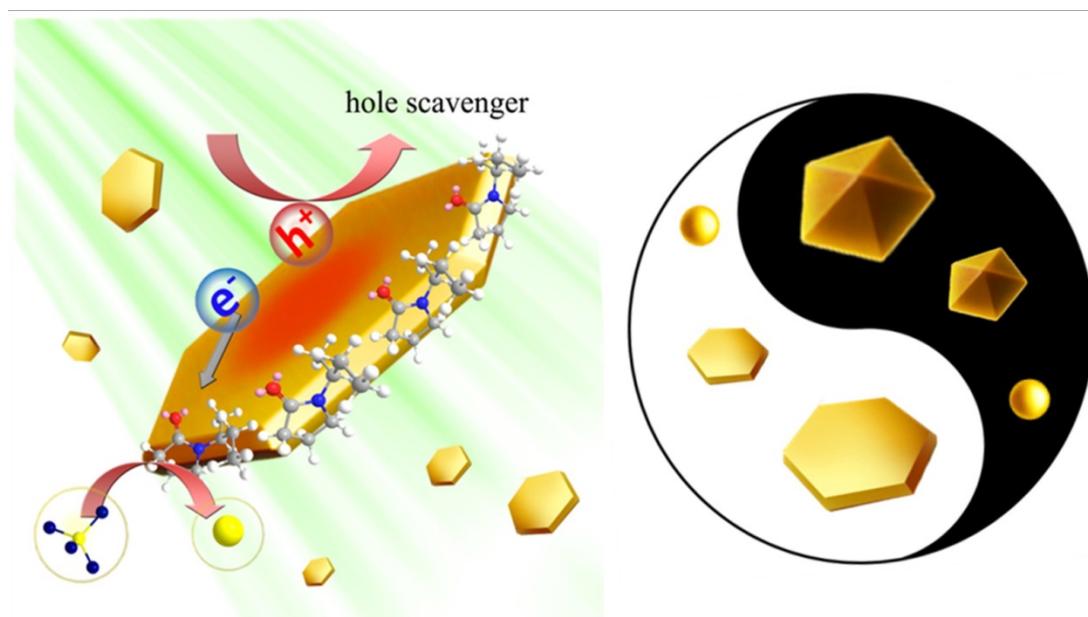
the electronic states, whose energy level spacing becomes larger than the thermal energy and maximum phonon energy in that size range. Modifications of the acoustic vibrational response of metal clusters in this size range will also be discussed.

COLL 442

Plasmon-driven growth of gold nanoprisms with implications for photocatalysis

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We report the SPR-driven growth of anisotropic gold nanoprisms, finally demonstrating the general applicability of plasmon-mediated photochemistry for nanomaterials synthesis. Single-nanoparticle growth studies reveal that SPR excitation must work cooperatively with the surfactant polyvinylpyrrolidone to afford the anisotropic growth of nanoprisms. This insight inspires the development of a novel seed-separation strategy for selectively preparing gold nanoprisms in unprecedented yields (>90%). We further extend this plasmon-driven photochemical process to *p*-nitrophenol photoreduction, highlighting the utility of plasmonic nanostructures for promoting important industrial reactions with visible light.



COLL 443

Plasmon enhanced sensing and catalysis

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Surface plasmons can efficiently capture incident light and focus it to nanometer sized hotspots which can enhance electronic and vibrational excitations in nearby structures. In this talk, I will discuss how plasmonic Fano resonances can be exploited in surface enhanced spectroscopy and photocatalysis applications. Plasmonic Fano resonances are caused by dark plasmon modes and can induce very large field enhancements making such modes particularly useful in LSPR sensing and surface enhanced spectroscopies such as SERS, Four-wave mixing, and SECARS. Plasmonic Fano resonances also provide very efficient hot carrier generation which can be exploited in photocatalysis and light harvesting applications.

COLL 444

Unique properties of metal nanocrystals for driving photocatalysis

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Photon driven chemical reactions at metal surfaces have been studied for over forty years with a majority of research focused on non-thermal, electron driven chemical processes in the context of controlling reaction selectivity and understanding fundamentals of non-adiabatic surface reactivity. A majority of these studies have been executed on metal single crystals, where surface electric fields have relatively small magnitudes and chemistry is typically driven through substrate-mediated excitation of adsorbate-metal bonds that competes with hot charge carrier diffusion into the bulk. These characteristics of photon driven reactions on metal single crystals results in processes with characteristically low yields and minimal, if any, ability to control the outcome of probed chemistry because the processes of photon absorption and induced chemical reactions are delocalized from each other.

Metal nanocrystals offer opportunities to overcome these limitations through enhanced electric fields created in response to excitation of localized surface plasmon resonance and large surface area to volume ratios that enable chemistry by direct photoexcitation of adsorbate-metal bonds. In this talk I will discuss recent results where we show that decaying plasmonic excitations at junctions of Ag nanocrystals can be efficiently funneled into catalyzing O₂ dissociation on the Ag surface. Associated with plasmon driven chemical reactivity are unique wavelength, intensity and isotope dependencies, which shed light on fundamental mechanistic insights. In a second example, I will describe how the large surface area to volume ratio characteristic of sub 5 nanometer

diameter metal crystals can be exploited to control the outcome of catalytic processes through direct photoexcitation of targeted adsorbate metal-bonds. The implications of these results and unresolved questions will be discussed.

COLL 445

Analysis of 2- and 3D plasmon coupling between nanoparticles on cellular and viral surfaces

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Near-field coupling between gold and silver nanoparticles generates interparticle separation-dependent spectral responses in the far-field that can provide information about the spatial distribution of nanoparticle-targeted functionalities on biological surfaces. In this presentation, we will review the underlying electromagnetic coupling mechanisms and show how the NP spectral response depends on the spatial NP distribution. Experimental approaches to effectively quantify this information will be discussed. Using selected examples, we will illustrate the application of this approach to characterize the spatial distribution of NP labels targeted at surface-expressed cancer biomarkers. The implications for the spatial distribution of the biomarkers will be discussed. In a second application example, we will outline how nanoparticle-based techniques provide new ways for quantifying targeted lipid species on enveloped virus (HIV1, Ebola) particles.

COLL 446

Impact of self-assembled monolayers on (oxidized) cobalt for Si-based molecular electronic junctions

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Understanding the complex interplay between molecular functionalities and ferromagnetic surfaces, such as cobalt, is of interest for many diverse technologies ranging from catalysis to organic spintronics. The formation of thiol-containing molecular monolayers on template-stripped cobalt and oxidized cobalt surfaces was followed with X-ray photoelectron spectroscopic (XPS) measurements and electronic transport measurements. We contrasted the self-assembly of octadecanethiol (ODT) and mercaptohexadecanoic acid (MHA), finding the self-assembly of the bifunctional molecule is profoundly different. In particular, the cobalt surface exhibits a very different interface following self-assembly of the MHA species. We examine two different models of the interface formation based on the results, and discuss the impact of this Co/molecule interface on electron transport through Co/molecule/Si molecular junctions. Our results provide insight into ex-situ modification and functionalization of

ferromagnetic interfaces. Nanometer-scale control of the oxide thickness at the MHA-Co interface is quite challenging and manifests in having profound effects on the electron transport by altering the effective tunneling distance or providing a more resistive current pathway. This work has provided insight into the reactive nature of the cobalt oxide in solution enabling the opportunity to prepare a nearly oxide-free ex-situ molecule-cobalt interface. The electrical measurements together with the interface structure derived from XPS provide comprehensive evidence that a molecular layer could have profound influence on the Co substrate and hint that further understanding could enable researchers to tune the local interfacial structures for desired applications in technologies where surface engineering could impact organic spintronics, medical implants, catalysis, pigments, and surface cobalt coatings.

COLL 447

Dynamics of self-assembled monolayers on Au(111) studied by time-resolved scanning tunneling microscopy

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Self-assembled monolayers (SAMs) of thiols on metal have been extensively studied by Scanning Tunneling Microscopy (STM) because of their potential applications in molecular electronics. Design and operation of future molecular electronic devices requires a proper understanding of the electronic properties, dynamics and interactions of the interfaces and molecules utilized. Due to the limitation in temporal resolution of a standard STM, i.e. seconds to minutes, dynamic events are often averaged out. Only a limited number of studies have been performed with a substantially higher time resolution, see for instance ref. 1.¹ The time resolution of a standard STM instrument can be improved by 6-7 orders of magnitude by recording tunnel current-time traces at a preselected position with the feedback loop disabled. In our case, the bandwidth of the current-voltage converter (≈ 100 kHz) limits our temporal resolution to 10 μ s. This motivated us to conduct our studies, in which the dynamics on various phases on decanethiol SAM on Au(111) were studied by recording the current-time spectroscopy with a temporal resolution of 10 μ s.¹ Time-resolved STM measurements for another SAM, which is 2,5-bis(4'-mercapto-phenylethynyl)benzene SAM on Au(111), revealed that the molecules continuously switched back and forth between two nearly degenerate configurations.² Given the simplicity and strength of our approach we believe that our findings will improve our understanding of the molecular structure of SAMs.

References:

1. Wu, H.; Sotthewes, K.; Kumar, A.; Vancso, G. J.; Schön, P. M.; Zandvliet, H. J. W., Dynamics of Decanethiol Self-Assembled Monolayers on Au(111) Studied by Time-Resolved Scanning Tunneling Microscopy. *Langmuir* **2013**, 29, (7), 2250-2257.
2. Wu, H.; Sotthewes, K.; Méndez-Ardoy, A.; Kudernac, T.; Huskens, J.; Lenferink, A.; Otto, C.; Schön, P. M.; Vancso, G. J.; Zandvliet, H. J. W., Dynamics of oligo(phenylene-

ethynylene) self-assembled monolayers on Au(111). *Chemical Physics Letters* **2014**, 614, (0), 45-48.

COLL 448

Polyurethane degradation and characterization of aerospace coatings

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Premature degradation of polyurethane coatings has received much attention due to the use of these coatings on military assets. Coatings are typically over-indexed so that complete reaction of the polyol occurs, providing required mechanical properties. However, in doing such, over-indexing promotes urea linkage formation. The role these urea linkages play in degradation is not fully understood. This work set out to determine if the degradation process was directly related to the concentration of urea linkages within the coating system. Poly(ether-urethanes) were synthesized with varying amounts of isocyanate to promote the formation of urea linkages. FTIR-ATR confirmed that urea concentration increased with indexing. Samples were then subjected several artificial weathering conditions, both with and without light, to correlate the effect of these linkages with observed premature coating degradation. Detailed surface analysis provided additional insight into the mode of action and facilitated correlation of environmental exposure factors with observed physical degradation.

COLL 449

Cyclic azasilanes: A kinetic approach to rapid silane surface modification

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The balance between hydrolysis and condensation in using silane coupling agents is crucial to the linking of organofunctional substituents onto inorganic surfaces. Understanding the kinetics and reactivity remains the key in obtaining the desired surface topography and silane surface coverage. Recently, a new class of silane coupling agents, called cyclic azasilanes, have been made, and these can couple to hydroxylated inorganic oxides and nanoparticles very rapidly. Such cyclic azasilanes have been shown to be effective surface modification substrates with minimal byproducts. Their rapid reaction with surface hydroxyls occurs in a fraction of the reaction time (generally less than one minute), compared to that of the conventional silane coupling agents. The effect of varying functionality, as well as the ring structure, was investigated, and the kinetics of rapid surface coupling determined by FTIR.

Comparisons to their conventional silane coupling agents were then made to afford a complete understanding of the advantages and surface chemistry of these cyclic azasilanes. The observed hydrolysis and ring opening reaction rates analyzed by FTIR and the surface chemistry analyzed by XPS will be presented.

COLL 450

Pyridinium as the electrocatalyst in carbon dioxide reduction on polycrystalline gold electrodes

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Pyridinium has been studied for its potential catalytic role in the electrochemical reduction of carbon dioxide to methanol. We report electrochemical analysis of the pyridinium + carbon dioxide interaction with gold electrodes, independently of the hydrogen evolution reaction. The present results show that gold electrodes exhibit unique pyridinium and carbon dioxide electrochemistry compared with previous work on platinum electrodes or photochemical systems. Analysis of the data show multi-layer adsorption of pyridine, an irreversible reduction wave associated with pyridinium as the pH approaches the pK_a of pyridinium, and a small but significant catalytic activity (0.15 mA/cm^2) for carbon dioxide reduction in the presence of pyridinium at $-1.0 \text{ V vs. Ag/AgCl}$.

This work aims to discern the electroreduction mechanism by analyzing the proposed pyridinium reduction process in inert purge gas environments using electrochemical and *in situ* infrared spectroscopic techniques. This information will guide the analogous exploration under carbon dioxide environments to determine the nature of the enhanced current response.

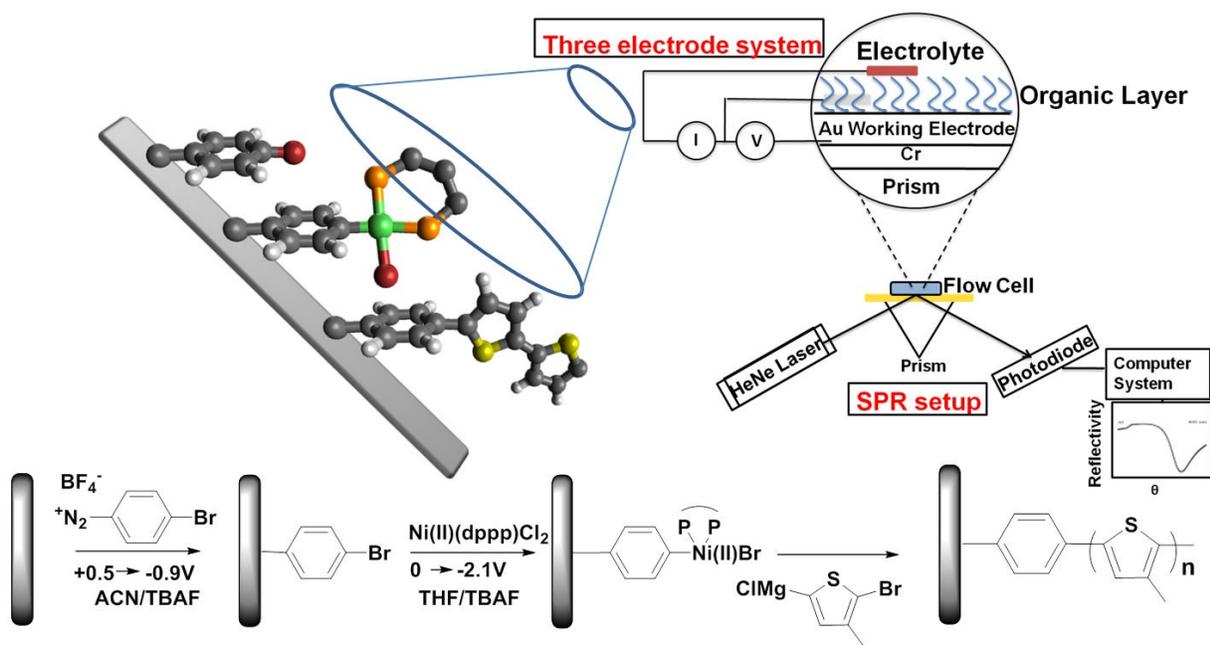
COLL 451

Rapid formation of reactive initiator monolayers for conjugated polymer brushes using electrochemical reduction of Ni(II)

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The talk will be focused on the development of a robust, one-step electrochemical technique to generate surface-bound initiators for conjugated polymers. The electrochemical reduction of arene diazonium salts at the surface of a gold electrode is used to generate tethered bromobenzene monolayers rapidly. The oxidative addition of reactive Ni(0) across the aryl halide bond is achieved *in situ* through a concerted electrochemical reduction of Ni(dppp)Cl_2 , thereby avoiding the use of sensitive Ni(0) as the primary catalyst and limiting the diffusion of Ni(0) species away from the surface. With this electrochemical technique, the formation of the reactive monolayer resulted in

a six-fold increase in surface coverage, over previously reported solution deposition techniques, and it allows the generation of polymer brush layers that show different degrees of orientation with respect to the surface normal.



COLL 452

Vibrational sum frequency generation studies for elucidating mechanisms and kinetics at surfaces

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The application of vibrational sum frequency generation studies for elucidating mechanisms and kinetics at surfaces relevant to catalysis and the environment are discussed.

COLL 453

Advancements in the determination of membrane zeta potential at high ionic strengths: Specific application to semipermeable polymeric membrane

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Surging interest in the characterization of polymeric membrane surfaces has demonstrated the importance of zeta potential measurements, especially on thin-film composite nanofiltration, reverse osmosis, and forward osmosis membranes. These membranes are tailored for brackish and seawater desalination and more recently, treatment of complex industrial waste streams such as oil and gas exploration and production wastewater. These membranes are exposed to high salinity feed streams in practice; however, traditional membrane zeta potential is measured in the presence of dilute aqueous solutions of low ionic strength (< 0.1 M). Therefore, membrane zeta potentials reported in the literature are representative of feed streams more than one order of magnitude below the salinity of seawater and even further below that of some oil and gas wastewaters.

In this study, we demonstrate a new approach for the determination of the zeta potential at high ionic strengths. The development of this new method allowed for the determination of membrane zeta potential for a series of polyamide thin-film composite and cellulose triacetate membranes at ionic strengths ranging from 0.1-3 M. These findings contradict the model of the electrochemical double layer (EDL), which predicts that membrane zeta potential approaches 0 mV at high ionic strength. We conclude that the EDL model does not suitably describe the membrane-water interface at high ionic strengths nor explains zeta potential equilibrium resulting from a saturation of (hydrated) counter-ions in the stagnant layer of the EDL due to steric hindrance. These results have significant implications on the rejection of charged organic contaminants and on the behavior of forward and reverse diffusing solutes across semi-permeable polymeric membranes.

COLL 454

Nucleation and crystallization kinetics of initial apatite nanocrystal formation within biological templates

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Apatite, one of the most important biominerals, is a main constituent of bones and teeth, where type I collagen forms a template for mineralization. Recent *in vitro* studies successfully simulated bone-like apatite nanocrystal formation within the gap channels of collagen fibrils with the aid of polyaspartic acid. However, the kinetics and development mechanisms of apatite with respect to its size, total volume, and crystallinity remain poorly understood. In this study, we utilized small angle X-ray scattering to evaluate the particle size and total volume evolution over the course of apatite formation within collagen matrices. Different scattering patterns were observed

for nanocrystals that formed within the gap channels and those that formed at the outer surfaces of collagen fibrils. Mineralization at the outer surfaces occurred faster than within the gap channels; however, it reached a plateau in a relatively short time due to the extensive formation of apatite at the outermost surface. On the other hand, mineralization within the gap channels occurred only after a time lag, and took longer to reach a plateau. X-ray pair-distribution function showed a higher degree of crystallinity in apatite formed on the outer surface of collagen. From these findings, a better understanding of the nucleation and growth of biologically inspired minerals within organic templates can be achieved. This knowledge is applicable to materials science, environmental studies, and tissue engineering.

COLL 455

Three column series approach to investigate role of desorption rates in colloid-facilitated transport of americium, cesium, and plutonium: Experiments and modeling

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We investigated the role of sorption kinetics in the colloid-facilitated transport of radionuclides (specifically Am, Cs, and Pu). We conducted batch and breakthrough experiments and modeled the results with a multi-site/multi-rate MATLAB code to elucidate radionuclide capacity and sorption rate coefficients. We used a series of three columns and injected unanalyzed effluent from the first column (conducted in duplicate) through a second column and injected unanalyzed effluent from the second column through a third column. Americium and cesium experiments used fracture fill material (FFM) from the Grimsel Test Site in Switzerland and bentonite colloids generated from a FEBEX bentonite brick. Plutonium experiments used natural colloids and groundwater collected from a well in a nuclear test cavity (Chancellor) from the Nevada Test Site. All materials were characterized (e.g., QXRD, XRF, SEM/EDS, BET, single particle counting) to better constraint the models. Colloids were pre-equilibrated with radionuclides before injection.

Americium/bentonite transport was consistent through each column, with nearly 50% of the sorbed americium desorbing in each of the three columns and suggesting a single type of binding site. For cesium and bentonite and plutonium and natural colloids; however, each subsequent pass resulted in a higher fractional breakthrough. This suggests that Pu and Cs bind more strongly to certain available binding sites. The weaker (or faster) binding sites release radionuclides that subsequently attach to the column geomaterials (FFM or Tuff) while the radionuclides bound to the stronger (or slower) sites remain attached to the mobile colloids and are transported through the column. The colloid properties were also measured with each subsequent pass through a column and did not show any changes with respect to mineralogy or colloid size. These results provide quantitative insights to help determine long-term fate and transport of radionuclides to aid risk assessment evaluations.

COLL 456

Structure-function relationships into layered solid oxide fuel cell cathode material

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The promise of direct and efficient conversion of chemical to electrical energy makes fuel cell development an area of great technological interest. Solid Oxide Fuel Cells (SOFCs) are one of the most promising technologies to meet this goal. However, current SOFCs operate at temperatures above 700°C. This high temperature increases costs and decreases cell lifetime. To overcome this challenge we must develop materials that demonstrate high electrocatalytic activity and facile ion and electron transport at lower temperatures. A significant barrier to progress is a lack of experimental techniques that can probe the properties of these materials under high temperature working conditions.

This presentation will discuss our efforts to generate bulk to surface structure-function relationships for SOFC cathode materials; focusing on our work related to double perovskite and Ruddlesden-Popper layered phases. In particular, we will present relationships derived from combined crystallographic characterization by *in-situ* neutron diffraction and synchrotron XRD, surface oxygen exchange rates determined by pulsed isotopic exchange, electrochemical performance from impedance spectroscopy, and surface composition from XPS and HS-LEIS. The combination of these techniques provides powerful insights into the links between structure and function of both bulk and surface properties, and the link between the surface and the bulk.

COLL 457

Tailoring the structure of active materials for solar thermochemical fuel production through templating

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A promising route toward renewable fuel production is thermochemical splitting of carbon dioxide or water to produce carbon monoxide or hydrogen using concentrated solar energy. To carry out this reaction at practical temperatures, two-step reactions using metal oxides, including ceria, are employed. These heterogeneous reactions benefit from having large accessible surfaces and short diffusion paths within the structure of ceria. Such features can be achieved by hard templating methods. Here, we describe methods to tailor internal and external morphology of templated metal oxides for enhanced performance in two-step thermochemical reactions. In particular, we will consider porous ceria and doped ceria materials prepared by colloidal crystal (CC) templating and wood templating. Both methods produce highly interconnected pore

systems with increased surface areas compared to nonporous active materials. In addition to controlling the internal pore architecture of the materials through the hard template, we employ polymerization-induced phase separation to alter the external morphology of ceria and other metal oxides, producing porous microspheres, hollow particles, porous sheet structures, or materials with hierarchical porosity. The predominant controlling factor of microstructural evolution in these syntheses is the degree of polymerization of the gel, which is controlled through tailoring reagent imbalance. We will describe the effects of structural morphology on carbon dioxide splitting, including effects on cycle kinetics and thermal stability of the porous materials. Ceria materials prepared by both CC templating and wood templating are capable of enhancing the kinetics of thermochemical CO production compared to nonstructured ceria. Whereas the CC-templated materials provide higher surface areas and greater peak production rates, wood-templated structures exhibit greater thermal stability and permit cycling at higher temperatures. Rapid cycling rates are feasible in these materials to increase the production of fuel over a given period of time.

COLL 458

Reducing cracks in photoanode of dye-sensitized solar cells based on binder-free TiO₂ nanoparticles by 1D electrospun metal oxide nanofibers

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Formation of cracks is a serious issue in the mesoporous film prepared with paste of binder-free TiO₂ nanoparticles for dye-sensitized solar cell (DSSC) applications due to the rapid solvent evaporation during the preparation process. Herein we report two approaches to significantly reduce crack formation in a film prepared using a binder-free paste of TiO₂ nanoparticles (sizes less than 8 nm). In the first approach, a flexible and thin mat of electrospun SiO₂ nanofibers was used to cover the binder-free TiO₂ nanoparticle film right after the doctor blading process. The network of the SiO₂ nanofibers prevented the crack formation and helped maintain the film integrity during solvent evaporation. In the other approach, ~33 wt.% electrospun TiO₂ nanofibers with lengths of ~3 mm and diameters of ~300 nm were added to the binder-free paste of TiO₂ nanoparticles. The nanofibers in the paste served as a skeleton structure to reinforce the integrity of the film and to reduce the crack formation in the TiO₂ film. The morphology of the TiO₂ films was investigated using optical microscopy and scanning electron microscopy. The results showed the photoanodes of TiO₂ prepared by our methods were uniform and had few cracks. Photoanodes of as-prepared binder-free TiO₂ film sensitized with organic dye were assembled into quasi-solid DSSCs using polymer gel electrolyte and Pt/FTO counter electrode. The quasi-solid devices showed power conversion efficiency of 4.5 % with stable performance over long storage time.

COLL 459

Metabolic characterization of nonmodel microalgae for sustainable biofuel production

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Adaptation to various growth environments cause major shifts in the metabolism of microalgae species. Specifically, environments where nitrogen source is limited cause upregulation of neutral lipids, such as triacylglycerols while overall growth and proliferation rates are decreased under these limiting conditions. In this study, we aim to delineate the cellular metabolic processes under varying nitrogen- and phosphorus-growth conditions by utilizing transcriptomic and metabolomic analyses. Specifically, comparative analysis of the metabolome and transcriptome in time-series will allow us to study the expression and the crosstalk between anabolic and catabolic reactions. We have established an LC-MS based platform for metabolic analysis of a non-model, oleaginous microalgae, *Ettlia oleoabundans*. Our data suggests degradative cellular processes activated under nitrogen-limited conditions are likely to impact overall lipid accumulation. We are particularly interested in addressing these processes that affect lipid production and accumulation with the goal of maximizing lipid biosynthesis in *Ettlia oleoabundans*.

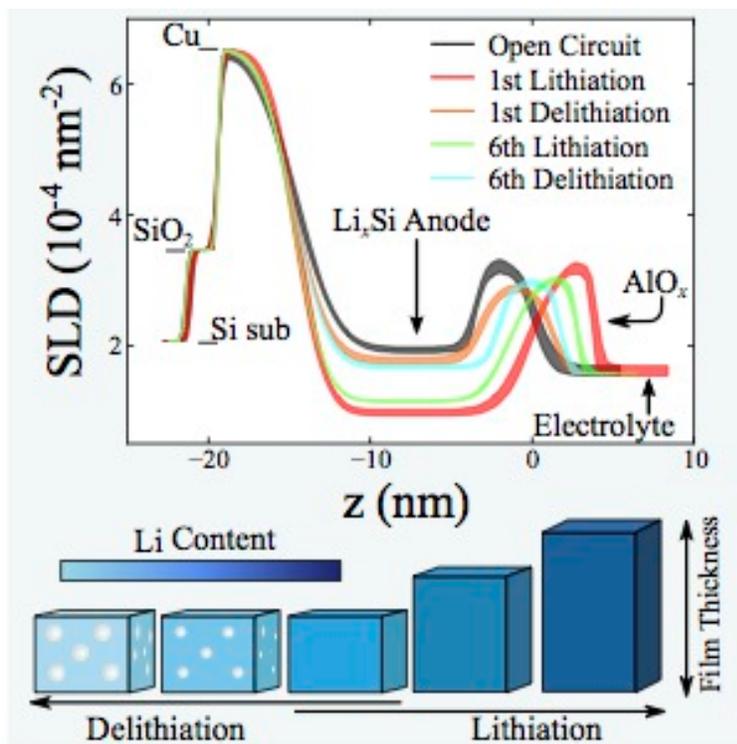
COLL 460

Pore collapse and regrowth in silicon electrodes for rechargeable batteries

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Numerous strategies have been attempted to improve the durability of Si anodes for high-capacity rechargeable Li-ion batteries, including thin-film anodes and protective coatings. However, efforts have yet to identify a mechanically robust anode design that maintains a stable capacity. Part of the difficulty is due to a paucity of *in situ* techniques to observe definitively how proposed modifications impact the correlation between structure, mechanical properties, and function in Si anodes.

This presentation reports the structural and composition changes of an 11 nm thick amorphous Si thin film anode, capped with a 4 nm thick alumina film, measured *in operando* by neutron reflectivity (NR) and electrochemical impedance spectroscopy in a lithium half-cell. NR data are analyzed to quantify the Si layer thickness and composition at various states of charge over six cycles. The Si anode expands and contracts during cycling, while maintaining its integrity and low interfacial roughness (<1.6 nm). The apparently non-linear expansion of the Si film versus lithium content agrees with previous findings. However, a proposed pore collapse and regrowth (PCRG) mechanism establishes that solid domains in the porous film expand linearly with Li content at a rate of 8.48 cm³/mol-Li, similar to bulk Si. In the PCRG model, during lithiation the solid Li_xSi expands both isotropically, to fill the pores, and anisotropically to expand the film. Porosity is reversibly reestablished at 5-28% upon delithiation. Data also show that the alumina protective on the Si film functions as an effective artificial solid electrolyte interphase.



Neutron Scattering length density (SLD) vs thickness (z) profiles for the Si anode as a function of charge state demonstrate reversible collapse and regrowth of the pores during lithiation and delithiation, respectively, shown in the illustration. SLD profiles are 68% confidence intervals.

COLL 461

Fast charging of dual lithium-ion-insertion cells

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An isothermal, physics-based, dual lithium-ion insertion cell sandwich model was used for simulating the galvanostatic charge performance of a graphite (Li_xC_6)/ liquid electrolyte/ $\text{Li}_y(\text{Ni}_a\text{Co}_b\text{Mn}_c)\text{O}_2$ cell at room temperature at various current densities [i]. The cell capacity vs. voltage data from simulations were validated with experimental results. The cell overpotential was higher at higher rates. The cell was charged only to 67% and 57% of the designed capacity at 2C and 3C rates respectively due to corresponding overpotential losses of 279 and 414 mV. The various contributions to the cell overpotential at the end of 2C charge rate were obtained as in Figure 1. Solid phase diffusion limitation in the negative, charge transfer overpotential, electrolyte concentration overpotential and ohmic (ionic) overpotential influenced the charge acceptance for the cell design and operating conditions chosen in this work. Lithium plating at the negative electrode was shown to be thermodynamically feasible during galvanostatic charging at 2C rate and above (Figure 2).

References:

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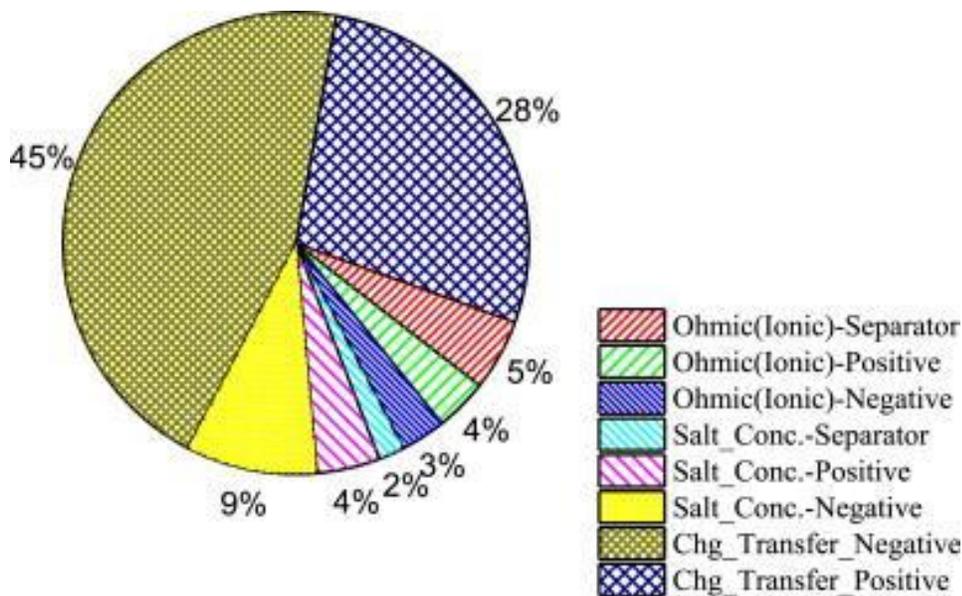


Figure 1. Contributions to the cell overpotential (279 mV) at the end of galvanostatic charging at 2C rate (42.6 Am^{-2}).

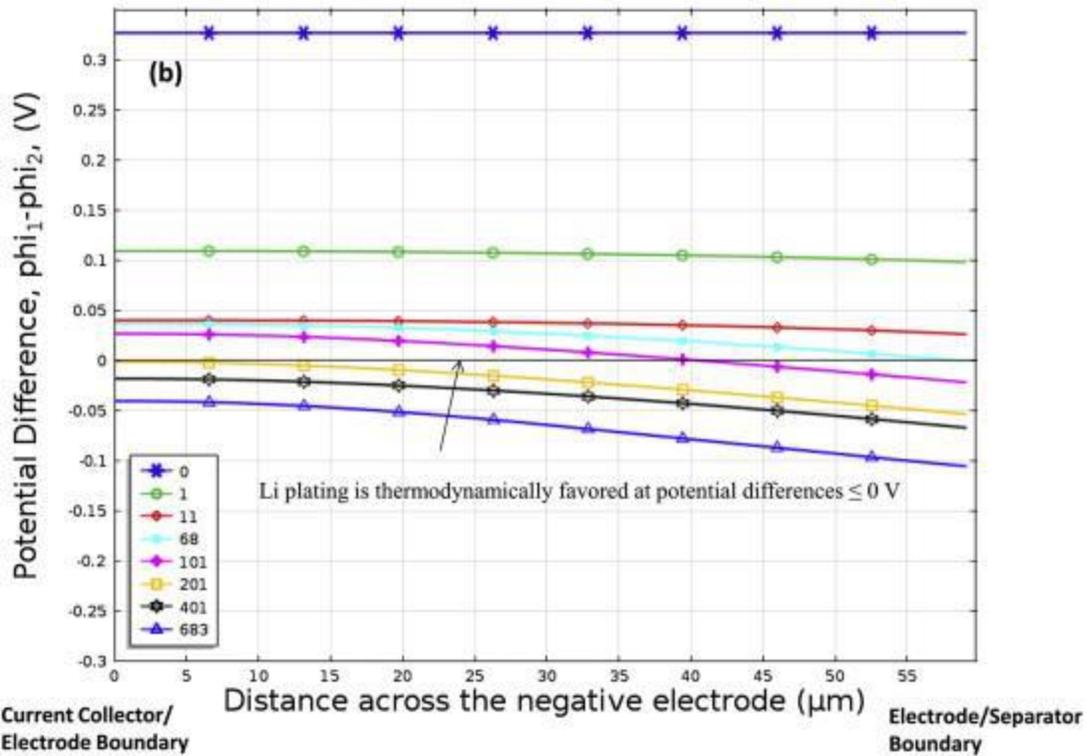
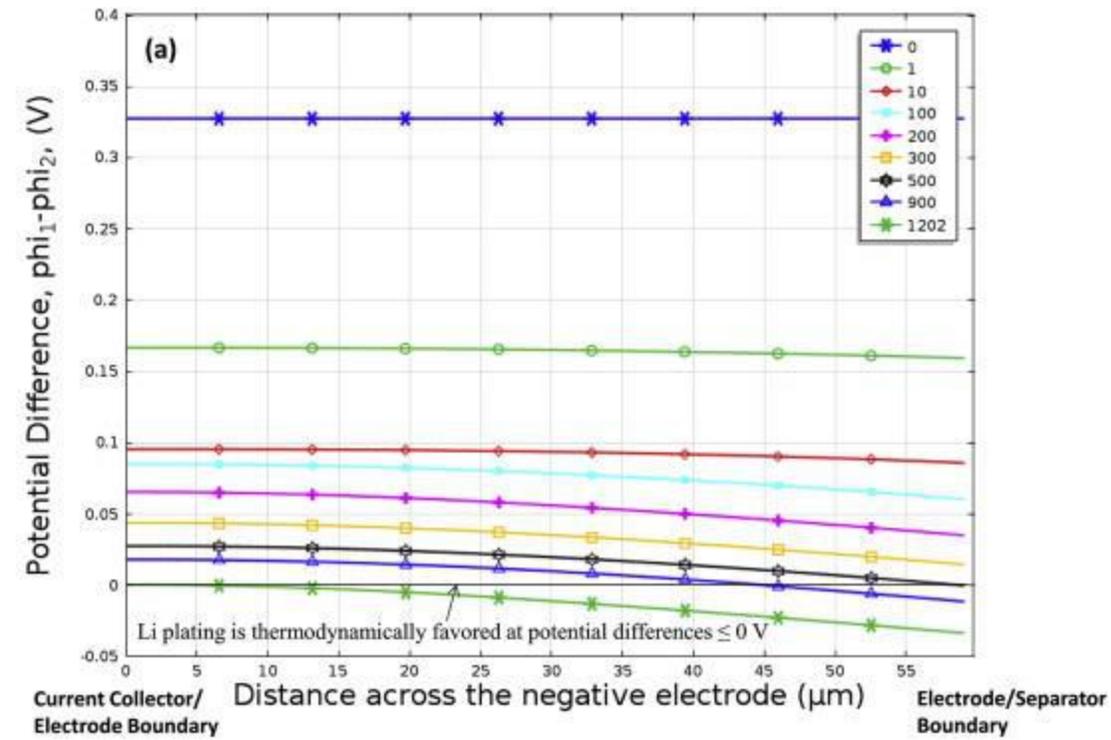


Figure 2. Potential difference between solid phase (ϕ_1) and liquid electrolyte phase (ϕ_2) in the negative electrode during galvanostatic charging at (a) 42.6 Am^{-2} (2C rate); (b) 63.9 Am^{-2} (3C rate). Legend is time in seconds from the start of the charge.

COLL 462

Hierarchical view of DNA based recognition, and the role of flexibility and shape

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Beyond its importance in biology, in the general area of materials science and engineering, the assembly of nanoscale objects on the basis of DNA hybridization is finding an increasing range of applications. In order to interpret results of DNA-based nanoparticle assembly experiments, for example, it is important to develop models capable of describing phenomena occurring at micron length scales while retaining a molecular-level representation capable of capturing hybridization. Similarly, in epigenetics, models capable of describing DNA-protein complexes would be useful.

This presentation will provide an overview of recent hierarchical models and computational approaches developed by our research group to investigate the effects of confinement, hydrodynamic interactions, salt concentration, and sequence on the structure and properties of DNA, both at equilibrium and beyond equilibrium. Particular emphasis will be placed on recently proposed detailed models and methods designed to describe the manipulation of DNA in microfluidic devices, the melting and rehybridization of DNA at the single nucleotide level, and DNA molecular recognition in DNA-protein complexes. The relevance of the models will be discussed in the context of nanofluidic designs for applications in optimal mapping, and in the context of recent experiments on DNA packaging in chromatin.

COLL 463

DNA motifs for recognition of single wall carbon nanotubes

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Single-stranded DNA forms a strong hybrid with single wall carbon nanotubes (SWCNT), dispersing them very effectively in aqueous media. Certain short strands of DNA recognize specific partner SWCNT, allowing them to be separated from a mixture of SWCNT chiralities by ion-exchange chromatography or aqueous two-phase partitioning. To understand the structural basis for recognition, we have studied these hybrids theoretically using molecular modeling. We show that a family of novel ordered and surface-adsorbed DNA structures emerge due to the interaction between DNA strands and the SWCNT. We have studied the energetics of the hybrid through experiments in which surfactant molecules displace the DNA off the SWCNT, by single molecule force spectroscopy to measure the forced desorption of DNA from SWCNTs, and by aqueous two-phase partitioning to study sequence-dependent solvation free energy differences. Surfactant exchange studies show that there is a strong correlation between activation energy for DNA removal and recognition. Single-molecule force

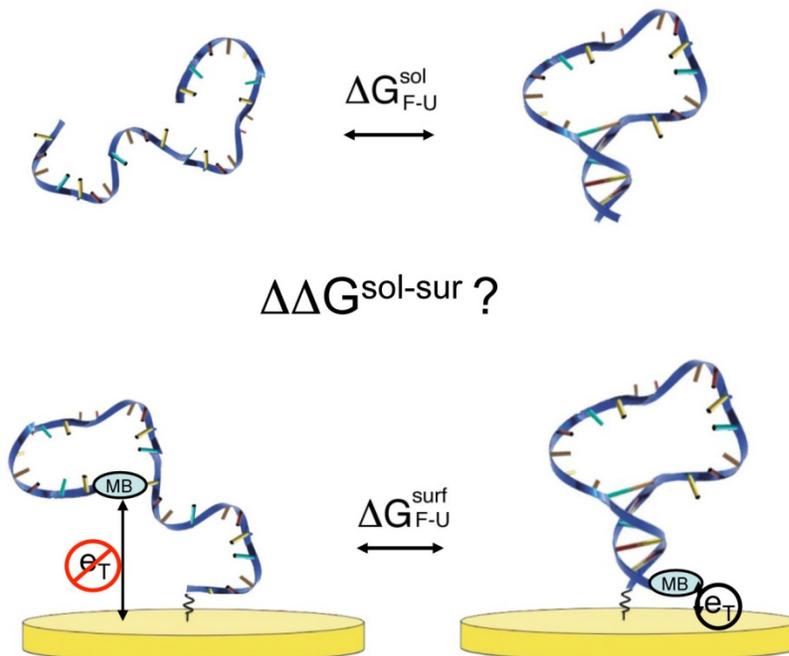
spectroscopy shows that DNA binds stronger to curved SWCNTs than to flat graphite. Aqueous two-phase partitioning shows that solvation free energies follow a different trend from activation energies.

COLL 464

Entropic and electrostatic effects on the folding free energy of a surface-attached biomolecule: An experimental and theoretical study

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Despite the importance of surface-bound biomolecules in biology and, increasingly, in biotechnologies, our understanding of the extent to which and mechanisms by which biomolecules interact with specific surfaces remain quite limited. In response, we have used a novel electrochemical method to experimentally measure the change in folding free energy that occurs when a simple DNA structure is attached to a number of chemically distinct, highly charged surfaces. Not surprisingly, the magnitude of the observed perturbation depends strongly on the charge of the surface, with increasingly negatively charged surfaces leading to increased destabilization. Conversely, attachment to a positively charged surface renders the folding of this negatively charged biomolecule irreversible. A simple model that considers only the excluded volume and electrostatic consequences of attachment quantitatively recovers the observed free energy on negatively charged surfaces as a function of charge and ionic strength, thus highlighting the important role that surface-biopolymer electrostatics can play in the physics of surface attached biomolecules.



We have developed an electrochemical method for monitoring the folding of surface-bound biomolecules which allows us, in turn, to measure their folding free energy. Comparison with the folding free energy of the same molecule in solution informs on the free energy of interaction between the biomolecule and the surface.

COLL 465

Surface-mediated DNA hybridization

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High-throughput single-molecule total internal reflection fluorescence microscopy was employed in conjunction with Förster resonance energy transfer (FRET) to observe the dynamic behavior of donor-labeled ssDNA at the interface between aqueous solution and a solid surface decorated with complementary acceptor-labeled ssDNA. In addition to the immobilized DNA, the surface was modified to display either hydrophobic alkyl or hydrophilic oligo-ethyleneoxide moieties. At least 100 000 molecular trajectories were accumulated and analyzed for both complementary strands and negative control ssDNA. FRET was used to identify trajectory segments corresponding to the hybridized state. The majority of molecules from solution adsorbed nonspecifically to the surface, where a two-dimensional search was performed with a chance of hybridization; unsuccessful searches resulted in desorption from the surface. The search process was significantly more successful on hydrophobic surfaces, and successful searches were also faster on hydrophobic surfaces. On both types of surface, searches were much faster than expected from simple two-dimensional Brownian motion, and qualitatively consistent with a more efficient search process associated with intermittent desorption-mediated surface diffusion. Hybridization was reversible, and two distinct modes of melting (i.e., dehybridization) were observed, corresponding to long-lived and short-lived hybridized time intervals. The hybridized state was longer-lived on hydrophilic surfaces. These observations provide new insights into the dynamics associated with surface-mediated DNA hybridization, and suggest that surface chemistry plays a complex role in influencing both the dynamics of the search process and the stability of the hybridized state.

COLL 466

Single molecule view of conformational changes and hybridization of DNA on dynamic surfaces

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The recognition of target molecules by DNA probe molecules tethered to surfaces is at the heart of a wide range of biosensors and microarrays. Yet, a molecular level understanding of the complex dynamics of DNA probes on surfaces, which is key to the development of reliable biosensors, remains in its infancy. A major challenge is the lack of knowledge of the spatial arrangement and conformations of these probe molecules, which dramatically influence molecular recognition on surfaces.

By exploiting the transient electrostatic pinning enabled by an applied electrochemical potential, we have enabled *in situ* AFM to visualize the conformational changes of single DNA molecules to gold. Our study has revealed an extreme sensitivity to the nanoscale environment: the electrostatic interaction of the DNA with the surface is dominated by defects in the passivating self-assembled monolayer (SAM) and that the SAM, often regarded as a static structure, is not only highly mobile but is actively remodeled by the DNA at different applied potentials. Moreover, by directly visualizing single hybridization events, we have provided nanoscale and single molecule level evidence that the hybridization efficiency is impacted by the presence of neighboring probe molecules. Such molecular level insights into hybridization on surfaces may inform new strategies to engineer more robust and reliable DNA sensors.

COLL 467

Quantitative single-molecule imaging of DNA hybridization at capture surfaces with sequence specificity

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Single-molecule fluorescence microscopy is a proven technique for measuring the kinetics of biomolecule interactions at interfaces, though these experiments must be designed with the intrinsic rates of specific biomolecule interactions in mind. DNA hybridization is difficult to measure using single-molecule techniques because the association rate constant for complementary strands is low, $\sim 10^6 \text{ M}^{-1} \text{ s}^{-1}$, requiring long observation times and high solution concentrations of target strand to gather significant statistics. Long exposure to high concentrations of target ssDNA leads to nonspecific adsorption, which is typically mitigated by complex readout sensitive to specific interactions, such as FRET or colocalization. In this work, we describe a scheme for immobilizing probe ssDNA at a glass interface passivated against nonspecific adsorption with anionic blocking groups, yielding surfaces that are sufficiently selective that complementary binding dominates the population of fluorescently-labeled target DNA on the surface. Interactions between probe and target DNA are highly sequence specific; surface populations of hybridized complementary target DNA are nearly 3 orders of magnitude greater than that of a scrambled sequence, eliminating the need for FRET to identify complementary interactions. The surface density of immobilized probe DNA can be controlled from 10^8 to 10^{10} cm^{-2} by the probe concentration during the immobilization reaction. At low density, individual probe molecules can be resolved so that hybridization and dissociation rates can be measured directly from single-molecule

trajectories. This assay has the potential to allow for the identification of oligonucleotides out of a mixture of immobilized ssDNA. At higher site densities the substrates are more efficient at capturing target strands from solution, making them excellent ssDNA sensors with very low detection limits. We have developed super-resolution techniques to quantify probe molecule density, so that high-density surfaces could be used to measure equilibria and kinetic constants of weaker interactions, such as short oligonucleotide hybridization and split-aptamer association.

COLL 468

Using nonlinear optical spectroscopy to monitor DNA molecular recognition and structure at the buried silica/aqueous interface

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Second-order nonlinear optical spectroscopy is well-suited to monitor interactions at buried interfaces as it is surface sensitive and provides molecularly specific information about species that are ordered at the interface. Such techniques that directly monitor biomolecular processes at interfaces are critical as the dynamics of molecular recognition at interfaces can differ substantially from similar interactions in solution given the unique environment of the interface. Using resonantly enhanced second harmonic generation we have determined the influence of confinement on the molecular recognition of DNA immobilized at the silica/water interface. These experiments, supported by the complementary technique vibrational sum frequency generation, reveal that immobilization on silica substantially destabilizes the DNA duplex, more so than what has been observed on other substrates. Additionally, we observe that the structure and net orientation of the DNA at the interface exhibits annealing effects for both the duplex and immobilized single strand, which suggests that DNA-surface interactions may contribute significantly to the properties of DNA on silica. As silica is one of the most common substrates for DNA microarrays and chip-based platforms, these results provide insight into optimizing biondiagnostic devices.

COLL 469

Rapid synthesis of faujasite/polyethersulfone composite membrane and application for CO₂/N₂ separation

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Because of the well-defined porous crystalline structure, zeolite membrane is promising in CO₂ capture. Reported zeolite Y membranes for CO₂ separation take long synthesis time, high cost and has low reproducibility.

Rapid growth of faujasitic membrane on a polyethersulfone support is investigated in this study. The membrane growth takes place in a novel zeolite reactor, where the

extent of supersaturation of the synthesis gel is controlled by removal of water from the reaction system. The gel remaining after removal of half the water from the reaction is isolated and used as a coating on the polymer support. Along with this reactive gel, optimal coating of nanozeolite seed deposition on the porous polymer support was also investigated. Eight variations of the gel-seed combinations are examined for optimum membrane growth. Polymer supports with the gel and the seed layer are then reintroduced back into the reactor, and the hydrothermal synthesis continued with the water being added back to the reactor system. Based on the electron microscopy of the membrane formed after one hour of reaction, the optimal membrane synthesis conditions was defined. Further characterization included X-ray diffraction, optical microscopy and more detailed scanning electron microscopy. Leak test of a dye through the membrane and the mechanical stability of the membrane via a tape test was performed. The transport properties of these membrane for CO₂/N₂ separation was evaluated. With a silicone polymer (PDMS) covering mesoporous defects of the grown zeolite membrane separation characteristics included CO₂ permeance is in the range of 500 - 1200 GPU and CO₂/N₂ selectivity is 50 - 110. With this membrane design, a planar geometry during handling and use is necessary, since bending can introduce cracks that degrade the transport properties of the membrane.

COLL 470

Relationship between polyelectrolyte bulk complexation and kinetics of their layer-by-layer assembly

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The effect of pH and salinity on bulk phase behavior and layer-by-layer (LbL) growth kinetics are investigated for oppositely charged polyelectrolytes with the goal of relating phase behavior to LbL growth kinetics. Depending on salinity, pH and mixing ratio, the complex formed in the bulk is either a precipitate or a gel-like coacervate and multilayers grow either linearly or exponentially with deposition time. In addition to primary Coulombic interactions, we observe that polymer-specific interactions have a profound effect on both bulk complexation and LbL growth of the polyelectrolytes. The overall strength of interaction between polyelectrolytes, as indicated by their phase behavior, has a non-monotonic affect on LbL growth rate, because stronger interactions increase the driving force for diffusion, but also reduce the effective diffusion coefficient of a polyelectrolyte molecule through LbL multilayer. As a result, there is little correspondence between coacervation and exponential growth on one hand, and precipitation and linear growth on the other. Salt concentration has a non-monotonic effect on LbL growth at pH 7, with exponential growth found over the range 15-60% of the critical salt concentration (C_s^C) needed to transition from coacervation to a clear solution in the bulk, regardless of the physical chemistry of polyelectrolytes employed, whereas salt concentrations both below and above this range result in linearly growing

films. Finally, we report a “universal curve” for the dependence of LbL growth rate, normalized by its maximum value, against salt concentration, normalized by C_s^C , which could be useful for designing conditions for optimal LbL growth.

COLL 471

Adsorption of bacteria into electrospun cellulose nanofiber mats: Development of a dynamic model

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Removing bacteria from potable water sources is a universal challenge traditionally achieved using industrial standard cellulose filters. Here, we employ electrospun cellulose mats, ideal for filtration and separation, to elucidate variables that effect the ability of the porous sorbent to adsorb high concentrations of bacteria. Cellulose acetate (CA) solutions were electrospun and post-treated to form regenerated cellulose (RC) mats with an average fiber diameter of $\sim 1 \mu\text{m}$. Experimentally, the ability of the mats to adsorb the model microorganism, *Escherichia coli* K-12, out of a phosphate buffered saline solution was quantified. Systematically, changes in cellulose mat diameter, initial bacteria concentration, and state of bacteria were explored. An increase in cellulose mat diameter or an increase in initial bacteria concentration led to an increase in total bacteria collection. A dynamic model was developed from the experimental data to relate the systems variables. Our model could potentially be used to tailor nanofibrous cellulose mats to obtain the highest collection of bacteria for industrial applications.

COLL 472

Multilayer chromophore thin film fabrication via layer by layer deposition technique

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The fabrication of well-organized multilayer thin films composed of various chromophores on solid substrate has attracted significant research attention because of their potential optical, electrochemical, and catalytic properties leading to possible applications as building blocks for artificial photosynthetic solar cells, gas sensors, nonlinear optics, and molecular electronic devices.

Layer by-layer (LBL) deposition technique is a powerful, low-cost, method to transfer chromophore assemblies from solution onto a solid surfaces (such as glass, quartz and various electrode substrates) while maintaining predictable nanoarchitectures and

function. In this presentation, we will provide strategies developed in our group to fabricate multi-chromophore (in particular, using perylene diimides, and porphyrins) containing multilayer thin films on glass substrate. Importantly, our LBL fabrication technique uses sustainable aqueous media as the immersion solvent and harnesses cyclodextrin-based host-guest interactions. We will also discuss the photo-physical properties of these well-organized thin films.

COLL 473

Modulating the uptake of dextran coated SPIONs in stem cells: The effect of surface charge

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Stem cell therapies have potential to combat many diseases, especially those that have no known cure. Stem cells can be monitored in vivo using non-invasive imaging techniques such as magnetic resonance imaging (MRI), where cells are labelled with a contrast agent prior to transplantation. MRI contrast agents are normally split into T_1 and T_2 categories. Super paramagnetic iron oxide nanoparticles (SPIONs) generate much attention as T_2 agents, and are often preferred due to high sensitivity and biocompatibility. This high sensitivity allows the visualization of stem cells within certain organs. Synthesis of SPIONs for biomedical applications typically involves synthesis of an iron oxide core, followed by some type post modification technique to render the materials hydrophilic.

We have used a co-precipitation method to create a library of differently charged SPIONs simply by altering the ratio of dextran to DEAE-dextran in the co-precipitation synthesis. Increasing the charge leads to higher uptake of SPIONs thus increasing the MRI contrast.

COLL 474

Effect of membrane structural dopants on charge transport through conjugated oligoelectrolyte modified phospholipid bilayers

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The properties of lipid bilayers can often be strongly altered by the presence of low concentration additives. For example, recently developed conjugated oligo-electrolytes (COEs) are known to readily incorporate into cell membranes to dramatically increase electron transport across these membranes. This charge transport enhancement has been shown to enable a wide range of electrochemical applications, particularly in areas such as microbial fuel cells and water treatment. However, it remains poorly understood how additives like the COEs interact in phospholipid membranes to facilitate novel

properties such as enhanced electron transport. Here we examine how COE incorporation and charge transport are influenced by COE solution concentration, as well as by phospholipid membrane properties such as fluidity and charge. The electrochemical properties were characterized using cyclic voltametry for COE-containing phospholipid membranes prepared with and without common cell membrane species (e.g., cholesterol, choline) that influence membrane fluidity and charge. It was found that the uptake of COE and its charge transport properties are modestly influenced by the COE solution concentration and by the membrane fluidity. In contrast, altering the charge of the phospholipid membrane strongly influences the electrochemical properties of the COE-containing membranes.

COLL 475

Uniform cross-linked cellulase aggregates prepared in millifluidic reactors

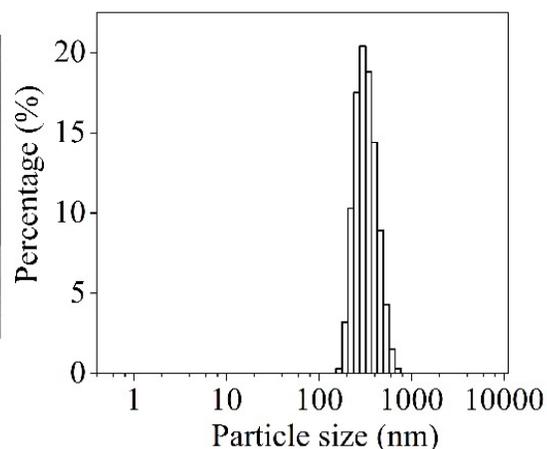
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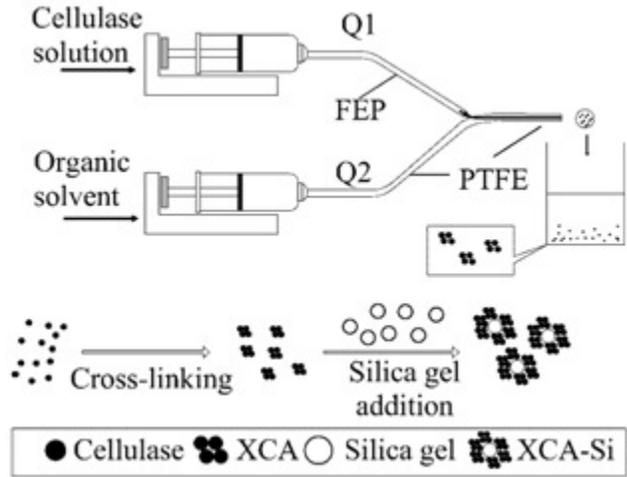
Cellulase is a group of enzyme which catalyzes the hydrolysis of cellulose to produce oligosaccharides and glucose. However, cellulase is highly soluble in water. In this study, we report the preparation of uniform cross-linked cellulase aggregate (XCA) by using a millifluidic reactor which consists two inlets and a Y-junction. In this reactor, the cellulase solution is mixed with acetonitrile (as a precipitant) and 20 mM of glutaraldehyde (as a cross-linker) at the Y-junction. Subsequently, uniform XCA, with an average size between 200 nm and 400 nm, can be formed inside the reactor. Unlike free cellulase, XCA is insoluble such that it can be filtered out from the solution. It can be used alone or absorb on silica gel (XCA-Si) as a catalyst for hydrolyzing cellulose. Interestingly, XCA-Si shows highest activity at pH 4.8 and 50 °C, which is similar to the optimal condition of free cellulase. Moreover, XCA-Si is more stable than free cellulase at high temperature (>60°C). It precipitates naturally and can be recycled at least 5 times after the hydrolysis of cellulose.

Cellulase



**Acetonitrile
and glutaraldehyde**





COLL 476

Self-healing and disruption of arborol fibrils

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Controlling and reversing the self-assembly of small molecules into the support network of a gelatinous phase is important for the production of molecular scaffolds and the design of microfluidic devices. Such mastery over molecules can also contribute to fundamental understanding of amyloid diseases. Self-assembled fibrils made from two-directional arborols were filtered. Their subsequent growth revealed details of the self-assembly of the two-directional bolaform molecules. Fibril fragments remained extended and relatively uniform in length while healing at a rate that depended on concentration. Introducing a one-directional disruptor to the system and studying fibril-induced reduction of gold ions to nanoparticles additionally probed network disruption. The disruptor slowed fibril healing and subsequent gelation, while reduction of gold ions reversed gelation. The latter observation suggests a route to a scaffold that can take itself down after directing the production of gold nanoparticles.

COLL 477

Two-photon absorption properties of chromophores in polyelectrolytes

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Materials with large two-photon absorption (2PA) cross-sections have received enormous research attention in recent years mainly for their applications in two-photon microscopy, optical limiting, optical data storage and 3D imaging. Our research group has been working on enhancing the cross-sections of chromophores by stationing them in an environment with aligned electric fields. Polyelectrolytes offer one such possibility where one can alter the electric fields by changing their folding/unfolding conditions. In this study, we aim to study the 2PA cross-sections of chromophores in polyelectrolytes in an effort to probe the folding and unfolding of polyelectrolytes. The investigations are carried out with anionic (Coumarin 519), cationic (Hoechst 33258, Thioflavin T) and neutral (Coumarin 485) dye molecules dissolved in two anionic polyelectrolytes (Poly (sodium 4-styrenesulfonate) PSS, and Poly [5-methoxy-2-(3-sulfopropoxy)-1,4-phenylenevinylene]). These systems are chosen specifically to understand the influence of electrostatic interactions and in turn the electric fields on the 2PA cross-sections of chromophores. The 2PA cross-sections measurements have shown interesting trends wherein the 2PA cross-section of cationic dyes were enhanced by as much as 10-fold when they are bound to the polyelectrolytes while neutral dyes have shown no effect. However, there was some enhancement with anionic dye molecules. Fluorescence upconversion and time-correlated single photon counting measurements were carried out to understand the binding interactions of chromophores and polyelectrolytes. The results shed light on the role of the electrostatic interactions in enhancing the nonlinear optical properties of chromophores.

COLL 478

Substrate mediated stability of DNA origami at elevated temperatures and in diverse solvent environments

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The highly specific, designable self-assembling nature of DNA origami has prompted exploration of applications in electronic nanosystems. However, the relative fragility of the DNA biomolecule calls into question whether DNA nanostructures are compatible with current nanoelectronic and lithographic techniques using high temperatures and harsh solvents. We explored the stability of DNA origami adhered to both mica and functionalized silicon substrates at high temperatures and after treatment with solvents commonly used in nanofabrication processes. Using atomic force microscopy (AFM), it was found that the dimensions of DNA origami adhered to a substrate were retained when heated to 150°C as well as after treatments with acetone, methylene chloride, and other solvents. Even after much longer exposure times, the DNA origami retained their shape. The chemical characteristics of the structures at higher temperatures were

monitored using x-ray photoelectron spectroscopy (XPS), indicating possible chemical degradation at temperatures above 200°C. These results indicate that DNA origami, when adhered to a substrate, attains a much higher stability than is seen in solution and can withstand temperatures and solvents used in nanofabrication. This expands the possible application of DNA origami in nanoelectronics.

COLL 479

Exploring biomedical applications of nanoparticles by their surface functionalization

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With the increasing use of nanoparticles in both science and industry, their chemical modification became a significant part of nanotechnology. We've explored several applications of nanoparticles that will benefit from the controlled surface functionalization: dentifrices and filling materials, drug delivery, improvement of bone implants and sunscreens. Functionalization of titanium dioxide and silica nanoparticles improves their adhesion to human dentin, which opens their future use for treating tooth hypersensitivity by occlusion of dentin tubules and carriers of remineralizing and other active components. Functionalization of carbon nanofibers helps control their alignment for enforcement of mechanical strength of dental fillings. Functionalization of titanium dioxide improves adhesion between titanium dioxide nanotube-coated implants and bones and imparting antibacterial properties. The relationship between morphology of nanoparticles and their affinity to organic molecules (salicylic and caffeic acid) using multiple adsorption isotherms, and toward material surfaces using TEM-imaging, let us suppress photodegradation of caffeic acid in the presence of titanium dioxide and work toward new formulations of sunscreens, containing both components. The developed reliable quantitative procedures for photometric determination of primary and secondary surface amino-groups was employed for characterization of the synthesized new materials.

COLL 480

DNA nanotubes and nanotapes via self-assembly of ssDNA-amphiphiles

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DNA is a popular material for constructing complex, multi-dimensional nanostructures due to its ability to organize via Watson-Crick base-pairing in a precise and predictable manner. Popular approaches to create nanostructures from DNA include DNA origami,

DNA tile and DNA brick assembly, each of which rely on numerous strands of single-stranded DNA (ssDNA) with different and complimentary sequences to direct the DNA assembly process. These approaches and others have been used to create numerous structures including three-dimensional polyhedra, two-dimensional lattices, nanoribbons and nanotubes. An alternate approach to direct the assembly of ssDNA is to conjugate a hydrophobic moiety (i.e., polymer or lipid) to the ssDNA to form an amphiphilic molecule that spontaneously self-assembles when added to aqueous solutions.

We have recently shown that the type of molecular spacer linking a ssDNA headgroup to a lipid-like molecule affects the amphiphile's binding properties (when an aptamer-amphiphile is used) its secondary structure and assembly, producing spherical micelles or bilayer nanotapes (flat or twisted) depending on the type of spacer used in the amphiphile design.

DNA nanotubes were created for the first time using molecular self-assembly of ssDNA-amphiphiles composed of a hydrophobic dialkyl tail and polycarbon spacer and a hydrophilic ssDNA headgroup. The nanotube structures were formed by bilayers of amphiphiles, with the hydrophobic components forming an inner layer that was shielded from the aqueous solvent by an outer layer of ssDNA. The nanotubes appeared to form via an assembly process that included transitions from twisted nanotapes to helical nanotapes to nanotubes. Amphiphiles that contained different ssDNA headgroups were also created to explore the effect of the length and secondary structure of the ssDNA headgroup on the self-assembly behavior of the amphiphiles in the presence and absence of the polycarbon spacer. It was found that nanotubes could be formed using a variety of headgroup lengths and sequences.

The ability to form structures of great interest, such as nanotubes, via ssDNA-amphiphile self-assembly offers an alternative to the other purely DNA-based approaches, like DNA origami and DNA tile assembly, for constructing these structures and may be useful for applications in drug delivery, biosensing, and electronics.

COLL 481

Connections between nanoparticle (NP) surface chemistry and protein corona formation: Influence of the corona on small ($d_{\text{core}} < 5.0$ nm) NP- supported lipid bilayer interactions

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Understanding the fundamental chemistry that governs the interactions of functionalized nanomaterials with biological membranes is essential in order to fully understand the possible implications of nanomaterials as environmental contaminants or potential therapeutics. The potential bio-interactions of functionalized nanomaterials are governed not only by nanoparticle physicochemical properties, but also by their interactions with biomacromolecules in serum or natural waters (e.g. formation of a protein corona). Here, we use a library of 4.0 nm functionalized gold nanoparticles (AuNPs), stabilized with either ω -functionalized thiols or layers of polyelectrolytes, to investigate how nanoparticle surface chemistry influences bio-interactions for small engineered NPs. First, the functionalized AuNPs were incubated in fetal bovine serum, and the composition of the resulting protein coronas were determined by LC-MS analysis. Subsequently, the interaction of corona-protected AuNPs with supported lipid bilayers possessing various phospholipid compositions was investigated by QCM-D, and compared to the interaction of as-synthesized AuNPs with the same bilayers. We find that the composition of the AuNP protein corona and AuNPs stability in serum both depend upon AuNP ligand shell composition. Through our QCM-D results, we find that the presence of a protein corona can either increase or decrease the extent of NP-bilayer interaction, dependent on both the composition of the bilayer and AuNP ligand shell.

COLL 482

New generation of well-defined lipid-based magnetic nanoparticles for theranostics

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Bio-imageable nanoscale assemblies that can be activated and controlled through external stimuli represent the next generation multifunctional *theranostics* (therapeutics + diagnostics). MRI contrast agents such as iron oxide nanoparticles, which generate thermal energy by an external alternating magnetic field (AMF), can be effectively used to induce localized hyperthermia or heat-triggered drug release when co-encapsulated with drugs in thermo-sensitive lipid nanoparticles (**LNP**). We have developed well-defined, reproducible, easy to scale up, and size controllable (from 30 nm to 60 nm) hybrid **LNP** systems that consist of either hydrophobic or hydrophilic magnetic iron oxide nanoparticles encapsulated in various lipid components. We herein present their synthesis and biophysical characterization, as well as their effects in *in vitro/in vivo* MRI imaging and AMF-induced drug release.

COLL 483

Robust and tailored wet adhesion in biopolymer thin film with wet adhesion and toughness superior to wet adhesion in bone

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Model layer-by-layer (LbL) assemblies of poly(allylamine hydrochloride) (PAH) and hyaluronic acid (HA) were fabricated in order to study their wet adhesive behavior. The film characteristics were investigated to understand the inherent structures during the assembly process. Subsequently, the adhesion of these systems was evaluated to understand the correlation between the structure of the film and the energy required to separate these LbL assemblies. We describe how the conditions of the LbL fabrication can be utilized to control the adhesion between films. Based on our results, we discuss how the fabrication procedure can create tailored adhesive interfaces with properties surpassing analogous systems found in nature. The characteristics of the film formation are examined in the absence and presence of salt during the film formation. The dependence on contact time and LbL film thickness on the critical pull-off force and work of adhesion are discussed. Specifically, by introducing sodium chloride (NaCl) in the assembly process, the pull-off forces can be increased by a factor of 10 and the work of adhesion by two orders of magnitude.

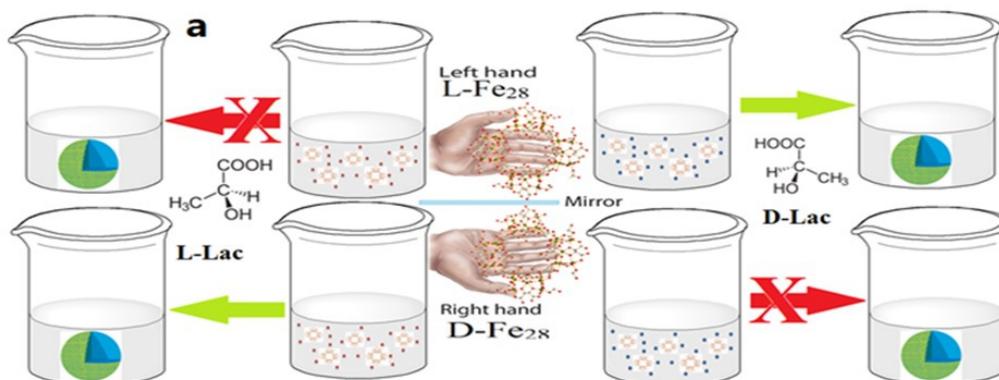
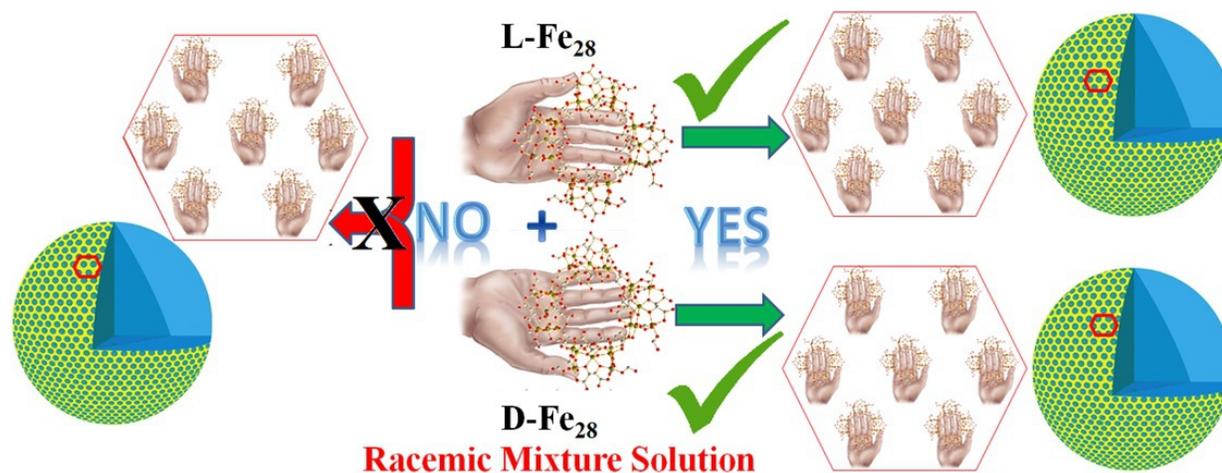
COLL 484

Chiral recognition and selection during the self-assembly process of protein-mimic macroanions: the effect of long-range electrostatic interactions

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The homo-chirality of basic biological molecules such as amino acids and sugars, as one of the biggest puzzles in understanding the origin of life, is still not clearly understood¹⁻⁵. A few sketchy theories have been developed to explain how homo-chirality originated, was amplified in macromolecules and supramolecular assemblies, and was transmitted to other biomolecules/assemblies during the evolution of life^{2, 6}. This process certainly involves recognition and competition between the enantiomers during their organization into supramolecular structures^{7, 8}. Herein, we report the chiral recognition and chiral selection during the self-assembly process of two enantiomeric wheel-shaped macroanions, $[\text{Fe}_{28}(\mu_3\text{-O})_8(\text{Tart})_{16}(\text{HCOO})_{24}]^{20-}$ (Tart = D- or L-tartaric acid) *via* counter-ion mediated interactions. The enantiomers are observed to remain strictly self-sorted and self-assemble into their individual single-layer spherical assemblies ('blackberry' structures^{9, 10}) in their racemic mixture solution. The addition of chiral co-anions can selectively suppress the self-assembly process of one type of enantiomeric macroanions while promoting the other one. This leads to the separation of two enantiomers from their

mixtures. This study suggests that delicate long-range electrostatic interactions could be responsible for such high-level chiral recognition and selection.



COLL 485

Synergetic DNA delivery with pyridinium amphiphiles with different packing parameters – toward composite DNA delivery systems

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Pyridinium amphiphiles – simple surfactants, gemini surfactants, lipids, lipophilic polycations can act as efficient synthetic transfection systems with reduced toxicity in vitro and in vivo, as previously shown by our group [1-4]. We recently optimized pyridinium cationic lipids and gemini surfactants through comprehensive tuning of the self-assembling process of these amphiphiles at the level of counterion, hydrophobic chain, added co-lipids, their nature and molar ratio [5,6] and we have establish structure-activity and structure-property relationships across different classes of

pyridinium amphiphiles [1-6].

We proved that a synergetic effect can be generated by of blending these second-generation pyridinium cationic gemini surfactants into cationic pyridinium lipid bilayers and we established the impact towards plasmid DNA compaction and delivery process. [7].

In the current study we have generated new pyridinium amphiphiles supported on gold nanoparticles and we assessed their physicochemical parameters in parallel with their transfection efficiency as previously described [1-7]. We established that the synergetic action of pyridinium amphiphiles with different molecular curvatures can be extended to composite systems containing amphiphiles supported on highly curved Au nanoparticles and pyridinium lipids. We correlate the composition of these nanoparticles with the dynamics of the DNA compaction process, and with transfection efficiency and cytotoxicity of resulted nucleic acid complexes. We confirmed the broad validity of the concept of synergetic action of pyridinium amphiphiles with different packing parameters and we expanded it to new composite metal-amphiphile DNA delivery systems with high transfection efficiency and negligible cytotoxicity, useful for therapeutic gene delivery.

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COLL 486

Distinct Adsorption Configurations and Self-assembly characteristics of elongated proteins on chemically uniform and alternating surfaces

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Understanding protein-surface interactions is crucial to solid-state biomedical applications whose functionality is directly correlated with the precise control of the adsorption configuration, surface packing, loading density, and bioactivity of protein molecules. Due to the small dimensions and highly amphiphilic nature of proteins, investigation of protein adsorption performed on nanoscale topology can shed light on subprotein-level interaction preferences. We examine the adsorption and assembly behavior of a highly elongated protein, fibrinogen, on both chemically uniform and varying surfaces. By focusing on high resolution imaging of individual protein molecules

whose configurations are influenced by protein-surface rather than protein-protein interactions, fibrinogen conformations characteristic to each surface are identified and statistically analyzed for structural similarities/differences in key protein domains. By exploiting polystyrene-block-polymethylmethacrylate (PS-b-PMMA) nanodomains whose repeat distance is commensurate with the length of the individual protein, we determine that fibrinogen exhibits a more neutral tendency for interaction with both PS and PMMA blocks relative to the case of common globular proteins. Factors affecting fibrinogen-polymer interactions are discussed in terms of hydrophobic and electrostatic interactions. In addition, assembly and packing attributes of fibrinogen are determined at different loading conditions. Primary orientations of fibrinogen and its rearrangements with respect to the underlying diblock nanodomains associated with different surface coverage are explained by pertinent protein interaction mechanisms.

COLL 487

Superhydrophobicity and oleophobicity via increased modified surface topography

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Super-hydrophobicity and oleophobicity of a surface means that water and oil liquids have a contact angle on a surface greater than or equal to 150°, low contact angle hysteresis and a sliding angle of less than 10°. Synthetic hydrophobicity and oleophobicity are applied to a surface to make the surface self-cleaning, anti-corrosive and anti-fouling to a variety of possible contaminants. Here, we report an aqueous suspension of micro-particles for the fabrication of super-hydrophobic and oleophobic substrates. In our experiments, the deposition of hollow glass spheres on a glass substrate provides the necessary increased microscale topography needed for super-hydrophobicity. By depositing aqueous suspended glass spheres on a substrate, we can bake off the aqueous media at high temperatures leaving behind fused micro-glass topography. Nano-roughness is then added by assembling monolayers of n-octadecyltrimethoxysilane and (tridecafluoro-1,1,2,2-tetrahydrooctyl) triethoxy silane. The hydrophobic chains on our self-assembled monolayers provide the necessary functionality on the structures to allow for Cassie-State formation at an air/liquid/ solid interface (i.e. hydrophobicity of water). Our substrates are repellent to water with static contact angles in 140-150° range. The substrates also repel oily substances with a static contact angle of >100°. Dynamic contact angle measurements on our modified surfaces showed low contact angle hysteresis, with only a 5° between advancing and receding contact angles. Low hysteresis suggests that the liquid of interest will symmetrically roll off the substrate rather than spread and/or slide down the substrate. Fusion and chemical cross-linking of our micro and nano- topography affords necessary durability to our substrates as they maintain their super-hydrophobic/oleophobic properties after washing and drying of the substrate. In this project, we report a simple

two-step method for preparing super-hydrophobic and oleophobic substrates on a large scale.

COLL 488

Reconfigurable anisotropic coatings via magnetic field-directed assembly and translocation of locking magnetic chains

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A method for the generation of remotely reconfigurable anisotropic coatings is developed. To form these coatings, locking magnetic nanoparticles (LMNPs) made of a superparamagnetic core and a two-component polymer shell are employed. Two different polymers form phase-separated coaxial shells. The outer shell provides repulsive interactions between the LMNPs while the inner shell exerts attractive forces between the particles. Applying a non-uniform magnetic field, one gathers the particles together, pushing them to come in contact when the internal shells could effectively hold the particles together. When the magnetic field is turned off, the particles remain locked due to these strong interactions between internal shells. The shells are thus made stimuli-responsive, so this locking can be made reversible and the chains can be disintegrated on demand. In a non-uniform magnetic field, the assembled chains translocate, bind to the solid substrate and form anisotropic coatings with a “locked” anisotropic structure. The coatings can be constructed, aligned, realigned, degraded, and generated again on demand by changing the magnetic field and particle environment. The mechanism of the coating formation is explained using experimental observations and a theoretical model.

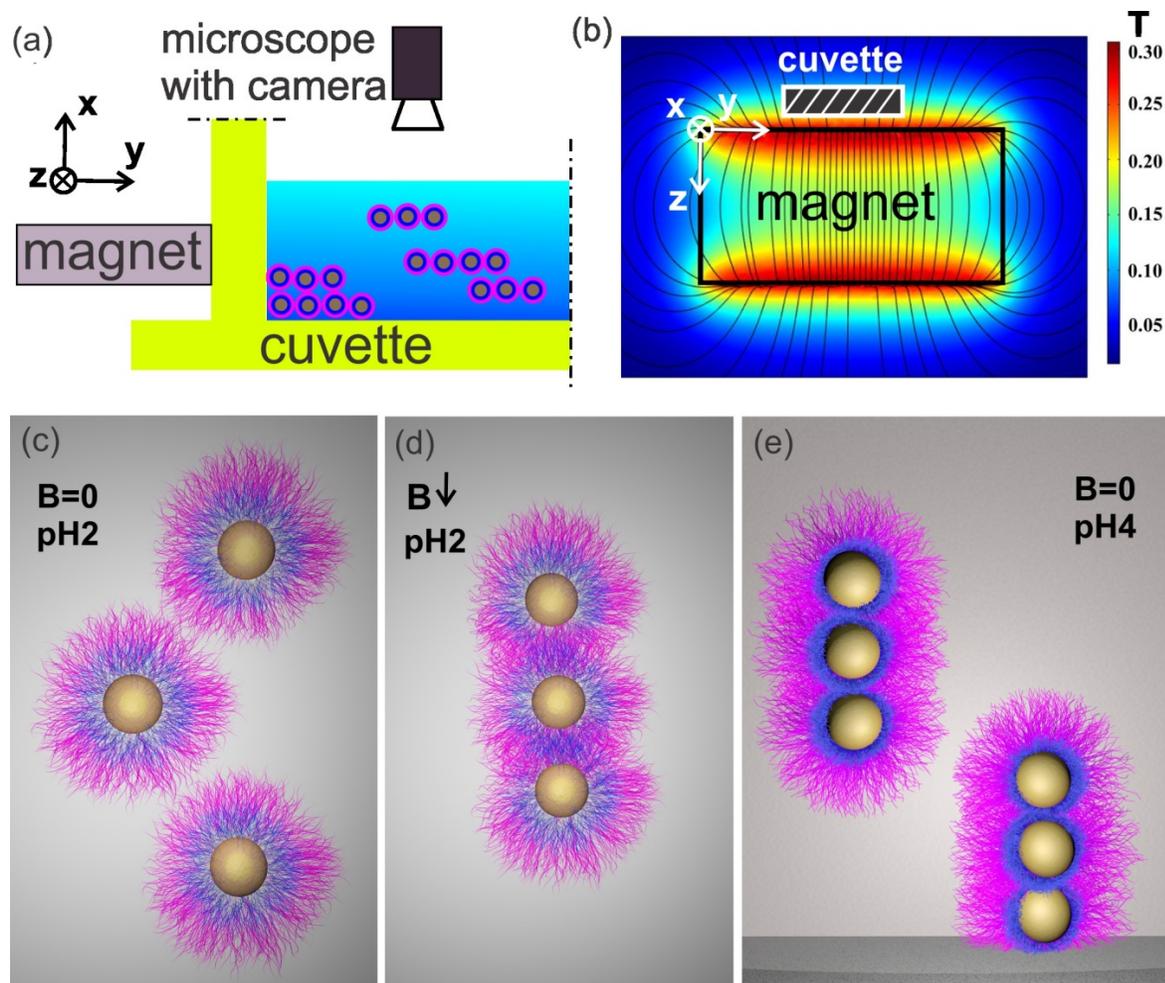


Figure 1. Schematics of the experimental set up and mechanism of locking

COLL 489

Assembly of surface-anchored metal-organic frameworks: Controlling deposition conditions to tune film morphology

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Surface-anchored metal-organic frameworks (SurMOFs) have potential for incorporation as smart interfaces for applications ranging from sensors to photonics. When thin nanoscale films, such as these, are integrated into device architectures, it is unfortunately common for film “defects” to negate or dominate the desired properties of the material. Therefore it is important for the nanostructure of SurMOF films to be well characterized. This emerging nanomaterial’s potential may not be fully realized in part because of improper fabrication due to a lack of fundamental understanding regarding how the film forms at the substrate interface. This research systematically investigates layer-by-layer deposition of six related SurMOF systems altering deposition variables

such as temperature, concentration, time, and coordinating metal ion. Formation of the first five foundational layers was characterized by scanning probe microscopy, ellipsometry, and reflectance infrared spectroscopy. Quantitative image analysis determined film morphology properties, such as surface roughness and coverage, providing insight regarding growth and structure at the film-substrate interface. The HKUST-1 MOF system was the benchmark studied here to which other systems were compared. Deposition variables such as temperature and coordinating metal ion were found to dramatically alter film morphology, while concentration and time were found to have a more subtly effect. Systems with different organic components and the same inorganic components yielded distinctly different film structures ranging from the nucleation and growth of crystallites to the formation of a conformal film. To a lesser degree, systems with the same organic components and different inorganic components revealed that reactivity of coordinating metal ion influenced both surface coverage and structure. Temperature control demonstrates potential to have a great impact on surface coverage, particle size, and roughness. Beyond how these variables affect film morphology, preliminary investigations have examined the absorption of gases within these frameworks and future research will explore the crystallinity of these structures.

COLL 490

Estimating sorption kinetics from the transient shape of a pendant drop

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A method for determining the adsorption and desorption kinetics for a single component aqueous surfactant solution is presented. Estimates for the ratio of these quantities typically involve determining equilibrium surface tensions at different bulk surfactant concentrations, however the individual sorption rates themselves are unknown. These sorption rates are important in modeling many physical phenomena. Here we present a technique that utilizes transient surface tension measurements to directly estimate adsorption and desorption rates. It will be shown that both adsorption and desorption rates are concentration dependent. Several surfactant systems such as aqueous sodium oleate (NaOL) and aqueous sodium dodecyl sulfate (SDS) in mineral oil will be used to demonstrate the technique. The surfactant systems can be classified by one of three general sorption regimes based on how kinetics vary with bulk concentration. A fast pattern-search algorithm for measuring surface tension based on error minimization is also presented.

COLL 491

Probing the effect of the HC–FC dipole on the properties of thin films formed from hydrocarbon-terminated perfluorinated alkanethiols

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This presentation describes the synthesis of *w*-alkylated perfluorinated alkanethiols and the surface properties of the corresponding partially fluorinated self-assembled monolayer films (FSAMs) formed on gold surfaces. The general structure of these adsorbates is $\text{H}(\text{CH}_2)_n(\text{CF}_2)_6(\text{CH}_2)_{11}\text{SH}$; where $n = 1, 3-6$ (**H_nF₆H₁₁SH**). These amphiphiles are designed to aid in evaluating the influence of the dipole arising from the upper *methylene-difluoromethylene* (HC-FC) junction upon the properties of the partially fluorinated thin films. A broad range of contacting liquids was used to probe changes in the interfacial energies for this series of FSAMs. In addition, the structural characteristics and packing densities of the adsorbed chains were evaluated using optical ellipsometry, X-ray photoelectron spectroscopy (XPS), and polarization modulation infrared reflection-absorption spectroscopy (PM-IRRAS). The resulting data collected for these newly generated thin films show an odd-even effect that correlates with the terminal hydrocarbon moiety and is independent of the total number of carbons in the chain backbone. These findings can aid in the design of partially fluorinated surfaces, where the fluorinated segment reinforces the structural properties of the organic thin film while exerting nanoscale-controlled effects on the interfacial energy of the exposed surface.

Keywords: Fluorinated Self-Assembled Monolayers (FSAMs), *w*-Alkylated Perfluorinated Alkanethiols, Wettability, Odd-Even Effects.

COLL 492

Synthesis and characterization of partially fluorinated self-assembled monolayers having an inverted surface dipole

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The synthesis of a new series of partially fluorinated alkanethiol adsorbates of the form $\text{CH}_3(\text{CF}_2)_6(\text{CH}_2)_n\text{SH}$ (where $n = 10-13$), along with analysis of the resulting monolayer films on gold, are described in this presentation. The fluorinated self-assembled monolayers (FSAMs) were characterized using optical ellipsometry, polarization-modulation infrared reflection-absorption spectroscopy (PM-IRRAS), X-ray photoelectron spectroscopy (XPS), and contact angle goniometry. To shed light on the effect that the inverted HC-FC dipole has on the surface character of these partially fluorinated thin films, the wetting behavior of several contacting liquids was examined on the FSAMs and compared to that of analogous monolayers formed from CF_3 -terminated alkanethiols and normal alkanethiols having equivalent alkyl chain lengths.

Keywords: Fluorinated Self-Assembled Monolayers (FSAMs), Odd-Even Effects, Gold, Wettability.

COLL 493

Analysis of interactions at fluid-solid interface: Exploring the complete slip boundary condition

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At the fluid-solid interface, chemical and physical interactions play a role in molecular slip and flow influencing a broad spectrum of industrial, commercial, and research applications. Hydrodynamic theories state that when a fluid comes into contact with an ultra-smooth surface (< 5-7 nm RMS roughness), the no-slip boundary condition can be violated. This could result in complete slip and can greatly improve fluid transport properties. To investigate this transition, a dynamic wetting technique was combined with vibrational spectroscopy and ellipsometry to allow direct investigation of molecular fluids at smooth and rough silver surfaces (RMS roughness between 1 and 30 nm). The wetting technique allows control of the wetting velocity, which is critical to provide perturbation of wetting film thickness. Such films of chlorobenzene, o-dichlorobenzene, and hexamethylphosphoramide were analyzed for thickness and molecular orientation. The present results of planar molecules show no film formation which supports the possibility of complete molecular slip. Hexemethylphosphoramide is analyzed due to its non-planar property.

COLL 494

Multilayered metallic nanostructures with an embedded internal standard as surface enhanced Raman substrates

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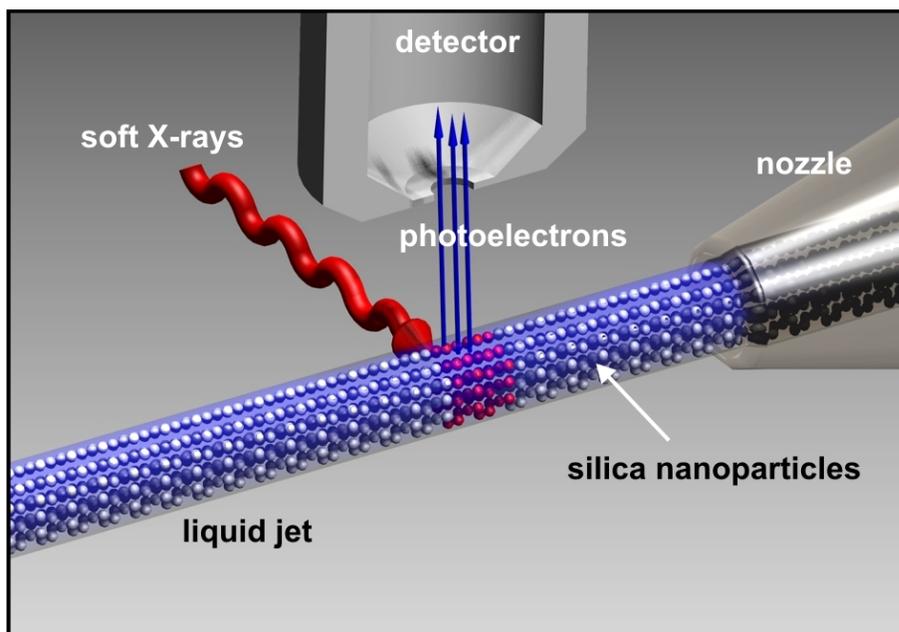
Metallic nanostructures have been the subject of considerable research due to their unique mechanism for light interaction and the considerable number of applications that result from, or are enhanced by, these interactions. Recently, the synthesis of highly crystalline Ag:SiO₂:Ag core:spacer:shell (CSS) particles of varying geometries by the hydrogen reduction method was reported. Herein, we report the synthesis of CSS particles with 'reporter' molecules embedded in the spacer layer. SERS and SEF enhancement factors of the embedded molecules are reported with respect to concentration within the spacer layer and layer thickness. Finally, the utility of the reporter molecule as an internal standard for SERS spectroscopy is explored.

COLL 495

X-ray photoelectron spectroscopy at the liquid-nanoparticle interface: Opportunities for colloidal science

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We begin by describing our new Near Ambient Pressure Photoemission (NAPP) endstation at the Swiss Light Source and how it allows for the extension of in situ X-ray Photoelectron Spectroscopy (XPS) to the liquid-nanoparticle interface of colloidal suspensions. Our measurements to date have primarily focused on geometric and electronic structures of silica (9 nm α -SiO₂), tin oxide (3 nm SnO₂) and hematite (30 nm Fe₂O₃) dispersions at the solution-air interface in both aqueous and non-aqueous solvents. These measurements have revealed (i) the spatial distributions of the NPs at the air interface and (ii) their true surface potential. The latter has been extensively investigated in relation to the effects of specific anions and cations, pH and temperature and has allowed for a complete measure of the electrical double layer structure at a water-nanoparticle interface. In the case of α -SiO₂, interpreting our data using the simplest assumptions and most straightforward understanding of Guoy-Chapman-Stern theory reveals an outer Helmholtz plane whose thickness corresponds to a single layer of water molecules hydrating the silica surface, plus the radius of the hydrated monovalent cation. Our results subject electrical double layer theories to direct and falsifiable tests that have proven elusive for well over a century, and reveal a physically intuitive, but quantitatively verified picture of the Stern layer that is consistent across multiple electrolytes and solution conditions.



The experimental setup depicting the extension of in situ XPS to the aqueous-nanoparticle interface. A free-flowing liquid microjet is injected into vacuum where it is spatially overlapped

with synchrotron radiation. Photoelectrons are collected using a near ambient pressure (NAP) spectrometer.

COLL 496

Interfacial liquids, Most soft surfactants probed by AFM

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Scanning tunneling microscopes operated in electrochemical environments have provided much knowledge about solid topography buried in liquids. However, our knowledge is still limited about liquids structured over solids. Frequency-modulation AFM (FM-AFM) is a promising tool to observe the solid topography and also the liquid structure at liquid-solid interfaces. The cantilever with a tip is resonantly oscillated in this mode of operation. The shift of the resonance frequency, Δf , represents the force pushing or pulling the tip to be related to liquid local density. Microscopes with force sensitivity of 10 pN or better in water have been developed [1] and commercialized to date.

Kimura et al. [2] and Fukuma et al. [3] first observed Δf as a function of vertical and lateral coordinates over water-mica interfaces. Following their achievements, the author and coworkers have successfully examined structured liquids at a number of interfaces including water-TiO₂ [4], water-Al₂O₃ [5], water-hydrophilic monolayers [6, 7], water-*p*-nitroaniline [8, 9], water-CaCO₃ [10], water-peptide nanotubes [11], alcohols-hydrophilic monolayers [12], alcohols-graphite [13, 14], hydrocarbons-hydrophobic monolayer [15] and hydrocarbons-salicylic acid [16]. The observed Δf slices were sensitive to the composition of the solid and liquid, while insensitive to tips of different apex radii [17]. This suggests that the observed force distribution was not much affected by the presence of the tip above the interface.

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COLL 497

Selenium: The better anchor group for self-assembled monolayers (SAMs) on gold?

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Self-assembled monolayers (SAM) became a very powerful tool in the materials sciences, biochemistry, and engineering. In particular SAMs of thiolates are renowned for their ease of formation, their stability and their high order. Nevertheless, not all thiols can form densely packed monolayers and for some cases even the best thiolate monolayers are not well ordered enough.

Based on the idea that a softer anchoring atom would fit better to the soft gold atoms (according to Pearson's HSAB principle), we prepared a number of selenium-containing precursors and studied their assembly on gold (and in some cases on silver). Data obtained by surface infrared spectroscopy, different photo-electron spectroscopies, and STM hint on the formation of very stable monolayers with improved order.[1-4]

In this talk we will present the preparation methods for the starting materials and the respective monolayers, give details on the surface characterisation, and offer explanations for the superior behaviour of the selenolate SAMs.

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COLL 498

Dissociation of formic acid on metal oxide surfaces probed by UHV-IRRAS

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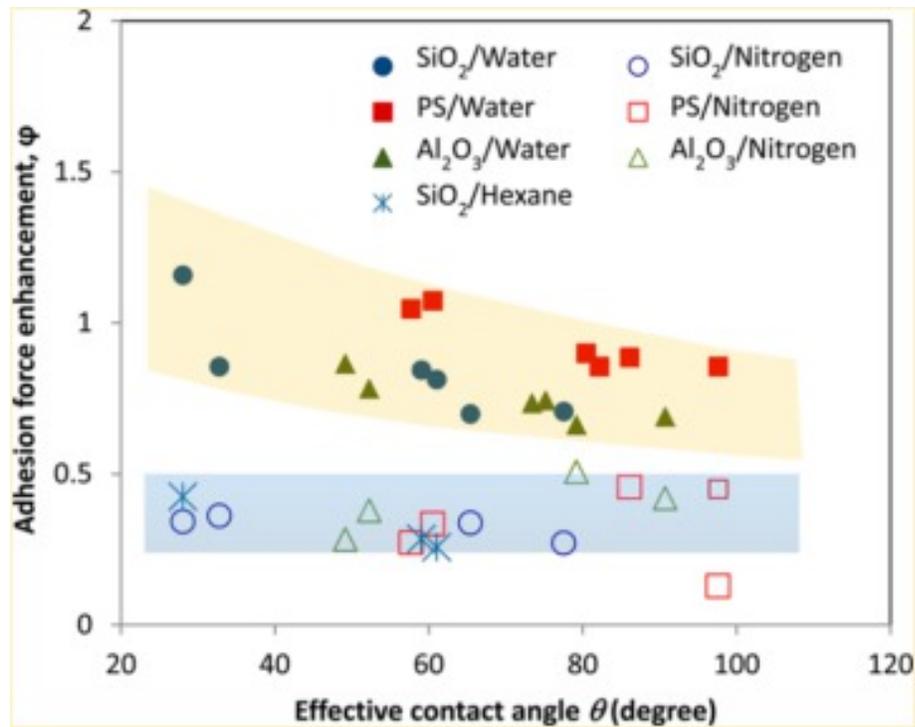
Carboxylate groups are frequently used to anchor photosensitizers and other functional molecules to oxide substrates. As a result the binding of HCOOH, the simplest carboxylic acid, to oxides substrates is an important model system with regard to understanding the grafting of more complex molecules via carboxylate groups with this important oxidic substrate. Here, the interaction of formic acid with different oxide single crystal surfaces (TiO₂(101), ZnO(10-10), Fe₃O₄(001)) has been monitored by infrared reflection absorption spectroscopy (IRRAS). The high-quality IR data are further combined with other complimentary techniques, such as X-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED) and scanning tunneling microscopy (STM). We found that the interaction of HCOOH with TiO₂(101), ZnO(10-10) and Fe₃O₄(001) leads to dissociative adsorption yielding different formate species via an acid-base reaction on oxide surfaces. The adsorption geometry of reacted formate species will be discussed in detail.

COLL 499

Dynamic adhesion forces between microparticles and substrates in water

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The interactions between micrometer-sized particles and sub-strates in aqueous environment are fundamental to numerous natural phenomena and industrial processes. Here we report a dynamically induced enhancement in adhesion interactions between microparticles and substrates immersed in water, air, and hexane. The dynamic adhesion force was measured by pulling microsized spheres off various substrate (hydrophilic/hydrophobic) surfaces at different retracting velocities. It was observed that when the pull-off velocity varies from 0.02 to 1500 μm/s, there is 100–200% increase in adhesion force in water while it has a 100% increase in nitrogen and hexane. The dynamic adhesion enhancement reduces with increasing effective contact angle defined by the average cosine of wetting angles of the substrates and the particles, and approaches the values measured in dry nitrogen and hexane as the effective contact angle is larger than 90°. A dynamic model was developed to predict the adhesion forces resulting from this dynamic effect, and the predictions correlate well with the experimental results. The stronger dynamic adhesion enhancement in water is mainly attributed to electrical double layers and the restructuring of water in the contact area between particles and substrates.



COLL 500

Formation of luminescent inorganic precipitation tubes

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Using reaction conditions far from equilibrium, we investigate the dilatatory growth of hollow tubes formed from reactant-loaded pellets. The latter pellets are composed of phosphorescent zinc sulfide and zinc sulfate by mass. During the experiment, a single pellet is placed in a small volume of concentrated sodium silicate. Tube growth is directed by a single gas bubble which is monitored by a time-lapse camera. Using procedures of image acquisition and processing we are able to quantify the spatio-temporal dynamics. Systematic measurements include induction period and growth velocity. This presentation will discuss two distinct morphologies located in upper and lower zones of growth at reactive interfaces. The resulting tubes can range from 1.1-1.8 mm and 450-900 μm in radii depending on the morphology. Moreover, the radii distinguishes between the two morphologies. Lastly, scanning electron microscopy reveals that the precipitation tubes have intricate patterns on the outside surface.

COLL 501

Incorporation of nanoparticles into tunable, highly-ordered, porous silica films

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Incorporating metal nanoparticles into inverse opals has attracted significant attention in the literature since the high surface area and photonic properties of inverse opals coupled with the plasmonic properties of metal nanoparticles greatly expands the possible applications of these materials as catalysts, sensors, photonic structures, and in Surface-Enhanced Raman Spectroscopy. Using a new three-phase co-assembly method, we are able to create highly ordered inverse opal films with homogeneously distributed and accessible gold nanoparticles embedded within the walls of the structure. This highly-ordered, large-scale porous structure, combined with a uniform functional composition, cannot be fabricated by typical inverse opal synthetic methods. We show that the synthesized films possess unique optical properties, combining an angle-dependent Bragg peak of typical inverse opals with the angle-independent absorption peak of gold nanoparticles. These optical properties are tuned by changing the concentration of nanoparticles added to the colloidal solution before assembly or by the selective growth of embedded nanoparticles within the prepared porous thin film. We also demonstrate that due to the functional tunability of our structures and the accessibility of its pores and nanoparticles, the wetting and subsequently the optical properties of these films can be spatially patterned.

COLL 502

Ionic and molecular modifiers of calcium oxalate crystallization: Tailoring Interfacial Interactions

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Crystallization is inherently an interfacial phenomenon that can be mediated through the use of additives, termed modifiers, which adsorb at specific crystal surfaces and influence the anisotropic rates of crystal growth. In pathological biomineralization, the formation of minerals is believed to be regulated *in vivo* by the interaction of urinary constituents with crystal interfaces. Here we examine the role of native growth modifiers of calcium oxalate monohydrate (COM), which is the most prevalent crystalline constituent of human kidney stones, and serves as a model for examining modifier-crystal molecular recognition [1]. Many species, such as proteins and trace metals, are putative growth modifiers that display an affinity for binding to specific surfaces of COM

crystals to suppress (or in some cases promote [2]) crystal growth. Our studies have revealed interesting trends among modifiers with varying charge density and hydrogen-bonding moieties that suggest the diffuse double layer surrounding COM crystal surfaces plays a significant role in modifier-crystal interactions. In this talk we will discuss the effects of alkali metals and alkaline earth metals on COM crystallization. To this end, we employ a combination of bulk crystallization assays and interfacial studies. To obtain better understanding of the interfacial phenomena during COM surface growth in the presence of modifiers, we have employed atomic force microscopy (AFM) to observe *in situ* the dynamics of layer-by-layer surface growth and the mechanisms of modifier inhibition. We couple these studies with bulk assays to assess the influence of growth modifiers on the crystal size and habit. Collectively, these studies are a basis for ongoing initiatives to design novel drug candidates for pathological diseases [3] and a generalized platform for the rational design of inorganic and advanced materials with tailored properties.

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COLL 503

Colloidal particle dispersions for the synthesis of full color electrophoretic inks

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Colloidal polymer particle dispersions are routinely used as electrophoretic inks. The principal method of synthesising these is through non-aqueous dispersion polymerisation (NAD) in non-polar solvents. PHSA-g-PMMA stabilisers were used, resulting in monodisperse, spherical particles of varying sizes but the stabiliser synthesis was complex and was often difficult to reproduce.¹ This led to the development of novel stabilisers –block copolymers synthesised by atom transfer radical polymerisation (ATRP).²

Poly(methyl methacrylate)-*block*-poly(octadecyl acrylate) (PMMA-*b*-PODA) stabilisers^{3,4} with varying chain lengths were synthesised, and successfully incorporated into colloidal dispersions synthesised by non-aqueous dispersion (NAD) polymerisations.⁵ These reactions allowed for the synthesis of particles from <100 nm to 1.1 µm, with the option to incorporate cross-linkers and polymerisable dyes. These properties have all been

achieved whilst maintaining low polydispersities, hexagonal close-packing and layering.

A significant drawback to the PMMA-*b*-PODA stabiliser was the propensity of the particles to precipitate or gelate below 15 °C. These gelation properties were investigated using DLS and viscometry; the gelation (or UCST) was consistently seen to occur at 15°C. This is evident from a dramatic increase in viscosity, polydispersity and hydrodynamic volume below this temperature. The introduction of a comonomer, ethylhexyl acrylate (EHA), into the PODA block at various molar percentages lowered the temperature at which this behaviour is observed, and at high enough concentrations of EHA the gelation was prevented completely.

Full colour polymeric particle dispersions have been successfully incorporated into electrophoretic cells and demonstrated all the required behaviours to be used in electrophoretic displays.

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COLL 504

Selecting the swimming mechanisms of colloidal particles: Bubble propulsion vs. self-diffusiophoresis

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Studies in synthetic micro-motors have thrived over the last decade utilizing different propulsion mechanisms. Among all the propulsion strategies, the self-diffusiophoresis and bubble propulsion, using hydrogen peroxide as the fuel, have been widely studied. The well known platinum-polystyrene Janus particles usually move primarily due to the self-diffusiophoresis. The platinum films on those Janus spheres were typically coated by physical evaporation. This two dimensional templating method limit the throughput of the Janus particles.

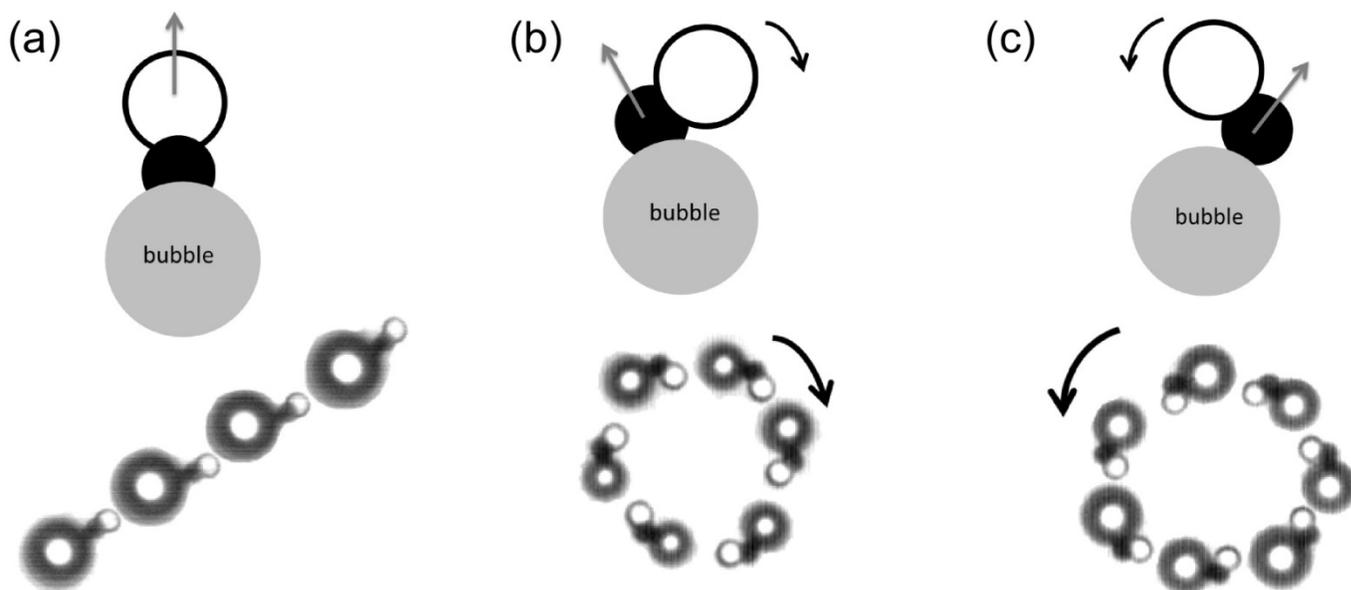
We use a simple bulk chemical deposition method to make platinum-polystyrene Janus dimers. Surprisingly, those particles are propelled by bubbles on the platinum-coated lobes. We followed a same synthetic strategy to chemically deposit platinum on Janus spheres initially with physically deposited platinum. We observed that the motion behavior of the spheres were being switched from self-diffusiophoresis to bubble propulsion. By comparing the platinum deposition methods, platinum surface coverage, and surface roughness on polymer spheres, we confirm that both high catalytic activity

and rough surface are necessary to form bubbles on particle surface.

Compared with spheres, our Janus dimers, with combined geometric and interfacial anisotropy, also exhibit distinctive motions at the respective stages of bubble growth and collapse, which differ by 5-6 orders of magnitude in time. We have observed three types of motions from the hybrid dimers: linear, clockwise and counterclockwise motions, which are determined by the relative position of the bubble to the dimer. The motions follow the same growth curve in the bubble growth stage which proved to be a diffusion controlled process.

Interestingly, our Janus dimers exhibit opposite behaviors at the bubble burst moment in linear and circular motions.

Our study not only provides insight into the link between self-diffusiophoresis and bubble propulsion, but also reveals the intriguing impacts of the combined geometric and interfacial anisotropy on self-propulsion of particles.



COLL 505

Characterization and dispersion behavior of quaternary ammonium encapsulated polyoxometalates in polyurethane

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Progress toward the understanding of the polymeric distribution of a series of novel reactive polymer additives designed to impart active chemical and biological protection

is presented. A series of quaternary ammonium biocides that exhibit a range of amphiphilic character were coordinated to chemically reactive polyoxometalate species. The effects of quaternary ammonium biocide composition on the polymer distribution and surface segregation of the conjugate compound in polyurethane solvent cast films were investigated by SEM, ATR-IR, laser confocal microscopy, contact angle analysis, and XPS depth profiling. Furthermore, effects of additive concentration, polymer concentration, and solvent selection on additive dispersion were examined, in addition to phase separation kinetics. The relative lengths of ethylene oxide and alkyl tail moieties of the quaternary ammonium biocides, additive concentration, and polymer drying time were identified as significant factors in distribution of additive in polyurethane. Results from antimicrobial and simulant decontamination challenges are also presented.

COLL 506

Janus particles for probing and manipulating immune functions

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Multifunctionality of Janus particles enables many promising biomedical applications that are not offered by homogeneous particles. To realize those applications requires understanding how properties of Janus particles influence the particle-cell interactions. We study the effect of anisotropic functionality in Janus particle-cell interactions and explore new applications of Janus particles in immune modulation. In this talk, I will discuss our recent progress on two aspects of Janus particle-immune cell interactions: cellular uptake and immune cell activation. I will show how surface anisotropy of Janus particles can be exploited to probe and manipulate immune cell functions.

COLL 507

Intra-phase mixing in binary drops translating through corrugated microchannels

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The intra-phase mass transport in a translating spherical drop containing two components will be studied numerically at zero capillary number. The study is motivated by intra-phase mixing in microfluidic systems where two drops containing different species of unequal or nearly equal volume are formed in channels where they merge, forming a binary drop and then translate. To enhance mixing it is possible to add periodic-alternating expansions/contractions or corrugation to the channel. The species conservation equation is solved using 4th order finite difference discretization in space with an adaptive explicit Runge-Kutta-Merson (RKM) scheme to advance in time.

Volume fraction for the initial species concentration range from 0.5 to 1.0, Peclet number of 10,000 and dimensionless frequency, or Strouhal numbers, ranging from 0.1-10 will be used to estimate the variation in global concentration and unmixed volume as a function of time.

COLL 508

Molecular dynamics simulations of colloidal nanoparticles solvation

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We use atomistic molecular dynamics simulations to model the solubility of colloidal nanoparticles in different solvents. We consider nanoparticles of diameters 2nm and 8nm core with perfluoroalkane ligands and three different solvents (acetone, isopropanol and perfluorohexane). We analyze the distributions of ligands configurations for different nanoparticles and solvents, and evaluate the approximate binding energies of the particles and solvents. From these data, we deduce that the nanoparticle solubility is controlled by the solvent type, the particle diameter, the density of its ligands, the solvent-accessible surface area of the ligands, the dipole moment orientation of the ligands, and other features of the nanoparticle surface. The simulation results are compared in detail with the experimental data obtained by our collaborators.

COLL 509

Theoretical description of architectures of nanoparticles

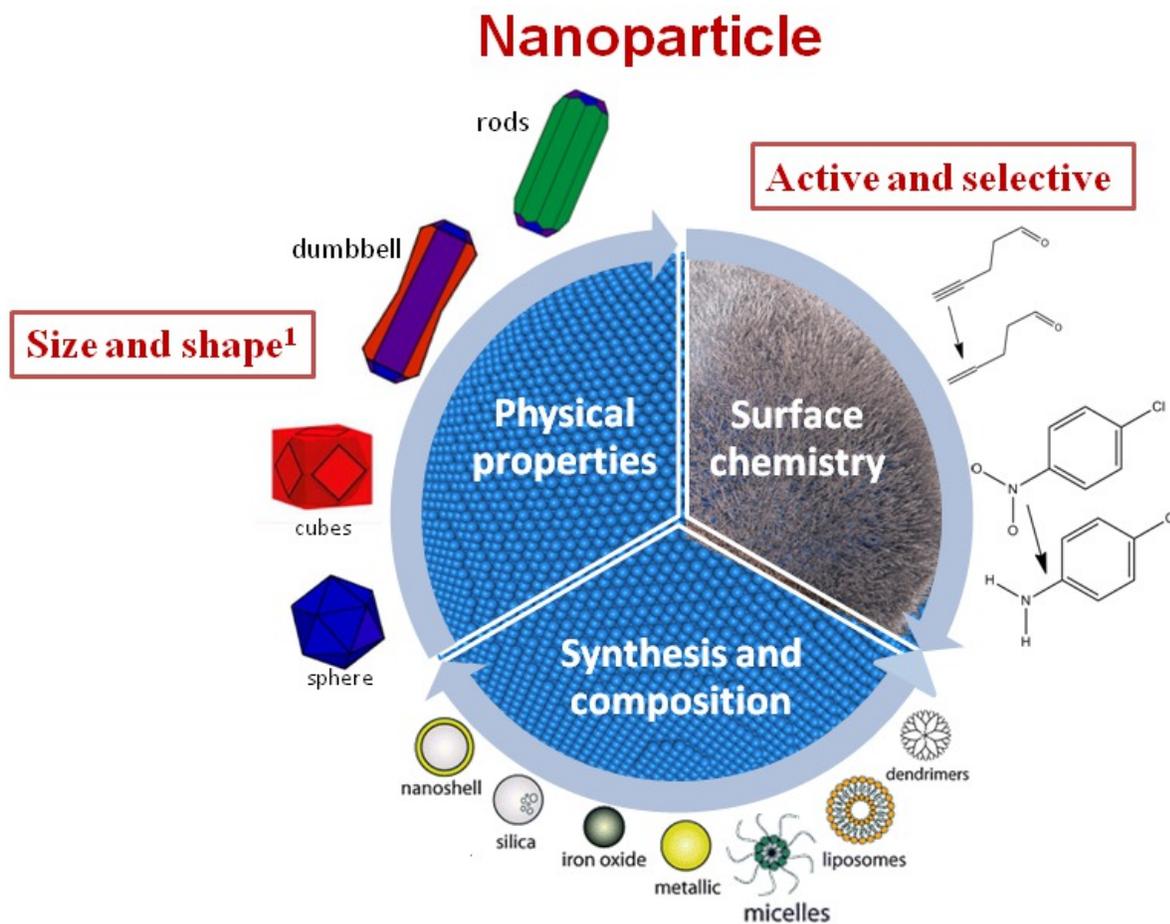
Neyvis Almora Barrios¹, *nalmora@iciq.es*, Nuria Lopez². (1) THEORETICAL HETEROGENEOUS CATALYSIS, Institute of Chemical Research of Catalonia (ICIQ), Tarragona, Spain (2) Theoretical Heterogeneous Catalysis Grp, Inst Chemical Research of Catalonia, Tarragona, Spain

Density Functional Theory simulations including dispersion provide a detailed atomistic model for understanding of synthesis-structure relationships in the study of material sciences and catalysis.[1, 2] We have investigated the atomic structure of the NanoSelect™ catalysts and deriving selectivity descriptors which can be generalized to other ligand-modified palladium catalysts. These results lead to an improved understanding of the performance of colloidal nanoparticles in alkyne hydrogenation, opening new pathways for the design of highly selective catalysts with tailored properties.[3]

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Scheme 1. Representation of the nanoparticle, showing the relations between synthesis and properties

COLL 510

Understanding abiotic:biotic interface: Molecular-level insights into the behavior of enzymes covalently immobilized on surfaces

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Surface-immobilized enzymes are important for a wide range of technological applications, including industrial catalysis, drug delivery, medical diagnosis and biosensors. However, our understanding of how enzymes and proteins interact with abiological surfaces on the molecular level remains extremely limited. We have compared the structure, activity and thermal stability of two variants of a β -galactosidase attached to a chemically well-defined maleimide-terminated self-assembled monolayer surface through a unique cysteinyl residue. In one case the enzyme is attached through an α -helix, in the other case through an adjacent loop. Both enzymes exhibit similar specific activities and adopt similar orientations with respect to the surface normal, as determined by sum frequency generation and attenuated total reflectance FT-IR spectroscopies. Surprisingly, however, the loop-tethered enzyme exhibits a thermal stability 10 °C lower than the helix-tethered enzyme and 13 °C lower than the enzyme in free solution. Using coarse grain models, molecular dynamics (MD) simulations of the thermal unfolding of the surface-tethered enzymes were able to reproduce these differences in stability. Thus, revealing that tethering through the more flexible loop position provides more opportunity for surface residues on the protein to interact with the surface and undergo surface-induced unfolding. These observations point to the importance of the location of the attachment point in determining the performance of surface-supported biocatalysts and suggest strategies for optimizing their activity and thermal stability through molecular simulations.

COLL 511

Direct synthesis of single layer layered double hydroxide nanosheets

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Layered double hydroxides (LDHs) are known to be prepared in layered structure with a thickness of tens to hundreds of nanometers. In order to maximize the utilization of LDHs, single layer LDH nanosheets with large aspect ratio are most desirable, since such nanosheets have found a wide range of applications including oxygen evolution catalysis, polymer composites, and supercapacitors. Up to date, exfoliation of pre-synthesized LDH layered structure is the main approach to obtain single layer LDH nanosheets. However, due to their time consuming process and complexity, the exfoliation method is hard to be scaled up, which limits the large scale application of LDH nanosheets. In this work, we aim to directly synthesize colloidal single layer LDH nanosheets from metal cations and hydroxides at the presence of a layer growth inhibitor in the Z-direction, formamide. The proposed mechanism is that formamide will attach to the surface of LDH layers, weakening the interactions between the positively charged layers and counter anions, thus inhibiting the growth in the third dimension.

Factors such as formamide concentration, M^{2+} to M^{3+} molar ratio, and the role of aging were discussed and evaluated in the direct synthesis of LDH single layer nanosheets.

COLL 512

Silyl electrolytes for lithium-ion battery applications

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Novel silyl solvents as components of electrolytes for lithium-ion batteries have improved lithium ion transport and safety in comparison to the conventional carbonate solvents most in use in lithium-ion electronic devices. This talk will explore the ion transport of a variety of electrolytes composed of the silyl solvent families (Figure 1): 1NM2 and related compounds where the number of ethylene oxide chain units (2 in 1NM2) on the trimethyl silyl fragment has been varied, 1ND2 where there are two ethylene oxide substituents directly covalently bound to the dimethyl silyl moiety and 1FS₃M2 where there is a three carbon spacer between the ethylene oxide chain and the silicon and a fluorine atom replaces one methyl substituent. Electrolytes of the solvents with the salts LiPF₆, LiTFSa and LiBOB have been prepared and their variable temperature ionic conductivities measured by impedance spectroscopy. We have also measured lithium and anion diffusion in PFG-STE NMR experiments which yield lithium and anion transference numbers. From both the ionic conductivity and NMR diffusion measurements, we have calculated the extent of ion association in these electrolytes. We also report the viscosities, glass transition temperatures and dielectric constants of the silyl solvents which impact the variations in ion transport we find for lithium salt electrolytes. Full carbon/lithium cells of some of these electrolytes have been prepared and cycle well.

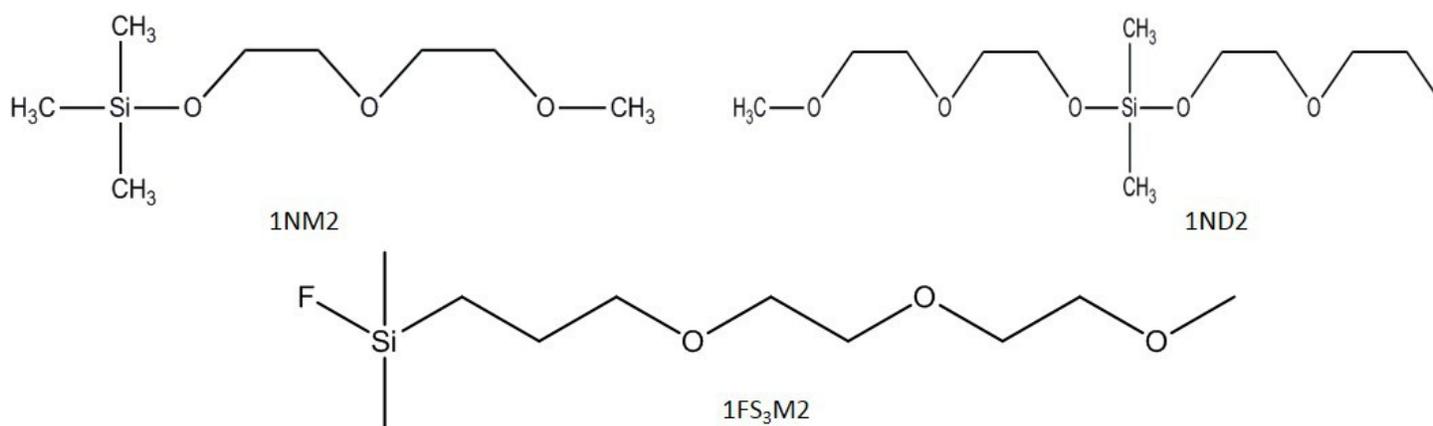


Figure 1. The chemical structures of the silyl solvents 1NM2, 1ND2 and 1FS₃M2.

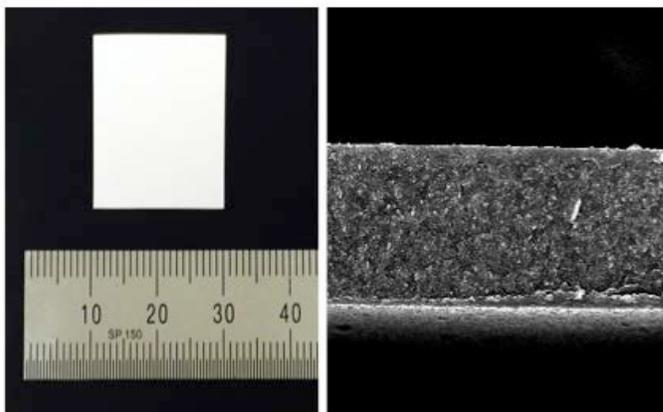
COLL 513

Recent advances in the synthesis and processing of single and mixed-metal nano-oxides using liquid feed flame spray pyrolysis (LF-FSP). Thin, flexible ceramic membranes that can act as lithium electrolytes with properties equal to liquid electrolytes

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Liquid-feed flame spray pyrolysis (LF-FSP) of metal alkoxide and carboxylate complexes dissolved in ethanol generates a wide variety of phase pure single and mixed-metal oxide nanopowders. These nanopowders typically have average particle sizes of 20-60 nm with surface areas of 70-200 m²/g and are often single crystals with limited agglomeration and essentially no aggregation.

LF-FSP provides routes to nanoparticles with exact compositions for example Y₃Al₅O₁₂, 2SiO₂·3Al₂O₃, or even single phase materials that are off expected stoichiometry including spinels with compositions of (MO)_x(Al₂O₃)_{1-x} (M = Mg, Ni, Co) where x = 0.1-0.3. We have also made nanopowders targeting ceramic oxide electrolytes for lithium batteries including: Li_{1.7}Al_{0.3}Ti_{1.7}Si_{0.4}P_{2.6}O₁₂ nanopowders. Efforts to transform these powders to dense, composite ceramic materials with controlled grain size do not necessarily generate monoliths with final densities better than mixtures of the individual powders. However the Li electrolytes perform better than expected from previous literature data. The reasons for this and several novel results concerning processing will be discussed.



Thin Flexible Ceramic Electrolyte with Superionic Li Conductivity

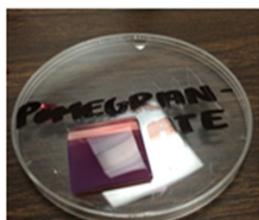
COLL 514

Creation of natural dye sensitized solar cell by using nanostructured titanium oxide

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This research focuses on improving the methodology of producing chlorophyll dye-sensitized solar cells by the process of amalgamation with anthocyanin dyes to maximize cell efficiency and power production at the most economical cost and mass manufacturing process. The methodology of producing a dye-sensitized solar cell divided into three sections: dye extraction, TiO₂ paste application, and solar cell structure. These three important factors contribute significantly to the maximization of a dye-sensitized solar cell. This research conducted explores different ways of improving the current-voltage potential of the solar cells. The solar cell's performance in terms of efficiency, voltage, and current was tested with 1.5 AMU solar simulator as the light source.

In the case of H₂, we identify trends and promising adsorbents from amongst 4,000 known metal-organic compounds mined from the Cambridge Structure Database.



(a)



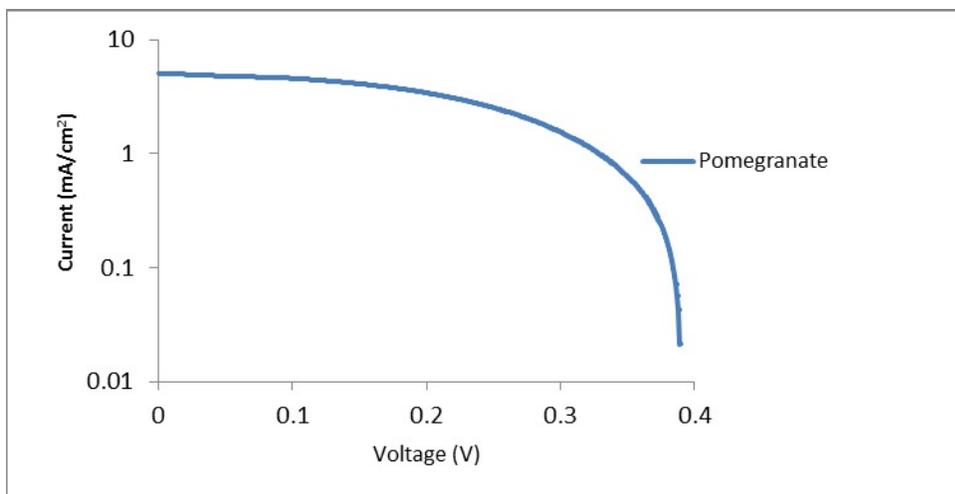
(b)



(c)



(d)



The experimental results show that Pomegranate produced the greatest photoelectric conversion efficiency (η) up to 2%, an open-circuit voltage (V_{oc}) of 532 mV, and a short-circuit current density (J_{sc}) of 5 mA/cm².

COLL 515

Amphiphilic functionalization of cathode catalyst to advance electrochemical reactivity of fuel cells

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Fuel cell (FC) systems have drawn significant attention, because they meet all requirements for future sustainable energy generation such as high electrical efficiency, low emission, good partial-loading characteristics and fuel supply flexibility. One design of FCs is PEMFCs, which consist of a solid Nafion membrane as the electrolyte, utilizing H₂ or bio-fuel as a fuel supply; and noble metal as the catalyst. PEMFCs provide direct electricity for stationary and portable applications with high energy conversion efficiency, low pollutant emissions, simple design and operation, and flexible fuel supply. However, current PEMFC designs encounter problems in materials compatibility, manufacturing cost, and performance degradation. Numerous attempts have been made to improve the performance and durability of PEMFCs. This study developed functionalized catalyst composed of carbon nanotubes (CNT) arrays, which were decorated with platinum (Pt) as cathode catalyst. The novelty of this approach lies in amphiphilic post-functionalization. It was found that PEMFCs displayed power density (900 mW/cm²) under lowered Pt loading (< 0.2 mg/cm²). This performance gain is attributed to greater accessibility to electrochemical active-sites, allowing generation of energy and reduced environmental burden. Additionally, the hydrophobicity of the catalysts also provides a new tool to prevent cathode flooding, resulting in long-term device stability.

COLL 516

Aiding developments of single-molecule force spectroscopy for biosensing via molecular simulation

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Interest in the use of single-molecule force spectroscopy (SMFS) to investigate the interactions between biomolecules and solid substrates has developed in recent years.¹⁻³ SMFS studies have shown that the adhesion forces of single-stranded DNA (ssDNA) to the aqueous interface of substrates is reduced in the presence of the complementary ssDNA chain. Such behavior raises the possibility of using SMFS as a novel biosensing technique in dilute solutions (< 1nM).^{2,3}

Molecular simulation can provide valuable assistance in the development of SMFS by providing a greater understanding of how the interaction of ssDNA with different substrates depends on the oligomer sequence. To this end, the free-energy of adsorption of the four nucleobases, nucleosides and nucleotides to two different substrates, graphene and gold, has been calculated using newly developed polarizable force-fields.^{4,5} These data provide a baseline that can be used to (1) compare the results of experiment and simulation and (2) help isolate the factors that cause specific ssDNA oligomers to bind more or less strongly to a specific substrate. We find good agreement between our results and the available experimental data. Our findings also highlight the differences and commonalities in adsorption behavior of the DNA fragments at the two substrates. By combining data obtained from experiment and simulation we can advance our understanding of the driving forces for the interaction of DNA with different substrates and expand the possibilities of SMFS.

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COLL 517

Use of surface-specific spectroscopy techniques to unravel molecular recognition in biosensing

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Molecular recognition is key to many biological applications, including biosensing. Yet, little is known about the actual molecular forces behind such recognition, which has motivated intensive research into theoretical and experimental methods that can probe interactions with biomolecules. In this presentation, results will be reported of the use of surface-specific techniques to address several issues associated with biosensing [1]. With sum-frequency generation (SFG) spectroscopy, for example, one may correlate detection of lactose with a sensing unit containing galactosidase to changes in this enzyme structuring in a layer-by-layer (LbL) film [2]. SFG is also suitable to study the organization of adsorbed water at interfaces during sensing experiments. Polarization-modulated infrared reflection absorption spectroscopy (PM-IRRAS) is another useful method which can be used to monitor formation of supramolecular structures in sensing devices, in addition to adsorption of analytes [3]. The adhesion force between a functionalized atomic force microscopy (AFM) tip and an analyte adsorbed on a solid support can be determined experimentally with force curves obtained with atomic force spectroscopy (AFS). The measured values for an enzyme attached to an AFM tip could be compared with the theoretical adhesion force estimated using steered molecular dynamics [4], and this can be applied to design novel nanobiosensors. A discussion will also be presented on how manipulation of nanomaterials can be combined with computational methods to exploit biosensors for clinical diagnostics [5].

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COLL 518

New roles for antifreeze proteins in recognizing non-ice surfaces

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Antifreeze proteins (AFPs) are a structurally diverse group of proteins produced in many cold-adapted organisms to allow these organisms survive in sub-freezing temperatures. AFPs are well-known for their abilities to depress the freezing point of water in a non-colligative manner and to inhibit the growth and recrystallization of ice by recognizing specific ice crystal faces for more than three decades. The latter presents an intriguing example of protein-surface interactions in the natural world. Hydrogen bonding and/or hydrophobic interactions are suggested for their affinity to ice surfaces. Based on recent identification of interactions of small molecules with AFPs in solutions, a speculation that the recognition ability of AFPs is beyond ice was raised. We have demonstrated that AFPs can control the crystallization of some non-ice like crystalline solids in a

highly-effective manner by recognizing the specific non-ice surfaces. In the progress, we have also modelled the proteins on the surfaces to understand the interactions of the proteins with non-ice surfaces. Progress on these efforts in connection with the potential applications of AFPs will be described.

COLL 519

Studying receptor-mediated liposome fusion kinetics at aqueous/liquid crystal interfaces

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Liquid crystal (LC) based sensors offer several advantages over traditional devices because they offer fast, label-free detection of molecules at the aqueous-LC interface through the observation of LC alignment. For example, phospholipids will spontaneously adsorb at the interface, realigning the LC and changing the optical properties of the sample. This spontaneous liposome fusion can be inhibited by the presence of poly(ethylene glycol) (PEG), which acts as a steric barrier at the LC interface. Complementary DNA strands incorporated at the interface and in the liposomes can be used to control specific fusion events. Hybridization of these DNA oligonucleotides leads to vesicle rupture and fusion with the LC interface, increasing the local phospholipid concentration and modifying the LC orientation and optical signal. To expand the scope of our system, we can employ DNA aptamers as molecular recognition elements to detect a number of molecular targets.

We have performed a systematic study of system parameters to optimize the conditions required for fast and specific liposome fusion at the LC interface. This study focused on liposome composition, the steric barrier at the interface, and the DNA oligonucleotide recognition element. Results show that all of these parameters will affect the kinetics of vesicle fusion with the interface. Optimization of these conditions suggests the ideal system contains a liposome mixture of unsaturated phospholipids and cholesterol along with a DNA recognition element that is 30-40 base pairs in length. These properties improve the current design of our LC-based sensor by increasing the kinetics of the system, while still maintaining high sensitivity and selectivity. Exploring these parameters is also important to improve understanding of the mechanism of liposome fusion with a soft interface. Future work will attempt to pinpoint specific parameters (e.g. oligonucleotide length, lipid composition) and observe their influence on individual steps in the fusion mechanism.

COLL 520

Effect of nanoparticle surface chemistry and salt concentration on binding to RNA and DNA

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The design of nanoparticles that can induce specific structural transitions in nucleic acids is important for nanotechnology applications including gene delivery and nanoelectronics. It is known that in biological systems, the binding of cationic proteins induces structural changes in DNA or RNA, which can affect gene expression or cause the compaction of DNA into chromatin. The anionic backbone of the nucleic acids DNA and RNA allow for non-specific electrostatic interactions with cationic proteins, nanoparticles, or dendrimers. The interaction of nucleic acids and nanoparticles may be tuned through changes in nanoparticle size, charge, polarity, or shape. However, the factors that affect structural transitions are not fully understood. We performed atomistic molecular dynamics simulations of the binding of nucleic acids to monolayer-protected gold nanoparticles to elucidate structural changes that take place for nanoparticles and DNA upon binding. Results from these simulations were analyzed to determine modes of DNA and RNA bending with nanoparticles. Our simulations show that highly charged nanoparticles cause DNA to bend with little damage to the helix structure, similar to DNA in the nucleosome. Nanoparticle shape as well as charge is shown to affect the wrapping of nucleic acids with the nanoparticle. Because RNA is less flexible than DNA, RNA bends less than DNA. Similarly, low salt concentrations and high nanoparticle charge cause greater disruptions to DNA structure. We find that the roll parameter is the most important base-pair parameter for DNA bending. These results may be used to construct pseudo-phase diagrams showing the behaviors of nucleic acids and nanoparticles under different conditions.

COLL 521

Ultrasound biosensing techniques based on biomolecule-induced aggregation of nanodroplets

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Aggregation of droplets has excellent potential as a mechanism for biosensing both in vitro and in vivo. In this talk, a novel method is presented in which a unique signal is generated in response to the presence of an analyte in solution using ultrasound-based detection of phospholipid-coated perfluoropentane nanoemulsions. Ultrasound is a safe and widely available technique for contrast imaging. Superheated droplets produce low signal-to-noise ratios, thus making them poor ultrasound contrast agents under normal conditions; they can, however, be vaporized into high contrast microbubbles in situ through application of a high-intensity focused ultrasound (HIFU) pulse. The surface

chemistry of the nanodroplets was designed such that an analyte in solution would bring about aggregation of the nanodroplets by binding to the functionalized droplet shell. This aggregation was seen to affect the vaporization threshold of the droplets. For a proof-of-concept study, aggregation was first induced via interactions of biotin-streptavidin, followed by the use of complementary antibodies. This talk will describe the properties of droplets that affect their transition to bubbles, and how aggregation can be used to selectively vaporize one set of droplets in the presence of another. Finally, this work will be placed into context of how to create in-solution, 'label-free' biosensing assays.

COLL 522

Impedimetric biosensors for detecting VEGF based on PEDOT carboxylic acid/PEDOT copolymer

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Age-related macular degeneration (AMD) is the leading cause of irreversible visual impairment in the developed world. The precise, rapid detecting and monitoring of vascular endothelial growth factor (VEGF) are critical for improving anti-VEGF clinical treatments of AMD. An impedance biosensor based on poly(3,4-ethylenedioxythiophene) (PEDOT) carboxylic acid/PEDOT copolymer was developed as a promising technique for detecting VEGF. Carboxylic acid modified 3,4-ethylenedioxythiophene (EDOT)/EDOT was electrochemically polymerized on the surface of an interdigitated gold electrode. The thin nanopolymer films of PEDOT carboxylic acid/PEDOT were characterized using optical microscopy, SEM/EDS and FIB techniques. Anti-VEGF monoclonal antibody from Mayo Clinic was electrostatically or covalently immobilized on the surface of the polymer films, and used to detect VEGF by electrochemical impedance spectroscopy (EIS). By fitting the impedance spectra to an equivalent circuit model, the leakage resistance was found to have a linear relationship with VEGF concentration.

COLL 523

SiC porous materials derived from apple for high-performance electromagnetic interference shielding

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Following rapid development of the electronics industry and wireless communication, electromagnetic interference (EMI) shielding of radio frequency radiation has been a more serious concern in this modern society. EMI shielding materials has thus become a hot research topic, and considerable attention is being devoted to their design and

fabrication. In this research, porous SiC with high-performance EMI shielding property was fabricated by using apple as the template. The obtained porous material was characterized by techniques including SEM, EDS, XRD, mercury intrusion and vector network analysis. The formation mechanism of the porous SiC materials is discussed related with their structure evolution. It is found that the porous SiC well inherits the honeycomb structure of apples. The porosity and pore size could be tuned by controlling the precursor concentration and sinter temperatures. The special configuration endows the porous SiC with shielding effectiveness (SE) above 40 dB covering a wide frequency of 2-18 GHz at a thickness of 2 mm. The maximum SE reaches 60 dB at 18 GHz. These results suggest that the developed porous SiC derived for apples will be valuable in EMI shielding devices.

COLL 524

Modeling fullerene aggregation in electrolyte solutions: A combined deterministic-stochastic framework

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Understanding the aggregation mechanism of nanoparticles such as fullerenes and carbon nanotubes, in various solvent media is of importance in myriad applications that use solution processing. For instance, the structure of thin film nanocomposites, used in a range of organic electronic devices such as organic photovoltaic cells, is determined by the size and shape of nanoparticle agglomerates that form during solution processing. We present a novel multi-scale model, based on molecular dynamics (MD) and kinetic Monte Carlo (kMC), to study the growth of nanoparticle agglomerates. A well-studied system, comprising fullerenes in NaCl electrolyte solution, was simulated to validate the model. The concentration of the electrolyte was varied from 0.01 M to 0.4 M in order to understand the effect of electrolyte concentration on the agglomerate size and shape of fullerenes. The model included two steps: 1) coarse-grained molecular dynamics (CGMD) simulation to determine the relevant events and their corresponding rate constants, and 2) kMC simulations using the estimated rate constants to track the growth of fullerene agglomerates with time. Under the simulated conditions, the agglomeration process evolves from a diffusion limited cluster-cluster aggregation (DLCA) regime to percolating clusters in transition and finally to a gelation regime. The fractal dimension of the aggregates was ~ 1.9 for the DLCA regime, which is in good agreement with existing data in the literature. The fractal dimension of the percolating clusters was ~ 2.5 , while that for the gelation regime was calculated to be ~ 3 , and occurs when the radius of gyration of fullerene clusters is 5 times larger than that in DLCA aggregation regime. The fullerene agglomeration showed similar trend at various electrolyte concentrations. The results indicated that beyond a certain fullerene concentration, the electrolyte concentration has minimal effect on the aggregation mechanism of fullerene nanoparticles. Overall the data from our multi-scale numerical model showed good agreement with existing theory of colloidal particle growth.

Although we validated our model by specifically simulating fullerene aggregation in electrolyte, the model can be applied to a multitude of systems where agglomeration of small molecules is of importance.

COLL 525

Synthesis of carbon-based nanoscale composite particles for imaging applications

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The development of carbon-based nanoscale composite particles, especially those combining optical and magnetic methods, are currently of considerable interest in many areas of biomedical imaging applications. Today despite some improvements in diagnostic protocols, for example early detection of cancer still remains a significant diagnostic challenge. The ideal imaging agents should be bright, magnetic, nontoxic, biocompatible, and stable against photobleaching. Among the attractive multifunctional imaging agents currently investigated are ones based on semiconductor quantum dots (QDs) such as CdSe/ZnS coupled with magnetic elements. However, these QDs containing cadmium or other heavy metals are unfortunately known for their significant toxicity even at relatively low concentrations. In this study, we report the synthesis of new platforms of carbon-containing nanoscale composite particles for eventual biomedical imaging use. The resulting nanoparticles are evaluated for their structural, chemical, and optical properties using various techniques such as UV-vis and fluorescence spectroscopy, Fourier Transform Infra-Red, elemental analysis, and SEM. The as-prepared nanoparticles exhibit excellent water solubility, good photostability, and a high quantum yield.

COLL 526

Label-free two photon imaging of live cells using graphene dots

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Targeted imaging using near infrared (NIR) light is the key to improve the penetration depth and it is highly promising for clinical tumor diagnostics. Here we will discuss our recent report on the synthesis of PEG coated graphene quantum dots for label free imaging of tumor cells. We will discuss synthesis and characterization of polyethylene glycol (PEG) coated graphene oxide quantum dots using one-pot hydrothermal reaction. The two photon luminescence measurement shows it can be used as very strong two

photon absorbing material. Our result demonstrate that two-photon luminescence signal remains almost unchanged even after two hours of illuminations, as a result, we are able to use them for label free selective imaging of tumor.

COLL 527

Developing carbenes as surface modifiers

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Carbenes have found utility in a variety of fields such as organometallic-/organo-catalysis, metal complex and allotrope stabilization, and recently surface functionalization. For instance, *N*-heterocyclic carbenes (NHCs) form more stable surface coatings on gold than traditional thiols with respect to several harsh conditions. We will present surface functionalization and stabilization strategies that employ functional carbenes. We focus on the stability of gold nanoparticles coated with NHCs compared to those coated with thiols. This work continues to diversify the application of carbenes for surface chemistry.

COLL 528

Carbon dots preparation and effect on protein fibrillation

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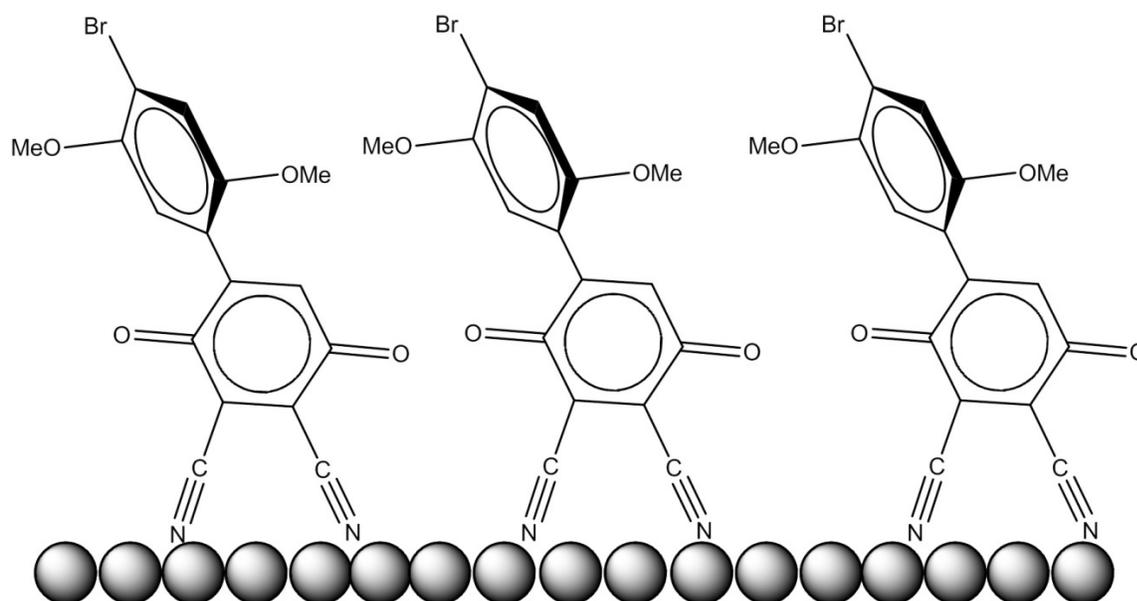
Carbon dots have recently emerged as a new class of photoluminescent nanomaterials with size less than 10 nm. They have competitive advantages over the semiconductor-based counterparts (ZnS/CdSe quantum dots) in biological and biomedical applications due to their unique properties, such as excitation wavelength dependent photoluminescence, excellent biocompatibility, low cytotoxicity, and optical stability. In our experiments, water soluble carbon dots were prepared from carbon powders. The products were characterized using UV-Vis, fluorescence, FTIR, XPS, AFM and TEM. As carbon dots have potential applications in biological systems (e.g. cell imaging, biosensing, and drug delivery), it is necessary to study interactions between carbon dots and proteins, and evaluate effects on protein fibrillation. Human insulin was chosen as a model protein to investigate these topics. It was found that these carbon dots have strong interaction with insulin and can inhibit its fibrillation. Cytotoxicity studies showed that these carbon dots have no or low toxicity in vivo. The results show potential applications of carbon dots to prevent amyloid fibril formation.

COLL 529

Conductance and rectification through asymmetric biphenyl molecule systems

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Understanding the electronic and physical properties of molecules in nanometer-scale electronic circuits is a key goal for material scientists. Knowing the possible conformations of a molecule and making predictions about how it will act within a system is important to the design of single molecule electronics. Here, we present the synthesis of a 4,4'-dibromohemibiquinone (Br,Br-HBQ) backbone which consists of a dimethoxybenzene bonded to a para-benzoquinone. The dimethoxybenzene acts as an electron-rich (n-type) donor and the quinone acts as a hole-rich (p-type) acceptor. From this backbone, a series of hemibiquinone derivatives have been synthesized and characterized. Predictions of the electronic properties of the derivatives by DFT are discussed with emphasis on the connection to molecular geometry. The self-assembly of a dinitrile-substituted hemibiquinone on a template-stripped gold surface and the properties of the resulting monolayer are presented. NMR spectroscopic, X-ray crystallographic, and cyclic voltammetric data will be used to rationalize the results of absorbance and conduction measurements.



COLL 530

Electron transfer and molecular binding to nanostructured carbon for supercapacitor materials

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To make renewable energy technologies truly sustainable we must also incorporate efficient energy storage strategies. We will present methods and materials that can enhance the store and transport of electrical energy. Several of our metal coordination complexes bind strongly to SWCNTs. We have synthesized and characterized hybrid nanomaterials capable of enhancing the specific capacitance of thin film supercapacitors. These complexes act to enhance available Electrical Double Layer Capacitance and add a significant pseudocapacitance increasing the specific capacitance, specific energy, and power. Compounds like $[\text{Ni}(\text{dibenzo}[a,c]\text{dipyrido}[3,2-h:2',3'-j]\text{phenazine})_3]^{2+}$ use earth abundant metals. Structure determination of assembled SWCNT supraparticles by electron microscopy, and light scattering. Optical properties of the assemblies in solution will be by UV-vis-NIR spectroscopic methods. Redox properties of surface adsorbed assemblies will be measured by electrochemical and spectroelectrochemical methods. The capacitance of thin film composites were determined using standard electrochemical methods including galvanostatic charge-discharge measurements. Equivalent circuit analysis of the composite electrodes were measured using electrochemical impedance spectroscopy. Experimental studies will be compared to computational modeling of these systems. Our objectives are to understand and control the morphology and directed assembly of SWCNTs upon adsorption of charged coordination complexes to form porous films for supercapacitor applications.

COLL 531

Synthesis of layered polyoxometalate/organic polymer-coated metal nanoparticles

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Hollow nanospheres have received considerable attention because of their potential application in a variety of fields including chemical sensing, drug delivery, catalysis, and separation science. Beyond the now well-studied silica-based nanospheres, most of the hollow nanospheres featured in the literature are composed of nested polymer shells that are formed through the sequential layer-by-layer (LbL) deposition of organic polycation and polyanion layers onto a sacrificial colloidal template that is subsequently dissolved. Rather than using organic polyanions, we employ inorganic polyoxometalates (POMs) in the synthesis of hollow nanospheres. POMs are well-defined anionic metal-oxygen clusters that maintain their structural integrity in acidic environments and during stepwise, multielectron redox reactions, making them attractive for use in electrocatalysis applications. Here we present our work on the synthesis of nanoparticles composed of alternating polycation (Poly) and polyoxometalate (POM) shells on a gold nanoparticle (AuNP) core. We have successfully created POM1Poly1@AuNPs using silicotungstic acid (STA) and polyallylamine (PolyA) as the

POM and polycation, respectively. These samples have been characterized with a battery of analytical techniques including UV-vis spectroscopy, dynamic light scattering (DLS), zeta potential, and transmission electron microscopy. DLS results show an increase in hydrodynamic diameter of greater than 5 nm as each successive layer is added to the AuNP core. The zeta potential measurements reveal a change in surface charge of more than 80 mV and a change in the sign on the charge that matches the expected for the either the cationic (positive) or anionic (negative) terminal layer. Continued work focuses on adding more STA and PolyA layers to the gold nanoparticle core.

COLL 532

Bimetallic $\text{Na}_4\text{Au}_x\text{Ag}_{44-x}\text{pMBA}_{30}$ molecular nanoparticles

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Mixed metal nanoparticles can have the best of both or the worst of both properties of the respective metals, therefore careful study of mixed metal systems is needed to realize their benefits. Studies have begun to learn the rules behind adding silver atoms to molecular gold nanoparticles, but the consequences of adding gold atoms to molecular silver nanoparticles are poorly understood. Here, we use co-reduction of gold and silver thiolates to study the effects of mixed metals on the structure, chemical properties, and optical properties of $\text{Na}_4\text{Ag}_{44}\text{pMBA}_{30}$ nanoparticles. We found that substituting gold into $\text{Na}_4\text{Ag}_{44}\text{pMBA}_{30}$ nanoparticles produced $\text{Na}_4\text{Au}_x\text{Ag}_{44-x}\text{pMBA}_{30}$ species where x ranged from 0 to 12 and where excess gold beyond 12 atoms instead formed large gold nanoparticles. The distribution of Au atom substitutions was found to be Gaussian, which indicated that the substitution was random rather than driven toward a thermodynamic sink. This is in contrast to a previous report. The stability as a function of Au atom substitution was studied in both the gas phase and solution phase and in both cases Au was found to improve stability. Differences in stability were used to bias the distributions toward high gold content, which facilitated the study of optical absorption spectra as well as structure determination by single-crystal x-ray diffraction.

COLL 533

Phase transport of citrate stabilized gold nanoparticles using nonspecifically adsorbed polymers

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Many synthetic approaches for gold nanoparticles (GNPs) rely on an aqueous media, resulting in water-soluble nanoparticles, which usually constrains the ability to

incorporate GNPs into other organic solvents or hydrophobic composites. In this paper we report an approach to transport citrate capped GNPs into a variety of solvents, including ones that are hydrophobic and not miscible with water. Our approach does not require the use of phase transfer agents such as alkylthiols or alkylamines, which strongly bind the gold surface. We employed a polar organic solvent, in which the particles were metastable, to suspend GNPs and dissolve the hydrophobic polymer, which will provide stabilization and allow for transport to various solvents after drying. The polymers used in this work (polymethylmethacrylate and polyvinylacetate) have approximately equal chain lengths and are structurally similar. Interestingly, a significant difference in their ability to stabilize the transport of the GNPs is observed and discussed.

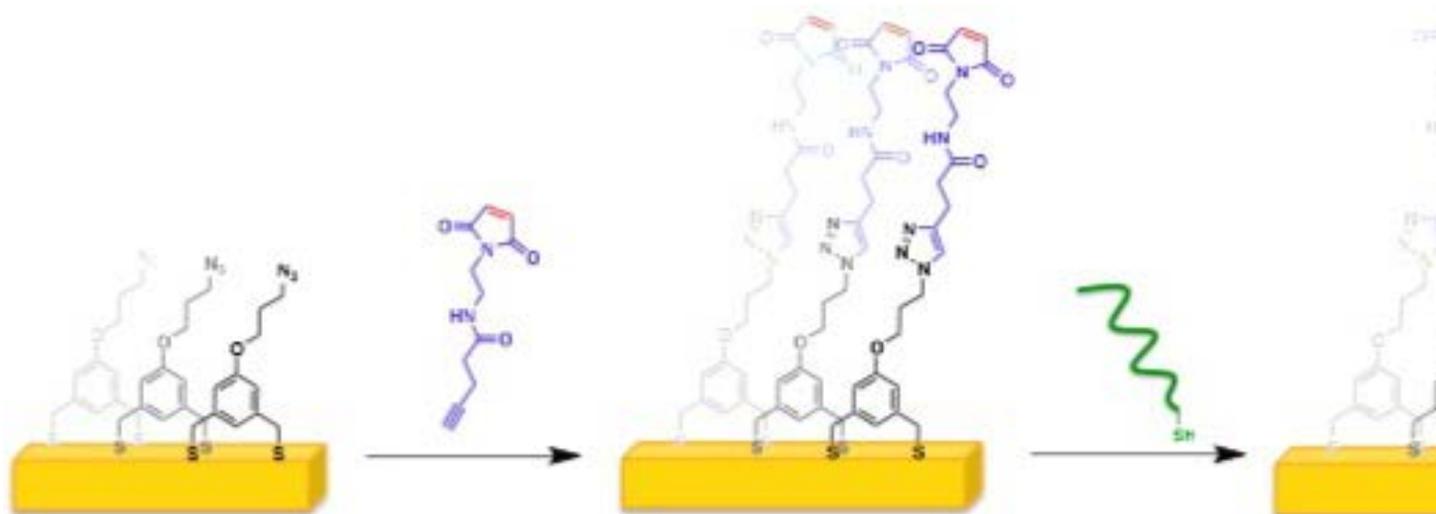
COLL 534

Highly efficient poly-lysine functionalization of gold surfaces by dual click reactions utilizing dithiol adsorbates

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Abstract: Functionalization of surfaces with poly-L-lysine is frequently used to immobilize molecules electrostatically. This report presents the preparation of self-assembled monolayers (SAMs) of azide-terminated adsorbates to determine the parameters that would most effectively produce a poly-L-lysine-modified SAM surface. Three different azide-terminated adsorbates were synthesized and used to prepare SAMs. A maleimide linker was attached to the azide-terminated surfaces via a copper-catalyzed click cycloaddition to offer an active platform for the attachment of the polypeptide. A thiol-Michael addition was used to immobilize the cysteine-terminated poly-L-lysine on the gold surface. Each step in this process was analyzed by ellipsometry, X-ray photoelectron spectroscopy (XPS), polarization modulation infrared reflection-absorption spectroscopy (PM-IRRAS), and contact angle goniometry to determine the most suitable adsorbate structure for such click attachments. Additionally, a series of mixed SAMs using an azidoalkanethiol in combination with a normal alkanethiol with an equivalent alkyl chain was prepared to determine whether dilution of the azide-reactive site on the SAM surface could provide comparable results to our bidentate SAMs. Overall, the collected data demonstrate the advantages of the aromatic bidentate adsorbate and its potential to form effective platforms for surface attachments via click reactions.

Keywords: Self-Assembled Monolayer (SAMs), Click Reaction, Maleimide Linker, Aromatic Dithiol Adsorbate, Poly-L-Lysine, Mixed-SAMs.



COLL 535

Toward understanding electronic and optical properties of colloidal germanium nanocrystals as a function of size and surface ligand

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Fundamental knowledge of size dependent properties of nanocrystals (NCs) is crucial for their application. Our interests lie in expanding synthetic size control and surface functionalization of colloidal Ge NCs. The work presented here focuses on the characterization of solution-based, microwave-synthesized Ge NCs with amine and thiol ligands. Cyclic voltammetry was used to determine the valence band energy based on the oxidation potential as a function of size for amine terminated NCs. NIR-UV-vis spectroscopy was used to investigate bandgap energy changes with different surface ligands. The optical gaps followed the expected trend for quantum confinement, however the absolute value depended on the ligand. For the size range considered, it is shown that the size of the NCs has less of an effect on the properties than the surface ligand employed.

COLL 536

Model for the phase transfer of nanoparticles using ionic surfactants

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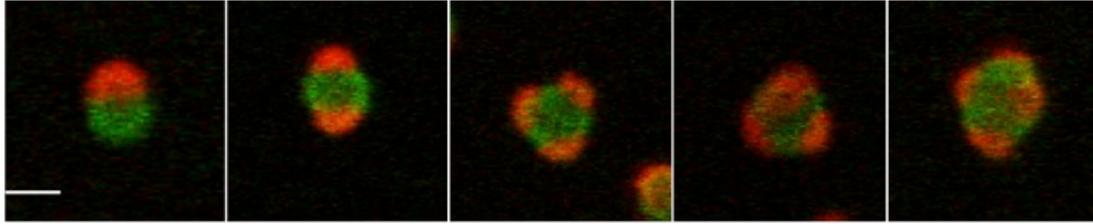
Ionic surfactants are widely used for the phase transfer of nanoparticles from aqueous to organic phases, however a model that can be used to select ionic surfactants based on the nanoparticle solution properties has yet to be established. Here, we have studied the phase transfer of a variety of nanoparticles and have identified hydrophobicity, steric repulsion, and interfacial tension as key factors in determining whether or not phase transfer will occur. Based on these studies, we have developed a simple model for phase transfer wherein the success of the surfactant depends only on three criteria. The phase transfer agents must (i) efficiently load onto or cross the interface, (ii) solubilize the nanoparticles in the receiving phase, and (iii) sterically stabilize the nanoparticles to prevent aggregation due to van der Waals forces between the inorganic cores. Using these criteria, the effectiveness of ionic surfactants could be predicted based on their molecular geometry and the properties of the nanoparticle solutions. These rules provide a basis for choosing surfactants for phase transfer of spherical nanoparticles up to 16 nm in diameter and advances the development of a general model of nanoparticle phase transfer, which would include all nanoparticle shapes, sizes and solvents.

COLL 537

Orthogonal functionalization of patchy particles

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Colloids with chemical distinct and precisely located patches, so called “patchy particles”, are expected to be useful for the construction of open structured colloidal architecture. However, most synthetic pathways only generate mono-functionality lying on patches so far, which limit their more sophisticated potential applications, such as artificial self-replicating colloids. Patch particles bearing dual functionalities both on patches and matrixes are achieved. By attaching two orthogonal DNAs on each part, spatial and temporal controlled self-assembly are demonstrated. And the patch particles can behavior two-stage assembly/melting when tuning the length of “stick end” on patches and matrixes.

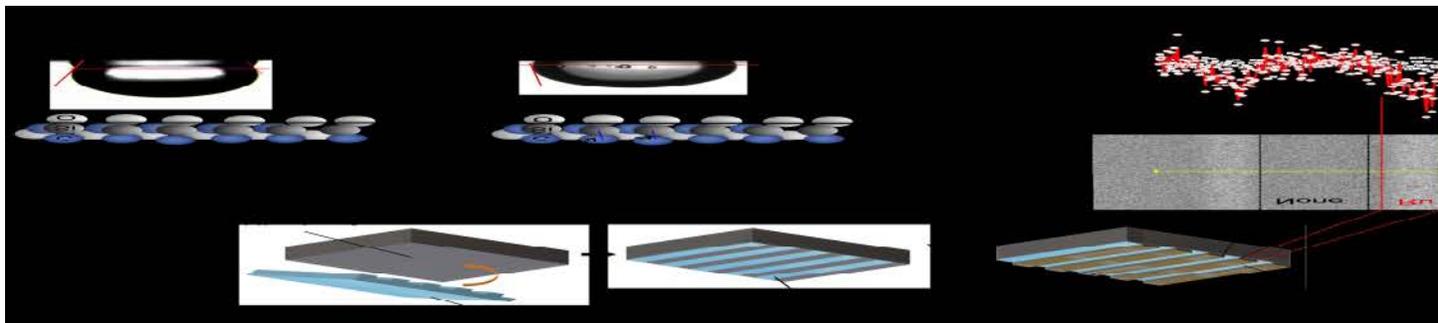


COLL 538

Strong hydrophobizer: Laterally chemisorbed low-molecular-weight polydimethylsiloxane

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Techniques to make a surface hydrophobic have been widely developed for various applications, such as self-cleaning, anti-frosting, and condensation heat transfer enhancement. In particular, the self-assembled silane agent, which consists of a non-polar functional group and a long alkyl-chain spacer, is primarily used to chemically modify surfaces to make them hydrophobic. However, this silane agent is not robust because of thermal and chemical instability of the alkyl chain, which remains a challenge for its practical use under harsh environmental conditions. Here, we introduce a siloxane chain-based hydrophobizer that exhibits superior thermal and chemical stability compared to the conventional hydrophobizing silane agent under conditions of over 300°C and pH 2-13. To demonstrate the capability of the siloxane chain-based hydrophobizer to serve as a highly robust chemical surface modifier, we present two applications: the formation of fine metal nanoparticles with a narrow size distribution by thermal dewetting of a metal thin film and the selective deposition of a ruthenium thin film by atomic layer deposition, which required robust hydrophobicity even up to 300°C.



COLL 539

Elucidating structure/property relationships of peptide-decorated Au nanoparticles using advanced molecular simulations

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The ability to exploit the structure-function relationship of peptide-decorated metal nanoparticles (NPs) in aqueous solutions offers a promising method for the production of catalytically active nanomaterials with controllable functionality.¹ Experimental studies are able to determine the structure of the NPs as well as investigating their catalytic ability.^{1,2} However, establishing clear connections between the structure of the adsorbed peptide overlayer and the catalytic performance of these systems, under aqueous conditions, via experimental techniques is challenging. Recent studies have highlighted the ability of molecular simulation to provide valuable information about the behavior of materials binding peptides at the aqueous interfaces of inorganic substrates.^{3,4} However, the majority of these studies have investigated the structure of peptides at planar surfaces or with ideal faceted NPs rather than surfaces that possess irregularities at the nanoscale. In contrast, recent experimental evidence shows that using peptides to cap the growth of metal NPs can lead to NPs that possess irregular surface features.² By employing Hamiltonian replica-exchange molecular dynamics (H-REMD) simulations⁵ the structure(s) of overlayers of multiple peptides adsorbed on the surface of AuNPs, with irregular surface features, have been predicted under aqueous conditions. Ten different peptide/AuNP systems have been investigated, allowing connections between the structure and catalytic behavior of the different systems to be elucidated.

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COLL 540

Optical signatures of crystal phase in semiconductor nanocrystals

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Semiconductor nanocrystals (NCs) have recently been employed as emitters and absorbers for a broad range of applications spanning bioimaging, solar energy conversion, and optoelectronic devices. A major challenge impeding their further development is the difficulty in characterizing their crystalline structure when the domain sizes are small and when the crystals are polytypic or defective. Conventional crystal structure determination using powder X-ray diffraction (XRD) provides poorly defined diffraction signals, and processing is low-throughput due to the requirement of large quantities of highly pure material. Here we report optical signatures of crystal phase in II-VI NCs and demonstrate the utility in determining the phase of NCs in solution using absorption spectroscopy. Both *ab initio* calculations and experimental measurements confirm that CdSe NCs with two different crystal phases, wurtzite (WZ) and zinc-blende (ZB), exhibit crystal phase-specific absorption features (E_1) at energies much higher than the bandgap energy (E_0). E_1 transitions enable unambiguous crystal phase identification in very small NCs (~2 nm in diameter) for which XRD patterns provide vague phase information. Moreover E_1 transition features allow the prediction of polytypic NC structures based on absorption spectra by differential contributions of both WZ and ZB phases. These insights can lead to the development of a simple, accurate, and high-throughput structural characterization methodology in liquid suspension for NCs compatible with continuous readout.

COLL 541

Shape controlled narrow-gap tin chalcogenide nanostructures

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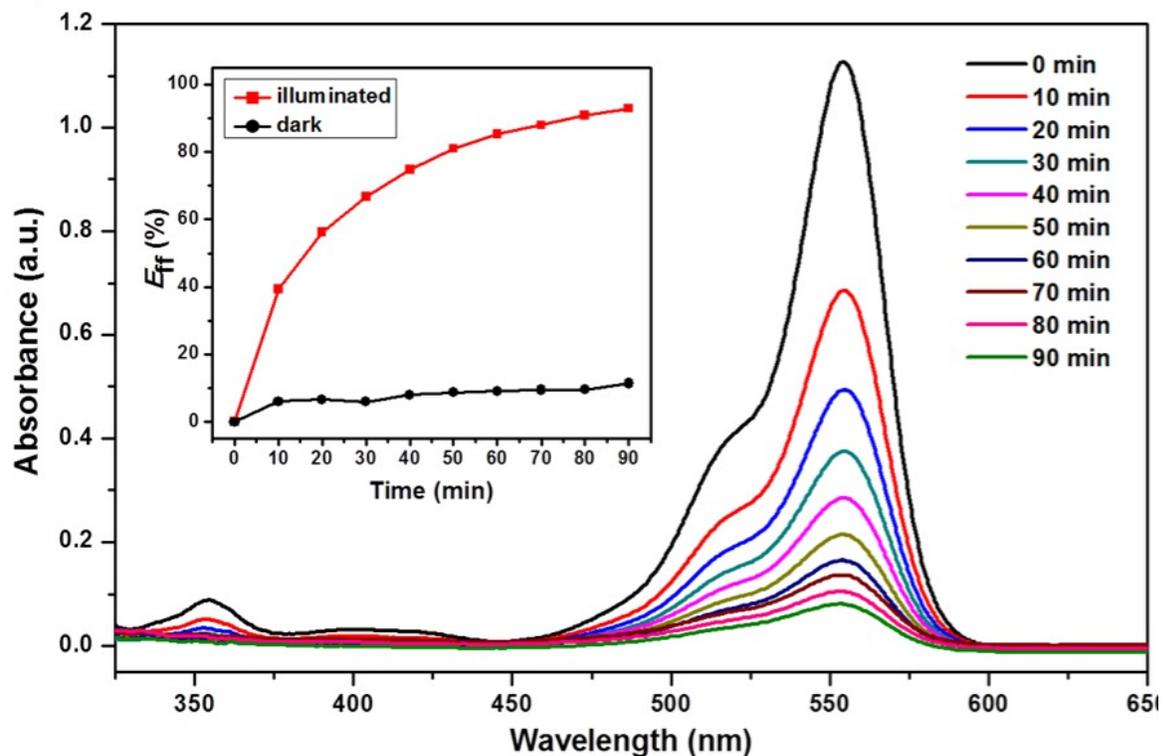
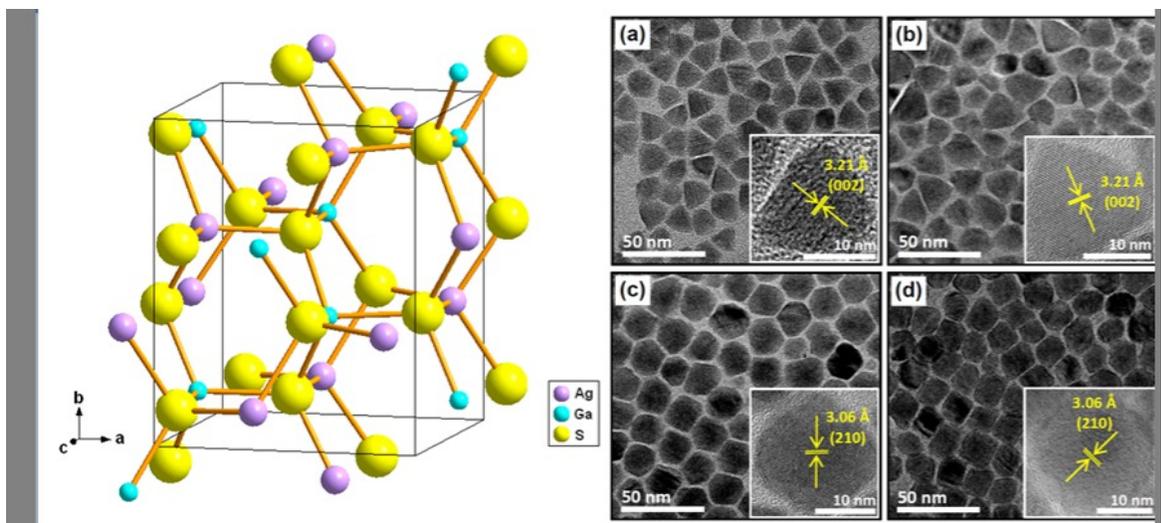
The rational design and synthesis of narrow-gap colloidal semiconductor nanocrystals (NCs) may be the key to the development of photovoltaics, photodetectors and thermoelectrics with advanced performance. SnTe is particularly attractive as Pb- and Hg-free semiconductors with a direct band gap of 0.18 eV. Initial efforts to synthesize SnTe NCs have succeeded only in producing monodisperse spherical SnTe NCs with no report of further shape control. In this talk, I will show our recent progress on use of a solution-phase synthesis strategy for achieving SnTe nanocubes. In addition to the synthesis, the spectroscopy and preliminary field-effect transistor performance of these materials will be also discussed.

COLL 542

Colloidal synthesis and photocatalytic properties of orthorhombic AgGaS₂ nanocrystals

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Ternary I–III–VI₂ semiconductors (where I = Cu, Ag; III = Ga, In, VI = S, Se) have been gaining considerable interest in nanoscale research primarily due to their band structures, which are suitable for light-harvesting and light-emitting applications. While a great deal of attention has been given to the Cu-based systems, there are relatively few reports on their Ag-based counterparts. Much of the studies have been limited to AgInS₂ (AIS), which has been known to exist in the tetragonal and orthorhombic form. Meanwhile, AgGaS₂ (AGS), an attractive material for optoelectronics and photocatalytic applications, is not as well-explored. Unlike in the case of AIS, the orthorhombic phase has never been previously observed for AGS. Using a simple non-injection colloidal synthetic approach, we present the first successful synthesis of AGS nanocrystals that have the wurtzite-derived orthorhombic crystal structure. The synthetic strategy involves the co-thermal decomposition of Ag(I) and Ga(III) dithiocarbamates in suitable coordinating solvents. It was found that the formation of the orthorhombic polymorph of AGS can be promoted with the use of long-chain alkanethiols and primary alkylamines as coordinating solvents. Using the crystallographic data for orthorhombic AIS as reference, we have carried out Rietveld analysis of our diffraction data and determined the lattice parameters for orthorhombic AGS. From optical absorption data, we have determined the band gap of orthorhombic AGS to be ~2.7 eV, which lies in the visible spectrum. The photocatalytic potential of the orthorhombic AGS nanocrystals for organic dye degradation was investigated under visible-light illumination. We have found that 93% of RhB dye molecules could be degraded within 90 min, demonstrating the effectiveness of orthorhombic AGS nanocrystals as a visible-light-responsive photocatalyst. **References:** Chem. Commun., **2014**, 50, 7128–7131.



COLL 543

Careful control of confinement potential and interfacial lattice strain in colloidal quantum dots to improve radiative recombination and fluorescence blinking

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Adding shells onto core colloidal quantum dots (QDs) is a widely-used method to increase their photoluminescence quantum yield. However, choosing the shell composition and thickness is not trivial, since both the band-edge energy offset and interfacial lattice strain play roles in influencing the fluorescence properties at the ensemble and single-particle level. Using a shell material with a high band-edge energy offset better confines the charge carriers to the core, but such a material usually has a large lattice mismatch to the core and balancing these two effects is non-trivial. Multiple combinations of multi-shells and gradient-alloyed shells have been reported, but a comprehensive model of how the different combination of material affect charge carrier recombination dynamics through wavefunction overlap and trap states is not yet available. We have used a systematic approach of controlling the thicknesses of multi-shells or gradient-alloyed shells onto CdSe, CdTe and CuInS₂ cores and analyzed the radiative and non-radiative recombination rates as well as fluorescence blinking. We have found that the relationship between the ensemble radiative rates (leading to changes in ensemble quantum yield) and the blinking rates is not always correlated. This suggests multiple mechanisms underlying blinking that are individually affected by confinement potential and interfacial trap states. We discuss physical models of wavefunction overlap and charge-carrier trapping at the various interfaces in order to controllably-synthesize QDs with specific properties tailored to specific applications.

COLL 544

Size characterization and alternative synthesis of monolayer-protected quantum dots

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Water-soluble, monolayer-protected quantum dots (QDs) were synthesized using several water-soluble thiols and alternative metal salts (e.g., cadmium acetate, zinc sulfate). QDs were synthesized at temperatures as low as -55 °C in attempts to control the growth of the nanoparticles. The optical properties of QD solutions were characterized using UV-visible and fluorescence spectroscopies. The hydrodynamic radius of the QDs was determined using pulsed field gradient (PFG) NMR. The diffusion coefficient of the nanoparticles, in concert with a small reference molecule, was determined using PFG-NMR. For reference, the diffusion coefficient of a redox-active molecule was calculated using cyclic voltammetry. Subsequently, the size of the nanoparticles was calculated using a modified version of the Stokes-Einstein equation. This work is funded, in part, by the National Science Foundation (CHE-1126231).

COLL 545

Excited state dynamics in doped quantum dots

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Better understanding of the excited state dynamics in doped quantum dots will play a crucial role in improving the efficiencies of next-generation electronic devices such as solar cells and LEDs. Doping ZnSe quantum dots with manganese (Mn^{2+}) or copper (Cu^+) to alter the emission color provides an ideal system to study the electron transfer from conduction band energy levels to dopant energy levels using transient absorption (TA) spectroscopy. Introducing Mn^{2+} or Cu^+ into ZnSe increases the rate of electron relaxation in the conduction band levels compared to undoped ZnSe. Transient absorption measurements also indicate that “nucleation doping” and “band doping” lead to significantly different excited state dynamics in ZnSe: Mn^{2+} QDs. The rapid rates of electron transfer to dopant atoms increase the emission stability of the quantum dots when exposed to air and light.

COLL 546

Investigating interactions between CdSe nanocrystals and dithiocarbamate ligands in solution

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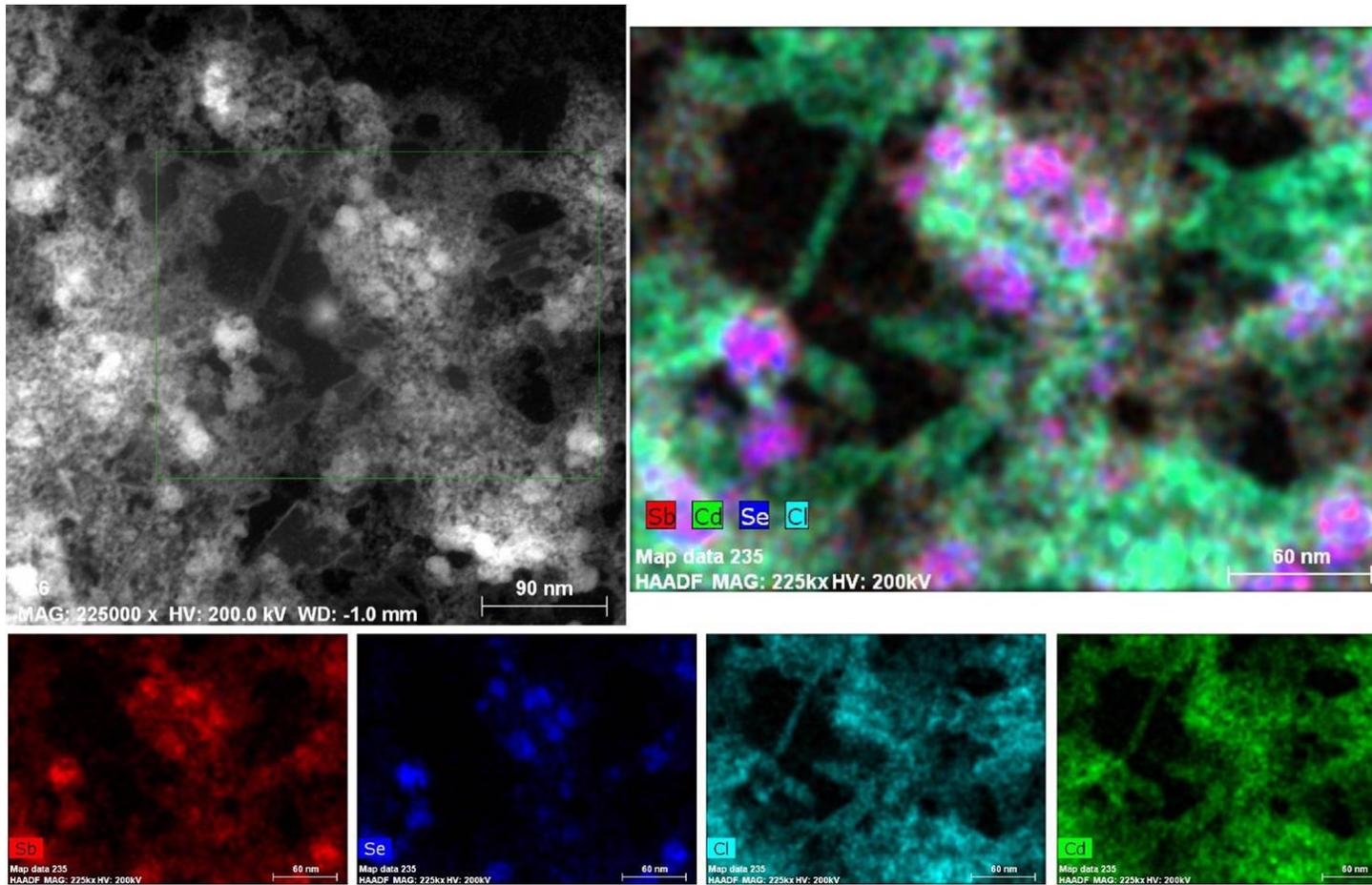
Studies have shown that the addition of dithiocarbamate molecules to films of CdSe nanocrystals can increase the nanocrystal band gap and can increase film conductivity. These reports indicate that studying the interactions between dithiocarbamate derivatives and CdSe nanocrystals may help increase the efficiency of nanocrystal based electronic devices. Previous studies of these ligands have primarily examined the effects of ammonium dithiocarbamate molecules on nanocrystal films, because colloidal nanocrystals precipitate when ammonium dithiocarbamate molecules are added to nanocrystal solutions. To address this issue we have synthesized dithiocarbamate molecules using a bulkier cation (1,1,3,3-tetramethylguanidinium (TMG⁺)) following synthetic methods from the literature. We report that when TMG⁺ dithiocarbamates are added to solutions of colloidal nanocrystals, that the nanocrystals remain soluble in chloroform and that we still observe red-shifting of the nanocrystal band gap for spherical nanocrystals. This allows us to investigate the interactions between dithiocarbamate ligands and colloidal CdSe nanocrystals in solution as well as in nanocrystal films. We investigate the effects of TMG⁺ 3,5-dimethylphenyldithiocarbamate on CdSe nanocrystals by characterizing nanocrystal solutions with absorbance, photoluminescence, and NMR spectroscopy and electrochemical cyclic voltammetry.

COLL 547

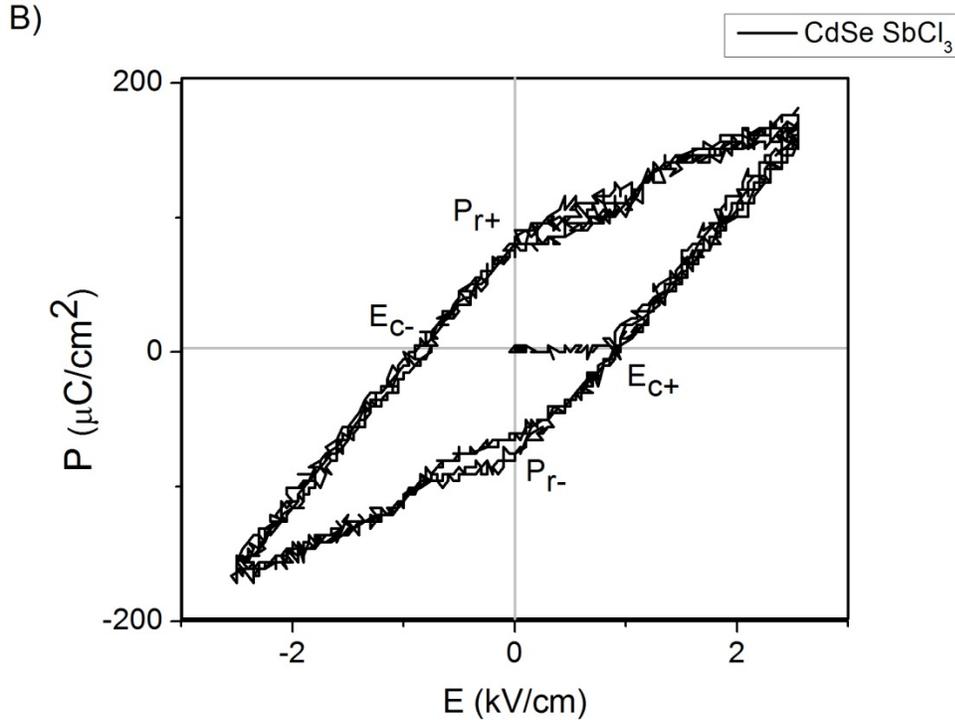
Characterization of the transformation of colloidal CdSe quantum dots into ferroelectric particles

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Ferroelectric particles were generated through a simple, room-temperature treatment of colloidal CdSe quantum dots with SbCl₃. STEM-EDS, XRD, ATR-IR, and TGA are utilized to observe changes in surface stabilization, elemental composition, and d-spacing of lattice planes to ascertain the nature of the reaction steps. Correlation of the observed chemical and physical changes with ferroelectric polarization elucidates the probable sources of the ferroelectric property.



STEM-EDS of CdSe quantum dots treated with SbCl₃



Hysteretic polarization response of CdSe quantum dots treated with SbCl_3

COLL 548

Formation of 1D-nanostructures using surface-directed vapor-liquid-solid growth process

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The classic epitaxial thin film growth has been utilized in its super confined form in the metal-catalyzed Vapor-Liquid-Solid (VLS) process where the metal catalyst acts as a material concentrator resulting in a rapid and localized nanocrystal growth at a specific site. As an extension of this approach, previously, we as well as others demonstrated the surface-directed VLS growth of nanowires, which results in horizontal growth of nanowires on a single crystal substrate [1-3]. In this presentation we discuss interactions of Au catalyst droplet on different III-V semiconductor substrates to grow different 1D-nanostructures including nanowires. Results also are presented on epitaxial relationship between the epilayer and the underlying substrate; however, despite what is observed in the non-VLS lateral growth of nanowires, here we show that the nanowire growth direction is orthogonal to the lattice match direction. We also demonstrate a rare example of Au droplet reaction with the semiconductor surfaces that results in volatile reaction products rendering formation of oriented assemblies of inverted nanowires.

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COLL 549

Electric field-directed nanowire assembly

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Ordered particle arrays are sought after for applications including electronics, optics, and solar cells. Innovation will require complex functional structures that are difficult to achieve with current methods. Understanding the mechanisms of particle assembly will enable spatial control and organization necessary for the development of functional arrays. Here, a hybrid top-down/bottom-up approach to particle assembly is presented. Interparticle and particle-field interactions were investigated using multi-component nanowires assembled in AC electric fields. By varying metal composition and/or selective etching of metal segments, we synthesized a variety of particle types. Control of the field profile was enabled through a lithographically patterned electrode geometry that facilitated the concentration of nanowires by funneling them towards regions of high field strength. Dielectric forces were manipulated through frequency and voltage variation, organizing nanowires parallel to the field lines within the electrode gap. Typically, the nanowires assembled into a structure that spanned the entire electrode gap. Electric field-directed assembly is especially useful for annealing structures by cycling the field on and off. Annealing allows individual particles to sample multiple interparticle interactions with varying van der Waals forces, settling into the most stable configuration. We took advantage of the reconfigurable nature of this system to produce ordered, particle-dense structures. This dynamic system could be further investigated for use as a rapidly configurable material.

COLL 550

Designing a super-assembly using mixed biological and synthetic nanostructures

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Exploiting selective and programmable interactions at nanometer scale is important to increased understanding of many cellular processes and for the development of controlled assembly of functional nano- and micro-materials for potential applications in life- and materials sciences. Native Tobacco Mosaic Virus (TMV), a non-encased virion labeled with biotin (Bt) on its surface were trapped within the lipid bilayer of liposomes during self-assembling process of the liposomes. A new super-assembled hierarchical structure resulted from interactions between Bt-TMV-liposomes with a partially blocked streptavidin (SA). $-(\text{Bt-TMV-Liposome-SA})_n-$ polymeric configurations were obtained where SA provides a microscopic hinge between liposomes. As proof for TMV insertion into self assembled liposomes, TMV was removed from bilayer after sequential addition of phenol and enzymatic cleavage using trypsin that increased bilayer fluidity thereby releasing self-quenched calcein fluorescent marker kept within the aqueous cavity of the liposomes. UV-Vis and anisotropy fluorescence spectroscopy indicated local structural changes at the interface between TMV and lipid bilayer of liposomes. Fluorescent anisotropy (FA) provided quantitative information of Bt-TMV trapped within lipid bilayer of liposomes. SEM, TEM, and fluorescence spectral imaging confirmed the formation of super-assembled hinged assembly. Overall, $-(\text{Bt-TMV-Liposome-SA})_n-$ assemblies may provide useful structural information for potentially important for designing biocompatible super-hierarchical materials.

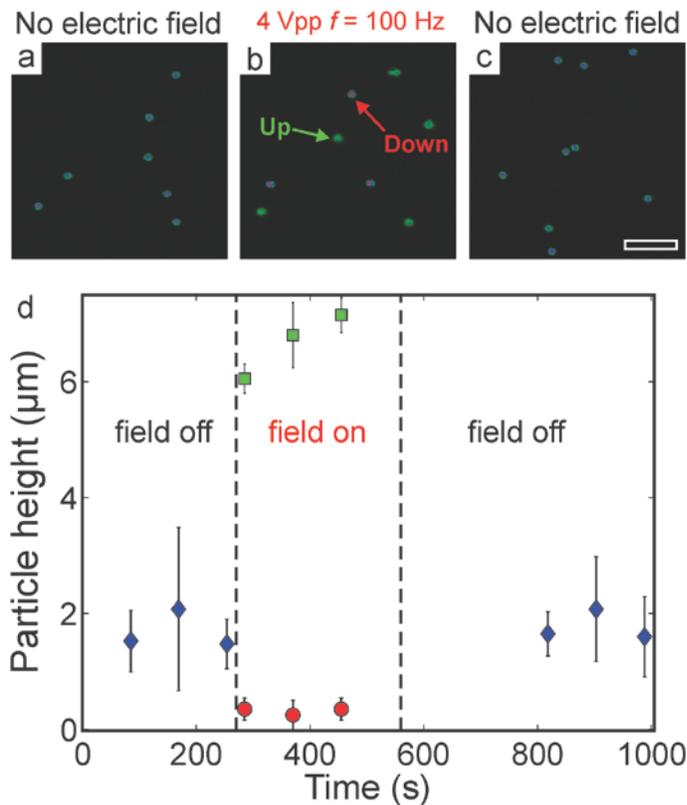
COLL 551

Bifurcation in the equilibrium height of colloidal particles near an electrode in oscillatory electric fields

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Application of an oscillatory electric field is known to alter the equilibrium separation distance between micron-scale colloidal particles and an adjacent electrode. This behavior is believed to be partially due to a lift force caused by electrohydrodynamic (EHD) flow generated around each particle, with previous work focused on identifying a single equilibrium height of the individual particles over the electrode. Here we report the existence of a pronounced bifurcation in the equilibrium particle height in response to low frequency electric fields. Optical and confocal microscopy observations reveal that application of a ~ 100 Hz field induces some of the particles to rapidly move several particle diameters up from the electrode, while the others move closer to the electrode. The fraction of particles that exhibit this "extreme levitation" increases with increased applied potential and decreased frequency, in a fashion qualitatively consistent with an energy landscape predicated on competition between EHD flow, colloidal interactions,

and gravity. Taken together, the results provide evidence for the existence of a deep tertiary minimum in the electrode-particle interaction potential at a surprisingly large distance from the electrode.



Representative confocal microscopy images of the particle height bifurcation exhibited by 2 μm particles in NaOH. (a) Prior to application of the field, the particles are all in the same focal plane adjacent to the electrode. (b) 30 seconds after applying the electric field the particles have moved to two distinct focal planes. Particles with red centers are approximately in focus, bright green particles are several microns above the electrode. (c) Five minutes after the field is removed, the particles have moved back to their original focal plane. The scale bar in (c) is 10 μm. (d) Electrode-to-surface particle heights extracted from confocal microscopy z-scans.

COLL 552

Self-assembly of colloidal nanoparticles into chiral ribbons and hollow capsules

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We discuss our atomistic and coarse-grained simulations of colloidal nanoparticles self-assembled into complex superstructures, which were observed in recent experiments. We study the formation of chiral superstructures formed by 1) superparamagnetic magnetite nanocubes self-assembled in magnetic fields, and 2) chiral CdS (truncated

tetrahedra) nanoparticles self-assembled in the presence of circularly polarized light. We also model the formation of hollow nanoparticle-based capsules with their sizes dependent on the parameters of the solution. We show how the parameters that control the self-assembly processes of these unique systems.

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COLL 553

Self-assembly of nanometer scaled macroions in dilute solution

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Hydrophilic macroions, with sizes ranging between simple ions (point charges valid for the Debye-Hückel Theory) and colloidal suspensions (usually described by the DLVO theory), demonstrate unique solution behavior by self-assembling into ordered, single layer, hollow, spherical “blackberry” structures. Counterion-mediated attraction is considered as the main driving force for the self-assembly behavior.

Herein, we investigated the solution behavior of ionic polyhedral oligomeric silsesquioxane (POSS) and cyclodextrin (CD) which have well-defined size, shape, mass, and charge density using laser light scattering (LLS). Sub-nanometer sized ionic POSS provides a valuable opportunity to explore the unknown size boundary between simple ions and macroions. Whereas studying ionic CD, a simple biomolecule-based macroion, expands our understanding beyond inorganic macroion. We found the transition from single macroions to blackberries, as well as the sizes of blackberries, can be achieved by adjusting the parameters such as the macroionic charge density, solvent polarity, or adding extra electrolytes.

Understanding the solution behaviors of macroions is of great significance in polymer, biology, and many other fields of science, since polyelectrolytes and biomacromolecules are all complex macroions.

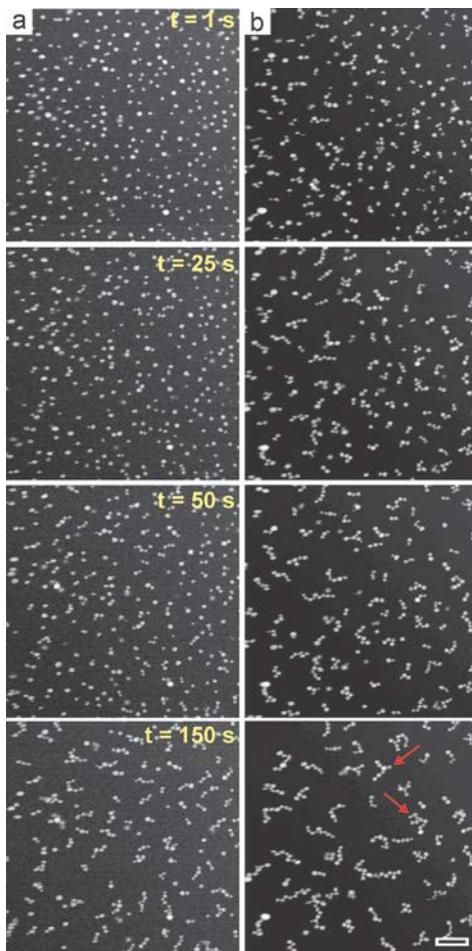
COLL 554

Direct nanoscale visualization of the kinetics of colloidal gold nanoparticle chain assembly

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Various types of colloidal nanoparticles are known to self-assemble into hierarchical mesostructures *via* anisotropic interparticle interactions. Previous modeling and experiments have suggested that dipolar and/or electrostatic interactions may be responsible for assembly of one dimensional nanoparticle chain structures; however,

due to a lack of *in situ* observations little is known about the kinetics of the self-assembly. Here we use real-time nanoscale observations to measure the self-assembly kinetics of colloidal gold nanoparticles into one dimensional chains. Gold nanoparticles suspended in acetate buffer were observed *in situ* liquid electron microscopy to self-assemble into chains of up to 20 nanoparticles over a time of minutes. Self-assembly was initiated upon irradiation of the nanoparticles with the imaging electron beam. Measurements of the self-assembly kinetics revealed that the chains formed *via* second order aggregation kinetics during the first tens of seconds. We investigate the effects of the electron beam current on the effective aggregation rate and chain formation mechanism, and find that the aggregation rate increases linearly with beam current. Our observations suggest that the increase in aggregation rate with beam current is due to an increase in the effective diffusivity of the nanoparticles.



Time-lapsed series of *in situ* liquid cell dark field scanning transmission electron microscopy images showing assembly of gold nanoparticle chains over 150 s at beam currents of (a) 107 pA and (b) 634 pA. The scale bar in the final panel of (b) is 200 nm. Red arrow denote the formation of branched structures during the most rapid self-assembly conditions.

COLL 555

Biomimetic hydrogel microparticles for controlled local presentation of extracellular matrix proteins to pancreatic β -cells

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Pancreatic islets are one of the most important multicellular aggregates in which cell-cell contact and the interaction of cells with extracellular matrix (ECM) proteins are important for regulating many cellular functions. In such aggregates, the interactions of cells with ECM proteins are crucial at the periphery of the clusters as well as throughout them. In this work, local presentation of ECM proteins throughout multicellular aggregates was achieved using biomimetic soft hydrogel microparticles that were modified with immobilized cell-cell communication cues such as Eph-A5 and Ephrin-A5. Furthermore, the surface of microparticles was functionalized with ECM components by the assembling of biocompatible layer-by-layer nanofilms.

MIN6 cell, a pancreatic β -cell line was cultured with different types of biomimetic hydrogel microparticles. It was observed that the survival and glucose responsiveness of MIN6 cells were dependent on the following properties of multilayer nanofilm coatings on the surface of microparticles: 1) the thickness of nanometer sized multilayers, 2) the polymer species of LbL nanofilms, and 3) the nature of the outer layer of LbL nanofilms. Furthermore, multiple ECM protein combinations were presented to β -cells in concert by incorporating different population of microparticles throughout the aggregates.

The results of this study demonstrated that components, charge and mechanical properties of LbL nanofilms prepared on hydrogel microparticles strongly affected cell functions, and the effect of these LbL nanofilms on cell functions differed vastly as compared to LbL films prepared on flat hydrogel surfaces. Controlling the bulk and surface properties of microparticles synergistically increased the survival and insulin production of β -cells. Therefore, three-dimensional presentation of ECM proteins using LbL nanofilms on hydrogel microparticles could be a novel and unique technique for making tunable biomaterial interfaces to control cell behaviors.

COLL 556

Magnetoactive hydrogels for dynamic modulation of pro-angiogenic signaling from mesenchymal stem cells

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Patient derived mesenchymal stem cells (MSCs) are a promising cell-based autologous therapy for cardiovascular diseases due to dynamic secretion of pro-angiogenic molecules following implantation. However, the efficacy during clinical trials has proven variable. In our laboratory we have noted a gradual loss of the multipotent phenotype during expansion on tissue culture plastic. Recently we showed how extracellular matrix stiffness and composition has a significant influence on the MSC secretome and its pro-

angiogenic properties. In this presentation we will demonstrate a dynamic magnetically-tunable hydrogel that can stiffen in response to permanent magnets for ex vivo culture of MSCs. Hydrogels were fabricated to contain chemically functionalized magnetic iron particles embedded in a polyacrylamide matrix. Matrix protein was covalently immobilized on the surface of the gels followed by MSC culture and 'switching' between soft and stiff conditions. MSC spread area increased in response to the magnetic field and this effect was reversible. Conditioned media from the MSC cultures were used in a functional angiogenesis assay that employs human microvascular endothelial cells (hMVECs) within 3D matrigel. Conditioned media from MSCs cultured under a magnetic field showed higher angiogenic potential than those cultured without a magnetic field. These novel magnetoactive hydrogels may prove a useful tool for controlling the microenvironment of cells ex vivo prior to implantation for cell-based therapies.

COLL 557

Monodisperse polymeric ionic liquid microgels by post modifications and their versatile biomedical applications

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Monodisperse poly(2-vinyl pyridine-co-N-isopropylacrylamide) (p(2-VP-co-NIPAM)), Poly(2-vinyl pyridine-co-glycidyl methacrylate) (p(2-VP-co-GMA)), poly(4-vinyl pyridine-co-N-isopropylacrylamide) (p(4-VP-co-NIPAM)) and poly(4-vinyl pyridine-co-glycidyl methacrylate) (p(4-VP-co-GMA)) microgel was synthesized via surfactant free polymerization technique in the argon atmosphere. The prepared mono disperse particles were exposed to chemical modification reactions by using bromo/dibromo alkanes as modifying agents with various lengths (C_n , $n = 4, 6$ and 8) to prepare polymeric ionic liquids (PILs) particles of p(2-VP-co-NIPAM)⁺, p(2-VP-co-GMA)⁺, p(4-VP-co-NIPAM)⁺, p(4-VP-co-GMA)⁺ microgels [1-3]. Furthermore, the p(2-VP-co-GMA)⁺ and p(4-VP-co-GMA)⁺ microgels containing epoxy groups were further exposed to post modification by using various chemical reagents such as NaOH, NH₄OH and so on. The prepared microgels were characterized by SEM, DLS and Zeta potential measurements, and FT-IR spectroscopy for visualization, size and surface charges and structural analysis. Also, the all microgels were tested for antimicrobial properties against bacteria such as *Staphylococcus aureus* ATCC 6538, *Escherichia coli* ATCC 8739, *Bacillus subtilis* ATCC 6633 and *Pseudomonas aeruginosa* ATCC 10145. The potential use of these microgel as drug delivery vehicles, and biological molecule separation for biomedical application were investigated [4,5].

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COLL 558

Supercooled water in nanoconfinement: Molecular simulation study of single-molecule and collective dynamics

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Liquids in nanoscopic confinement freeze at temperatures much lower than the normal freezing temperature of bulk liquids. This presentation will focus on our molecular simulation results for the structure and dynamics of supercooled water confined in approximately cylindrical pores with diameters ranging from 20 to 40 Å. The primary focus of our work is on porous amorphous silica, resembling MCM-41 materials. We have calculated and analyzed the self-intermediate scattering function (ISF) of water hydrogens, the observable in quasi-elastic neutron scattering (QENS) and the collective polarizability anisotropy time correlation, measured in optical Kerr effect (OKE). We characterized the effects of the temperature and reduced molecular translational and rotational mobility in the layers near the interface on both single-molecule and collective dynamics of water.

COLL 559

Ionic liquids and water: the surprising connection

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Since ionic liquids (ILs) are composed solely of ions, theories of diffuse electric double layers are typically presumed to be inapplicable for modeling their electrostatic screening properties. In this work, we use temperature-dependent, force-distance

measurements to demonstrate that the electric double layers formed by ILs can exhibit a near surface regime featuring a pronounced layering of ions that is in series with a longer range, exponentially decaying diffuse double layer regime. Increasing the temperature decreased the measured diffuse layer decay lengths, whereas colloidal interactions that are purely entropic or osmotic in nature will increase in range at higher temperatures. Thus, outside of strongly surface bound ion layers, ILs can be conceptualized as dilute electrolyte solutions, where only a small fraction of the IL ions thermally dissociate to behave as effectively free, diffuse layer ions, while the remaining ions behave as a highly correlated dielectric medium. This framework is analogous to the autoionization of pure water. Our results resolve several scientific paradoxes concerning ILs, and provide a general, molecular-scale framework that may guide the design of high or ultra-low conductivity ILs for energy storage applications.