

COLL 1

Structuring materials through droplet templating

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This talk will describe methods to create new structures using emulsion drops as templates. By making very small drops in a continuous fluid that is a gas, it is feasible to create a new class of spray drier which produces nanometer-scale particles of a very wide range of materials. If these nanoparticles are small enough, their structure can remain amorphous even if the material has a strong propensity to form crystals. In addition, the talk will describe method to create new types of vesicle-like structures using multiple-emulsion templates

COLL 2

Behaviors of thermotropic liquid crystals 'caged' inside partially filled polymer capsules

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Microscale droplets of thermotropic liquid crystals (LCs) suspended in aqueous media (e.g., LC-in-water emulsions) respond sensitively to the presence of contaminating amphiphiles and thus provide promising platforms for the development of new classes of colloidal droplet-based sensors. We have developed new approaches to the encapsulation of microscale LC droplets in partially filled polymer capsules (so-called 'caged' LCs) that introduce several new properties and droplet behaviors and expand the potential utility of LC droplet-based sensors. These 'caged' LC droplets can undergo rapid and diagnostic changes in shape, rotational mobility, and optical appearance upon the addition of amphiphiles to surrounding aqueous media, including many useful changes in these features that cannot be attained using freely-suspended or surface-adsorbed LC droplets. The polymer 'cages' also provide means to immobilize LC droplets on surfaces, including the surfaces of living mammalian cells, without impacting optical appearance or diagnostic responses to contaminating amphiphiles. These advances have enabled the design of new LC droplet-based arrays and the deployment of these responsive materials in complex biological environments (including the insides of living mammalian cells) to report rapidly, and in real time, on the presence of analytes and toxins in extracellular environments. Recent results in each of these new areas will be discussed.

COLL 3

Thermoresponsive nanoemulsions: Quenchable colloids through molecular self-assembly

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The suspension microstructure and rheology of polymer-colloid mixtures is critical to their performance in a wide range of formulated products. However, because colloidal interactions in these systems arise from mixing, there is often little opportunity to dynamically control their properties. We have recently developed nanoemulsions whose polymer-droplet and droplet-droplet interactions can be finely tuned with temperature through molecular self-assembly, enabling their dynamic colloidal assembly into structures ranging from associative transient polymer networks to arrested colloidal gels. In particular, they show potential as a new class of colloids whose microstructure and properties can be tailored using thermal quenching and annealing strategies, similar to what is already done for biphasic metals, ceramics and polymers. In this talk, I will show how the thermoresponsive properties of these nanoemulsions both make them model systems to understand the rheology of colloidal suspensions and gels, as well as provide new routes for creating hierarchically structured materials.

COLL 4

Photoinduced demulsification and two findings from the study

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This paper reports on the influence of light irradiation on stability of emulsions prepared using a photoresponsive gemini surfactant (**C₇-azo-C₇**) having an azobenzene skeleton as a spacer. When mixtures of *trans* **C₇-azo-C₇** aqueous solution and *n*-octane are homogenized, stable emulsions are obtained in a specific region of weight fraction and surfactant concentration. UV irradiation of stable O/W emulsions promotes the *cis* isomerization of *trans* **C₇-azo-C₇** and leads to the coalescence of the oil (octane) droplets in the emulsions, i.e., demulsification. The occupied area per molecule for **C₇-azo-C₇** at octane/water interface decreases with the *cis* photoisomerization of *trans* isomer. Dynamic interfacial tension measurement shows that UV irradiation to the interface between aqueous *trans* **C₇-azo-C₇** solution and octane brings about an increase in the interfacial tension, indicating that the Gibbs free energy at the interface increases. From these results, the *cis* isomerization of *trans* **C₇-azo-C₇** molecules at the O/W interface due to UV irradiation leads to direct contact between the water and octane phases, because of the reduction of molecular area at the interface, and subsequently makes the emulsions demulsified.

In the course of the research, we have found that the synthetic intermediate (**DN-azo**) of **C₇-azo-C₇** forms gold-colored plate-like crystals. The thin film obtained by accumulating the crystals has a maximum specular reflectance of ca. 15% for visible light. UV-vis measurements show that the molecules in the crystal produce J-aggregates. Furthermore, XRD measurements estimate the long-range *d*-spacing for the crystal as 1.51 nm. These results indicate that the azobenzene moieties are oriented diagonally

against the crystal surfaces. The gold-colored crystals may be useful as a substitute for conventional metallic pigments in specific coating applications.

COLL 5

Complex emulsions as stimuli-responsive soft materials

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Invited Talk delivered on behalf of Professor Daniel Blankschtein

Emulsification is a powerful age-old technique for mixing and dispersing immiscible components within a continuous liquid phase. Consequently, emulsions are central components of medicine, food, and performance materials. Complex emulsions, including multiple emulsions and Janus droplets, are of increasing importance in pharmaceuticals and medical diagnostics, in the fabrication of microparticles and capsules for food, in chemical separations, for cosmetics, and for dynamic optics. As complex emulsion properties and functions are related to the droplet geometry and composition, the development of rapid and facile fabrication approaches allowing precise control over the droplets' physical and chemical characteristics is critical. Significant advances in the fabrication of complex emulsions have been accomplished by a number of procedures, ranging from large-scale less precise techniques that give compositional heterogeneity using high-shear mixers and membranes to small-volume microfluidic methods. However, such approaches have yet to create droplet morphologies that can be controllably altered after emulsification. Reconfigurable complex liquids potentially have greatly expanded utility as dynamically tunable materials.

Using theories of interfacial energetics, we have modeled the interplay between interfacial tensions during the one-step fabrication of three- and four-phase complex emulsions displaying highly controllable and reconfigurable morphologies. The fabrication makes use of the temperature-sensitive miscibility of hydrocarbon, silicone, and fluorocarbon liquids and is applied to both microfluidic and scalable batch production of complex droplets. We demonstrate that droplet geometries can be alternated between encapsulated and Janus configurations via variations in interfacial tensions as controlled with hydrocarbon and fluorinated surfactants including stimuli-responsive and cleavable surfactants. Therefore, we have discovered a generalizable strategy for the fabrication of multiphase emulsions with controllably reconfigurable morphologies to create a diversity of responsive materials.

COLL 6

Benzoic acid penetration of surfactant interfaces in the context of *Mycobacterium tuberculosis*

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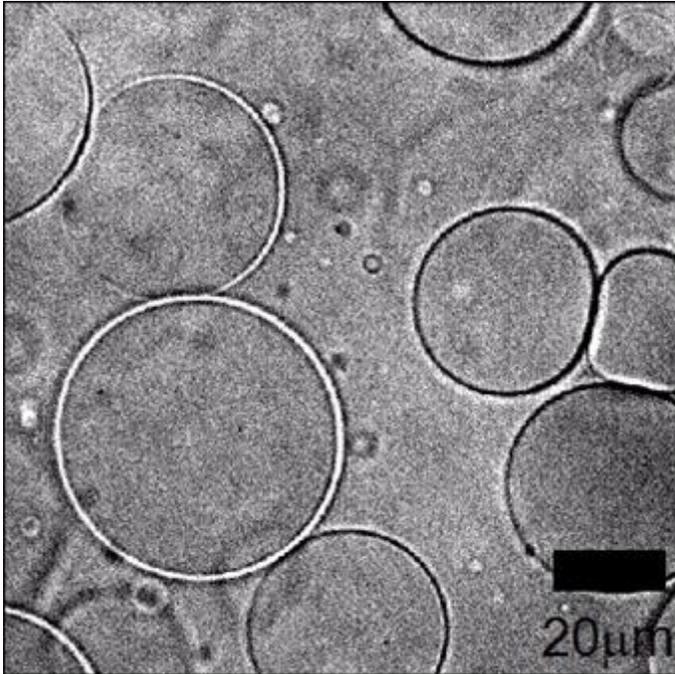
Membrane penetration is a critical event for a drug to have a desired therapeutic effect. Penetration of a mycobacterial membrane can be especially difficult due to its thick and waxy outer coating. The mycobacterial membrane and the rise in multi-drug resistance are two major reasons why tuberculosis is still an issue today. As a first line drug, pyrazinamide has been shown to have a pH dependent effect on *mycobacterium tuberculosis* and in a similar way, benzoic acid does as well. Both pyrazinamide and benzoic acid were able to dissipate the proton motive force across a membrane. To explore the pH dependence and ability of benzoic acid to dissipate the proton motive force across a membrane, two model membranes were employed. The first model membrane employed was the reverse micelle. With the combination of ^1H , ^1H - ^1H NOESY NMR and altering the AOT reverse micelle sizes, we were able to determine the penetration ability of benzoic acid at a water-surfactant interface. Langmuir monolayers were also used to evaluate the effects of benzoic acid on a membrane and when these two methodologies are used in conjunction, it was possible to determine how benzoic acid interacts with an interface modeling a membrane.

COLL 7

From thermal fluctuations to extreme mechanics of polymer vesicles

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Too little is understood from direct local measurement about local mechanical properties of membranes or (more generally) living cells. Here, we infer these properties from thermal fluctuations on the one hand, and extreme deformations on the other hand. Polymer vesicles ("polymersomes") composed of diblock copolymers (polyethylene oxide/polybutadiene) were prepared. Extreme mechanics was studied by direct imaging in a specially-designed microfluidic device. Thermal fluctuations were studied spotwise at different locations on the vesicles and power spectra were obtained over a wide frequency range, up to 50 kHz, which is more than 4 orders of magnitude, providing access to the bending modulus κ and the membrane tension, σ with surprising results.



COLL 8

Optimizing fluidity versus stability in planar supported and suspended lipid bilayers using mixtures of polymerizable and fluids lipids

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The use of phospholipid bilayers as platforms for biosensing applications and models for membrane protein studies have been developing fields for several decades. One of the major limitations with using such bilayer systems has been their fragility, specifically their susceptibility to chemical disruptions and mechanical shock; the latter is particularly problematic for black lipid membranes (BLMs). One strategy to address this issue is the use of polymerizable lipids, which have been shown to greatly increase the mechanical stability of BLMs. However, cross-linking decreases the fluidity of the bilayer and may limit the diffusion of transmembrane proteins, preventing subunit association or interactions with other transmembrane components. Using mixtures of polymerizable and non-polymerizable lipids offers an approach to maintain fluidity while achieving enhanced mechanical stability. This presentation will discuss studies of planar supported lipid bilayers (PSLBs) and BLMs composed of single lipids and lipid mixtures. Fluorescence recovery after photobleaching (FRAP) and atomic force microscopy (AFM) are being used to characterize lateral diffusion and phase segregation in PSLBs composed of polymerizable dienoyl lipids and non-polymerizable fluid lipids. The results show that the apparent fluidity of the bilayer can be tuned by adjusting the lipid ratio, and that phase segregation produces nanoscale-domains of fluid and polymerized

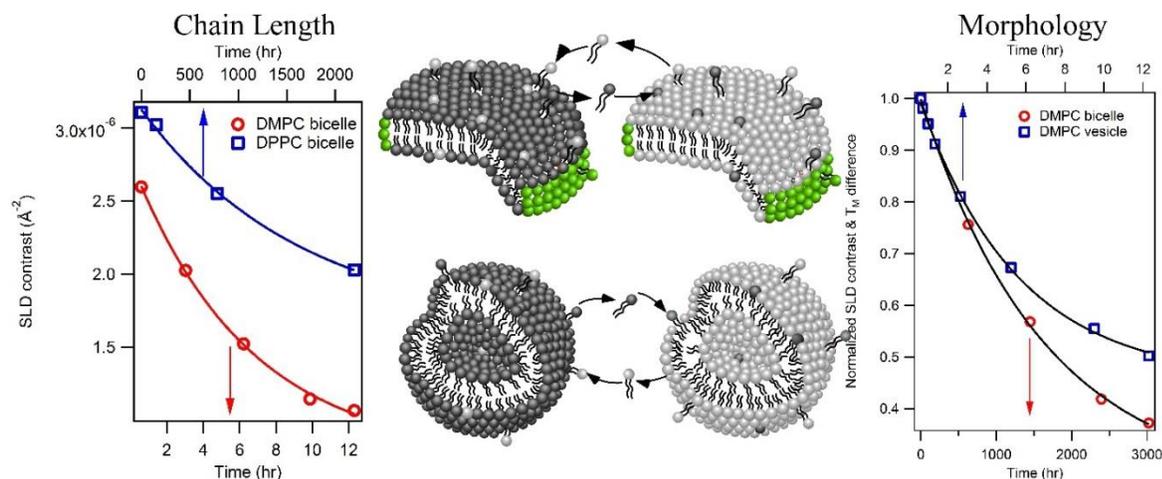
lipids. Results from studies of BLMs also will be presented. The results of these studies will inform the design of membrane-based biosensors that offer both a suitable environment for maintaining the activity of membrane proteins and the stability needed for a variety of sensing applications.

COLL 9

Spontaneous lipid transfer and its implication of membrane lateral organization and structural stability

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The spontaneous lipid transfer (SLT) rates are studied and found to be strongly related to the heterogeneity of the distribution of species on the bilayer. We obtained consistent SLT rates between vesicles (liposomes) and bicelles (nanodiscs, spontaneously forming in a long- and short- chain lipid mixture), respectively, using a variety of techniques differential scanning calorimetry, small angle neutron scattering and fluorescence cross spectroscopy. The obtained SLT rate between bicelles is at least two orders of magnitude faster than that of the same species between vesicles. This enhanced rate cannot be not completely explained by the slow flip-flop process that only occurs in vesicles and is most likely attributed to the reduction of the activation energy for the transfer process, taking place at the intermediate domains between the gel long-chain lipid phases. The SLT rate also increases with decreased long- to short- chain ratios, implying larger intermediate domains are forming in mixtures at higher short-chain compositions. Moreover, we have found that SLT rate does not directly correspond to the stability of the nanoparticles.



The lipid transfer rates of DMPC (di-C₁₄ Phosphatidylcholine) and DPPC (di-C₁₆PC) bicelles and DMPC vesicles, indicating strong dependence of morphology and acyl chain length.

COLL 10

Studying intracellular pathways of cationic liposome–nucleic acid nanoparticle assemblies with applications in gene delivery

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Cationic liposomes (CLs) are synthetic carriers of nucleic acids (NAs) for gene delivery and gene silencing therapeutics. The physicochemical characteristics of the CL lipids and membranes, and of their self-assemblies with NAs determine the nanostructures and delivery efficiencies of the assemblies. We have used custom synthesis of multivalent lipids and a range of PEG-lipids with attached targeting ligands and hydrolyzable moieties to study delivery mechanisms and barriers to efficient transfection. In recent work geared toward *in vivo* applications, we have focused on surface-functionalized PEGylated CL–DNA nanoparticles (NPs) optimized for cell targeting, uptake, or endosomal escape. Fluorescence microscopy colocalization experiments with members of the family of Rab GTPases shed light on NP pathways after endocytosis, e.g. directly revealing interactions with endosomal membranes. We expect the *in vitro* optimization of CL–DNA and CL–siRNA NPs with relevant primary cancer cells to impact the development of nucleic acid therapeutics.

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COLL 11

Confocal Raman microscopy for *in situ* characterization of hybrid supported phospholipid bilayers within individual C₁₈-functionalized chromatographic particles

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Measuring lipid-membrane partitioning of small molecules is critical to understanding drug-bilayer interactions. A model membrane for such studies has been developed where non-covalent interaction between a phospholipid and an n-alkane-modified surface produces a stable hybrid-bilayer membrane (HBM). Recently, HBMs have been adapted to C₁₈-modified porous silica for chromatographic retention studies where partitioning of some small-molecules are in agreement with vesicle bilayer partitioning. However, structure of the hybrid-bilayer within highly-curved pores of chromatographic silica has not been characterized.

To understand the structure of HBMs in chromatographic silica, we investigate formation and temperature-dependent structure of HBMs within C₁₈-modified porous-silica chromatographic particles using confocal Raman microscopy. Porous chromatographic silica provides a large surface area where 1,2-dimyristoyl-*sn*-glycero-3-phosphocholine (DMPC) forms a stable monolayer with covalently-bound C₁₈-chains. To explore HBM formation, DMPC adsorption was monitored as a function of time from 15% isopropanol. Self-modeling curve resolution (SMCR) analysis of the spectra indicates a four-component process: disordered phospholipid is initially adsorbed to the C₁₈ surface followed by an ordering step where phospholipid and C₁₈ acyl chains adopt trans conformations with increasing lipid coverage. As the solution is switched from isopropanol-water to pure water further acyl-chain ordering is observed accompanying elimination of isopropanol. DMPC surface coverage ($2.8 \pm 0.1 \mu\text{mol}/\text{m}^2$) was quantified by carbon analysis which agrees with relative Raman scattering from C₁₈ chains and the acyl chains of adsorbed DMPC. The corresponding phospholipid head group area ($61 \pm 3 \text{ \AA}^2$) is in close agreement with DMPC vesicles. By monitoring acyl chain conformation versus temperature, it was possible to observe the HBM main-phase transition which is broad and shifted to higher temperature than a DMPC vesicle, in agreement with differential scanning calorimetry (DSC) results. To understand the nature of HBM melting, Raman scattering from lipid acyl chains was resolved from C₁₈-chains through the use of deuterated DMPC. Raman and DSC measurements indicate HBMs within C₁₈ chromatographic particles are interdigitated and immobility of C₁₈-chains likely leads to the shift and broadening of hybrid-bilayer thermal phase transitions.

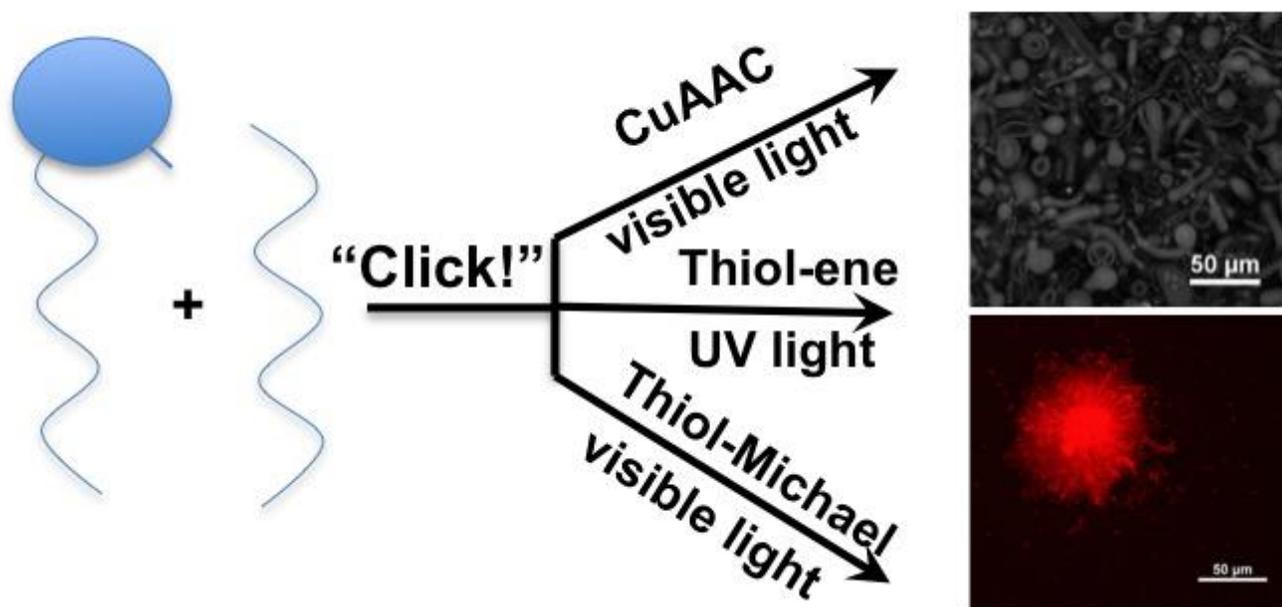
COLL 12

Photo-induced vesicle formation using "click" chemistries

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Since their characterization as enclosed membrane sacs, vesicles have garnered great attention in applications ranging from drug and cosmetic delivery to cell membrane dynamics studies as well as microreactors and artificial cells. In order to pursue these

goals, simple and highly controllable formation techniques become necessary. With this in mind, photo-induced micelle to vesicle transitions have been achieved through the use of a variety of “click” reactions. First, a visible light, radical generating photoinitiator was used to reduce copper (II) to copper (I), thereby catalyzing the Copper-catalyzed Azide-Alkyne Cycloaddition (CuAAC) reaction which has been used previously in the formation of vesicles through the addition of an azide functionalized, aliphatic tail to an alkyne functionalized lysolipid. Building upon this idea, new lysolipids were synthesized with either a thiol or a vinyl sulfone functionality. These new lipids could then undergo thiol-ene or thiol-Michael reactions to add appropriately functionalized aliphatic tails to the lysolipids upon exposure to visible light in conjunction with a photosensitizer and photo-base, UV light, or free base. This range in formation conditions greatly widens the ability to form vesicles in a simple, highly controllable manner while the range in chemistries opens up possibilities for specialized vesicles, responsive to multiple stimuli.



COLL 13

Renal clearable luminescent gold nanoparticles

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Inorganic nanoparticles have found broad applications in disease diagnosis and therapy; however, clinical translation of inorganic nanoparticles is still limited by their nonspecific and long-term accumulation in the body and potential health hazards. In this talk, we will discuss a class of renal clearable luminescent gold nanoparticles and their applications as contrast agents in fundamental understanding of how particle size, surface charge and hydrophobicity influence their renal clearance efficiencies, blood

retention and tumor targeting. Furthermore, their application in noninvasive kidney functional imaging will also be discussed.

COLL 14

Direct delivery of proteins and nucleic acids to the cytosol

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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. The direct access to the cytosol makes NPSCs effective tools for therapeutic delivery, particularly in conjunction with intracellular targeting as shown below for nuclear targeting. Applications and mechanistic studies of these vehicles will be discussed.

Figure 1. Cytosolar delivery of proteins coupled with nuclear targeting.

COLL 15

Enhancing tumor delivery and targeting with sub-5 nm ultrafine magnetic nanoparticles and anti-biofouling coating

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Nanomaterials are widely used for developing tumor targeted molecular imaging probes and drug delivery systems. The size and surface properties of nanoparticles are important factors controlling the biodistribution and effective delivery of theranostic nanoparticles to the disease tissue in vivo. Using magnetic resonance and optical imaging, we demonstrated that sub-5 nm ultrafine iron oxide nanoparticles (uIONPs, core size: 3 nm) have significantly high tumor tissue penetration and accumulation in the 4T1 breast cancer mouse model comparing to the nanoparticles with larger sizes (e.g., 10 or 20 nm core size). The advantages gained from reducing the core size are

attributed to that developed uIONPs facilitate enhance permeability and retention (EPR) effect that drives tumor specific delivery as they are highly dispersed in circulation for easy vascular extravasation and then undergo reversible self-clustering at pH below 7 to prevent re-entering the circulation after entering tumor interstitial space, evidenced by magnetic resonance imaging (MRI) contrast switching from bright T_1 contrast when uIONPs were in the blood to dark T_2 contrast when uIONP accumulated. Sub-5 nm uIONPs can be cleared from the body via both renal excretion and liver degradation, which can be observed in MRI. Furthermore, applying the anti-biofouling polymer for surface coating and functionalization significantly reduces the non-specific protein absorption on the surface of ligand-conjugated nanoparticles and interactions of the nanoparticles with non-targeted cells as well as uptake of nanoparticles by macrophages, all leading to improved biomarker targeting by protecting the affinity of the conjugated ligands and lowering off-target background interference and toxicity.

COLL 16

Nanolayered delivery for synergistic tumor therapies

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The layer-by-layer (LbL) approach toward construction of nanostructured nanoparticles provides multiple advantages for chemotherapy. We have generated LbL outer layers that provide effective stealth properties, with long systemic plasma blood half-lives and higher tumor accumulation over time. Modular layer-by-layer (LbL) nanoparticles can be engineered to “shed” or expand their nanoscale layers to release siRNA, alone or in combination with chemotherapy drugs, for effective tumor targeting. Furthermore, by creating highly controlled forms of layered polyelectrolyte complexes with the LbL approach, it is possible to control and minimize toxicity by limiting the amount and type of polycation used, while enhancing the loading of RNAi per particle and extending its rate of release. We have demonstrated efficacy in triple negative breast cancer, and most recently in genetically induced non-small cell lung cancer mouse models in which key siRNA targets have been selected with chemotherapy drug in the same nanoparticle system. By staging release of different drug components via the adaptation of the nanoparticle structure, we can achieve highly synergistic release behavior in these systems. In advanced ovarian cancer cell lines, we have optimized targeting of ovarian cancers and examined nanoparticle uptake for increased efficacy. Ongoing work that includes new ovarian cancer efforts utilizing siRNA and combination drug therapies will be discussed.

COLL 17

One-component nanomedicine

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One-component nanomedicine (OCN) represents an emerging class of therapeutic nanostructures that contain only one type of chemical substance. This one-component feature allows for fine-tuning and optimization of the drug loading and physicochemical properties of nanomedicine in a precise manner through molecular engineering of the underlying building blocks. Unlike traditional carrier-based nanomedicines that are inherently multicomponent systems, an OCN does not require the use of additional carriers and could itself possess desired physicochemical features for preferential accumulation at target sites. I present here our recent progress in the molecular design and fabrication strategies of OCN, and discuss the opportunities that this emerging platform could open for the new and improved treatment of devastating diseases.

COLL 18

Mageto-optical nanoparticles for ultrasensitive tumor imaging

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Nanoparticles in the 1-100 nm size range are of considerable current interest, not only because of their unique size-dependent properties but also their dimensional similarities with biological macromolecules (e.g., nucleic acids and proteins). These similarities could allow an integration of nanotechnology and biology, leading to major advances in medical diagnostics, prognostics, and targeted therapeutics. In this talk, I present recent development of multifunctional nanostructures for ultrasensitive detection of tumors in vivo.

COLL 19

Surface chemistry effect: Renal clearance and tumor targeting of NIR-emitting gold nanoparticles

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PEGylation and zwitterionization, two most popular surface chemistries used in minimizing protein adsorption and nonspecific liver uptake of nanoparticles, have distinct impacts on tumor targeting of luminescent gold nanoparticles (AuNPs) although both strategies render AuNPs effective renal clearance. High tumor-targeting efficiency and specificity were obtained with PEGylated AuNPs, whereas rapid tumor detection was more readily achieved with zwitterionic AuNPs, which is because two types of AuNPs are different in enhanced permeability and retention effect, normal-tissue

clearance and pharmacokinetics. These differences suggest that appropriate surface chemistries for nanoparticles should be rationally selected upon their exact applications in cancer diagnosis and therapy.

COLL 20

B-glucan/ODN carrier conjugated with TAT peptide: Specific delivery to cytosol

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Antisense-oligonucleotides (AS-ODNs) are not able to protect the bound ODN against degradation enzyme in biological fluids and be taken up by targeting cells. To solve these issues, the development of drug delivery systems to deliver AS-ODNs has been studied.

We have studied a polysaccharide schizophyllan (denoted by SPG), a member of β -glucans, as a delivery carrier of oligonucleotides. SPG can form a complex with polydeoxyadenosine (denoted by $dA_{\text{base numbers}}$) and prevents degradation by enzymes. We have reported that the complex comprising of SPG and the dA_{40} that was beforehand connected with AS-ODNs (AS-ODN- dA_{40}). The complex can deliver AS-ODNs to dectin-1-expressing cell and silence mRNA, then, eventually suppress protein expressions.

TAT peptide: human immunodeficiency virus type 1 protein fragments is known one of the major arginine-rich cell penetrating peptides. We prepared TAT peptide conjugate phosphorothioate dA_{40} oligonucleotide (denoted by TAT- dA_{40}) by the click chemistry reaction. The TAT- dA_{40} /AS-yb-1- dA_{40} /SPG complexes showed a higher cell uptake and more cell-growth suppression than AS-yb-1- dA_{40} /SPG complex that had not TAT. We suppose that this improvement can be ascribed to TAT-induced cellular ingestion of the complexes.

COLL 21

Ligand-protected gold superatoms and superatomic molecules

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Icosahedral gold cluster with 8 valence electrons, Au_{13}^{5+} , has been found as a stable core in ligand-protected Au clusters. Such a core can be viewed as “superatom” in which valence electrons confined within small particles occupy atomic-like, discrete electronic orbitals. Recent X-ray crystallographic studies demonstrated formation of a variety of dimeric structures of Au_{13}^{5+} via different bonding modes: a vertex-sharing Au_{25}^{9+} (16 e), face-sharing Au_{23}^{9+} (14 e) and non-sharing Au_{26}^{10+} (16 e). These examples suggest that one can artificially create a new class of molecules made of superatoms (superatomic molecules), which will serve as building blocks of novel

functional materials. The talk will introduce our recent efforts to elucidate the bonding nature of the gold superatoms and superatomic molecules and to synthesize these materials with novel electronic structures and morphologies.

COLL 22

Controlling colloidal gold nanoparticles with atomic precision: Fundamentals and opportunities

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Recent advances in colloidal gold nanoparticle research have led to atomically precise nanoparticles. A series of magic-sized $Au_n(SR)_m$ nanoparticles have been created, at least in the ultrasmall size range (below 3 nm). More importantly, significant progress has been attained in determining the total structures of size-specific $Au_n(SR)_m$ nanoparticles, ranging from $Au_{18}(SR)_{14}$ to $Au_{133}(SR)_{52}$. New structures have been discovered, such as the body-centered cubic 38-gold-atom nanoparticles, and structural isomization has been for the first time revealed. Such ultrasmall nanoparticles exhibit interesting electronic and optical properties with clear manifestations of strong quantum size effects. Correlation of the properties with structures offers deep understanding of the fundamentals of colloidal nanoparticles. These well-defined nanoparticles hold great potential in catalysis, energy conversion, optics and sensing applications.

COLL 23

Gold and silver in nanoscale, dispersed by ligands to molecular precision

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Nanometer-scale, ligand-stabilized noble metal clusters have emerged in recent years as a novel form of nanoscale matter with potential applications in molecular electronics, optics, sensing, drug delivery and biolabeling. Tremendous advances have been achieved in understanding their stability and structure due to contributions from synthetic work, X-ray crystallography and density functional theory computations. The general features of their electronic structure can be understood surprisingly well from the simple concepts that have been used in the related field of bare gas-phase metal clusters since 1980's, particularly from the so-called "superatom model" that accounts for the delocalized sp-electrons in the metal core. Forming in most cases the frontier orbitals of the cluster, these electrons are responsible for low-energy optical transitions and much of the chemistry. The organic ligand layer facilitates chemical functionality and imparts in many cases chirality. Some recent highlights in understanding the structure and properties of these novel nanomaterials composed of gold, silver, or their intermetallics are discussed, and a novel application for site-specific conjugation to enteroviruses for TEM imaging is demonstrated.

COLL 24

High-resolution separation of thiolate-protected gold clusters by reversed-phase high-performance liquid chromatography

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Thiolate (SR)-protected gold clusters ($Au_n(SR)_m$) have attracted much attention as building blocks of functional nanomaterials. Our group has been studying the high-resolution separation of $Au_n(SR)_m$ clusters using reversed-phase high-performance liquid chromatography. In this presentation, I talk our recent results on the separation of $Au_n(SR)_m$ clusters and their doped clusters according to the core size, charge state, ligand composition, and coordination isomer. Additionally, I talk new findings obtained by using high-resolution separation and future prospects for the separation of such types of metal clusters. We believe that the techniques and knowledge gained in this studies would contribute to the creation of $Au_n(SR)_m$ clusters with the desired functions and associated functional nanomaterials.

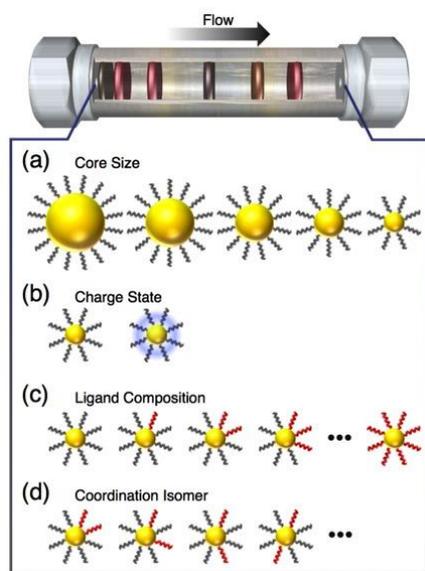


Fig. 1 High-resolution separation of $Au_n(SR)_m$ clusters based on the core size, charge state, ligand composition, and coordination isomer using RP-HPLC.

COLL 25

Comparative studies on ligand binding stability on Au(111) surface

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Self-assembled monolayers (SAMs) of organic ligands on gold have attracted lots of research interest in recent years. The protecting ligands are given many functions in

addition to their basic role as surface stabilizers, which in turn generate significant applications in the fields of electronics, sensing, drug delivery and nanotechnology. The classical coating ligands are sulfur-containing thiols, which has been widely studied and the Au-S interface structure has been well understood and characterized. Besides thiols, a lot of alternative ligands have been explored as stabilizers for gold, such as phosphines, amines, aryl radicals, as well as the recently discovered alkynyl groups and N-heterocyclic carbenes (NHCs), and new interfacial structures and functionalities have been reported. The ultimate utility of SAMs-derived gold nanosystems will be critically dependent on their stability. To our knowledge, however, there has been no systematic comparison between these ligands in terms of their bonding strength to gold. In this work, using Au(111) surface as the model system, we performed density functional theory (DFT) calculations to examine the bound stability of different classes of anchoring groups to the perfect and “adatom” Au(111) surface. Our results indicated that NHCs with bulkier substitutes and the terminal alkynes (e.g., phenylacetylene) form stronger bonds to gold as compared to thiols, phosphines or aryl radicals, while amines form the weakest bonding. The theoretical picture provided here will give enlightening insight for experimental peers in the future selection of the promising groups for any given application.

COLL 26

Controlling synthesis of atomic precision alloy nanoclusters and their structure related properties

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It has been known that alloyed nanoclusters can dramatically enhance the properties of homo-metal counterparts. The atomically precise doping in gold nanoclusters allows us to deeply understand nanocluster's physical and chemical properties, as well as to tailor the nanoclusters with new properties. Particularly, metal compositions, precise atom numbers, and metal doping site play important roles on revealing their new enhanced functions and application potentials. For example, the superior catalytic performance and optical properties of silver-gold bi-metallic nanoclusters over homometal nanoclusters have been proposed in recent years. Herein, we present the controlling synthesis of doping nanoclusters with atomic precision, and their structure related optical and catalytic properties.

COLL 27

What do you get when you cross a virus with a polymer?

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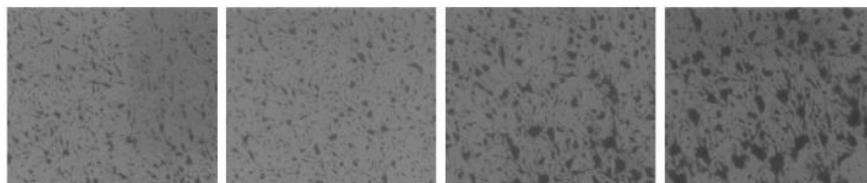
As near-monodisperse nanoscale objects, virus-like particles (VLPs) are attractive starting materials for the construction of a variety of higher-order materials. We have explored the marriage of VLPs with organic polymers in several ways, including entrainment in novel degradable materials, and graft-to or graft-from methods on both the exterior and interior of the particles. We have also attempted to modulate the catalytic activities of packaged enzymes with polymeric coatings. These studies will be described with illustrative examples of synthesis, characterization, and functional assays.

COLL 28

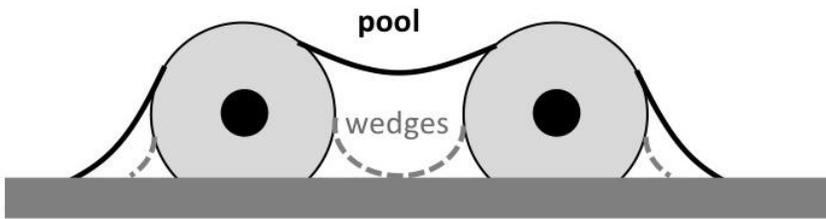
Water at the tobacco mosaic virus

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The interaction of water with viruses is key to understanding details of their structure and function. More important, for many virus infections, including epidemics, the presence or absence of water is crucial for transmission. Our first step towards understanding more complex virions is investigating the well-known Tobacco Mosaic Virus (TMV), which retains its shape even in vacuum. This allows studying wetting by water on the nanoscale on immobilized virions. Depending on the substrate (carbon, mica, oxidized silicon, gold) and on the humidity, we explore scenarios such as wet wedges, layers, droplets (on TMV), and water pools (confined by TMV). Our tools are environmental electron microscopy (SEM and STEM) in up to 10 mbar water vapor, and AFM (various modes) in humidified air at 1 bar. We found that most wetting processes are reversible, as expected from other experiments. The virions remained adsorbed even when completely covered by water. TMV is hydrophilic, as might be assumed from the many polar and ionic residues on its surface. However, we also found inhomogeneities, which can explain the unexpected observation of nanoscale droplets (as opposed to layers).



**Wetting of adsorbed virions, formation of water pools
(15 μm SEM images, 7.09 mbar water vapor, 2°C)**



**Wetting of adsorbed tubular virions:
Pools (>99% humidity) and wedges
of water. Side view along the viral axis.**

COLL 29

Protein-templated self-assembly of hierarchical nanoarchitectures

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Discrete nanoparticle (NP) ensembles have attracted increasing attention because of their distinct properties and potentials in fundamental researches and novel functionalities. Here we show the controllable assembling of three-dimensional hierarchical nanoarchitectures of quantum dots (QDs) and gold NPs (AuNPs) with mutated virus-based NPs (VNPs) as scaffolds by simultaneous use of their inside and outside space. QDs are first encapsulated into the icosahedral VNPs. Then AuNPs bind to the outside of the QD-containing VNPs (QD-VNPs) through interactions with rationally introduced semi-exposed cysteines on the VNP surface. By tuning the ratio of AuNPs to QD-VNPs, we have obtained a series of hybrid nanoarchitectures in high yields, in which there is one QD at the center surrounded by a tunable number of AuNPs. Surface plasmon resonance (SPR) coupling of AuNPs and fluorescence quenching of QDs by AuNP clusters were observed in these structures. The findings demonstrate that VNPs can be a robust platform to controllably organize nanomaterials. The diversity in structure and size and the feasibility in structural manipulation of VNPs make this strategy versatile for fabrication of various structures and devices.

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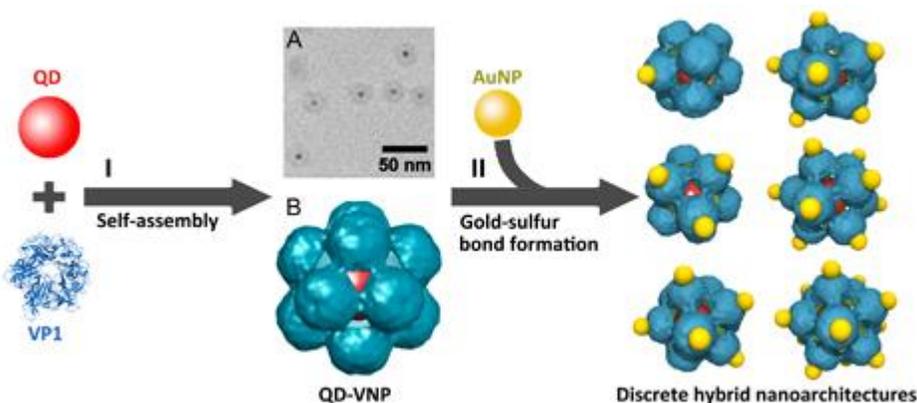
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COLL 30

Engineering virus-like nanotubes and rods

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Advances in nanotechnology offer significant improvements in a range of applications including, lightweight materials with greater strength, increased energy efficiency from electronic devices, and better sensors for a range of medical and environmental uses. However, these advances require the development of systems for the design, modeling, and synthesis of nanoscale materials. Interestingly, many biological molecules function on this scale and possess unique properties that impart the ability to assume defined conformations and assemblies as well as interact with specific chemical or biological substrates. Studies in our laboratory focus on the engineering of simple protein based nanorods and tubes derived from the structures of filamentous plant viruses. The uniform dimensions and known structures of filamentous viruses make them attractive templates for the defined assembly and display of functional groups used in materials science, sensor applications and vaccine development. However, active virus replication and recombination often result in the loss of engineered functional groups, limiting the usefulness of these viruses for such applications. To circumvent these limitations genetic modifications of selected negatively charged intersubunit carboxylate residues within the coat protein of *Tobacco mosaic virus* (TMV) were neutralized so as to stabilize the assembly of rod-shaped virus-like particles (VLPs) within a bacterial expression system. This system is genetically tractable and produces stable rod-shaped TMV-VLPs that can be used to display functional groups and peptides in a multiple configurations with potential applications in sensor, electrode and therapeutic

development. Specific studies have produced VLPs that display sensitive receptor peptides from both external and internal rod surfaces. These VLPs can also be programmed to self-assemble from their rod ends onto a variety of surfaces and substrates. Combined this VLP system increases the functionality of these rod-shaped nanoparticles while simplifying their production.

COLL 31

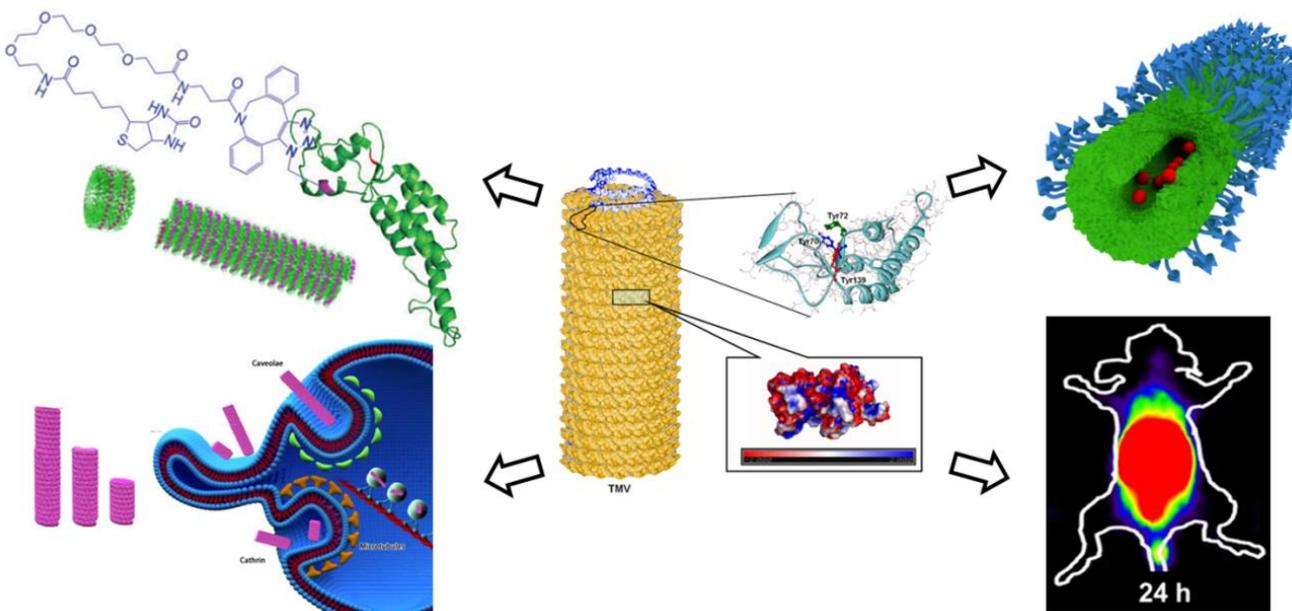
Rod-like plant virus: Functionalization, self-assembly, and bioapplications

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Viruses, although extremely simple in structure and composition, provide an ideal basis for tumor therapy due to their naturally evolved high efficiency in cellular transfection. Especially, plant viruses, showing no infection toward mammals, provide viable drug delivery platforms. Take tobacco mosaic virus (TMV) as research subject, we: a) established the method for site-specific and high yield modification of TMV coat protein utilizing genetic code expanding technology and copper free cycloaddition reaction, and built biotin-functionalized virus-like particles by self-assembly of the protein monomers; b) exploited a facile strategy to prepare rod-like TMV with different aspect ratio by sucrose density gradient centrifugation separation following ultrasonic treatment, and elucidated the effect of aspect ratio on the cellular internalization mechanism and in vivo biobehavior, completely discarding the influence of surface chemistry and diameter; c) constructed 1D tumor-targeted anti-cancer drug carrier by chemical conjugation, with comparable tumor inhibition to free drug while greatly reduced side effect on tumor bearing nude mice. It is anticipated that TMV and other plant virus will be further finely installed in biomedical applications.

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COLL 32

Dynamic assemblies of virus-like particles in solution and on surfaces

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Self-assembled viral protein cages like the cowpea chlorotic mottle virus (CCMV) are widely used in material sciences, medicine and catalysis. These particles are symmetrical and monodisperse, have the ability to encapsulate functional cargo and have been decorated with a variety of drugs, fluorescent dyes, polymers and carbohydrates. CCMV is an icosahedral plant virus consisting of 180 identical coat proteins that self-assemble around the viral RNA. The spherical capsid is 28 nm in diameter and has a Caspar and Klug triangulation number $T = 3$. A particularly interesting feature of CCMV, is its defined and reversible assembly behavior. Depending on pH and ionic strength, CCMV can disassemble into coat protein dimers and reassemble into non-infectious virus-like-particles (VLP). This makes it possible to use CCMV as an encapsulation vesicle.

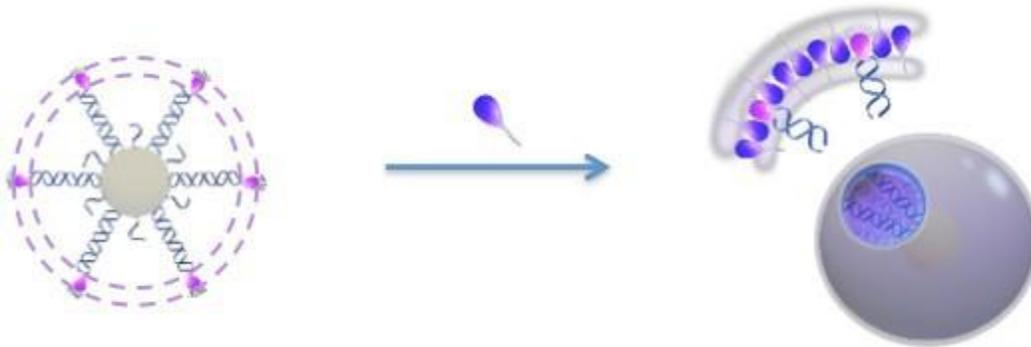
Here we report on the assembly of virus-like particles in defined clusters or hydrogels and the immobilization of CCMV on monolayers. The latter can be achieved *via* the formation of a heteroternary complex between curcubuteril, azobenzene and methyl viologen. To this end, the outer surface of CCMV was functionalized with alkyne moieties and post-functionalized *via* click chemistry with an azobenzene switch, resulting in the immobilization of the VLP's in a dynamic supramolecular fashion. The reported assembly methods may open new routes to study biologically relevant materials organized by multi-valent, dynamic interactions.

COLL 33

Frame-guided assembly

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How to precisely control the shape and size of final assemblies, especially using same amphiphilic molecules and under the same environmental conditions, is always a challenge in molecular assembly. Inspired by the cytoskeletal/membrane protein/lipid bilayer system that determines the shape of eukaryotic cells, we proposed and 'the Frame Guided Assembly' (FGA) strategy to prepare heterovesicles with programmed geometry and dimensions. This method offers greater control over self-assembly: with same molecular system, the size of final assemblies could be tuned at 1 nm level and their shape could vary from spherical to cubic, and even given sized two dimensional sheets. Most importantly, the principle of the FGA could be applied to various materials such as block copolymers, small molecules including surfactants and lipids, which is a general rule in self-assembly.



Scheme 1. Schematic illustration of the frame guided assembly

COLL 34

Degradation of colloids *in vitro* and *in vivo*

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Colloids are typically hybrids, comprising the actual colloidal particle, a surface coating, and a corona of adsorbed biological molecules from the environment. Degradation of the 3 distinct parts will be discussed.

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COLL 35

Biological interactions of layer-by-layer engineered particles

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The design and assembly of responsive materials underpins the development of particle carriers for biomedical applications. This presentation will detail various assembly strategies and chemistries to generate multifunctional and responsive particles. Recent studies on the development of nanostructured polymer particles for efficient cargo encapsulation, triggered release and antibody-mediated targeting will be highlighted. Examples on the application of these particles loaded with oligonucleotides and peptides to stimulate immune responses will be given. It will be shown that engineered particles with well-controlled physicochemical properties can be used to uncover several key principles that govern particle-cell interactions. For example, redox-responsive capsules associate with cells in a time-dependent manner, which is mediated by the exofacial thiols on cell membranes, and during endocytosis, the particles distort in shape and accumulate in lysosomal compartments. Furthermore, the role of shape of engineered particles on cellular interactions will be discussed. The assembly of organic ligands with metal ions will also be presented, highlighting metal-ligand complexation as a facile approach to generate particles that can disassemble under cellular conditions. It is expected that such engineered particle systems represent a class of novel materials for therapeutic delivery as well as an interesting paradigm to attain detailed knowledge of complex nano-bio interactions. This knowledge may aid in the rational design of nanoengineered materials (beyond particle systems) for biological applications.

COLL 36

Peptide-mediated cytosolic internalization of luminescent quantum dots

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Advancements in the synthesis of biocompatible nanocrystals offer a promising opportunity to develop platforms for use in molecular imaging and as diagnostic tools. A crucial criterion to successfully employ them in biology requires devising strategies to promote their intracellular uptake while circumventing endocytosis. We report on the use of a cationic anti-microbial peptide as means of promoting the cytosolic uptake of QDs. The peptide is synthesized with a terminal cysteine to allow conjugation onto amine-modified QDs. The QDs have been coated with metal-coordinating ligands. Using fluorescence imaging and flow cytometry we find that incubating cells with the QD-peptide leads to delivery into the cytoplasm without affecting the cellular morphology or viability. A homogeneous distribution of QD staining has been observed throughout the cytoplasm without co-localization with labelled endosomes. Furthermore, inhibition of endocytosis using incubation at 4°C or pre-treatment with inhibitors has shown minimal effects on the intracellular QD uptake.

COLL 37

Co-precipitation of SPIONs for stem cell tracking: How synthesis conditions affect particle properties, stem cell labelling, and MR contrast

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Superparamagnetic iron oxide nanoparticles (SPIONs) are widely used pre-clinically as contrast agents for stem cell tracking using magnetic resonance imaging (MRI). The total mass of iron oxide that can be internalised into cells without altering their viability or phenotype is an important criterion towards the generation of contrast, and SPIONs designed for efficient labelling of stem cells can allow an increased sensitivity of detection.

We have synthesised a series of cationic SPIONs with very similar hydrodynamic diameters and surface charges and report how subtle changes in the amount of polymer used in the co-precipitation synthesis can affect the core size and therefore modulate not only the magnetic properties of the SPIONs but also their uptake into stem cells. SPIONs with the largest core size presented the highest relaxivity and uptake into stem cells, significantly affecting the amount of contrast that can be generated. We explore how cell internalisation affects the relaxometric properties of SPIONs and how that can affect the imaging of SPION labelled stem cells. Physicochemical properties of SPIONs were characterised using DLS, zeta potential, UV-Vis, TGA, pXRD, magnetic resonance

and SQUID magnetometry. We also used magnetic separation to investigate how the size and surface charge of SPIONs can change after exposure to cell culture medium.

COLL 38

Multicompartmental particles for combined imaging and release

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Nanoparticles that are comprised of two distinct hemispheres have the potential to serve as simultaneous imaging and drug delivery modalities. The fact that these functions are separated within the nanoparticles allows for functional decoupling, i.e., the release can occur without affecting the ability to image the carrier particles. Specific examples will be presented that show combined imaging and delivery of SiRNA as well as small-molecule drugs.

COLL 39

Perfluorocarbon-loaded polymeric nanoparticles for cell tracking using multimodal *in vivo* imaging

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Cellular therapeutics show great promise for the treatment of immunogenic tumors, for example melanoma. In this context, long-term tracking and the quantification of therapeutic cells *in vivo* is essential to effectively optimize the therapy. Cell tracking with ultrasound is especially attractive, as it is an easy-to-use and cost-effective imaging modality. Moreover, using perfluorocarbon-based ultrasound contrast agents would allow for quantification of labeled cells with ¹⁹F MRI. However, most current ultrasound contrast agents, are not sufficiently stable over time and therefore not suitable for long-term imaging, and particularly cell tracking.

Aiming at development of contrast agents with prolonged stability, we investigated the encapsulation of selected perfluorocarbons (PFCs) into polymeric nanoparticles. We compared different polymers, including poly-D,L-lactide-co-glycolide, poly(ϵ -caprolactone) and poly(dimethylsiloxane) and their block-co-polymers. By changing different formulation parameters, we obtained contrast agents with varying efficiency, some of which were stable to ultrasound for at least several days.

We prepared nanoparticles through a combination of solvent evaporation and miniemulsion, modifying the diameter between 100-300 nm and labeled the particles with fluorophore during synthesis. We characterized the particles by electron microscopy, dynamic light scattering, X-ray scattering, fluorescence spectroscopy and

calorimetric methods. To study the ultrasound performance of our agents we carried out high-resolution ultrasound and compared different imaging phantoms. Furthermore, we quantified the amount of encapsulated PFC by ^{19}F NMR before and after ultrasound treatment. These results indicate that the structures of our contrast agents as well as the acoustic contrast generation mechanism are different from the structure of currently established microbubbles or phase-change nanodroplets. In particular, no gaseous or vaporizing component appears to be present.

To assess the ultrasound performance of our agents, we carried out ultrasound *in vitro* and *in vivo*, using particles or labeled therapeutic cells for injections. The results of ultrasound imaging were confirmed by ^{19}F MRI and fluorescence microscopy.

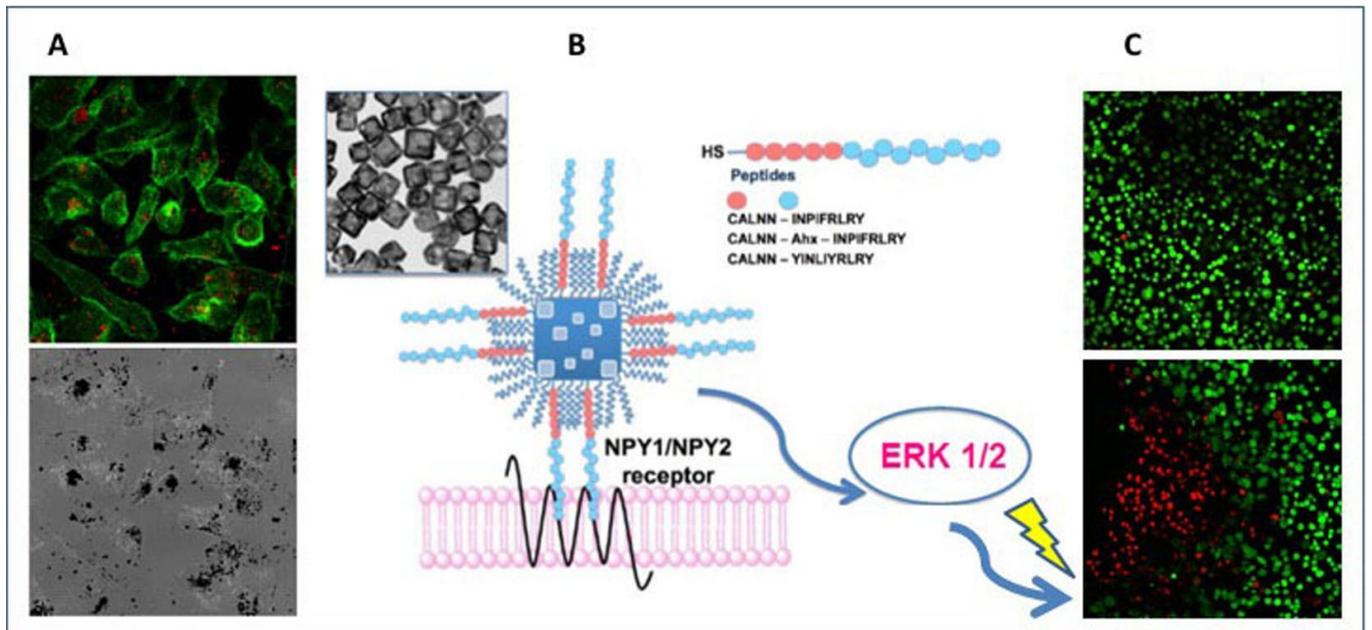
COLL 40

Gold nanocages for imaging and therapy of prostate cancer by active targeting of neuropeptide Y-receptor

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Gold nanocages (AuNCs) have been shown to be a useful tool both for imaging and hyperthermia therapy of cancer, thanks to their outstanding optical properties, low toxicity and facile functionalization with targeting molecules, including peptides and antibodies. Here, we use AuNCs for selective targeting of prostate cancer cells *via* specific interaction between neuropeptide Y (NPY) receptor and peptides conjugated to the AuNCs surface. Three different peptides derived from NPY have been synthesized *ad hoc* and covalently conjugated to AuNCs, giving stable nanoconjugates. UV-vis band of the nanoconjugates was set around 800 nm for subsequent hyperthermia experiments, which is particularly promising for next preclinical investigations. Long-term stability of nanoconjugates in different media has been confirmed both by UV-vis and DLS studies. Active NPY receptor targeting was observed by confocal microscopy showing large time-dependent AuNCs cellular uptake. Activation of ERK1/2 pathway has been evaluated by Western blot analysis to confirm specific interaction. Moreover, cellular uptake kinetics were compared as a function of peptide structure. Cytotoxicity of nanoconjugates has been evaluated by MTS and Annexin V assays, confirming their safety within the concentration range explored. Hyperthermia studies were carried out irradiating the cells, previously incubated with AuNCs, with a pulsed laser at 808 nm wavelength. Different laser power densities and irradiation times were used and the cellular viability was compared using both MTS assay and confocal microscopy. In particular, calcein AM/propidium iodide assay showed the presence of dead cells after 10 min irradiation at relatively low power density of 2.6 W/cm^2 . Caspase-3 and Annexin V assays has been used in order to understand the cell death mechanism by apoptosis

or necrosis. Moreover, ATP levels as indicator of cell viability was measured by ATP-bioluminescence assay. In summary, our peptide-NC conjugates proved to be an efficient theranostic nanosystem for targeted detection and activatable killing of prostate cancer cells.



A) Confocal microscopy images of PC-3 cells after 5 h incubation with Au-CALNNYINLIYRLRY-NCs; B) Schematic representation of peptide-AuNCs; C) Confocal microscopy images of PC3 cells incubated with Au-CALNNYINLIYRLRY-NCs and irradiated by 808 nm pulsed laser: control live cells (upper) and live/dead cells (lower). Staining: Calcein AM for live cells (green), propidium iodide for dead cells (red).

COLL 41

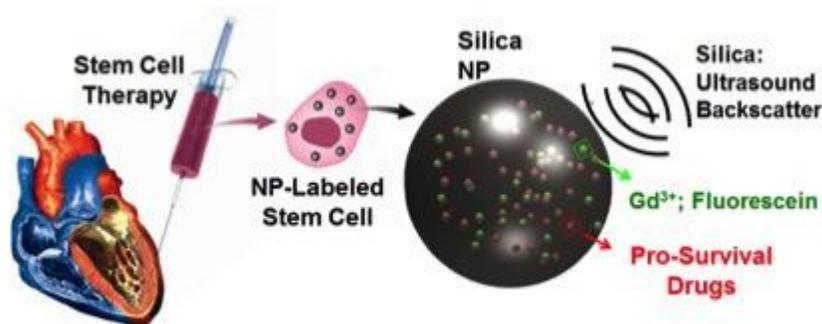
Mesoporous silica nanoparticles for ultrasound/magnetic resonance imaging and therapeutic drug delivery for stem cell therapy

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Increasing stem cell survival in vivo is an important challenge for the field of regenerative medicine. Strategies include both in vivo imaging and the co-injection of pro-survival agents to increase cell viability in these hypoxic environments. Here, we deploy mesoporous silica nanoparticles (MSNs) for theranostic imaging of mesenchymal stem cells. The nanoparticle offers real time ultrasound data to

understand the cell location and number in the treated region and to guide implantation into the peri-infarct zone and away from the most necrotic tissue. Chelated gadolinium provides T1-weighted MRI signal for high resolution follow-up. The MSN also provided sustained release of insulin-like growth factor (IGF) to increase cell survival. We could detect as few as 9000 cells with no cytotoxicity at the 250 $\mu\text{g}/\text{mL}$ concentration required for labeling. We also studied the degradation of the nanoparticles and showed that they experience interesting morphology changes and are completely cleared by three weeks. Finally, we showed that the IGF increased cell survival by 40% ($p < 0.05$) relative to MSN-free cells under serum-free tissue culture challenge.

Ref: Kempen et al. *Theranostics*, 2015. DOI: 10.7150/thno.11389



COLL 42

Direct measurement of the functionalization of metal oxide nanoparticles through radioanalytical methods

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In this work we have developed a method utilizing ^{14}C -labeled ligands which can quantitatively measure the concentration and ligand exchange rates of surface bound ligands on iron oxide nanoparticles. Ligand exchange is a common method for the modification of nanoparticles in which a sacrificial ligand is displaced with a competitive ligand. Such surface modification of nanomaterials represents one of the most prevalent methods to control the interface of these novel materials. Various factors, such as binding group chemistry and nanoparticle age, can influence the ligand exchange

reaction. To quantify the effects of these factors, we have produced radiolabeled (^{14}C -labeled) and unlabeled iron oxide nanoparticles via thermal decomposition. The presence of ^{14}C -labeled ligands was monitored using liquid scintillation counting (LSC), then the ratio of $^{12}\text{C}/^{14}\text{C}$ was used to estimate the total ligand behavior. Oleic acid on the surface of radiolabeled nanoparticles was challenged with small molecule ligands with catechol, phosphonate, sulfonate, thiol, carboxylic acid, or silane functional groups. Measurements indicated that the functionality of the end group has a strong effect on the amount of oleic acid remaining on the surface, with catechols displacing the highest amount of oleic acid. To quantify aging effects, unlabeled nanoparticles were exposed to free ^{14}C -oleic acid in solution after different periods of aging. Periodic measurements allowed for the determination of the effect of nanoparticle age on the exchange rate of oleic acid. Results showed an increase in exchange after approximately 8 hours of exposure.

COLL 43

Synthesis and optical characterization of cysteine- and cystine-coated metal nanoparticles

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A nanometer (nm) is one billionth of a meter (10^{-9}) and represents the collection of few molecules or atoms. At this scale (1-100 nm), the properties of materials become dependent on their size and shape and differ from their bulk or individual states. These deviations in behavior observed at the nanoscale are due to electron or quantum confinement, surface to volume ratios, and unique interfaces not present as size increases for a given material. The properties can be tuned by the size of a given structure and not the nature of the material itself. This allows for the possibilities of designing and building structures at the nanometer scale for a variety of applications.

Noble metal (copper - Cu, gold - Au and silver - Ag) nanoparticles (NPs) have size and shape dependent optical properties as well as strong absorption in the visible spectrum. Much of the interest in metal nanoparticles has involved Au and Ag as the metals. Au and Ag nanoparticle solutions are usually colored and as the size or shape of the nanoparticle changes, the observed color will also change. These unique size and shape dependent optical properties of are interest and can be characterized using spectroscopic techniques. The metal surfaces are also easily functionalized with a variety of substances including organic ligands with thiol groups that have an affinity to form metal-S bonds.

The Turkevich method is the traditional synthesis method for metal nanoparticles. This research explores the use of amino acid cysteine and cystine (dimer of two cysteine molecules) to not only synthesis metal nanoparticles, but also functionalize their surfaces. The procedures were optimized for use in biological systems and analyzed using optical methods such as UV-Vis and fluorescence spectroscopy.

COLL 44

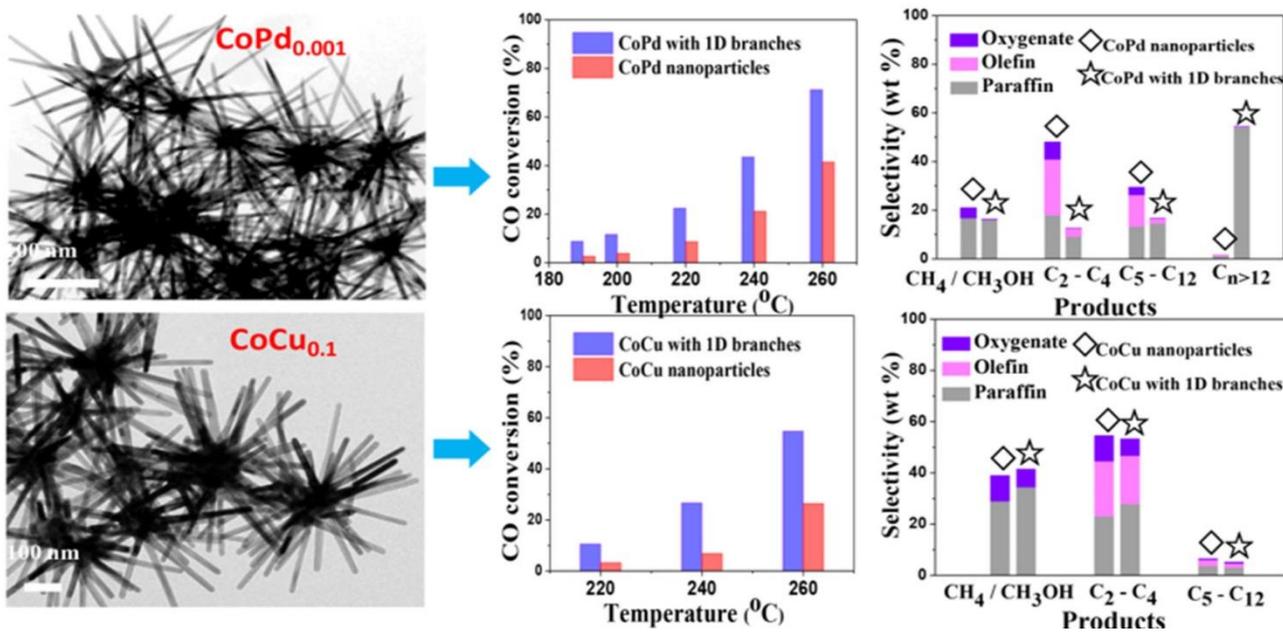
Synthesis of Co-based bimetallic nanocrystals with rod-like branches for selective hydrogenation of CO

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Co-based bimetallic nanocrystals with rod-like branches are synthesized by heterogeneous nucleation of Co atoms onto the pre-nucleated seeds such as Pd or Cu through a facile wet-chemical route. The peripheral branches (rod-like) of Co-Pd and Co-Cu nanocrystals outspread along (001) direction and are enclosed by (101) facets. By switching the pre-nucleated metals to form robust Co-Pd or Co-Cu bimetallic nanocatalysts, the selectivity of CO hydrogenation could be purposely adjusted towards heavy paraffins, light olefins or oxygenates. The Anderson-Schulz-Flory chain-lengthening probabilities for products are up to 0.9 over Co-Pd nanocrystals, showing that long-chain hydrocarbons can be formed with high selectivity using the targeted design of Co-Pd nanocrystal catalysts. These Co-based bimetallic nanocrystals with rod-like branches exhibit superior catalytic activities to the corresponding Co-based nanoparticles for synthesis gas conversion. Especially, Co-Pd nanocrystals with 1D branches favored carbon chain growth to obtain heavier hydrocarbons than those produced by CoPd nanoparticles, while Co-Cu nanocrystals with 1D branches showed a similar catalytic selectivity to CoCu nanoparticles for syngas conversion, indicating that the selectivity of syngas conversion is more sensitive to the structure of CoPd catalysts than that of CoCu.

Catalysts with 1D branches

Syngas conversion



Comparison of catalytic activity and product selectivity on Co-based catalysts.

COLL 45

Fluorescence properties of hybrid core-shell superparamagnetic Fe@C-CN_x nanoparticles

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Magnetic nanoparticles created tremendous interest in biological application for cancer treatment with targeted drug delivery and hyperthermia. Superparamagnetic materials based on iron oxides magnetic properties are strongly influenced by dispersion and particle size. Alternative materials having higher superparamagnetic properties such as iron carbides and carbon-coated Fe were explored. [1] The presence of carbon shell acts as a protective coating against chemical components of biological fluids and is inert to pH change. Along with magnetic properties, simulations of fluorescence properties by the same particles can eliminate the addition of organic fluorophores (dyes) required for biological imaging.

The paper presents the synthesis of hybrid Fe@C-CN_x core-shell nanoparticles exhibiting both superparamagnetic and fluorescence properties. Superparamagnetic Fe@C core-shell nanoparticles were used where the carbon shell was functionalized through the one-step free-radical addition of alkyl groups terminated with carboxylic acid moieties. [2] The method utilizes the organic acyl peroxide of dicarboxylic acid (succinic acid peroxide) as precursor for functionalization. Further, functionalized nanoparticles were coated with CN_x through a low-temperature, in-situ solution-based chemical reaction of cyanuric chloride with lithium nitride. [3, 4] A detailed physiochemical characterization and fluorescence property of the hybrid materials is presented.

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COLL 46

2D Cu_{2-x}S nanocrystals from thermolysis of a lamellar template

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Two-dimensional (2D) atomic crystals that support surface plasmon excitation have the potential to exhibit extraordinary field confinement, long plasmon propagation lengths, and are emerging as an exciting and transformative class of nanomaterials for “flat” optics. A major challenge is the synthesis, characterization, and device integration of 2D atomic crystals that enable plasmon excitation within relevant optical bandwidths. Here, we describe the synthesis and characterization of 2D Cu_{2-x}S nanocrystals that support plasmon excitation in the near-infrared wavelength range. 2D nanocrystal morphology is typically achieved through anisotropic diffusion during colloidal synthesis, yet here we utilize a templated approach through a Cu alkanethiolate precursor. Cu alkanethiolates adopt supramolecular, lamellar structures and also represent single-source molecular precursors for Cu_{2-x}S via thermolysis reactions. We demonstrate that supramolecular ordering can dynamically change during thermolysis due to lyotropic-like phase behavior of the supramolecular precursor at thermolysis temperatures. As an example of this 2D templating, we demonstrate the synthesis of 2D nanosheet structures that are several microns wide with thicknesses of approximately 4 nm. This result demonstrates bottom-up chemical synthesis as a powerful technique for the fabrication of 2D nanocrystals and low-dimensional plasmonic materials.

COLL 47

Electrochemical control of vanadium dioxide nanocrystal films

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Vanadium dioxide (VO_2) has received considerable attention from a variety of fields due to its relatively low temperature and reversible metal-to-insulator transition (MIT). This transition, which occurs at approximately 68°C, is characterized by a small structural transformation from the low temperature monoclinic phase to the high temperature rutile phase. Along with this structural change, the electrical and optical properties of VO_2 change dramatically, leading to interest in utilizing this material for solid-state memory devices and smart windows. The ability to lower the MIT is of critical importance for practical applications. Efforts in this area have focused on straining, doping, and electrical gating. Here, we demonstrate how nanocrystalline films of VO_2 can be generated from colloiddally synthesized and strained V_2O_3 bixbyite nanocrystals. The optical properties of these films could then be controlled electrochemically by application of various potentials. Using variable temperature spectroelectrochemical analysis under inert atmospheric conditions, we were able to identify four distinct optical states for the VO_2 nanocrystalline film. Additional analysis using X-ray and Raman spectroscopy enabled us to relate the structural properties to the different optical states.

The reversible electrochemical control of the optical properties in these VO₂ nanocrystal films provides a new avenue for the practical application of VO₂ at relevant temperatures. More broadly, the concept of using electrochemistry to influence the structural and optical properties of nanomaterials is of interest to the community studying the basic science of these systems.

COLL 48

Palladium nanoparticle seed mediated growth of palladium nanoshell on silica core

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Palladium shell of ~11 to 15 nm thickness has been synthesized successfully by reduction of surface bound palladium ions onto ~200 nm diameter silica core. The method for generating such nanoshells is based on seed-mediated growth technique. Palladium ions from complex palladium salt are adsorbed onto aminosilane functionalized silica core and subsequently reduce to create *in situ* palladium nanoparticle seeds. These nanoparticle seeds act as the nucleation sites to promote further growth of final palladium overlayer. Palladium nanoparticle seeds generated onto the functionalized silica surface are ~3nm in diameter and are uniformly distributed throughout the core surface as observed by transmission electron microscopy (TEM). The thickness of the final palladium shell can easily be tailored by varying the concentration of the seeded core during the shell formation step. An increase concentration of seeded core leads to decrease in shell thickness. In addition, use of ascorbic acid generates uniform shell compare to formaldehyde as reducing agent. The formation of the palladium nanoshells is extensively monitored using ultraviolet-visible spectroscopy and TEM, with zeta potential measurement to assess the surface charge of silica core and after surface functionalization. This present method reports the first time synthesis of palladium nanoshell from surface bound palladium nanoparticle seeds compare to all the earlier reports that use gold nanoparticle as seed to generate the final palladium shell.

COLL 49

Temperature dependence of the nanocrystal nucleation revealed through plasmon resonance of bimetallic nanoparticles

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Colloidal synthesis of inorganic nanocrystals is a rapidly evolving area of materials science that holds great promise for future technological applications. Our ability to control the evolution of nanoparticle shapes in growth reactions, however, is still just

developing. The grand challenge lies in understanding the effect of the reaction parameters, such as precursor concentration, solvent temperature, and ligand chemistry on the processes of nanocrystal nucleation and growth. Here, we develop an experimental strategy for monitoring the time-dependent monomer concentration during the hot-injection synthesis of Ag nanoparticles. By measuring the relative concentration of Ag-ions immediately before the nucleation burst, we were able to elucidate the role of reaction parameters on the rate of nucleation and the ensuing nanoparticle morphology. In particular, we show that the nucleation rate increases with temperature linearly, which is explained by increase diffusivity of monomers.

COLL 50

Photoluminescent zinc oxide nanoparticles: Surface chemistry and gas sensing

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Zinc oxide nanoparticles exhibit a strong room temperature bimodal photoluminescence (PL) spectrum upon excitation with ultraviolet light (e.g, 340 nm), with emission at 380 nm due to excitonic recombination of excited electrons in the conduction band with holes in the valence band. A visible peak (e.g., at 550 nm) is also present that arises from defect-related states, such as oxygen vacancies. The PL spectra of commercially available and synthesized ZnO nanospheres and nanorods are presented, with correlations drawn between the spectra and their morphology. Chemisorption on the nanoparticles affects the ratio of the emission intensities at these two wavelengths, and opportunities exist for opto-chemical sensing. Changes in the PL spectrum due to chemisorption of molecules such as sulfur dioxide, nitrogen dioxide and methanethiol are discussed. The effect of various atmospheres including hydrogen, oxygen, nitrogen, carbon monoxide, carbon dioxide and air on the PL spectra are also presented, and a model is given to explain the results. A portable, UV light-emitting diode based instrument to detect the PL changes of ZnO has been constructed and tested, and the future of opto-chemical sensing with respect to specificity and selectivity is discussed.

COLL 51

Remediation of organophosphates by mixed metal oxide nanocomposites

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Persistent organophosphorus compounds (OPCs) are environmental pollutants found in flame plasticizers, pesticides, and remaining stockpiles of nerve agents present in military arsenals. We applied the unique properties of synthesized and processed mixed metal metal oxides (MMO) (MTiO_3 , MTiO_3 , $\text{M} = \text{Fe}, \text{Zn}$) nanomaterials to remediate

methyl parathion and methyl-paraoxon OPCs. Electrospun TiO_2 , ZnTiO_3 , and FeTiO_3 nanofibers were synthesized along with heterojunctioned TiO_2 and hematite (Fe_2O_3) nanocomposites processed from base and acid hydrolysis of milled ilmenite rock. We evaluated OPC degradation kinetics and degradation yields using spectroscopy (NMR, UV-vis, FT-IR), chromatography (GC-MS, LC) and mass spectrometry. Processed TiO_2 and hematite (Fe_2O_3) nanocomposites were the most effective in degrading methyl parathion and methyl-paraoxon. Moreover, density functional theory calculations were used to map-out possible lowest activation free-energy profiles and to provide mechanistic insights into surface and solution induced reactivities.

COLL 52

Engineering cascade reactions via supraparticle assemblies

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Nature has developed highly specific and efficient catalyst which synthesize complex organic molecules via cascade reactions. A good example of a natural cascade is the reduction of carbon dioxide (CO_2) into carbohydrates via photosynthesis. Due to the efficiency of such biological systems, there has been a considerable effort directed towards the development of artificial multi-enzymatic systems that mimic natural processes. While there has been significant progress in the field, the practical application of such catalytic cascade reactions suffers from several limitations, that prevent the one-pot synthesis from being effectively used in practice. Furthermore, the complexity of natural cascade systems presents a challenge when attempting to reproduce these biological systems.

Cascade reactions require the use of compatible reaction parameters (i.e., temperature, pressure, pH, solvent, etc.), to obtain optimum conditions (i.e., favorable reaction rates and stability). In practice, obtaining optimal conditions for all the reactions are rarely met, which results in an inefficient cascade system. Additionally, the presence of side products may inhibit enzymes, leading to unwanted deactivation. Further research is required before efficient and robust one-pot cascade systems that mimic natural biological processes can be designed.

This study aims to implement a novel tool, i.e. a bionic supraparticle (SP) in cascade reactions, in particular, the multi-step reduction of CO_2 to methanol, to improve our understanding, and consequently, engineer better designs of such one-pot cascade reactions. Bionic supraparticles (SPs) are composed of inorganic and organic components and are capable of combining the functionalities of inorganic and biological nanostructures. For instance, they are capable of capturing sunlight photons and subsequently converting them into chemical energy, mimicking natural biological processes. Better understanding through the use of SPs can potentially lead to efficient,

robust, and favorable designs of multi-catalytic reactions, which can sufficiently mimic natural biological processes, resulting in favorable application in practice.

COLL 53

Saporin magnetic nanodrivers for suicide breast cancer therapy

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Breast cancer is a remarkably heterogeneous disease comprising multiple subtypes, each representing a distinct biological signature depending on gene expression profiling, including hormone (estrogen and progesterone)-sensitive, HER2-positive and triple negative breast cancer. A unique therapeutic regimen has not been identified so far, thus combined therapies are required to overcome the limited efficacy of the available treatments and the risk of recrudescence. To overcome the limitations of conventional anticancer therapies we propose a strategy combining gene therapy and nanotechnology.

Magnetic iron-oxide nanoparticles (MNP) has been armed with a plant protein toxin, namely saporin, a suitable candidate for cancer therapy due to its high enzymatic activity, stability and resistance to conjugation procedures and to the action of blood proteases. Saporin activity is exerted by irreversible inhibition of protein synthesis, leading to apoptotic cell death of target cells. Different approaches were pursued by MNP functionalization with either saporin protein as such or with the corresponding gene. Low concentrations were readily active since very few molecules of the toxin generated in the tumor cells were sufficient to kill them. Specific ligands designed to target membrane receptors, over-expressed in several malignant tumors and often correlating with poor prognosis, has been conjugated to MNP in order to address intrinsic breast cancer heterogeneity and cover tumors at different stages and scores. The activity and specificity of functionalized MNPs were assessed *in vitro* in model breast cancer cell lines. Results have been compared to the effect of conventional agents used in the therapy of breast cancer such as the monoclonal antibody trastuzumab. From these studies we expect to generate a multifaceted tool for the delivery of both toxin proteins and DNA in the treatment of breast cancer and, possibly, of other solid tumors.

COLL 54

Ternary sol-gel nanoparticle for ultrasound imaging of mesenchymal stem cells

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Ultrasound imaging offers high spatial and temporal resolution, but often suffers from low contrast. To solve this, we report here a phosphate-based glass nanoparticle with high acoustic impedance and good biodegradation and biocompatibility properties. This $(\text{P}_2\text{O}_5)_{55}\text{-(CaO)}_{30}\text{-(Na}_2\text{O)}_{15}$ phosphate-based glass nanospheres (PGNs) were synthesized and characterized as contrast agents for ultrasound imaging. Scanning electron microscopy indicated spherical nanoparticles that were 200-500 nm, and XRD, ^{31}P NMR, and FTIR data suggested amorphous and glassy materials consisting mostly of Q^1 and Q^2 phosphate units. The ultrasound detection limits were 5 $\mu\text{g/mL}$ in vitro and 9 $\mu\text{g/mL}$ in vivo. We used these materials for stem cell tracking and could count as few as 4000 cells via ultrasound imaging with no cytotoxicity at doses needed for imaging. The PGNs were located inside the cells suggested phagocytosis. We also conducted biodegradation studies to show that the PGNs biodegrade into aqueous media with degradation products that can be easily metabolized in the body—a key feature for clinical translation. Importantly, signal remained elevated for at least 4 hours before biodegradation decreased echogenicity—this is an ideal window for medical imaging.

Ref: Foroutan *et al.* *ACS Nano*, 2015. DOI: 10.1021/nn506789y

COLL 55

Molecular imprinted biosensor for rapid detection of CEA from pancreatic fluid cysts

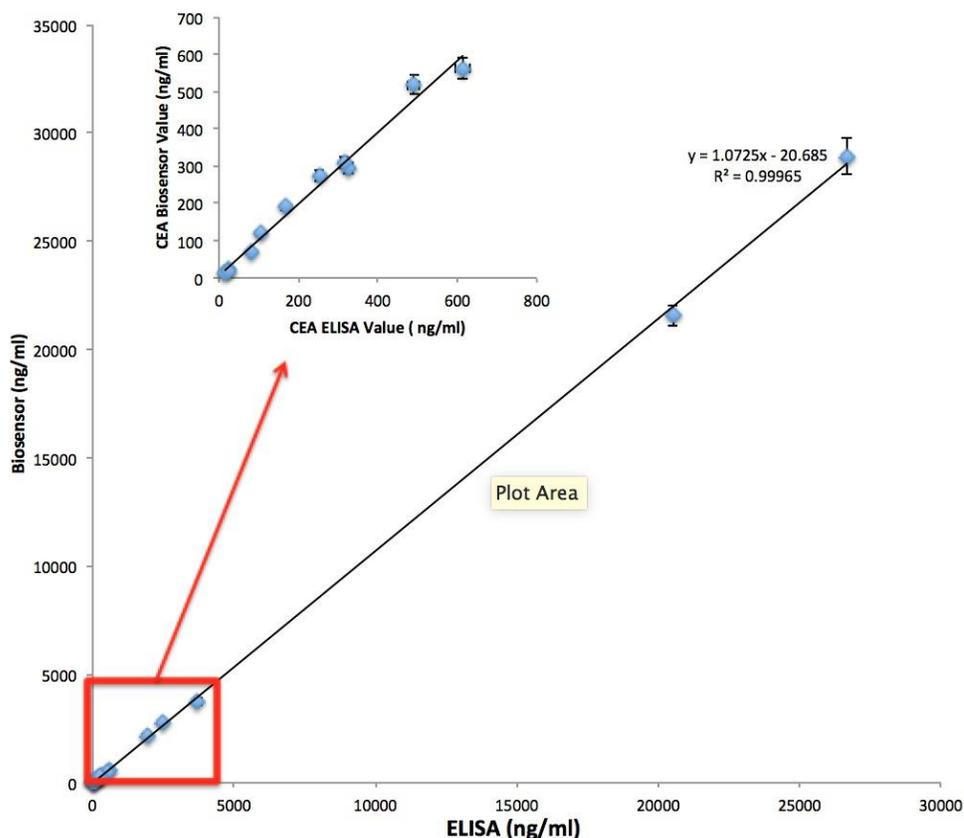
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Carcinoembryonic Antigen (CEA) is a glycoprotein whose levels can be used for early detection, detecting recurrence, assessing prognosis, and monitoring treatment of cancer patients. Currently, the most common detection method for CEA is the enzyme-linked immunosorbent assay (ELISA). Since this technique is time consuming and requires specialized equipment samples are sent away for analysis. Here we describe a new type of sensor based on molecular imprinting technology which can obtain quantitative results in less than 10 minutes using a portable potentiometric detection system, requiring a sample size of only ten microliters. Hence this sensor can be used immediately in samples at bedside. Here we report on a clinical study performed on 24 patients where we compare directly the results obtained with ELISA and the molecularly imprinted sensor. The results have an excellent correlation factor of 1.01, $p < 0.001$ confirming the equivalence of the two techniques.

The sensor is made via co-absorption of hydroxyl-terminated alkanethiol molecules and the template molecule a gold-coated chip. On the gold surface, the thiol molecules are chemically bound to the gold metal substrate and self-assembled into highly ordered monolayers, the biomolecules can be removed, creating the foot-print cavities in the monolayer matrix for this kind of template molecules. Here we present the results of extensive testing of the stability of the sensor surfaces using cyclic voltametry, and using potentiometry, the reproducibility of the results, the optimal templating kinetics, the selectivity of the surface imprint, and the optimal storage and shelf life conditions.

The adsorption isotherms, the surface imprint coverage, and the potential response calibration using CEA-ELISA. The results are consistent with calculations of the surface kinetics and confirm that the imprinting mechanism occurs via three-dimensional templating.

CEA ELISA & Biosensor data comparison



Quantity of CEA measured by ELISA and molecular imprinted biosensor

COLL 56

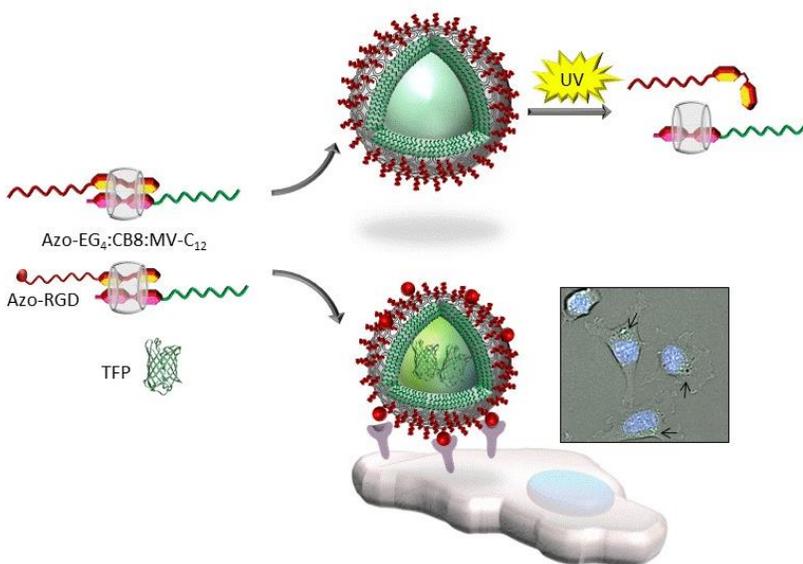
Light responsive supramolecular nanoparticles

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Supramolecular nanoparticles are biomimetic, responsive and powerful materials for biomedical applications. When the control over a stimuli-responsive host-guest complex is incorporated in nanoparticles, this can be used for encapsulation and targeted release of growth factors and other agents. The cavity of cucurbit[8]uril (CB8) handcuffs methylviologen and the light-responsive trans-azobenzene in a stable 1:1:1 ternary

complex.¹ Modifying these guests with a hydrophobic and a hydrophilic tail respectively, the ternary complex becomes an amphiphile (Azo-EG₄:CB8:MV-C₁₂). This supramolecular amphiphile self-assembles in light responsive hollow nanoparticles with a biologically relevant size of about 200 nm. Moreover, the nanoparticles void has been loaded with a cargo protein and the external leaflet of the nanoparticles has been functionalized with a targeting unit via host-guest chemistry. The targeting unit has been incorporated by simply adding small quantities of an azobenzene bearing the tripeptide arginine-glycine-aspartic acid (Azo-RGD) as a recognition site for the integrin receptors on the cell surface. In such a way, the nanoparticles have been selectively interacted with cells and a teal fluorescent protein (TFP) has been selectively delivered to living cells.

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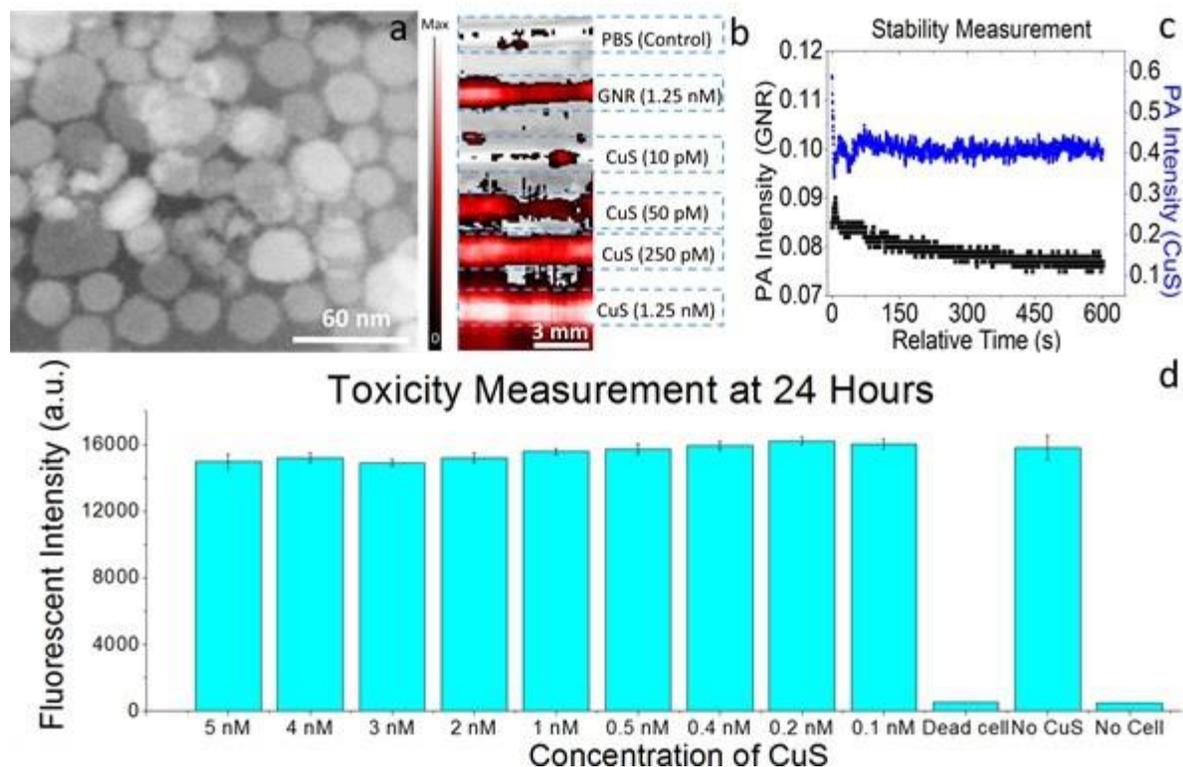


COLL 57

Copper sulfide nanodisks are photoacoustic imaging contrast agents

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Copper sulfide (CuS) nanodisks have tunable and directionally localized surface plasmon resonance excitation in the near infrared spectrum suggesting that they may be suitable as photoacoustic (PA) imaging contrast agents. To investigate the PA characteristics and cytotoxicity for *in vivo* imaging, CuS nanodisks were prepared by solvent based synthesis followed by surface modification with poly(ethylene glycol) methyl ether thiol (PEG-thiol, $M_w=1000$). The size (diameter= 31.1 ± 7.45 nm, aspect ratio= 4.54 ± 1.51 nm) and uniformity of CuS nanodisks were measured under scanning transmission electron microscope (**Figure a**). The synthesized CuS sample was diluted with ethanol and prepared in small tubing (ID=0.85 mm, OD=1.27 mm) placed in parallel for PA scanning. **Figure b** shows the ultrasound (grey) and PA (red) signal of the tubing. At isomolar concentrations, the CuS nanodisk has a stronger and more stable PA signal than gold nanorod (GNR)—a standard PA contrast agent. At a concentration of 1.25 nM, CuS offered 2.3-fold better signal than GNR at 700 nm (near maximum GNR absorption), where the maximum PA signal of CuS nanodisks occurs at 950 nm. The CuS signal was more stable over 10 minutes of excitation at 700 nm; the GNR decreased by 11 % ($P<0.001$) (**Figure c**). In addition, cell viability assays revealed little impact; 95 % of ovarian cancer cells were viable after being incubated with CuS nanodisk at 5 nM for 24 hours ($n=8$, $p<0.03$) (**Figure d**).



Synthesis and characterization of ash rice husk supported manganese nanocomposite and its application for adsorption of Cd(II), Pb(II) and Cu(II) ions

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Nanotechnology is an emerging aspect of science that is gaining relevance because of its copious effective applications. The release of Cd(II), Pb(II) and Cu(II) into the environment via anthropogenic activities has posed a number of threats on human beings, plants and aquatic organisms hence the need for efficient and effective nano-adsorbent. The synthesis of ash rice husk supported zerovalent manganese nanocomposite (ARH-nZVMn) was achieved via bottom-up approach in a single pot system by chemical reduction. ARH-nZVMn was characterized by Fourier transform infrared spectroscopy (FTIR), Transmission electron microscopy (TEM), Scanning electron microscopy (SEM), Energy dispersive x-ray (EDX), and X-ray Fluorescence (XRF). The BET surface area and point of zero charge (PZC) were determined. The effect of operational parameters such as pH, contact time, adsorbent dose, agitation speed, initial Cd(II), Pb(II) and Cu(II) concentrations, temperature, and salinity were investigated in a batch system. The kinetics data followed pseudo second-order and adsorption mechanism was governed by pore diffusion. The equilibrium sorption data were tested by Freundlich, Langmuir, Temkin, Dubinin-Kaganer-Raduskevich, and Halsey isotherm models. The Langmuir monolayer adsorption capacities (Q_{max}) found to be 172.41 mg/g, 84.04 mg/g and 84.75 mg/g for Cd^{2+} , Pb^{2+} , Cu^{2+} (181.818 mg/g) respectively were much greater compared to other nano-adsorbents used in adsorption of Cd^{2+} , Pb^{2+} , Cu^{2+} . The thermodynamics parameters (ΔH° , ΔS° , ΔG°) revealed a feasible, spontaneous, and endothermic adsorption process. Post adsorption characterization also supported the presence of Cu(II), Cd(II), and Pb(II) in the loaded ARH-nZVMn. Desorption was effectively achieved using HCl. ARH-nZVMn has a great potential for effective removal of these toxic heavy metal ions.

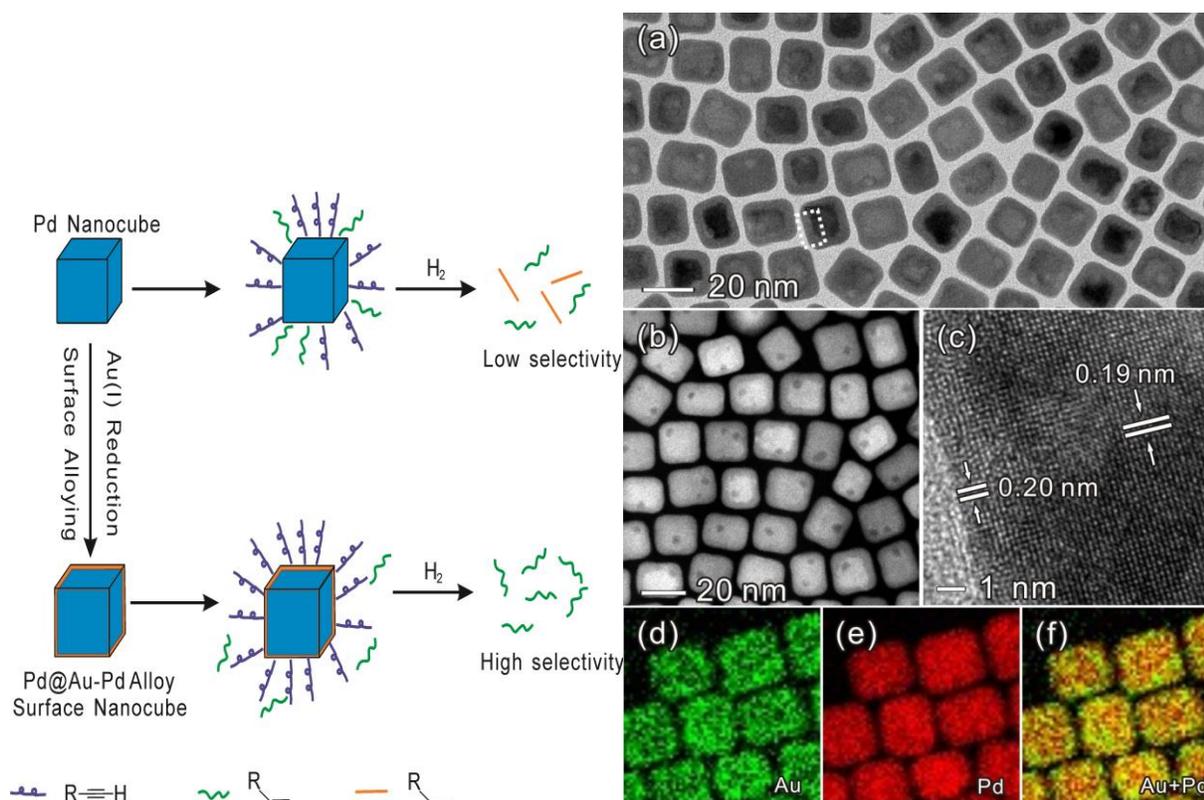
Key words: ARH-nZVMn Nanocomposite; Heavy metal ions; Adsorption; Desorption; Kinetics; Isotherm; Thermodynamics.

COLL 59

Design and preparation of surface Au-Pd alloy nanocatalysts for alkyne semihydrogenation

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One of the challenges in heterogeneous catalysis is to design and modify the surface structure of catalysts to achieve high activity and selectivity. Doping a metal surface with a second metal should be one of the most effective ways. In this work, gold atoms were doped onto the surface of palladium nanocrystals, and served as active sites to capture alkynes, thus enhanced both the activity and selectivity of alkynes semihydrogenation. Compared with commercial catalysts (Pd/C, Pd/Al₂O₃, and Lindlar catalyst), Au-Pd alloy surface shows the highest activity and the best selectivity. In addition, detailed alkyne-activation pathway has been identified in the alloy surface-catalyzed semihydrogenation reactions, elucidating the origin of high selectivity of the Au-Pd alloy surfaces.



COLL 60

Synthesis, characterization, viability assessment and silica encapsulation of thiol- capped CdSe quantum dots

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We report the synthesis and characterization of CdSe QDs, capped with four different thiol-ligands, in an aqueous medium, their internalization and biocompatibility with COLO-205 human colorectal adenocarcinoma and TK6 human spleen lymphoblasts. Furthermore, we report the silica encapsulation via ligand exchange and stability studies of the mentioned QDs. The thiol-ligands used for capping and stabilization were glutathione (GSH), thioglycolic acid (TGA), 3-mercaptopropionic acid (MPA), and L-Cysteine (L-Cys). Properties of the synthesized QDs were characterized with UV-Vis spectroscopy, XRD, FTIR and TEM. Stability of the encapsulated QDs was assessed by Z-potential analysis using DLS. To study the ligand effect on QDs biocompatibility, both normal and cancer cells were exposed to each synthesized QDs and viability was evaluated via Trypan Blue exclusion method. To further study the biocompatibility, their interaction with cells, and evaluate their bio-imaging potential, we performed measurements of intracellular QD uptake by cells and bacteria, monitored by confocal microscopy. Characterization results indicate that the non-encapsulated capped/QDs (bare-QDs) were successfully formed, exhibiting an improved optical response. FTIR spectrum analysis confirms the ligand exchange of the bare-QDs, which allowed silica encapsulation of the QDs with good stability, determined by Z-potential analysis. Silica clusters were observed with TEM. Viability studies of the bare-QDs indicate that COLO-205 and TK6 cells can tolerate the freshly prepared QDs with high viability values after exposure. Intracellular uptake imaging with confocal microscopy showed that synthesized QDs emit light efficiently, even after penetrating the treated cells or interacting with treated bacteria. The synthesized QDs have potential to be employed for bio-imaging studies with minimal effects. Future and ongoing work includes viability assessment of silica encapsulated QDs and establishing a relationship between cellular uptake over time and used concentrations of the experimental QDs, in order to determine if QDs uptake is time or dose-dependent.

COLL 61

Echogenicity of mesoporous and nonporous silica nanoparticles

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Silica nanoparticles are an intriguing theranostic biomaterial because of their tunable size and morphology, versatile surface chemistry modification, and good biocompatibility. Mesoporous silica nanoparticles (MSNP) in particular offer drug delivery applications because their pores/channels markedly increase drug loading capacity. However, these tools have yet to be rigorously characterized for imaging applications. Here, we studied both Stober silica nanoparticles (SSNP, Fig. a1-a2) at 160 ± 11 nm and MSNP (Fig. b1-b2) at 154 ± 15 nm. Dark field microscopy analysis showed that 5.1 mg/ml of MSNP has $(3.90 \pm 0.19) \times 10^{13}$ particles/ml and 11.4 mg/ml SSNP has $(4.18 \pm 0.27) \times 10^{13}$ particles/ml. Ultrasound images of MSNP and SSNP at the same particle concentrations were collected at 25 MHz and 40 MHz (Fig. c). At 25 MHz, the average gray values of SSNP at 0 , 2.5×10^{12} , 5×10^{12} , 1×10^{13} , and 2×10^{13}

particles/ml are respectively 2%, 54%, 55%, 46%, 42% higher than those of MSNP, while at 40 MHz, the average gray values of SSNP at the five concentrations are 0%, 38%, 48%, 36%, 38% higher than values of MSNP. Even at the same weight concentrations of 0.25 mg/ml, 0.5 mg/ml, and 1 mg/ml, SSNP show 30%, 28%, and 30% higher ultrasound signal than MSNP. These results have implications in cancer and cardiovascular medicine.

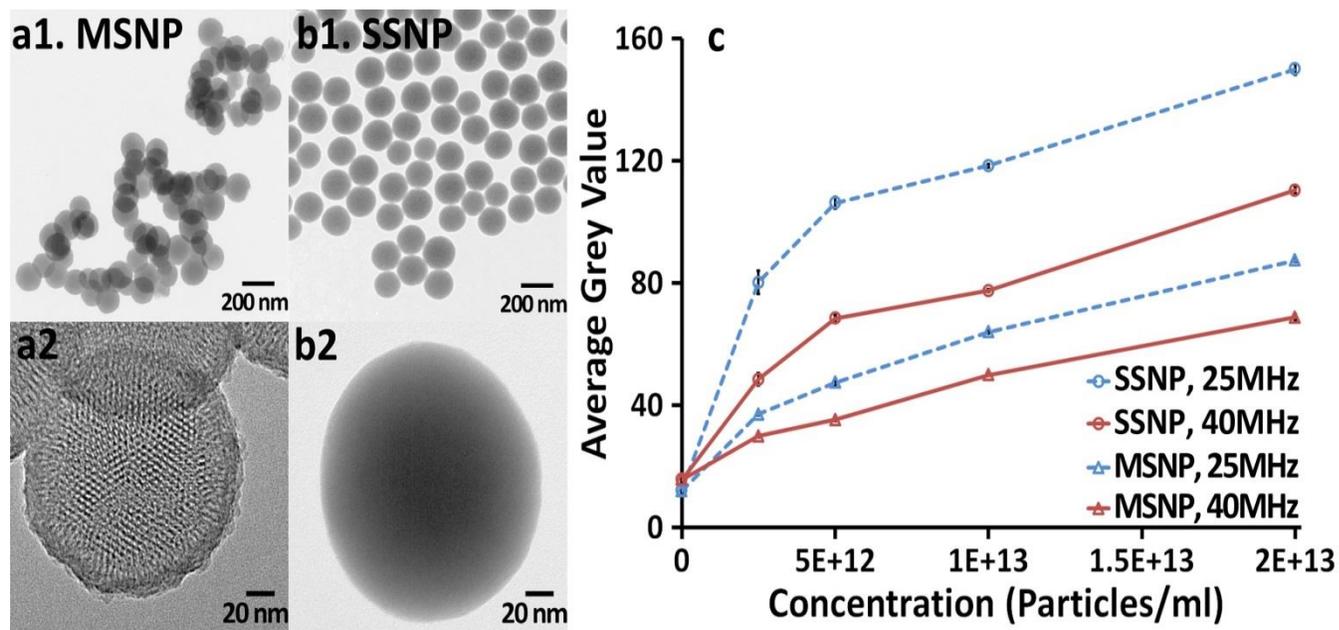


Figure 1. TEM images of MSNP (a1, a2) and SSNP (b1, b2). Average gray values of B fundamental ultrasound images of MSNP and SSNP at 25 MHz and 40 MHz.

COLL 62

Redox-mediated electrosorption for chemical and environmental separations

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We explore the use of asymmetric supercapacitor electrode assemblies of novel architecture for the selective electrosorption of a range of molecular species of environmental concern. The process relies on the strong interactions between targeted analytes and appropriate redox-active polymers when they are in one oxidation state and not the other. The release of the captured compounds can be realized on reversing the oxidation state of the polymers. A range of different process streams are amenable to treatment in this manner, and we will report on (i) selective separation of organic anions from a significant excess of supporting electrolyte, (ii) heavy metal ions from solution, and (iii) CO₂ from dilute gas feeds. The basic concepts, including the design, preparation and electrochemical characterization of the electrode assemblies and the dynamic uptake and release of the targeted compounds under a range of different operating conditions, will be discussed.

An important consideration in the electrochemically-mediated treatment of process streams is that side-reactions at electrode interfaces can be economically and energetically costly, since they can affect the electrode stability as well as impact electrochemical performance. In aqueous chemistry, for instance, water electrolysis at the cathode is a major challenge as it drains current density that could otherwise be applied in a useful process, can dramatically affect the solution chemistry through increases in pH, and can impact the stability of the anode itself. We conclude the presentation with a discussion on how appropriate matching of asymmetric redox electrodes can fully suppress the hydroxide generation reaction and enhance current efficiency.

COLL 63

Engineering responsive liquid crystal interfaces with surfactants, lipids, and nucleic acids

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The orientation of thermotropic liquid crystals (LC) is remarkably sensitive to the chemical and physical properties of vicinal interfaces; these phenomena are at the heart of traditional "alignment layers" that are ubiquitous in LC technology. The presence of long aliphatic chains at an LC interface has a particularly strong influence on LC anchoring, and even relatively small amounts of surfactants or lipids at an interface can be sufficient to trigger orientational changes of a macroscopic LC layer. At a fluid interface, such as that between an LC and an aqueous buffer, this can result in rich and complex behavior, involving the cooperative organization of surface-active molecules and the LC director field. Moreover, these phenomena can be exploited to engineer sensitive and selective sensing technologies, where molecular recognition events modify the structure of the interfacial layer, which in turn causes a change in the orientation of a macroscopic LC phase. Diverse examples involving nucleic acids will be described, where the changes in the interfacial LC alignment layer may be due directly to changes in secondary structure of adsorbed DNA or to interfacial events (e.g. liposome fusion) that are triggered by nucleic acid molecular recognition.

COLL 64

Surface engineering using vapor-deposited polymers

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The precise engineering of surfaces with respect to chemical functionalities, microstructure and nanoscale topography is an important aspect, when designing substrates for biological applications. A strategy based on the chemical vapor

deposition polymerization of [2.2]paracyclophanes will be presented that can yield a wide range of chemical functionalities for subsequent surface immobilization. Moreover, co-polymerization can yield multifunctional surfaces with orthogonal binding capacities as well as chemical gradients. Specific applications including the design of microstructured cell substrates, or surfaces for active transport along gradients will be discussed to exemplify the versatility of CVD based polymer surfaces.

COLL 65

Programming polymeric nanomaterials with enzymes, peptides and nucleic acids

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We describe polymers and nanoparticles with densely packed arrays of peptides and nucleic acids as biologically privileged materials capable of interacting in well-defined and programmed ways with cells and tissues. One class of structure renders 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. In addition, versions of these polymer-biopolymer conjugates show promise as transporters of proteins across cell membranes. These studies will be described with respect to their potential utility in therapeutic protein and peptide delivery to tissues. Similarly, densely packed nucleic acids on polymers and/or on particles will be described that are capable of efficient cellular uptake, while resisting degradation. We investigate the biological pathways by which the materials are taken up into cells via a novel screening approach, and will describe the development of siRNA versions of these materials.

COLL 66

Stimuli-responsive surfactants, polymers, and materials

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Imidazolium-based ionic liquid surfactant monomers (surfmers) are stimuli-responsive to select anions and solvents, and provide basis for many useful polymers that also are stimuli-responsive as well as highly useful dispersion stabilizers. We illustrate the synthesis of various homopolymers, diblock copolymers, triblock copolymers, random

copolymers and nanolatexes that exhibit LCST, reversible nanoparticle formation, stimuli-responsive dewetting, osmotic brush stabilization by adsorption from solution, stimuli-responsive destabilization and controlled coatings of submicron graphene platelets, and stimuli-responsive phase transfer. We also illustrate the first example of reversible colloidal crystal crystallization based on enthalpic rather than entropic driven free energy changes in a lyotropic nanogel system (see figure), and we illustrate a polymerized ionic liquid that yields an amorphous and heavily N-doped carbon, red carbon, that retains 66% of its mass up to 1480°C, while staying amorphous.



Colloidal crystals after recrystallization in water at 4C.

COLL 67

Approach to contact of soft or structured surfaces in fluids

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We characterize and model the spatiotemporal deformation of an elastic film during the radial drainage of fluid from a narrowing gap. Elastic deformation of the film takes the form of a dimple and prevents contact to be reached. Broadening of the dimple as the surfaces approach follows a relationship derived for droplets. With thinner elastic film the stress becomes increasingly supported by the underlying rigid substrate, the dimple formation is suppressed, which allows the surfaces to reach contact. Finally, we show that for a given fluid film thickness, the elastic deformation leads to stronger hydrodynamic forces than for rigid surfaces.

COLL 68

Molecular interactions between cell membranes and biological molecules

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Molecular interactions between model cell membranes and various peptide molecules have been investigated using sum frequency generation (SFG) vibrational spectroscopy, supplemented by attenuated total reflection (ATR) – FTIR spectroscopy.

A variety of antimicrobial peptides, such as magainin 2, MSI-78, cecropin P1, ovispirin-1 and LL-37 have been investigated while they interact with model cell membranes as a function of peptide concentration, lipid composition, and temperature. Alamethicin, serving as a model for ion channel protein, has also been examined using SFG and ATR-FTIR. In addition to the antimicrobial peptides, cell penetrating peptides, such as pep-1, have been studied and their interactions with model cell membranes were compared to those of antimicrobial peptides. Our research also demonstrates that isotope labeling method can be used in SFG studies to probe detailed local structure of peptides associated with cell membrane.

COLL 69

Quantifying molecular transport through cell membranes by nonlinear light scattering

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We demonstrate a nonlinear optical light scattering method for quantitative measurement of the cellular uptake and membrane transport rates of small/medium size molecules without the need of fluorescence tagging. In this method, we monitor the Second Harmonic Generation (SHG) from a 'probe' molecule with detectable hyper-polarization, in the presence of the 'target' molecule of interest while both molecules are crossing the cell membrane. The transport rate of the target molecule is extracted as a perturbation to that of the probe molecule. As a first example demonstrating this approach, we examine competitive transport of the strongly SHG-active cation, malachite green (MG), against the weakly SHG-active dication, propidium (Pro), across the outer-membrane protein channels in living *E. coli*. A one-site channel model is used to deconvolute from the MG transport kinetics the Pro transport rate. Comparison of model predicted and directly measured Pro transport rates validates the effectiveness of this method.

Applications of this method to a variety of systems have enabled the study of 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.

COLL 70

Molecular origins of cholesterol accelerated lipid flip-flop

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Cholesterol is a major constituent of cellular membranes which controls membranes fluidity, solubilization of immiscible lipid components and has even been implicated in

the formation of lipid rafts. Although our understanding of the structural role cholesterol plays in lipid membranes has been studied extensively, the effect cholesterol has on the transbilayer diffusion or flip-flop of lipid species is not well understood. We have previously shown that cholesterol increases the rate of flip-flop for the saturated lipid 1,2-distearoyl-sn-glycero-3-phosphocholine (DSPC) in a concentration dependent manner. The current study explores the chemical and physical origins which allow cholesterol to radically modulate the native rate of lipid translocation in membranes. These studies were conducted using the nonlinear technique of sum-frequency vibrational spectroscopy, which allows for the direct detection of lipid flip-flop dynamics. Several analogues of cholesterol are examined and their effect on the kinetics and thermodynamics of DSPC flip-flop will be discussed, with particular attention paid to 5 α -cholestan-3 β -ol (cholestanol) and 5-cholestene (cholestene). Cholestanol lacks a double bond between carbons 5 and 6 which alters the conformation of the sterol rings and cholestene lacks the hydroxyl group on the C3 carbon, changing the lipophilicity of the molecule. The effect of these chemical and structural changes on the activation thermodynamics for DSPC flip-flop will be discussed in detail.

COLL 71

Fluorescent lipids with selective partitioning to liquid ordered membrane domains

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Microscopic tracking of cellular processes is vital to understanding pathogen invasion, disease progression, and delivery of therapeutic material. Fluorescent labeling of phase separated membrane domains, also known as lipid rafts, are an important aid in this area but phase specific labels are few and their performance can be inconsistent. We have developed series of lipids that provide insights into fluorescent lipid probe design for selective partitioning to liquid ordered (Lo) membrane phases. Here, we investigated the role of the lipid's spacer region and the fluorophore situated at the head group position. With a lipid structure consisting of a glycerol backbone and two palmityl tails for favorable packing into ordered regions of the membrane, we found that hydrophobicity of the fluorophore plays a determining role in the lipid's partitioning behavior. Hydrophilic fluorophores, which display little membrane association (e.g., Atto488, OG488), enable the lipid tails to direct the lipid's partitioning towards the Lo phase. Hydrophobic fluorophore (e.g., rhodamine B), on the other hand, steers the lipid to the disordered phase (Ld). Using a polyethylene glycol (PEG) spacer can buffer some of the partitioning effect induced by the hydrophobic fluorophores, but only to an extent. For example, we find that fluorescein-labeled lipids partition to the Ld phase when the PEG spacer is short but partition well to the Lo phase at a molecular weight of 2000, however, rhodamine B partitions strongly to the Ld phase regardless of PEG length. Both red and green fluorescent labeled lipids that partition to the Lo phase will

be described.

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COLL 72

Kinetics of peptide-membrane interactions

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Biological membranes provide a unique environment for many peptides to fold, interact, and function. While we now know a great deal about how peptides fold in aqueous solution, we understand relatively little about the dynamics and mechanisms by which peptides fold in a membrane environment. This is due in part to the fact that it is experimentally more challenging to initiate and probe membrane-mediated peptide folding events with desired temporal and structural resolutions, as membranes create a more dynamic, heterogeneous, and crowded environment. In this talk, we will discuss our recent effort in combining several spectroscopic techniques and probes to dissect various kinetic steps involved in peptide-membrane interactions, including binding, folding, insertion, and association. Specifically, we will focus on membrane peptides that form well-defined and simple structural elements, such as alpha-helix, helix-helix dimer, and helix-turn-helix.

COLL 73

NMR structural studies on functional cannabinoid type II receptor in a lipid matrix

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The cannabinoid type II receptor, CB₂, belongs to the large class of rhodopsin-like G protein-coupled receptors (GPCR). It has been found at high concentrations in tissues of the immune system. The class of cannabinoid receptors, like other GPCR, has become the object of high interest because of its role as therapeutically important target of drugs. It is our goal to obtain insights into structure and function of CB₂ at near physiological conditions which can be achieved by NMR. The first and most important step for any structural study at high resolution is to obtain milligram quantities of pure

and functional receptor.

We express CB₂ recombinantly in *Escherichia coli* as a fusion with maltose-binding protein and several affinity tags. The CB₂-fusion protein is solubilized, purified, the fusion cleaved, and CB₂ purified again from cleavage products. The protein was successfully stabilized during purification and reconstitution by a proper mixture of detergents, lipids, and ligand. We demonstrate that a concerted action of an anionic cholesterol derivative, cholesteryl hemisuccinate (CHS) and high affinity cannabinoid ligands CP-55,940 or SR-144,528 are required for efficient stabilization of the functional fold of CB₂ in dodecyl maltoside (DDM)/CHAPS detergent solutions. Similar to CHS, the negatively charged phospholipids with the serine headgroup (PS) exerted significant stabilizing effects in micelles while uncharged phospholipids were not effective. Functionality of the purified and reconstituted receptor was verified by ligand binding and by a G protein activation assay. Composition, size, and homogeneity of proteoliposomes were investigated by analytical NMR, fluorescence spectroscopy using labeled lipid and CB₂, dynamic light scattering, and sucrose gradient centrifugation. The reconstituted CB₂ in a lipid matrix at sufficiently low temperatures has long-term stability that enables functional and structural studies. Exploratory NMR experiments conducted on a 2-mg sample of homogeneously ¹³C- and ¹⁵N-labeled CB₂ and comparison of experimental results with simulated spectra obtained from the atomic coordinates of a CB₂ model have demonstrated feasibility of the experimental concept. Specific isotopic labeling schemes have been developed to achieve the desired spectral resolution for a structural analysis of limited scope. An update on results will be presented.

COLL 74

Correlating lipid-protein interactions with single particle tracking and PIE-FCCS

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Dynamic associations between lipids and adsorbed biopolymers are central to assembly and function in biological membranes. The electrostatic component of these interactions has been recognized as a key feature, but is difficult to probe directly *in situ*. Phosphoinositides (PI) are anionic lipids that are particularly important in cell communication across the plasma membrane. Many proposals have been made about how PI lipids interact with cationic residues on the adsorbed protein, but these have been difficult to probe experimentally. Here we report on dynamic associations of phosphatidylinositol 4,5-bisphosphate (PI(4,5)P₂) lipids with adsorbed cationic peptides. We study these interactions in a novel asymmetric supported lipid bilayer using time resolved fluorescence methods like single particle tracking (SPT) and pulsed interleaved excitation fluorescence cross-correlation spectroscopy (PIE-FCCS). With SPT we observe individual lipid binding events, from which we quantify residence times and the dependence on solution ionic strength. With PIE-FCCS we observe and characterize a population of low-mobility lipid-peptide clusters. This approach allows us resolve the chemical details of electrostatic interactions in biological membranes.

COLL 75

Coating nanoparticles with cell membranes for targeted drug delivery

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Targeted delivery allows drug molecules to preferentially accumulate at the sites of action and thus holds great promise to improve therapeutic index. Among various drug targeting approaches, nanoparticle-based delivery systems offer some unique strengths and have achieved exciting preclinical and clinical results. This talk will focus on the recent development of cell membrane-coated nanoparticle system, a new class of biomimetic nanoparticles that combine both the functionalities of cellular membranes and the engineering flexibility of synthetic materials for effective drug delivery and novel therapeutics. Cell membrane-coated nanoparticles exploit a top-down approach to faithfully transfer entire cell exterior, including both lipids and membrane-associated proteins, onto synthetic nanoparticles. This new class of biomimetic nanoparticles has shown significant therapeutic potentials. From drug targeting perspective, they are capable of prolonging systemic circulation critical for both passive and active targeting mechanisms, while allowing for the use of synthetic nanoparticles to carry therapeutic agents. For cell-specific targeting, a lipid insertion approach has been introduced to provide these nanoparticles with desirable targeting ligands and controlled density without involving any chemical reactions that may potentially disrupt the protein makeup on the nanoparticle surfaces. Alternatively, when coated with membranes derived from selected cells, these nanoparticles achieve cell-specific targeting ability through inherent homotypic or heterotypic adhesions. Two specific areas will be highlighted in this talk, including (i) cell membrane coating to prolong nanoparticle circulation, and (ii) cell membrane coating to achieve cell-specific targeting.

COLL 76

Nucleic acid delivery systems for RNA therapy and gene editing

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High throughput, combinatorial approaches have revolutionized small molecule drug discovery. Here we describe our work on high throughput methods for developing and characterizing RNA delivery and gene editing systems. Libraries of degradable polymers and lipid-like materials have been synthesized, formulated and screened for their ability to delivery RNA, both in vitro and in vivo. A number of delivery formulations have been developed with in vivo efficacy, and show potential therapeutic application for the treatment of genetic disease, viral infection, and cancer.

COLL 77

Enzyme-instructed assembly to form nanostructures for selectively inhibiting cancer cells

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This talk describes that the nanoscale assemblies of small molecules or nanoparticles exhibit unique biological functions in extracellular and intracellular environment, such as selectively inhibiting cancer cells. We emphasize the spatiotemporal control of the nanoscale assemblies for controlling the cell fate, particularly illustrate a paradigm-shifting approach—enzyme-instructed assembly (EIA), that is, the integration of enzymatic transformation and self-assembly—for generating nanoscale assemblies from innocuous monomers for selectively inhibiting cancer cells. Moreover, we introduce the use of ligand-receptor interaction to catalyze the formation of nanoscale assemblies. By illustrating these experimental strategies for controlling the formation of nanoscale assemblies of molecules or nanoparticles and for identifying their corresponding protein targets, we aim to highlight that, though not being defined at the genetic level, EIA generated nanoscale assemblies are able to target cancer cells.

COLL 78

Surfactant additives to improve the distribution of inhaled drugs in the lungs

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Inhaled aerosol medications often do not distribute evenly within diseased lungs leaving some poorly ventilated regions untreated. Surface tension driven flows may be useful for dispersing medications over the internal surfaces of the lungs after inhalation and aerosol deposition, increasing the portion of the lung reached by the treatment. Surface conditions within the lung are complex with glycoprotein mucus overlying a thin, watery periciliary layer. Endogenous lipid and protein surfactants are present but their concentrations vary by location and are difficult to assess. We have utilized a series of model substrates to test surfactant-based liquid and powder formulations delivered with and without aerosolization. Surfactant formulations demonstrate improved drug spreading and up to multi-fold increases in treated area with small molecule, nano-, and micrometer sized drug analogs. Important formulation parameters affecting spread area include the surface tension gradient between the formulation and the airway surface

and surfactant inventory at the deposition site. Lipid surfactants, similar to those found naturally in the lung, can be used successfully if surfactant aggregates in the solutions are successfully dispersed through aerosolization or other means. We have demonstrated the presence of a surfactant spreading front that precedes formulation spreading and causes rapid and significant changes in surface tension at a distance from the deposition site. With a liquid aerosol, the escape of surfactant from individual droplets results in significant droplet field spreading after aerosol deposition. Surfactant and drug powder blends also demonstrate substantial dispersion. Challenges to further formulation development include the varying and poorly characterized surface conditions within the lung, the complex and vast architecture of the airways and airspaces, and the need for safe formulations with very low surface tensions. Successful development of self-dispersing formulations could significantly improve treatments for diseases such as cystic fibrosis.

COLL 79

Leveraging physiology for programmed precision nanomedicine

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Introduction: Co-delivery systems incorporating therapeutic protein/peptides with small-molecule drugs or macromolecular nuclear acids have been validated as a promising strategy for enhancement of cancer therapy. However, a co-delivery system capable of differentiating the extracellular and intracellular targets still remains elusive.[1,2,3]

Materials and Methods: We have developed a gel-liposome (Gelipo)- and a graphene-based nanosystems for sequentially delivering an anticancer protein and a chemotherapeutic agent. The gel-liposome co-delivery system is composed of a cell penetrating peptide (R8H3)-modified liposomal inner core for loading the small-molecule drug—Dox and a crosslinked hyaluronic acid (HA) gel based outer shell for encapsulating the therapeutic protein—TRAIL. In graphene-based co-delivery system, the GO nanosheet is applied to bear Dox due to the supramolecular π - π stacking. A linker NH_2 -PEG- N_3 was utilized for connecting the GO-COOH nanosheet and the furin-degradable peptide. Finally, TRAIL is conjugated to the sulfhydryl groups of the peptide using an amine-to-sulfhydryl crosslinker.

Results and Discussion: The gel-liposome co-delivery system showed synergistic anticancer efficacy. The IC_{50} of TRAIL/Dox-Gelipo toward MDA-MB-231 cells is 83 ng/mL (Dox concentration), which presents a 5.9-fold increase in the cytotoxicity compared to 569 ng/mL of Dox-Gelipo. Moreover, Gelipo significantly improves the inhibition of the tumor growth *in vivo*. For graphene-based sequential delivery system,

the A549 cells that overexpress furin were applied as a cell model to investigate the site-specific delivery of TRAIL and Dox. IC₅₀ of TRAIL/Dox-fGO was determined to be 14 ng/mL (TRAIL concentration) and 140 ng/mL (Dox concentration), which increased cytotoxicities of TRAIL-fGO, Dox-fGO and TRAIL/Dox-fGO to 8.5-, 3.6- and 2.4-fold, respectively. Furthermore, TRAIL-fGO showed the strongest tumor growth inhibition *in vivo*.

Conclusions: In summary, the new programmed co-delivery systems (Gelipo and fGO nanosheet) were able to efficiently deliver TRAIL and Dox to their distinct sites of action separately, in a site-specific manner.

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COLL 80

Neutrophil-mediated transport of nanoparticles across blood barriers

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Neutrophil-mediated Transport of Nanoparticles across Blood Barriers
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ABSTRACT: Inflammation disorders are underlying components of most diseases and exist in extravascular tissues. Intravenous administration of therapeutic nanoparticles rarely reach the diseased sites due to a blood-vessel barrier. Here we report the development of a novel strategy to deliver therapeutic nanoparticles across this blood vessel barrier via the neutrophil transmigration pathway. Using intravital microscopy of TNF- α -induced inflammation of mouse cremaster venules and a mouse model of acute lung inflammation, we demonstrated that intravenously infused nanoparticles made from denatured albumin were specifically internalized by activated neutrophils, and subsequently the neutrophils migrated across blood vessels and deposited nanoparticles into inflammatory tissues. Furthermore, nanoparticle internalization did not affect neutrophil mobility and functions. Using albumin nanoparticles we were able to deliver anti-inflammatory drugs or antibiotics to inflammatory or infected lungs, dramatically mitigating the lung inflammation induced by LPS (lipopolysaccharide) or

infection by *P. aeruginosa* bacteria. Our results illustrate that neutrophils can be exploited as novel vehicles to mediate the transport of therapeutic nanoparticles across blood vessel barrier, and using this approach we could significantly improve current treatments of acute inflammatory diseases and infection.

COLL 81

Nano-theranostics for photothermally triggered immunotherapy against cancer

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Immunotherapy has attracted tremendous attention in recent years to treat many challenging diseases including cancer. As a new comer in this area, our group recently has explored how to use nanotechnology to assist immunotherapy. On one other, we have developed antigen loaded nanoparticles, some of which could be tracked by imaging systems with high sensitivity, as potential vaccines to trigger in vivo immunotherapy. For example, using upconversion nanoparticles (UCNPs) as the antigen carrier, we have realized ultra-sensitive in vivo tracking of DCs, which in the meantime could be stimulated by nanoparticles to induce strong immunological responses after be administrated into animals. On the other hand, we have tried to combine photothermal therapy with immunotherapy using nano-agents which not only exhibit strong near-infrared (NIR) absorbance for efficient photothermal conversion, but also serve as nano-adjuvants to promote the immunological responses. Stimulated by the tumor-associated antigens released after photothermal tumor ablation, the triggered immunological responses if in combination with anti-CTLA4 therapy to suppress the activity of regulatory T cells could result in effective inhibition of tumor cells remaining in the body, promising for treatment of cancer metastasis.

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COLL 82

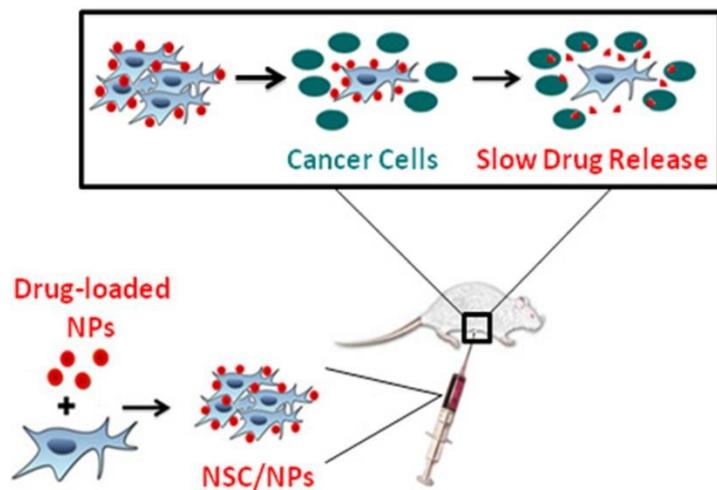
Using neural stem cell: Nanoparticle constructs to selectively deliver therapeutics to ovarian cancer

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Ovarian cancer is a deadly disease that afflicts approximately 22,000 women per year in the US. Once the disease reaches stage III and has metastasized to the abdominal

cavity, the 5-year survival rate is only 34%. Our goal is to develop stem cell/nanoparticle hybrids for targeted and selective tumor killing in patients suffering from late stage ovarian cancer. Neural Stem Cells (NSCs) are appealing for use as targeted delivery platforms in the abdomen, as they have demonstrated inherent tumor tropic properties to ovarian cancer cells *in vitro* and *in vivo* following IP administration. However, NSCs do not intrinsically have any anti-tumor efficacy. As NSC-based therapy moves into the clinic, there is a need to develop complementary techniques to enable targeted delivery of chemotherapeutics by NSCs.

An attractive complementary approach involves the use of nanoparticles (NPs), which can be loaded with a broad spectrum of chemotherapeutic agents for delivery and dissemination at tumor sites. Therefore, we are developing delayed-drug release NP/NSC constructs to realize a modular and general drug targeting system. Here, we synthesized a small library of model fluorescent silica NPs (SiNPs) with various surface functional groups, as well as cisplatin-loaded therapeutic silica NPs. The SiNPs were characterized by TEM, SEM, DLS, zetasizer, and the amount of Pt was quantified by ICP-MS. *In vitro* efficacy tests of these cisplatin-NPs demonstrated delayed drug release over 3 days. We then treated NSCs with cisplatin-NPs and injected these NSC-NP hybrids in mice bearing ovarian cancer tumors. In this biodistribution study, the amount of Pt in tumors and organs were quantified by ICP-MS 24h post injection. Our data demonstrated that NSC-NP hybrids have much superior accumulation of Pt in tumors than both free cisplatin and free cisplatin-NPs. Current work focuses on the long term survival of ovarian cancer-bearing mice treated with NSC-NP hybrids.



COLL 83

Distinguishing superatomic, metallic, and ligand-state electron dynamics in monolayer protected nanoclusters using femtosecond nonlinear spectroscopy

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Monolayer Protected Nanoclusters (MPCs) are photonic nanoparticles spanning the sub-nm to few-nm size range that can be isolated with structural and compositional control. The optical and electronic properties of MPCs often depend upon three structurally distinct components: i) metal atom core, ii) inorganic protecting units, and iii) organic ligands that aid nanocluster dispersion in colloidal suspension. In this talk, I will describe how femtosecond nonlinear spectroscopy can be used to examine and determine the influence of these three structural motifs on state-specific MPC electronic relaxation. Metallic electronic relaxation was identified for the $\text{Au}_{144}(\text{SC}_8\text{H}_9)_{60}$ nanocluster using excitation power-dependent 400-nm pump/visible probe spectroscopy. These data exhibited electronic relaxation rates that were linearly dependent on the excitation pulse energy, characteristic of metals. In contrast, excitation of $\text{Au}_{144}(\text{SC}_8\text{H}_9)_{60}$ using wavelengths spanning 480 nm to 800 nm yielded excitation-power-independent dynamics, resulting from primarily nonmetallic Superatom orbitals and ligand-based states of the MPCs. Electron dynamics for this manifold of states were resolved using state-selective pump and probe wavelengths. These methods were also applied to a series of $\text{Au}_{25}(\text{SR})_{18}$ MPCs, for which state-selective pumping and probing allowed isolation of electron and holes relaxation dynamics within the Superatom D and P states, respectively.

COLL 84

New design strategies for highly luminescent gold nanoclusters

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Luminescent nanomaterials, such as semiconductor quantum dots and organic dye molecules, have received broad attention in the scientific community for their applications in light emitting diode displays, luminescent sensors and biological imaging. Atomically precise gold clusters with well-defined core-shell structures present bright prospects to achieve high photoluminescence efficiencies. In this study, gold clusters with luminescence quantum yield higher than 60% were synthesized based on $\text{Au}_{22}(\text{SG})_{18}$ cluster, where SG is glutathione, by rigidifying its shell-gold with tetraoctylammonium (TOA) cations. Time-resolved and temperature-dependent optical measurements on $\text{Au}_{22}(\text{SG})_{18}$ have shown the presence of high quantum yield visible luminescence below freezing indicating that shell rigidity enhances the luminescence quantum efficiency. To achieve high rigidity of shell-gold, $\text{Au}_{22}(\text{SG})_{18}$ was bound to bulky TOA that resulted in greater than 60% quantum yield luminescence at room temperature. Optical measurements have confirmed that the rigidity of shell-gold was responsible for the luminescence enhancement. This work presents an effective strategy to enhance the photoluminescence efficiencies of gold clusters by rigidifying the Au(I)-thiolate shell.

COLL 85

Modulation of optical property and response of small gold clusters through the design of surface organic ligands

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The chemistry of ligand-protected gold clusters has attracted considerable interest due to their unique structure-dependent optical/electronic properties. Although their fundamental properties are known to be essentially governed by the nuclearity and geometrical structures, the protective organic ligands may also cause electronic perturbations on the cluster core to alter the optical properties. During the course of the recent study on atomically precise phosphine-ligated gold clusters, we have offered some novel examples with exceptional geometrical structures and optical features. Among them, heteroleptic clusters accommodating additional anionic ligands are interesting because a variety of organic functionalities can be introduced in the ligand moieties. Here we use acetylide- or thiolate-coordinated [core+exo]-type Au₈ clusters, and show that their optical properties and responses varied substantially with the organic ligands.

Au₈ clusters with two organic anionic ligands ([Au₈(dppp)₄L₂]²⁺) (L = C≡CR, SR) were synthesized by the reaction of the reduced form ([Au₈(dppp)₄]²⁺) with alkyne or thiol, and the structures were unambiguously determined by X-ray crystallography. Although there was no sign of the electronic coupling between the gold core and C≡C-units in the alkynyl-type clusters, the pyridyl-modified family (L = C≡CPy) showed reversible visible absorption and photoluminescence responses to protonation/deprotonation events. For example, 4-pyridylethynyl-modified cluster upon titration with HCl showed a clear red shift of the absorption band and photoluminescence quenching. The optical responses were highly dependent on the relative position of the pyridine nitrogen atom, implying the involvement of π-conjugated systems attached to the cluster moieties. In contrast, the thiolate-substituted Au₈ clusters showed marked different optical properties and responses. For example, the protonation the 4-pyridylthio-substituted Au₈ cluster resulted in a considerable photoluminescence enhancement. These observations demonstrate that the optical properties and responses can be tuned by the coordinating modules and organic functionalities.

COLL 86

Chirality of nanoscale gold particles and clusters

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Chirality at the nanoscale has gained considerable interest in recent years. The preparation of chiral nanomaterials and the properties they can have is important in pharmaceutical sciences, chemistry, physics and materials science. In this contribution

we will first provide some examples of chiral nanomaterials from different fields. We will then focus on a special class of materials: Thiolate-protected gold nanoparticles and clusters. These have promising potential applications as building blocks for nanotechnology, as catalysts or as sensors. We will discuss the preparation of chiral gold nanoparticles [1], their chiroptical properties and exchange reactions in their ligand shell. We applied Electronic and Vibrational Circular Dichroism (ECD/VCD) to study electronic transitions that are mainly located in the cluster core and to perform conformational analysis of the molecules in the ligand shell [2]. Ligand exchange reactions were performed and monitored by ECD, chromatography and mass spectrometry [3]. The chiroptical studies indicate that chirality can be bestowed to gold clusters through the adsorption of chiral thiolates. However, even with achiral ligands chiral clusters can be obtained. In this case a racemic mixture is obtained during the synthesis. Using chromatography we were able to separate the enantiomers of Au₃₈ [4] and Au₄₀ clusters. With the separated enantiomers at hand it was possible to study the properties of the gold – thiolate interface in detail. The cluster undergoes racemization involving a drastic rearrangement of its surface. This racemization is sensitive to the thiolates in the ligand shell but also towards doping of the cluster core with other metals. VCD furthermore reveals that the cluster can transfer its chirality to the environment. The latter property of the cluster may be of interest for applications in chiral technology.

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COLL 87

Nonlinear optical properties of thiolate-protected gold clusters: Second-harmonic scattering

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Thiolate-protected gold clusters have received a lot of attention in recent years, due to their intriguing, size-dependent properties. The clusters are of atomic definition and show molecular properties. While most efforts focus on structural elucidation and correlation of the structures with electronic and (linear) optical properties, including fluorescence, little work has been carried out on their nonlinear optical (NLO) properties. We recently presented the first study on second-harmonic generation (SHG) in Au₂₅(SR)₁₈ and Au₃₈(SR)₂₄ clusters, and noted a strong dependence on the properties on the structure of the clusters.¹ The findings are supported by a Density-Functional Theory (DFT) survey of the static first hyperpolarizabilities of a series of clusters. We experimentally determined the first hyperpolarizabilities of clusters composed of up to

144 Au atoms by Hyper-Rayleigh Scattering, and compare the hyperpolarizabilities with those of larger, metallic nanoparticles. The experiments also allow for benchmarking the DFT methods (e.g. ligand simplification, solvent effects) for further studies. Strong influence of the first hyperpolarizability on solvents and the choice of the ligand is observed.

The combined results represent the first systematic investigation of the second-order NLO properties of this particular class of nanomaterials, with potential in applications such as multimodal nonlinear optical imaging of biological tissue.

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COLL 88

Interconversion between superatomic electron configurations of $M@Au_{24}(SR)_{18}$ ($M = Au, Pd, Pt$) clusters

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For the past few years, owing to their unique electronic structures with high chemical and thermodynamic stability, thiolate ligand-protected gold nanoclusters have been extensively studied. In particular, the exceptional stability of thiolate-protected Au_{25} clusters, $[Au_{25}(SR)_{18}]^-$, arises from the closure of superatomic electron shells, leading to a noble-gas-like 8-electron configuration ($1S^21P^6$). Whereas the electronic properties of Au_{25} clusters are rather insensitive to the change in the ligand shell, they are likely to respond more sensitively to the change in core composition. In this presentation, we report that replacing the core Au atom with Pd or Pt results in stable bimetallic clusters, $[MAu_{24}(SR)_{18}]^0$ ($M = Pd, Pt$), having a superatomic 6-electron configuration ($1S^21P^4$). These clusters exhibit remarkably different optical and electrochemical properties from those of the 8-electron $[Au_{25}(SR)_{18}]^-$. The highest occupied molecular orbital–lowest unoccupied molecular orbital gaps of $[PdAu_{24}(SR)_{18}]^0$ and $[PtAu_{24}(SR)_{18}]^0$ determined by voltammetry were drastically decreased to 0.32 and 0.29 eV, respectively, indicating their electronic structures were significantly altered upon doping of the foreign metal. These results were strongly supported by the density functional investigations which revealed that the MAu_{12} core of the 6-electron $[MAu_{24}(SR)_{18}]^0$ is geometrically flattened to yield an oblate ellipsoid, accompanying the 1P orbital splitting. Furthermore, these clusters become 8-electron $[MAu_{24}(SR)_{18}]^{2-}$ upon electronic charging, demonstrating reversible interconversion between the 6-electron and 8-electron configurations of $MAu_{24}(SR)_{18}$. The unique electrochemical properties observed from the stable 6-electron clusters suggest that doping of a cluster is a powerful means to fine-tune the

redox properties of the cluster, which has practical implications in a variety of electrocatalytic applications.

COLL 89

Jahn-Teller effects in thiol protected gold nanoclusters and doped thiol protected gold nanoclusters

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We interrogate the relationships between structure, magnetism, and oxidation state for the three stable oxidation states of the thiolate protected nanoclusters Au₂₅(SR)₁₈ and PdAu₂₄(SR)₁₈. Characterization of each compound in multiple oxidation states by single-crystal x-ray crystallography and SQUID magnetometry suggests a first-order Jahn Teller effect.

COLL 90

From pathogen to cure: plant virus-based therapeutics

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Nanoscale engineering is revolutionizing the way we prevent, detect and treat diseases. Viruses are playing a special role in these developments because they can function as prefabricated nanoparticles. Genetic engineering and bioconjugation chemistry allow to introduce hundreds to thousands of copies of therapeutic payloads and/or targeting ligands to impart tissue-specificity. Functionalities can be introduced at the exterior and interior surfaces, and with spatial control. We have developed various strategies for therapeutic cargo loading and delivery; here, I will discuss applications in plant virus-based chemotherapy delivery targeting cancer. Furthermore, in addition to serving as a tool for drug delivery, the immune-stimulatory properties of the multivalent protein-based nanoparticles can be harnessed to stimulate the immune system, therefore potentiating the therapeutic outcome. I will highlight the potential for virus-based dual-pronged cancer therapeutics.

COLL 91

Dynamics of the adsorption and reduction of palladium on plant viruses

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A comprehensive understanding of the fundamental mechanisms governing electroless deposition on biotemplates has hitherto remained elusive. A firm grasp of these processes, which include adsorption of a metal precursor, its reduction and subsequent growth into metal nanostructures, is required for controlled and directed synthesis for applications. In this pursuit, a hydrothermal method that controls coating uniformity and efficiency is investigated.

Recent work has focused on studying the aforementioned processes in order to elucidate and replicate such controllable synthesis. Mineralization studies on four different biotemplates have been monitored with characterization techniques spanning XAS, UV-Vis, SAXS and TEM. These resulted in the successful decoupling of the surface adsorption and reaction processes. Salient mechanistic features affecting the dynamics of both processes have been revealed.

The well-known Langmuir and Freundlich adsorption isotherms describe the thermodynamics of surface adsorption by the different biotemplates. The governing adsorption parameters depend on the chemical functionalities on the biotemplate surface and the ionic species in solution, specifically metal complexes and anions.

Studies of the metal precursor reduction confirm an autocatalytic reduction mechanism mediated by the virus surface. Lastly, these populating nanoparticle growth rates were studied to confirm that the presence of cysteine groups on the TMV surface significantly affects the metal nanoparticle growth.

COLL 92

Viral templated palladium nanocatalysts

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Controlled and programmable fabrication of functional nanomaterials under mild aqueous conditions is an unmet challenge. Our approach to addressing these challenges is nanobiofabrication, that is to utilize the programmable functionalities of biologically derived materials and interactions. At the nanobiofabrication group of Tufts University, we exploit potent viral nanotemplates for controlled synthesis of metal nanocatalysts in conjunction with robust soft-lithographic fabrication for seamless integration of the as-prepared viral-nanoparticle complexes into polymeric hydrogel microparticle platforms. Specifically, we harness several unique properties of tobacco mosaic virus (TMV) for facile synthesis of catalytically active palladium (Pd) nanoparticles. We have examined and demonstrated size-controlled synthesis, high thermal stability and TMV template's fundamental role in the Pd nanoparticle formation via small angle X-ray Scattering (SAXS). We then employed two Pd-catalyzed model reactions, dichromate reduction for environmental remediation and Suzuki coupling reaction for efficient chemical synthesis of value-added chemicals, in order to investigate the catalytic activity, stability and reaction mechanisms. The results show

that the TMV-templated Pd nanoparticle synthesis offers attractive routes to highly active, controlled and stable catalyst systems in mild aqueous conditions. In this presentation, our recent progress on the spontaneous formation of small and uniform Pd nanoparticles, integration of the Pd-TMV complexes into shape-controlled polymeric microparticle scaffolds, as well as investigation of fundamental reaction mechanisms via Langmuir-Hinshelwood model, will also be highlighted.

COLL 93

Effect of nanotopography created by plant virus nanoparticles on osteogenic differentiation of bone derived mesenchymal stem cells

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One of the primary focuses in tissue engineering and regenerative medicine is optimizing a biomaterial surface at nanometer scale to control cell behaviors. In this study, virus nanoparticles with different structural features are chosen to generate 2D substrates with defined nanoscale topographies. Then the differentiation of bone derived mesenchymal stem cells (BMSCs) toward osteogenic lineage on these substrates is investigated. We observe acceleration and enhancement of osteogenesis in BMSCs cultured on the viral nanoparticles based substrates. These observations are evidenced by the upregulation of osteogenic markers, including bone morphogenetic protein-2, osteocalcin, and osteopontin, at both gene and protein expression levels. Moreover, alkaline phosphatase activity and calcium mineralization, both indicators for a successful bone formation, are also increased in cells grown on these nanoscale possessed substrates. These discoveries and developments present a new paradigm for nanoscale engineering of a biomaterial surface.

COLL 94

Virus-like-particles in advanced materials applications

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Virus Like Particles (VLPs) are the engineered and semi-synthetic derivatives of virus capsids—the shell-like structure that encapsulates the viral genome—which serve as the basis of new nanomaterials for drug delivery, *in vivo* detection of disease and in self-assembled materials. Their broad appeal arises from the fact that VLPs are highly extensible and can be modified by site-specific mutagenesis or chemical transformations post-expression to add new functionality. Our research has focused on developing methodology for organic chemical transformations within the current scope and beyond traditional bioconjugation techniques to create supramolecular nanocontainers that

enable environmentally responsive behavior. My talk will present our efforts toward this objective and the progress we have made during the initial two years of our research.

COLL 95

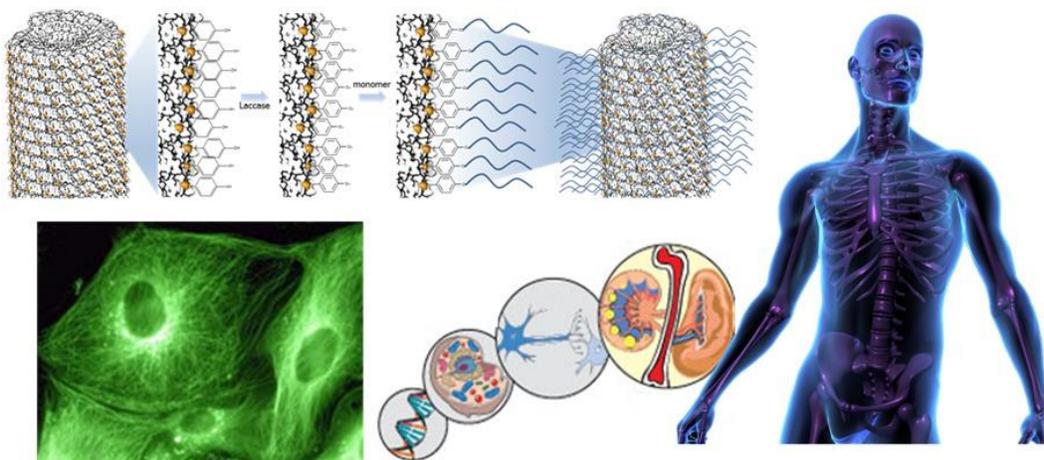
Virus bionanomaterials development and potential clinical applications

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Virus particles are an interesting class of materials for investigating new biomedical applications including drug/gene delivery, bio-sensing and bio-imaging. These virus particles can be engineered both genetically and synthetically to improve the drug targeting, prevent degradation, control release, in overall improve the treatment's efficiency. A novel synthetic approach for polymer-bionanohybrid particles will be discussed for Tobacco Mosaic Virus (TMV).

TMV which can be chemically functionalized in order to add various functionalities by targeting the surface tyrosine residues but requires some synthetic efforts. Here *Laccase* is used which is an enzyme able to selectively oxidize tyrosine. This work presents a new method to modify virus particles using *Laccase* as the biocatalyst for inducing a free radical polymerization reaction and thereby introducing a large variety of functional polymers onto the surface of the virus particle in a single step. Various monomers are used ranging from hydrophilic, charged and responsive to even hydrophobic monomers which shows the broad and easy applicability of the new synthetic method. Fluorescently labelled TMV-polymer hybrid nanoparticles were used to investigate the altered response towards cell internalization and it was found that the affinity towards cells can be tailored by changing the polymer composition.

It is envisioned that these mild and single-step approaches will greatly facilitate new biomedical applications due to the diversity and easiness of preparation. Initial attempts towards cell inclusion efficiency dependent on polymer-shell compositions have been made and ultimately more effective gene-delivery approaches are targeted.



COLL 96

Plasmonically active filamentous viruses as protein sensors

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For protein diagnostics to be of clinical value, it is necessary to develop sensors that have high sensitivity but favorable cost-to-benefit ratios. While nanotechnology has afforded novel sensing platforms, many of these require significant materials synthesis, engineering, or fabrication. In this talk, I will highlight our recent research efforts to engineer plasmonically active protein sensors by using filamentous M13 viruses. These viruses have five copies of the pIII protein, which can bind specifically to target antigens, and thousands of pVIII coat proteins, which can be genetically or chemically modified to react with signal-producing materials, such as plasmon-shifting or Raman active metal nanoparticles. We have recently shown that modified M13 bacteriophage can be used to rapidly induce a color change in the presence of a target protein yet also offer the ability to identify the detected antigen. To do this, the viruses were first modified with small molecules or DNA strands which were used to bind to metal nanocrystals. The identity of the antigen could then be easily determined by using either a DNA microarray or a micro-Raman analysis. The high surface area of the filamentous viruses also enabled generating highly sensitive signals over what be achieved by using antibodies alone. Finally, as a way to target a wide variety of biomarkers in solution, I will also demonstrate our recent protein engineering efforts to covalently attach monoclonal detection antibodies to the pIII proteins on the viruses without having to resort to expressing antibody single chain variable fragments or using biopanning techniques.

COLL 97

Influencing material properties using biomolecular interactions

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Biomolecules are being exploited in the synthesis and assembly of nanomaterials. In addition, there has also been an increasing interest in understanding the interaction between biomolecules and nanomaterials. The unique and diverse functions of biomolecules provide many opportunities in developing concepts, as well as new classes of materials and devices. The knowledge gained in understanding how biological materials are constructed and function has enabled the design of bioinspired/derived functional materials with tailored properties. We have employed experimental and computational approaches to understand structure-function relationships for the development of biomimetic materials, tailoring interfacial properties features and fabricating functional materials for a variety of applications. In this talk, I will highlight our efforts on using our fundamental understanding of biomolecular interactions, factors that influence bio-nanomaterials interactions and demonstrate the

fabrication of biomimetic materials for sensing, catalysis and decontamination applications.

COLL 98

Synthesis and characterization of metal-organic frameworks coated virus particle

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The goal of my research is to broaden the capability of a promising bionanomaterial, the tobacco mosaic virus (TMV), via surface mineralization with metal organic frameworks (MOF). Tobacco mosaic virus is the first purified and observed plant virus and has been intensively studied for decades. However, its high aspect ratio, rod-shaped morphology, various reactive sites for bio-conjugation and excellent stability in relatively broad range of conditions make it never out of fashion as robust building blocks in materials fabrication and medical applications. MOF is a type of coordinated polymer that contain highly ordered, 3-dimensional micropores and high surface area. Recent studies have demonstrated preparation of MOF under biocompatible conditions. These advanced synthetic strategies allowed MOF-coated biomaterials such as enzymes and proteins to obtain enhanced selectivity, catalytic efficiency and stability. In my project, I successfully prepared MOF-coated TMV, which retains rod-shape morphology and intact surface reactive tyrosine groups. More interestingly, the rod-shaped TMV@MOF composites can self-assemble into polyhedral microcrystals via modifying synthetic conditions. Both MOF-functionalized TMV and TMV@MOF self-assembly are novel in the field of nanotechnologies based on virus particles. With this encouraging discovery, a new type of bio-nanocomposite is emerging that will enable more robust, sophisticated and comprehensive integration of biological, inorganic and organic functional materials on the tens of nanometers scale.

COLL 99

Layer-by-layer near-IR II theranostic systems for ovarian cancer

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One of the frontiers of imaging is the use of the second near-infrared (NIR-II) window for fluorescence imaging in medical applications. Use of NIR-II provides greatly reduced tissue scattering and autofluorescence, and offers the ability to image deep into the body with fluorescence while achieving high resolution. These capabilities are particularly relevant for ovarian cancer, which is often diagnosed at late stages, when the potential for metastasis has greatly increased. The use of nanomaterials capable of providing fluorescence in this range, including quantum dots, nanotubes, and small molecule dyes, requires an appropriate surface functionalization to target tumors and enable accumulation of the nanoparticles, often via cellular uptake. Layer-by-layer (LbL) is an approach involving the alternating adsorption of positively and negatively charged polyelectrolytes. We have shown the ability to use this approach to coat a broad range of nanoscale materials, while providing properties that enable long and persistent circulation in the blood stream, and can be labeled to target tumors specifically. Importantly, layer-by-layer films can be designed to contain siRNA, proteins, or conjugated drugs within its interior layers, while allowing the formation of a targeting stealth exterior. We demonstrate the ability to coat several different NIR-II probe types, including quantum dots, carbon nanotubes, and polymer particles complexed with dye molecules to achieve LbL systems that target and direct these systems to tumors. Use of these systems in an orthotopic tumor model provided a measure of the targeting and the imaging capability of these systems. We have observed that both *in vivo* imaging and histology of the diseased tissues suggest preferential accumulation of LbL DCNPs in the orthotopic tumors, indicating great potential of using LbL NIR-II NPs as an effective theranostic platform. These concepts and methods will be further described and discussed.

COLL 100

Theranostics of tumoral cells with nanoparticles

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One of the areas of nanotechnology that has captured great interest by scientific community worldwide is the development of nanoengineered multifunctional systems which may be potentially used in a clinical strategy that simultaneously combine a (multi)diagnostic capability and single or combined therapies, the so-called nanotheranostic devices. In this talk, we will present some few examples developed within our research group in which hybrid nanoparticle-based systems are able to achieve a simultaneous multimodal therapeutic and imaging activity.

COLL 101

Tumor-specific nuclear targeting *in vivo* of graphene quantum dots via a mesoscopic interstitial fluid

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In multifunctional nanoparticle (NP) targeted diagnosis and treatment, the most important yet most difficult is the realization of precise and selective nuclear targeting throughout solid tumors. A great challenge is that pristine NPs have inability to identify cancer cells and overcome various biological barriers, and thus have to be constructed into complex, uncontrollable, and sluggish architectures coated with high-cost stabilizing agents, cross linkers, and targeting biomolecules by time-consuming, small-scale procedures. Ironically, such laborious efforts have proved futile for in vivo nuclear targeting applications owing to inevitable adverse systemic and tissue effects. Here we report that colloidal graphene quantum dots (GQDs)—the most promising, simplest, planar alternative to conventional toxic, complex, global quantum dots (QDs) —deliver an unprecedented in vivo targeting capability exactly to the nucleus only within malignant solid tumors for a wide range of types, without any additional surface engineering. Distinct from the conventional receptor-mediated targeting principle, our strategy is based on the smart synergistic utilization of two seemingly unrelated, conventionally alleged biological ‘barriers’ to perform the cancer-specific targeting: one is a repelling NP-cell interaction intentionally set as a pressure control switch that can switch off the uptake within normal healthy tissues, while the other is an interstitial fluid pressure (IFP) that is markedly enhanced within malignant solid tumors and thus serves as a pressure trigger to selectively switch on the cancer cell uptake. In vitro investigations confirm the pressure-trigger nuclear targeting mechanism and reveal a cell-dependent mechanical feature such as nuclear targeting driving threshold. In this design, the brightly fluorescent, plane-type QDs with unique intrinsic surface features behave like multifunctional, highly sensitive, ultrasensitive pressure sensors (2.5 nm) that can identify cancer cells by smart mechanical response to a wide range of cancer types, rather than by conventional antigen recognition for limited cancer types, and visualize their nuclei by targeted fluorescent imaging. Notably, the multifunctional QDs can be synthesized by the most practical approach (industrial scale, low cost, environmental friendliness), which highlights their applications in a wide range of fields beyond biomedicine.

COLL 102

^{99m}Tc-labeled multifunctional low-generation dendrimer-entrapped gold nanoparticles as a platform for targeted dual mode SPECT/CT imaging of tumors

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Development of cost-effective and highly efficient nanoscale contrast agents for targeted dual mode imaging of tumors still remains a great challenge. Here, we report the synthesis of folic acid (FA)-modified multifunctional low-generation dendrimer-entrapped gold nanoparticles (Au DENPs) labeled with ^{99m}Tc for targeted dual-mode

single photon emission computed tomography (SPECT)/computed tomography (CT) imaging of tumors. In this work, amine-terminated generation 2 poly(amidoamine) (PAMAM) dendrimers (G2.NH₂) modified with chelator DTPA *via* a amide linkage and FA *via* a polyethylene glycol (PEG) spacer were used as templates to entrap AuNPs. Further chelation of ^{99m}Tc led to the formation of multifunctional FA-targeted Au DENPs labeled with ^{99m}Tc (G2-DTPA-PEG-FA@Au-^{99m}Tc). The formed G2-DTPA-PEG-FA@Au NPs before and after ^{99m}Tc labeling were characterized *via* different techniques. We show that the formed G2-DTPA-PEG-FA@Au NPs with a mean Au core size of 1.6 nm are water-dispersible, colloidal stable under different temperature and pH conditions, and cytocompatible in the studied concentration range. Importantly, the co-existence of the AuNPs and ^{99m}Tc within the single multifunctional particles affords their uses as a nanoprobe for targeted SPECT/CT dual-mode imaging of FA receptor (FAR)-expressing HeLa cells *in vitro* and the xenografted tumor model *in vivo* within a time frame up to 3 h. With the demonstrated organ compatibility, the developed G2-DTPA-PEG-FA@Au-^{99m}Tc NPs using low-generation dendrimers may hold great promise to be used as a highly efficient and cost-effective nanoprobe for targeted SPECT/CT imaging of different FAR-expressing tumors.

COLL 103

Improved contrast in whole-body imaging with targeted colloids and membrane-impermeable quenchers and etchants

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There is considerable interest in using engineered colloidal particles to map the distribution of targeted cells in the body, to observe cell migration between and through tissues, and to better understand mechanisms of tissue transport for future nano-based drug delivery vehicles. Imaging specific cellular internalization of a drug or particle could improve our ability to detect disease and evaluate treatment efficacy, yet conventional imaging systems cannot distinguish intracellular particles from those still outside cells. The intracellular distinction can be made using core-etchable nanoprobe combined with a membrane-impermeable, biocompatible etching agent added prior to imaging. I will describe two etchable cores along with their *in vivo* etching chemistry – one system based on silver plasmonic cores and the other using semiconductor quantum dots. *In vitro* microscopy indicates efficient removal of extracellular signals (e.g. non-specifically bound particles). We translated the system to a tumor model in mice, and used whole-body longitudinal near-infrared fluorescence imaging to image tumors before and after the final etching step. We found greatly improved contrast in tumor/skin and tumor/liver when etchant was included in the procedure. *In vivo* etching can thus facilitate live animal tracking of targeting nanoprobe as they distribute and internalize into tissues and cells.

COLL 104

Size-selected imageable nanoparticles for effective image-guided vaccine delivery and cancer immunotherapy

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Although each imaging technique provides valuable information in basic research and preclinical studies, it suffers also from its own intrinsic limitations. In part, developing contrast agents which can be simultaneously detected by two or more complementary imaging modalities (e.g. multifunctional nanoparticles with multimodal imaging features) overcomes these limitations. Although these NPs are an exciting advance, it is widely accepted that a major trend in the future development of nanomaterials for biomedical research will be in combining imaging with therapy in a single construct so that diagnosis and treatment can occur together. In the context of theranostics, tackling cancer and emerging and re-emerging infectious diseases is a major goal and challenge. One of the key contributions of NP vehicles for developing safer and more effective vaccines is in improving the delivery and presentation of antigen and adjuvant to the immune system. A major challenge and opportunity will be in achieving efficient delivery of antigen/adjuvant to organs such as the lymph nodes (LNs) where immune responses are orchestrated. This *in vivo* trafficking is also desirable to monitor the invasion status of tumor-draining LNs.

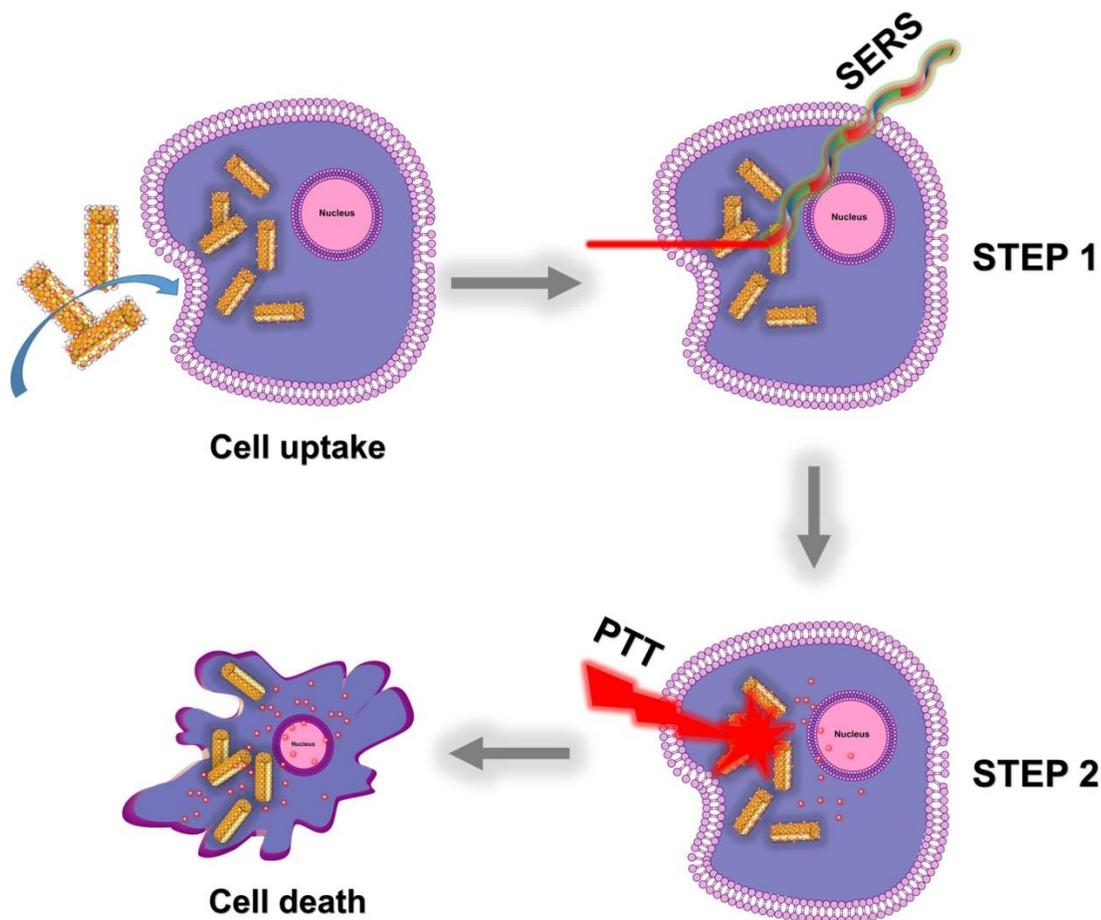
We have developed different NPs engineered to provide effective delivery of antigen, anticancer drugs and different immunomodulatory molecules to LNs whilst acting as multimodal imaging probes. We have found that subcutaneous and intratumoral administration of these structurally optimized imageable nanovaccines in mice allows effective imaging of drug delivery to LNs. We have recently investigated the immune responses and the therapeutic efficacy of several of these systems and the results show that the nanoconstructs provide significantly more effective antigen specific immune responses, cancer cell killing and anti-tumour efficacy than the free drugs. It will be shown that these nanoconstructs are easy to assemble and that may be applicable to a broad range of immunomodulatory therapeutics and imaging agents.

COLL 105

Two-step Raman imaging-guided chemo-photothermal cancer therapy

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Graphene oxide-wrapped gold nanorods (GO@AuNRs) offer efficient drug delivery as well as NIR laser photothermal therapy (PTT) *in vitro* and *in vivo*. However, no real-time observation of drug release has been reported to better understand the synergy of chemotherapy and PTT. Herein, surface-enhance Raman spectroscopy (SERS) is employed to guide chemo-photothermal cancer therapy via a two-step mechanism. In the presence of GO as an internal standard, SERS signals of DOX (doxorubicin) loaded on GO@AuNRs are found to be pH-responsive. Before DOX@GO@AuNRs are endocytic, both DOX and GO show strong SERS signals. However, only DOX signals start decreasing after the DOX@GO@AuNRs enter acidic microenvironment such as endosomes and/or lysosomes. This plasmonic antenna could be used to identify the appropriate real-time to apply PTT laser during chemo-photothermal therapy.



COLL 106

Targeting polydopamine-coated gold nanocages to tumor cells using the anti-angiogenic peptide anginex

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Tumor targeting is a crucial consideration when designing nanoparticle-based theranostic agents for *in vivo* use. The absence of targeting leads to low accumulation efficiency at the tumor site; small molecule targeting agents may lack specificity, and antibodies may not be robust enough to handle preparation and storage. Anginex is a synthetic 33mer, which can be exploited to inhibit tumor endothelial cell proliferation, tumor angiogenesis, and tumor growth. Anginex' activity arises from binding galectin-1, which is secreted by malignant tumor cells. The goal of the present study is to demonstrate the ability to conjugate anginex to polydopamine-coated gold nanocages, and then use these targeted particles to treat triple-negative, galectin-positive tumor cells. Photoacoustic flow cytometry was used to demonstrate that nearly 100 % of cells had bound particles and that the number of bound particles was reduced by ~20% when PEG is also conjugated to the polymer coating. Targeting of anginex-conjugated particles to galectin-1 positive cells was further confirmed using darkfield and photoacoustic microscopy. The untargeted particle was found to be a potent radiosensitizer, and anginex conjugation increased this effect resulting in a 4-fold reduction of surviving colonies. Photothermal heating of the nanocages was used to induce local hyperthermia which resulted in significant, tumor cell killing in the laser-irradiated region. The system's effect on angiogenesis is also under investigation. Overall, we find that anginex functions effectively as a targeting agent for these nanomaterials, which can be detected multiple ways and can be used to enhance a variety of therapeutic modalities.

COLL 107

Labelling of mesenchymal stem cells with gold nano: An initial *in vitro* study towards future *in vivo* tracking of mesenchymal stem cells

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The use of inorganic nanoparticles (NPs) for labelling mesenchymal stem cells (MSCs) for the purpose of future *in vivo* MSC tracking was investigated. Time dependent uptake efficiencies of NPs by MSCs at different exposure concentrations and times was investigated. Incorporated NPs were visualized with transmission electron microscopy (TEM). The fate of the MSCs was determined in terms of the amount of exocytosed

NPs versus the amount of initially endocytosed NPs, demonstrating that at high NP concentrations the internalized NPs are exocytosed over time, leading to a loss of label. While exposure to NPs did not significantly reduce cell viability and expression of MSC-characteristic surface markers, even at concentrations bigger than typically used for cell labelling, at those concentrations MSCs were significantly effected in their proliferation, migration. Thus, while labelling of cells with a large amount of NPs improves contrast for imaging, on the other hand the amount of added NPs should be reduced in order to avoid alterations in the MSCs.

COLL 108

Impact of the gold nanoparticle stabilizing ligands on catalysis

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During the past few decades, gold nanoparticles (AuNPs) have attracted enormous attention due to their unique catalytic activities, which are not revealed in bulk gold. Examples of the reactions catalyzed by AuNPs include the oxidation of hydrocarbons, alcohols, and glucose. In most nanoparticle applications, surface functionalization with ligands is essential to prevent from aggregation, however this surface passivation causes significant reduction of catalytic activity and selectivity. For example, Organo sulfur compounds are well known poisons of AuNP catalysis. The effect of stabilizing ligand on the catalytic property of AuNP is yet to be explored in detail. In this work, we perform an in-depth study of effect of nanoparticle stabilizing ligands such as thiolated polyethylene glycol (PEG) and 11-mercaptoundecanoic acid (MUA) on the nanoparticle catalytic activity. The AuNP catalyzed reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) by sodium borohydride (NaBH_4) is used as a model reaction. Our results show that decreasing PEG chain length and increasing surface coverage of PEG on AuNP reduces the catalytic activity. Moreover, the functionalization of AuNPs with MUA completely inhibits the catalytic activity. Studying the correlation between the ligand molecular structure and percent surface coverage on the AuNP catalytic activity is important for our fundamental understanding of the mechanisms and the rate of catalytic activity of AuNPs for different redox reactions. This work also reports the synthesis of thiolated poly(acrylic acid) (PAA) functionalized AuNPs and explored its application as a recoverable catalyst where the PAA provides pH responsive dispersibility in aqueous media. Thus PAA-AuNPs are easily and completely recovered from the reaction mixture and reused in subsequent reactions. It was found that the AuNP-PAA catalyst was highly active and reusable in the catalytic reduction of 4-NP to 4-AP with 100% conversion and modest reductions in the reaction rate with up to four catalyst recycles.

COLL 109

Probing the surface chemistry of ligand capped gold nanostructures by nuclear magnetic resonance (NMR) spectroscopy

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Gold nanostructures have attracted considerable attention in recent research due to their wide applications in various fields such as material science, physical science, electrical engineering, and biomedical engineering. Researchers have developed many methods for synthesizing different kinds of gold nanostructures, where the sizes and surface chemistry of the nanostructures are considered to be the two key factors. Traditionally, the sizes of nanostructures are determined by electron microscopy while the surface chemistry is investigated by optical spectroscopies such as IR spectroscopy and Raman spectroscopy. Compared with those techniques, Nuclear Magnetic Resonance (NMR) spectroscopy offers a more advanced and convenient tool for size determination and surface chemistry investigation by combining one and multiple dimensional NMR spectroscopy and diffusion-order NMR spectroscopy. NMR spectroscopy is a powerful tool for obtaining structural information of materials at molecular/atomic level and it has been frequently used in synthetic chemistry and molecular biology. Here, we show a proof-of-concept that NMR spectroscopy can be applied to characterize thiol-protected gold nanostructures, including size determination, surface chemistry investigation and structure study. Furthermore, we establish a general method for people to characterize nanostructures using NMR spectroscopy.

COLL 110

Changes in alkanethiolate chain length result in large changes to the electronic properties of the metallic core in gold nanoparticles, as probed by conduction electron spin resonance

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Alkanethiolate-protected gold nanoparticles are ubiquitous in nanoscience and technology, where they are valued for their ease of synthesis, stability, solubility, and emergent electronic properties. Often, chain lengths are varied in order to control solubility and stability, without concern for how the electronic properties might be affected. Here, we probe electronics within the gold core as a function of alkane chain length, using conduction electron spin resonance (CESR) -- a technique that is sensitive to the behavior of electrons near the Fermi Energy of metallic systems. We find that the properties of these *metallic* electrons are strongly affected by changes in chain length, and explore the chemical reasoning for this dependence.

COLL 111

Evaluation of thiolated ligand exchange on gold surfaces by using surface-enhanced Raman scattering

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We recently use Surface-enhanced Raman Scattering (SERS) methods to evaluate the extent of ligand exchange between different types of thiolated molecules on different types of gold surfaces. In this work, we have developed a SERS technique to evaluate the absorbance behaviour of 6-mercaptopurine (6-MP) and its glutathione-S-transferase (GST)-accelerated glutathione (GSH)-triggered release behaviour on the surfaces of gold nanostructures. The SERS signal was used as an indicator of absorbance or release of 6-MP on the gold surface. We found that GST can accelerate GSH-triggered release behaviour of 6-MP from the gold surface. Experimental results have proved that the presented SERS protocol can be utilized as an effective tool for accessing thiolated ligand exchange on gold surfaces. Compared with conventional methods, the novel SERS-based methods presented here with high sensitivity, rapid determination, relative ease of measurement may have wide application in biological analysis and nanodevice construction.

COLL 112

Synthesis of carbon-based nanomaterials loaded with silver and gold and their Raman and SERS characterization

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In this work, carbon-based nanostructured such as graphene, carbon nanotubes, and carbon nanosphere loaded with silver and gold were synthesized and characterized using various characterization techniques; scanning electron microscope, energy dispersive X-ray spectroscopy, thermogravimetric analyzer, X-ray diffractometer, Fourier transformed infrared spectroscopy, Raman spectroscopy and high-resolution transmission electron microscope. The average size of silver nanoparticles was around 40 nm and the size of gold nanoparticles was 60 nm. The UV spectroscopy showed a maximum absorbance of silver nanoparticles at ~ 400 nm while the maximum in the Au absorbance intensity was around 517 nm. The materials were evaluated by surface-enhanced Raman scattering. These nanomaterials are promising for SERS applications in drugs characterization.

COLL 113

Controlling gold nanorod synthesis via surface acoustic waves

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Gold nanorods (GNR) are very useful tools for imaging, nanomedicine, and cancer therapy, but their synthesis is often tedious and time consuming. Concurrently, surface acoustic waves (SAW) have been shown to enhance the diffusion coefficient, and hence mixing, of chemical reactions by a factor of two. Thus, we hypothesized that a SAW-mediated synthesis could modulate the reaction kinetics to accelerate the formation of GNR or produce novel morphologies. Applying 3W of power at a 50kHz frequency, the SAW-treated synthesis [JJ1] began to change color in about five minutes, whereas the control did not change until ten minutes. Vis-NIR spectrum showed a notable blue-shifted trend—the concentration of SAW-treated particles was 0.657 nM compared to 0.851 nM for the control—suggesting a change in the aspect ratio. STEM images confirmed GNR formation on samples prepared with and without the influence of the SAW, and we noticed a difference in the number of cuboidal particles between the two samples with more of these structures in the SAW treated group.

COLL 114

Synthesis and characterization of nanodiamond based hybrid nanostructures

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Understanding and manipulating the interaction between nitrogen-vacancy center in diamond and plasmonic nanostructures is crucial for many applications, including solid-state quantum devices and bio-imaging technology. We have developed a bottom-up approach to construct an emerging class of nanodiamond based hybrid nanostructures in a highly controlled manner. In these hybrid nanostructures, nitrogen-vacancy centers can be seamlessly integrated with plasmonic nanoparticles on the surface of nanodiamonds. We have achieved precise control of important structural parameters, including size, composition, coverage and spacing of external plasmonic nanoparticles, which offer a unique opportunity to investigate the underlying physics and achieve ultimate control of optical properties of nitrogen-vacancy centers. For example, substantial modification of emission characteristics of the nitrogen-vacancy centers has been observed when coupled to silver nanoparticles. These structures offer a rich toolbox to manipulate the properties of nitrogen-center from the bottom-up, and facilitate design guideline for novel nitrogen-vacancy centers based device applications.

COLL 115

***In situ* spectroscopy of the ligand exchange at the surface of colloidal Au nanoparticles**

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Gold nanoparticles with their tunable optical and electronic properties are of great interest for numerous applications. Often functionalization of the ligand shell is required in a second step after particle formation. For many techniques, this process is not accessible *in situ*. Here, we have applied second-harmonic light scattering (SHS) as an inherently surface sensitive and label-free technique to probe the ligand exchange at the surface of colloidal gold nanoparticles (AuNP) *in situ* and in real time. The original citrate shell was exchanged with the optically transparent 3-mercaptopropylsulfonate (MPS). Thiols bind strongly to Au surfaces and thereby alter their electronic surface structure. In fact, the formation of strong adsorbate-substrate bonds localizes surface electrons and leads to a reduction of the second-order polarization and consequently of SHS intensity. The SHS intensity decrease can be correlated to the MPS coverage and allows for the determination of the Gibbs free energy of adsorption and the surface coverage of MPS. We found that the ligand exchange with MPS must be described by a fast (<100 s) and a slow adsorption process (<23 min) which can be attributed to MPS adsorption on low- and high-coordinated Au surface sites. Upon MPS addition the SHS intensity decreases to an equilibrium value during 25 min whereas UV-Vis spectroscopy reveals negligible changes of the surface plasmon resonance before and after addition of MPS.

COLL 116

Plasmonic hedgehogs

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Hybrid nanostructures composed of semiconductor and plasmonic metal components have received extensive attention because of their extraordinary optical properties from synergistic interactions of localized surface plasmon resonance and the semiconducting material. In this work, gold nanoparticles (Au NPs) decorated highly uniform three-dimensional hedgehog particles (HPs), micrometre-sized particles coated with stiff nanoscale ZnO spikes, have been successfully fabricated through solution phase approach. Optical properties of these HP-Au hybrid particles were investigated with

absorption and photoluminescence (PL) spectroscopy. When HPs are decorated with Au, there is an apparent absorption enhancement in the visible range which indicates an increase of scattering in the system. PL quenching was observed for HP-Au hybrid particles compared to the original HPs. The cause for such quenching could be the intimate contact between the ZnO spikes and the Au NPs, therefore electrons transfer can easily occur from ZnO to Au. These interesting optical properties of HPs-Au hybrid nanostructures can potentially be used in a wide range of applications including photocatalysis, plasmon enhanced spectroscopy, biotechnology, and solar energy conversion.

COLL 117

Aryl bithiolate functionalized plasmonic nanoporous discs: New direction for detecting polycyclic aromatic hydrocarbons using surface-enhanced Raman spectroscopy

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This presentation describes the preparation and characterization of organic thin film-coated nano-porous plasmonic gold discs (NPGDs) as a substrate for detecting polycyclic aromatic hydrocarbons (PAHs) using surface enhanced Raman spectroscopy (SERS). NPGDs feature a unique combination of properties such as high-density plasmonic hot spots, intrinsic catalytic activities, clean surfaces, and large effective surface area. Hexyl-functionalized aryl-bithiol ($\text{H}(\text{CH}_2)_6\text{OC}_6\text{H}_3(\text{CH}_2\text{SH})_2$) (C6ArDT) was designed to be used as a robust adsorbate to form self-assembled monolayers (SAMs) on NPGD surfaces. The SAM molecules are used as a means for tuning the interfacial properties of the gold surface of the sensing substrate, thereby enhancing the interaction between the substrate with the target molecules. In addition, the incorporation of the bithiol headgroup as an anchoring moiety should offer long lifetimes for the organic monolayer. The performance of the generated NPGD random array was examined in the sensing of PAH molecules including pyrene, anthracene, benzo(a)pyrene, and benz(a)anthracene. In addition, the quality of the substrates was evaluated with respect to the adsorbate solution concentration-dependent gold-bound thiol percentage using X-ray photoelectron spectroscopy (XPS) analysis, and the Raman peak intensities of the PAH molecules as determined by SERS. This newly designed plasmonic substrate exhibits a SERS limit of detection of PAH molecules at concentrations as low as 2 $\mu\text{g}/\text{mL}$ (or 10 μM).

Keywords: Nano-porous Gold Discs (NPGD), Self-Assembled Monolayers (SAMs), Surface-Enhanced Raman spectroscopy (SERS).

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COLL 118

Sequence-dependent self-assembly of peptide amphiphiles via molecular simulations

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Stimulus-responsive biomaterials have been of great interest for a wide range of therapeutic applications including the design of biomimetic tissue scaffolds and drug delivery systems. Peptide amphiphiles (PAs), which are comprised of a bioactive peptide sequence that is chemically conjugated to a hydrophobic alkyl tail, have been shown to undergo self-assembly to form nanostructures (e.g., cylindrical nanofibers, spherical micelles) whose morphology is strongly dependent upon the solvent condition. In this study, we focus on a series of PAs to examine the effect of peptide sequence on self-assembly behavior and morphological properties of stimuli-responsive nanostructures via molecular simulations. Implementation of a newly extended intermediate-resolution protein model coupled with discrete molecular dynamic simulation technique enables the simulation of large PA systems to observe the whole self-assembly process. This allows us to elucidate kinetic mechanisms of self-assembly to form cylindrical nanofibers and spherical micelles as a function of the pH condition. Moreover, placing nonpolar peptide residues adjacent to the alkyl tail causes them shift the nanofiber-to-micelle transition in pH values due to the close proximity of charged residues. By manipulating the placement of peptide residues, the intermolecular interactions involved can ultimately be controlled and used as an effective parameter to design smart biomaterials.

COLL 119

Recognition in tight spaces

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Adhesion proteins function in confined spaces between cells or between cells and extracellular matrix. Using cadherins as model adhesion proteins, studies tested the postulate that confinement within quasi two-dimensional intercellular gaps enhances protein-protein interactions that are not detected in solution (3D). Micropipette-based measurements of cadherin-mediated cell-cell binding kinetics identified a unique kinetic signature that reflects both adhesive (*trans*) bonds between cadherins on opposing cells and putative lateral (*cis*) interactions between cadherins on the same cell. In solution, the adhesive extracellular domains only form *trans* bonds in solution (3D). Mutations postulated to disrupt the lateral interactions altered the kinetic signatures, but did not

affect the *trans* binding affinity. The kinetic signatures further correlated with cadherin organization at cell-cell junctions, with altered wound healing dynamics, and with the macromolecular permeability of inter epithelial junctions. These measurements thus revealed confinement-enhanced, quantifiable cadherin interactions that both influence adhesion protein organization within intercellular gaps and regulate tissue functions.

COLL 120

Colloid-enhanced polypeptide polydispersities: Synthesis of self-assembling, amphipathic β -sheets

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Synthesizing useful polypeptides is challenging in part because of the undesirable polydispersity index associated with the condensation polymerization growth mechanism. To offset this, we pre-synthesized amino acid dimers capable of polymerizing into amphipathic chains with alternating hydrophilic/hydrophobic side groups. Further, this alternating periodicity is typical of peptide sequences prone to self-assembly into beta-sheets. These two traits change the behavior of our growing polypeptide chains: as the strands grow longer, they become more prone to self-assemble and partition out of the reaction solvent and into colloids or interfaces. This interfacial affinity then changes the kinetics of chain growth to be transport-limited after some degree of minimum chain elongation. Our experiments show that in the absence of a colloid-rich reaction media, standard bulk-phase condensation polymerization occurs. In comparable, colloid-rich environments, the amphipathic character of the peptide narrows the polydispersity of the periodically-sequenced polypeptides and enhances subsequent interfacial self-assembly. We quantify polypeptide chain lengths and assembly using multi-angle light scattering and define the evolving β -sheet character through circular dichroism. We show that peptides grown in colloidal media show enhanced self-assembly and narrower polydispersity indices. These self-assemblies are then recharacterized as Langmuir-Blodgett films, paired with imaging through Brewster angle microscopy. From these, we show that the transport-limited peptide polymerization shows great promise for manufacturing low-cost, interfacially-assembling polypeptides.

COLL 121

Interactions between water-soluble peptoids and silica surfaces studied by second harmonic generation

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Peptoid coatings for biomedical or environmental applications have been explored towards new coating technologies. However, quantitative understanding of surface concentration and thermodynamic forces governing adsorption from aqueous phase to solid insulating surfaces is not available and can help accelerate potential peptoid-based technologies. Peptoid oligomers consisting of either six or fifteen (S)-N-1-(naphthylethyl)glycine residues, termed the 6-mer and 15-mer, respectively, were used in these studies. In this work, we quantified surface interactions between 6-mer and 15-mer peptoids and silica using the nonlinear optical tool, second harmonic generation (SHG). Equilibrium binding constants were determined for two peptoid lengths under varying pH, temperature and salt conditions.

COLL 122

Use of a unique protein model system to explore the effects of crowding by sol-gel confinement, polymeric crowding and small-molecule osmolyte crowding on different levels of protein structure

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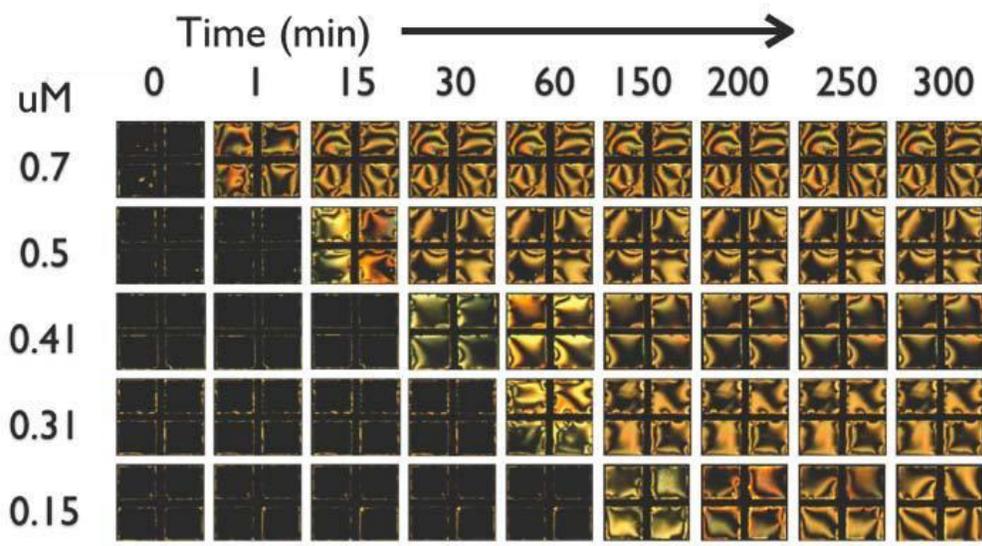
It is well-established in the literature that the structure and stability of proteins is influenced by co-solutes and other nearby structures. Recent reports on molecular crowding and confinement demonstrate that the effects of a protein's immediate environment are complex and involve several different phenomena, such as the protein's conformational entropy, changes in the properties of confined solvent molecules and enthalpic interactions. Changes in the secondary and tertiary levels of structure upon crowding were explored using a novel protein system. Osteocalcin is a small, three-helix protein with minimal tertiary structure. Jak-1 is a peptide that forms a single alpha helix with no tertiary structure. Both proteins are relatively disordered in dilute solution, and both transition to become more folded upon binding of calcium to their three gamma-carboxylated glutamic acid residues. This unique system permits direct comparison between a protein with and a protein without tertiary structure. We will describe our observations of the effects on structure and stability of osteocalcin and Jak-1 upon encapsulation in sol-gels, crowding with Ficoll-70 and crowding with the small molecule osmolyte TMAO. In brief, secondary structure stabilization was favored over tertiary structure stabilization for sol-gel encapsulation, while the opposite was true for osmolyte crowding with TMAO. Furthermore, we will discuss these results in the context of the current knowledge in the field of protein molecular crowding.

COLL 123

Dynamics of periodically sequenced polypeptides at the aqueous/liquid crystal interface

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We describe the rational design of amphiphilic helical peptides with controllable charge separation and tunable surface activity, where the dynamics of surface activity are an outcome of helical folding. The fundamentals of peptide folding and adsorption are investigated using a liquid crystal system. The thermotropic liquid crystals serve as a model fluid (i.e. oil) for the optical examination of dynamic molecular events at the aqueous/oil interface. This setup allows for the label-free detection of adsorbates with high sensitivity without limiting the mobility of the interface. Previously, similar liquid crystal experiments have been used to examine surfactants, lipids, and DNA. Our studies examine the time-dependent behavior of our periodically sequenced peptides and compare them with two well-cited protein systems, bovine serum albumin (BSA) and Lysozyme. We show that the dynamics can be quantified by the cooperative tilting of the liquid crystal (see figure), where proteins and peptides display unique organizational behavior at the interface. Subsequently, the adsorption behavior can be coupled to the bulk folded state of the peptide using circular dichroism to show that the folded population can be controlled with changes in electrolyte concentration. Taken together, we present a method to investigate surface patterning and peptide partitioning using liquid crystals, where competitive adsorption of peptides and proteins can be used to define the thermodynamics and kinetics of adsorption.



The phase transition of a nematic liquid crystal on the adsorption of a amphiphilic periodically sequenced peptide.

COLL 124

Scaling of polymer dynamics at an oil–water interface in regimes dominated by viscous drag and desorption-mediated flights

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Polymers are found near surfaces and interfaces in a wide range of chemical and biological systems, and the structure and dynamics of adsorbed polymer chains have been the subject of intense interest for decades. While polymer structure is often inferred from dynamic measurements in bulk solution, this approach has proven difficult to implement at interfaces, and the understanding of interfacial polymer conformation remains elusive.

Here we used high-throughput single-molecule fluorescence microscopy to track diffusion of isolated poly(ethylene glycol) molecules at oil–water interfaces (Figure a). Compared to diffusion in dilute aqueous solution, which exhibited the expected dependence of the diffusion coefficient (D) upon molecular weight (M) of $D \sim M^{-1/2}$ for a Gaussian chain, the behavior at the interface was approximately $D \sim M^{-2/3}$, suggesting a significantly more expanded polymer conformation, despite the fact that the oil was a poor solvent for the polymer (Figure b). Interestingly, this scaling remained virtually unchanged over a wide range of oil viscosity, despite the fact that at low viscosities the magnitude of the diffusion coefficient was consistent with expectations based on viscous drag (i.e., Stokes–Einstein diffusion), and for high viscosity oil, the interfacial mobility was much faster than expected and consistent with the type of intermittent hopping transport observed at the solid–liquid interface. The dependence on molecular weight, in both regimes, was consistent with results from both self-consistent field theory and previous Monte Carlo simulations, suggesting that an adsorbed polymer chain adopted a partially swollen (loop–train–tail) interfacial conformation (Figure c).

[1] Wang D, et al. JACS, 2015, 137, 12312–12320.

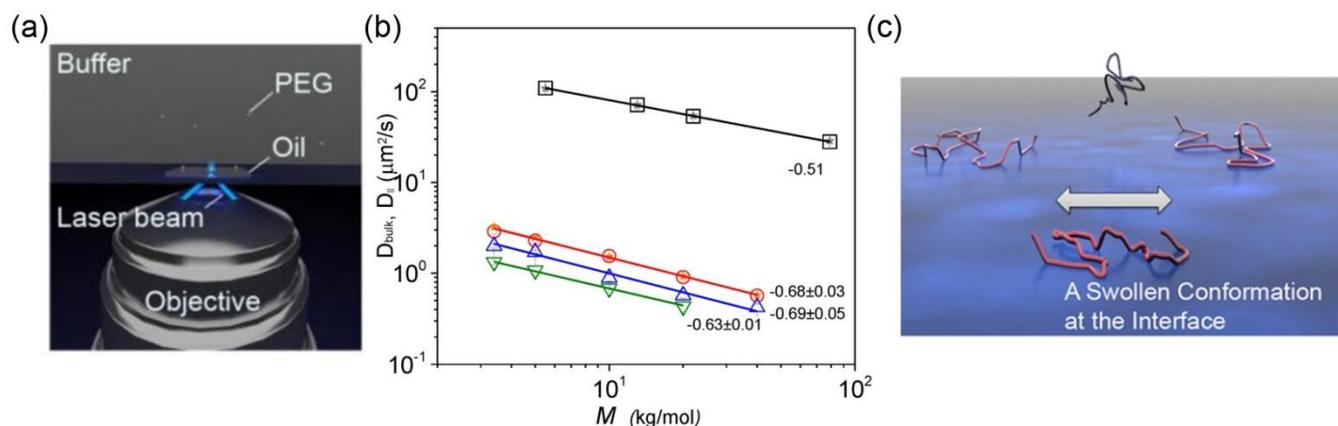


Figure (a) Schematic representation of total internal reflection fluorescence microscope at the oil–water interface; (b) Double logarithmic plot of diffusion coefficients versus molecular weight (M) in aqueous solution (squares) and at dilute coverage at the interface between water and PDMS with different viscosities. The scaling exponents associated with each data set are annotated at right. (c) Artistic presentation of adsorbed polymer chains (red) adopting a swollen interfacial conformation compared to the one in bulk liquid (black).

COLL 125

Surface tension of nano-confined lattice polymers

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Surface tension at solid/liquid interface is a key concept in understanding many important surface and interfacial phenomena such as wetting and capillarity. It is, however, not trivial to accurately calculate surface tension in lattice Monte Carlo (LMC) simulations, which are much faster (thus more accurate) than simulations in continuum. Here we propose a novel, efficient, and accurate method for calculating the surface tension of polymers confined between two parallel and impenetrable surfaces in LMC simulations, and examine how the surface tension varies with the degree of confinement (i.e., separation distance between the two surfaces). Direct comparisons between our LMC results and the corresponding lattice self-consistent field (LSCF) calculations also unambiguously and quantitatively reveal the fluctuation/correlation effects on surface tension neglected in LSCF theory.

COLL 126

Frustration by shape design: A colloidal glass of hard Brownian kites

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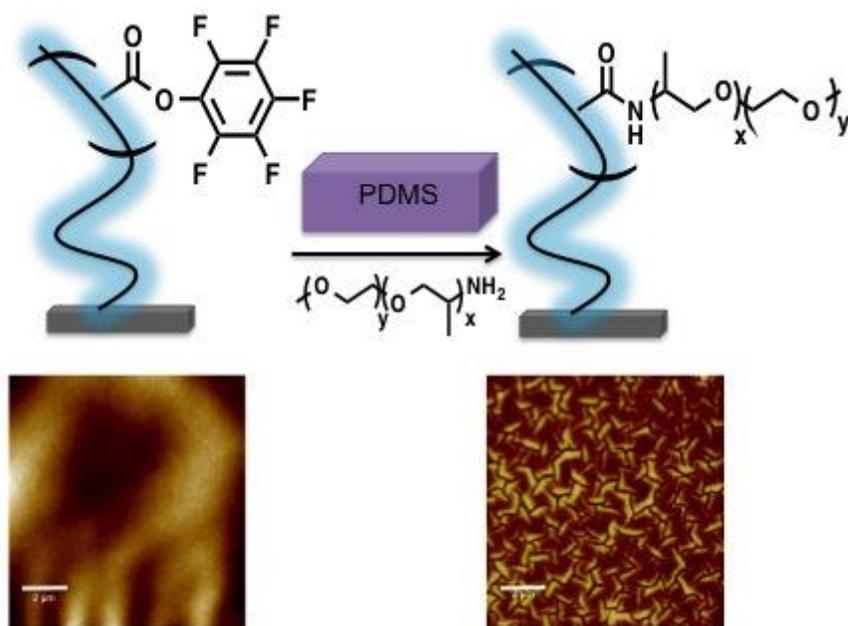
Using roughness-controlled depletion attractions, we create an idealized two-dimensional Brownian colloidal system of polymeric kite-shaped lithographic platelets that have been dispersed in an aqueous surfactant solution. Each microscale kite has one 144 degree and three 72 degree internal angles and two different edge lengths which are incommensurate. Although these kites have the geometric capacity to fully tile space in an alternating stripe crystal (ASX), upon very slow osmotic compression from a dilute isotropic fluid phase to higher densities, they do not crystallize, but instead robustly form a disordered glass, as revealed by optical transmission microscopy. We link this experimental demonstration of near-equilibrium glass formation to specific geometrical aspects of the particular designed shape of this kite, which favors the formation of local polymorphic configurations (LPCs), such as the pentagonal star, that are 5-fold and topologically incompatible over the 4-fold LPC associated with ASX. Thus, we have demonstrated a method of making a near-equilibrium glass that is directly linked to the diversity, topology, and incommensurate nature of few-particle LPCs. This mechanism of glass formation by shape-designed frustration is distinctly different than jamming colloidal particles by a rapid quench in density, and it could play a role in the suppression of crystallization of certain proteins.

COLL 127

Nanoscale surface creasing induced by post-polymerization modification

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Creasing in soft polymeric films is a result of substantial compressive stresses that trigger instability beyond a critical strain and have been directly related to failure mechanisms in different materials. However, it has been shown that programming these instabilities into soft materials can lead to new applications. In this talk, we present a method for fabricating reproducible nanoscale surface instabilities using reactive micro-contact printing (μ CP) on activated ester polymer brush layers of poly(pentafluorophenyl acrylate). We show that the sizes and structures of the nanoscale creases can be modulated by varying the grafting density of the brush substrate and pressure applied during μ CP. Stress is generated in the film under confinement due to the molecular weight increase of the side chains during post-polymerization modification, which results in substantial in-plane growth in the film, and leads to observed nanoscale creases.



Post-polymerization modification of poly(pentafluorophenyl acrylate) brushes using reactive microcontact printing with a PDMS stamp inked with Jeffamine® M-2070.

COLL 128

Synergistic enhancement of antibiotic activity with silver nanoparticles

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As time goes on, certain bacteria are becoming resistant to our seemingly antiquated antibiotics. This along with the exponential decline on the development of new drugs poses an issue concerning future treatment of bacteria. Scientists are now considering nanotechnology to be the forefront of drug development since it provides innovative approaches to current and future problems that have been perceived as nearly unsolvable. In the case of silver, which has been intensely studied and deemed an antimicrobial agent, colloidal silver not only retains antimicrobial character, but also exhibits new properties unknown to the scientific world. These properties in cooperation with antibiotics can perhaps synergistically enhance the effectiveness of the antibiotic versus it standing alone. This study tests the effects of Oxacillin on gram-negative bacteria when used in conjunction with silver nanoparticles.

COLL 129

Enhanced solid state fluorescence of nano-colloid and its application on a immunofluorescence labeling

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Fluorescent materials are generally used to visualize the cell membrane to study a biological mechanism of a cell. The immunofluorescence labeling is one of the analytical techniques to probe the structure of living cells. Two types of materials have been utilized in the fluorescence applications. Organic molecules are weak and soon lose their fluorescence under harsh environmental conditions, while inorganic materials have critical cyto-toxicity problem when they are used in a living cell. Inevitably a new fluorescent material is needed to overcome these problems. Here, a new organic fluorescent nano-colloid is introduced to overcome these problems by using a heterocyclic structure having excited-state intramolecular proton transfer and it is further applied in the immunofluorescence labeling. As expected, synthesized quinoline nano-colloid assembly has the fascinating optical property.

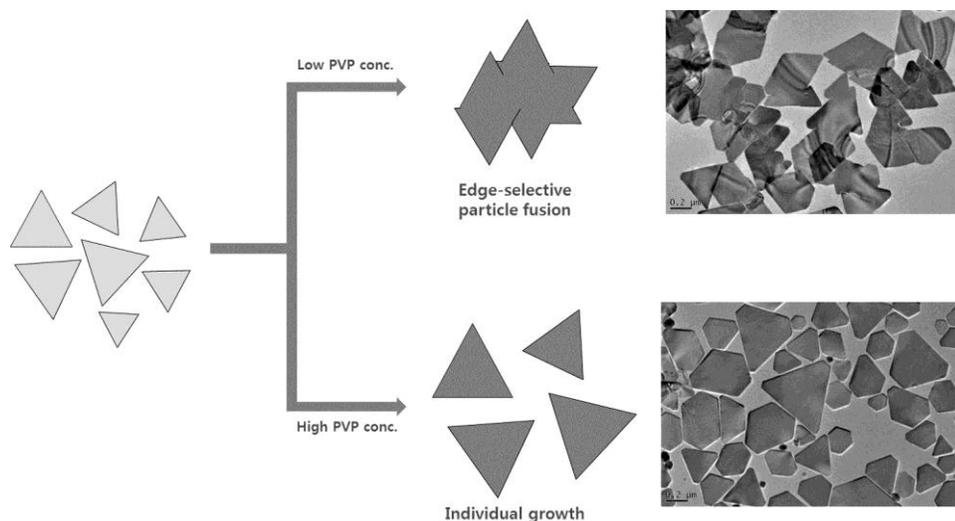
COLL 130

Maneuvering the growth pathways of silver nanoplates in kinetically controlled synthesis

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Two-dimensional (2D) conducting nanosheets such as graphenes have been of great interest because they can be applied to the bendable or stretchable electrodes for

displays. However, the 2D metal nanostructures including silver (Ag) nanoplates have not been considered as a promising material for these applications. To reduce the percolation threshold for conductivity and enhance the barrier property, Ag nanoplates with a high aspect ratio are preferred. Although several different routes to the synthesis of Ag nanoplates have been developed, most Ag nanoplates prepared from single-step synthetic routes based on solution-phase methods generally provide lateral sizes of less than 500 nm. In this presentation, a new route to the synthesis of Ag nanoplates with a high aspect ratio via particle fusion process will be reported. Ag nanoplates were synthesized by reducing silver nitrate (AgNO_3) with poly(vinyl pyrrolidone) (PVP) in N,N-dimethylformamide (DMF). In the synthesis, the hydroxyl end groups of the PVP served as a mild reductant in the kinetically controlled synthesis, and DMF played a critical role as a reaction medium (solvent) for the formation and growth of the nanoplates. Interestingly, the growth of the nanoplates proceeded along different pathways, as evidenced by variations in the shape evolution, depending on the PVP to AgNO_3 weight ratio. When the concentration of PVP is below a certain value, a large number of small nanoplates with different sizes were initially formed and then fused together along their lateral planes, leading to the formation of a secondary large nanoplate (bimodal particle growth). When the PVP concentration became higher and the surface capping was enhanced, the small nanoplates continued to grow individually without fusing (unimodal particle growth). This study not only advanced our understanding of the role played by PVP in the kinetically controlled synthetic reaction but also allows us to produce Ag nanoplates with a high aspect ratio in a single step.



Schematic illustration of the growth pathways of Ag nanoplates depending on the PVP to AgNO_3 weight ratio (Bimodal versus unimodal growth).

COLL 131

Synthesis of multilayer organic thin film with variable densities by layer-by-layer (LBL) deposition technique

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Research on multilayer organic thin film gains much attention for its many applications like optoelectronics, purification membranes, sensor, fuel cell etc. One of the simple and versatile techniques to prepare multilayer thin film is solution based LBL deposition technique.¹ In this research, we focus on the synthesis of variable densities polyurea multilayer thin film on solid surface by sequential dipping into the solution of bi-functional 1,3-Phenylene diisocyanate (PDI) and tetra-functional Tetrakis (4-aminophenyl) methane (TAM) reactive moieties. (Layer-by-Layer) multilayer growth was inspected by UV-Vis absorption spectroscopy. The linear increase of absorption intensity with deposition cycles represents the multilayer deposition. Three characteristic infrared bands of amide I, amide II and asymmetric (N-C-N) stretching band, confirmed the formation polyurea networks. XPS studies also unveiled the formation of polyurea networks.

The structural periodicity was measured with GI-SAXS technique. It was found that the structural periodicity enhanced along with layer growth at surface normal (q_z) direction on substrate surface. This result indicates that a threshold thickness is required to get molecular ordering at surface normal direction. Film thickness and film mass density were measured by X-ray reflectivity (XRR). It revealed that film mass density increased significantly with layer growth. While, 10 cycles film exhibits linear mass density throughout the film. In contrast, 20 and 30 cycles deposition case, film extending away from substrate surface is ca. 16% more dense than film proximate to the surface (Figure 1). This variation of mass density can be explained by different degree of cross-linking phenomena among film proximate to the surface and extending away to the surface.

References:

(1) Lee, B. H.; Ryu, M. K.; Choi, S. Y.; Lee, K. H.; Im, S.; Sung, M. M. *J. Am. Chem. Soc.* **2007**, 129, 16034.

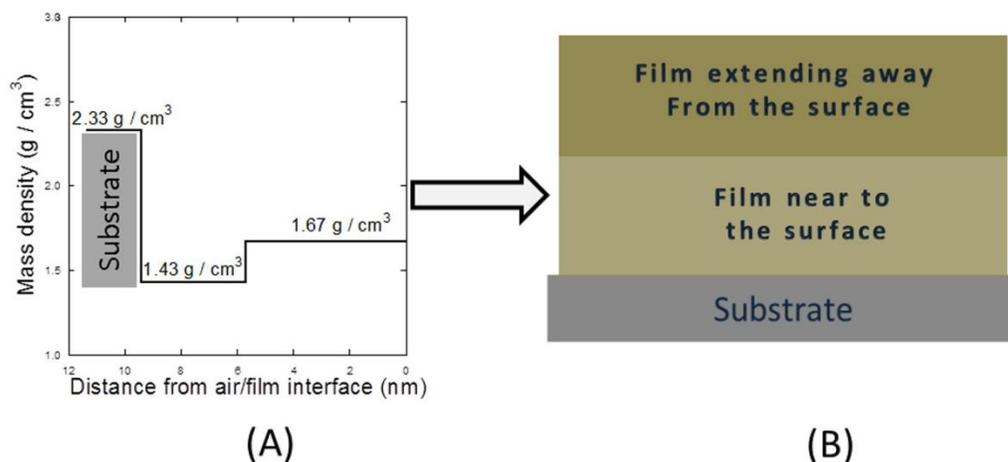


Figure 1. (A) XRR mass density (g/cm^3) profile of 30 cycles film. (B) Schematic presentation of variable densities thin film.

COLL 132

High throughput protein biomarker studies for early cancer detection

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We report progress towards the development of a novel high throughput platform to detect low abundance cancer-related protein biomarkers from body fluids. Our approach employs immobilization of anti-peptide antibodies (mAbs) onto amino-functionalized polyethylene glycol (PEG) coated magnetic nanoparticles (mNPs) with cobalt cores (which have high magnetic susceptibility) utilizing Matrix Assisted Laser Desorption Ionization Mass Spectrometry (MALDI-MS) for the quantitation of target proteotypic peptides. Details of the immobilization scheme will be described in conjunction with results describing the pros and cons of PEG coating the mNPs in terms of dispersibility and long-term storage. This novel approach, in conjunction with high speed MALDI-MS using a 5 kHz laser, will enable multiplexed quantification of protein biomarkers at a rate of 60 target proteins (180 target peptides) per sample in less than 6 minutes. This approach represents a 10-fold improvement in throughput, which is faster than standard LC-MS/MS approaches based on Multiple Reaction Monitoring (MRM) at comparable sensitivity, reproducibility, and dynamic range. This employs Labcyte's acoustic liquid handling technology, which enables multiplexing to increase the throughput. We are developing a method for analyzing 16 biomarkers initially and the same process has the potential to expand to a greater number of biomarkers and is thus scalable.

COLL 133

Tobacco mosaic virus stabilized by coordination polymers

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This project seeks to enable traditional organic chemical transformations particularly in organic solvents on large proteins. Our strategy is to utilize a biomimetic mineralization process to coat the entirety of the tobacco mosaic virus (TMV) in the porous confines of a coordination polymer. I will present my project toward extending this work into the modification of exposed amino acids on TMV to attach small molecules that would otherwise be insoluble in the traditional aqueous media normally required for such transformations.

TMV is a helical tube-shaped plant virus consisting of 2130 identical coat proteins spiraled around a single strand of viral RNA. The virus is 300 nm long, 18 nm in diameter, and has a 4 nm pore lengthwise down the middle of the tube. TMV can be disassembled and reassembled in physiological (aqueous) conditions, and it is stable under a wide range of pH and temperatures. TMV coat proteins have exposed tyrosine and glutamate residues that may be exploited for bioconjugation, allowing TMV to act as a scaffold for building larger macromolecules.

This project seeks to coat TMV with a hydrolytically stable crystalline coordination polymer in order to provide stability in a wide range of solvents that TMV cannot normally withstand. While embedded in the crystals, the exposed tyrosine and glutamate residues are still exposed, as reactants are able to diffuse through the pores and react with the TMV outer surface. These bioconjugation reactions will now be able to be performed in normally denaturing organic solvents, something not done before.

COLL 134

Synthesis of PbS/CdS core/shell nanocrystals for emerging optoelectronics applications

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Ultrathin silicon photovoltaic devices are emerging candidates for the low-cost replacement of thick, wafer-based solar cells. Energy transfer (ET) into thin crystalline silicon substrates from colloidal nanocrystals have been used to increase light absorption and hence electron-hole pair generation in the assembly. Here we demonstrate synthesis of near-infrared lead sulfide/cadmium sulfide core/shell nanocrystal quantum dots (NQDs) with bandgap lower than that of silicon (1.1 eV), suitable for the implementation in hybrid NQD/Si architectures. Optical absorption and emission spectra have shown high luminescence stability of the nanocrystals in solid state geometries. NQDs were drop casted onto Si substrates pre-functionalized with a

monolayer of self-assembled ligands (SAMs) to increase its ambient stability and prevent surface oxidation. Using time-resolved photoluminescence (PL) spectroscopy, we have measured kinetics of the NQD donors and found them to become considerably shorter in hybrid geometries, indicating effective interaction with the underlying Si substrate. This study demonstrates the feasibility of an advanced thin-film hybrid solar cell that relies on energy transfer between proximal strong light absorbers and high-mobility Si layers.

COLL 135

Optical detection of phosphatase activity with fluorescent graphene oxid

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We designed a fluorescence biosensor consisting of functionalized graphene oxide (fGO) and metal ions for the optical detection of phosphatase activity. Pristine GO was functionalized by a phosphate ligand, and followed by chelation of various metal ions, which induced quenching responses in GO fluorescence. The fGO biosensor was capable of sensitively detecting the phosphate activity through its turn-on fluorescence response. Furthermore, the fGO biosensor was able to detect an inhibitor for phosphatase.

COLL 136

Behavior of nanoscopic quantities of water in reverse micelles using NMR and fluorescence spectroscopies

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The behavior and interactions between water molecules and their environment vary greatly depending on whether they are presented in bulk or nanoscopic quantities. In our research we observe the behavior of water in small isolated environments using reverse micelles (RMs) as model systems. The behavior of water was observed for varying sizes of RMs formed using the cationic surfactant, cetyltrimethylammonium bromide (CTAB), with alcohol co-surfactants. We were able to distinguish between core and interfacial water as well as determine the relative ratio of core to interfacial water using ¹H NMR. The core to interfacial ratio appears to be dependent on the co-surfactant used, while maintaining the expected increasing trend as w_0 , a measure of the radius of the RM, increases. After establishing baseline data with previously studied straight chain alcohol co-surfactants, we applied NMR experiments to determine whether or not RMs containing cholesterol in the interfacial layer could be formed. Our goal was to create more complex lipid boundaries as models that more closely mimic cellular membranes. We found that cholesterol could not be used as the sole co-

surfactant in CTAB RMs. Cholesterol required a second co-surfactant with a limited range of ratios of CTAB to cholesterol to the other co-surfactant. Once we established that CTAB mixed micelles could be formed, acidic properties of the nanopools of water were analyzed. Aqueous acidity, in terms of pH, is generally conceptualized in ways that require a sizeable fraction of Avogadro's number of water molecules. However, in RMs with only nanopools of water there are only a few hundred to a few hundred thousand water molecules. Interesting questions arise when one proton might effectively shift the pH by more than a pH unit. We explored shifts in these environments via fluorescence and ^{51}V NMR spectroscopy. This poster will summarize our ^1H NMR, ^{51}V NMR and fluorescence data in support of our conclusions about the behavior of water in these RM environments.

COLL 137

Preparation of octanoic acid coated $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles monolayers using a mixed solvent system

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Highly crystalline and monodispersed octanoic acid coated $\gamma\text{-Fe}_2\text{O}_3$ magnetic nanoparticles were synthesized by the thermal decomposition of iron(0) pentacarbonyl. Different ratios of chloroform and methanol (5:1 to 1:1 by volume) were used as the dispersing agent for the nanoparticles in order to determine if mixed solvent system would prevent nanoparticles aggregations by creating a significantly larger solvent sphere that would further stabilize these nanoparticles in solution. By using the Langmuir-Blodgett (LB) technique, compressed monolayers of nanoparticles at the air-water interface were prepared. The monolayers were then transferred onto carbon coated Transmission Electron Microscopy (TEM) grids using either the LB or Langmuir-Schaefer (LS) methods. TEM images reveal that highly crystalline packing of nanoparticles can be achieved by preparing LB films using a chloroform and methanol mixture in a 4:1 ratio. The average diameter of the nanoparticles and the average interparticle spacing were determined to be 2.8 ± 0.7 nm and 1.9 ± 0.4 nm, respectively. The interparticle spacing is comparable with the theoretical prediction of 1.8 nm, which shows octanoic acid does not interdigitate during the packing process. Results suggest that applying a mixed solvent system of chloroform and methanol to disperse octanoic acid coated maghemite nanoparticles can reduce aggregation of these particles in a thin film thus promoting more ordered nanoparticle packing.

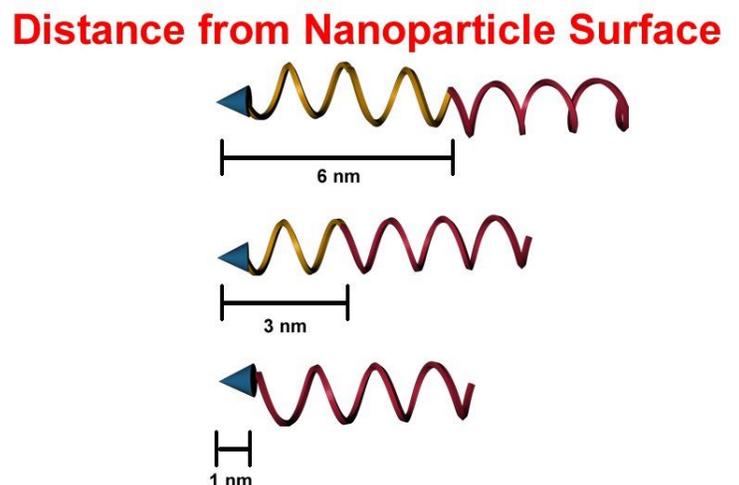
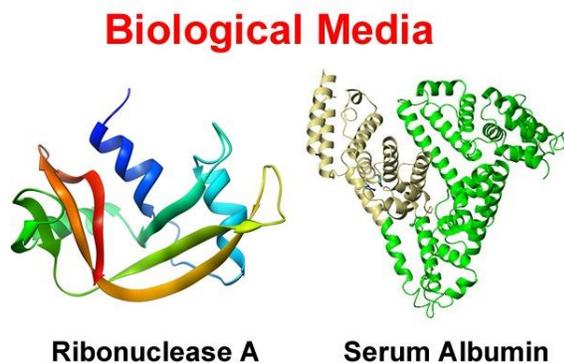
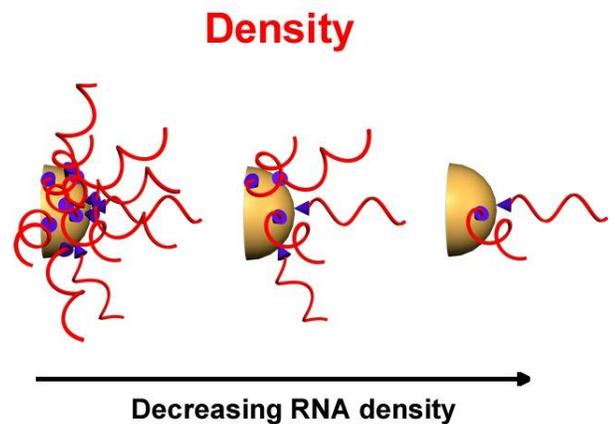
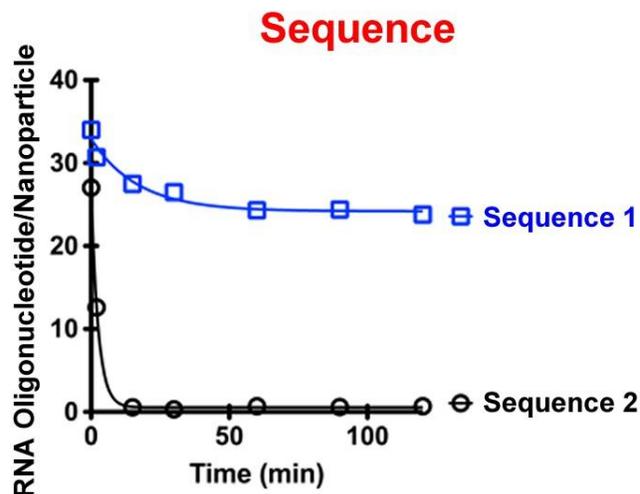
COLL 138

What controls the biological stability of RNA immobilized on nanoparticle surfaces?

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Stability in biological media is a requisite for the effectiveness of RNA *in vitro* and *in vivo* for applications such as gene regulation and immunomodulation. For example, small interfering RNA (siRNA) is a powerful and highly effective method to regulate gene expression. Spherical nucleic acids (SNAs), which consist of dense shell of oriented double stranded RNA on a nanoparticle surface, confer advantages over traditional RNA delivery such as high cellular uptake and enhanced stability compared to linear nucleic acids. While research has focused on the stability of RNA oligonucleotides free in solution, a comprehensive understanding of the factors that affect the stability of RNA immobilized on nanoparticle surfaces remains incomplete. The SNA provides an ideal system to study the stability of RNA immobilized on nanoparticle surfaces because it is a modular platform that allows one to control a number of different parameters such as sequence, oligonucleotide density, backfill molecule, and distance from the nanoparticle surface. Therefore, a comprehensive examination of how the chemical environment around the immobilized RNA affects the stability in biological media can inform the rational design of stable and active SNAs in biological media.

What Affects the Biological Stability of RNA-SNAs?



What affects the stability of RNA immobilized on nanoparticle surfaces? (1) Sequence: 12 different sequences were explored and it was determined that sequence plays a large role in the biological stability of immobilized RNA; (2) Density: By tuning the density of oligonucleotides on the surface of the nanoparticle, it was determined that the chemical environment of the RNA affects its stability; (3) Biological Media: Both complex media (ie. serum) and purified enzymes (ie. ribonucleases and serum albumin) were explored to determine which enzymes and proteins in biological media affect the stability; (4) Distance from Nanoparticle Surface: Different length linkers were utilized to determine how proximity from the nanoparticle surface affects stability.

COLL 139

PbS/CdS and PbS/ZnS all inorganic quantum dot thin films for solar cells

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Quantum dots are nanoparticles of semiconductors that can release energy of exciton as electrical current or fluorescent light. Because of this, the use of quantum dots has become an area of interest in the replacement of conventional silicon with quantum dots in solar cells as it would offer a wide range of benefits such as reducing cost, simple fabrication, and variability of band gaps. However, several issues with the potential use of quantum dot solar cells exist. These problems include the instability of films, charge recombination, and bulky ligands. To surpass these problems, research focuses on encapsulating quantum dot cores of PbS with an outer shell of CdS or ZnS on an all inorganic thin films using a low temperature method. To monitor the effectiveness of our films, absorbance and fluorescence measurements were taken. Thin films made of a specific ratio of PbS to ZnS spacers were then encapsulated with CdS or ZnS using modified Atomic Layer Deposition method displayed partially restored fluorescence of the original PbS+ZnS films. The results show that these films if further improved have the potential to be used in photovoltaic applications (Supported by the Welch Foundation Departmental Grant U-0047).

COLL 140

Morphologies of poly(vinyl alcohol) films adsorbed on polydimethylsiloxane substrates with and without plasma treatment

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Polydimethylsiloxane (PDMS) is a silicone polymer that is widely used in industry and scientific research, but its intrinsic hydrophobicity has been an impediment in many of its applications. Poor wettability, weak adhesion and nonspecific protein adsorption are undesirable properties associated with the hydrophobicity of PDMS. In order to make

PDMS surface more hydrophilic, 88%-hydrolyzed poly(vinyl alcohol) (PVOH) was adsorbed on PDMS substrates prepared by attaching PDMS polymers from 2 kDa to 116 kDa to silicon wafers. AFM images of the PVOH films illustrated a range of film morphologies. Continuous and smooth films are only obtained on the PDMS substrate with the lowest molecular weight of 2 kDa, giving rise to wettability similar as PVOH; as PDMS molecular weight/thickness increases, PVOH films become more discontinuous and eventually break into droplets, resulting in hydrophobicity similar as PDMS. The lower water receding contact angle of PDMS^{2k} relative to other PDMS substrates was hypothesized to prevent the PVOH film from dewetting. In order to test this hypothesis, oxygen plasma treatment was performed on PDMS substrates of higher molecular weights to reduce their dynamic contact angles to a comparable level as those of PDMS^{2k}. After 2 s of plasma treatment, the morphology of the PVOH film adsorbed on PDMS^{49k} changed from droplets to continuous honeycombs, which have similar features and wettability of the PVOH film adsorbed on the native PDMS^{2k}. This study establishes that the morphologies of the adsorbed PVOH films depend on the physical properties of the PDMS substrates.

COLL 141

XPS and SERS characterization of plasma-treated Ag colloids

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Plasma treatment effect on Ag colloids was investigated using X-ray photoelectron spectroscopy (XPS) and surface-enhanced Raman scattering (SERS) techniques. XPS showed that O₂ plasma was critical in removing organic contaminants on Ag colloids. With O₂ plasma treatment, Ag colloids were oxidized to form flower-like Ag₂O microclusters. The SERS spectral intensity of methyl orange (MO) adsorbed on Ag colloids became deteriorated with O₂ plasma treatment. Followed by H₂ plasma treatment, the SERS intensity of MO on Ag colloids regained, which indicated that Ag₂O has been reduced to Ag. However, the reduction by H₂ plasma could not bring Ag back to the original as-synthesized morphology. The flower-like microcluster morphology still remained. The formation mechanism of Ag₂O microclusters is discussed.

COLL 142

Performance of a new anti-fouling coating on biofilm growth on nanofiltration membranes

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Membrane biofouling is a major impediment limiting a more widespread use of membrane technologies. The formation of biofilm on the membrane surface can cause considerable technical problems and economical losses, especially in reverse osmosis

(RO) and nanofiltration processes. This work describes a new multi-functional formulation that permits either reversible or irreversible coating of membrane during normal operation. Tests show that the coating exhibit both contact-killing and anti-adhesion properties that are effective in retarding biofilm formation on the membrane surface. The treated membranes can maintain better than 2 log reduction (99 %) of *E. coli* and effectively prevent surface colonization even in the presence of soiling agents. Comparisons made with uncoated membrane showed no reduction in water permeation and dye rejection rate, indicating minimal impact of the treatment on the original membrane filtration property. Moreover, stability tests showed that the membrane retained better than 85% of the filtered anti-biofoulant after normal cross-flow operation.

COLL 143

Synthesis and biomedical applications of carbon nanomaterials: Investigation of PEG-HCCs in the treatment of ROS-mediated conditions and glioblastoma

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Carbon nanomaterials represent an expanding field with broad applications in many disciplines of chemistry and biology, and have been applied as drug delivery vehicles, biosensors, imaging agents, tissue scaffolds, and therapeutics. This work covers the use of highly oxidized carbon nanomaterials called PEG-HCCs (PEGylated hydrophilic carbon clusters) as drug delivery vehicles and as antioxidants. PEG-HCCs have been studied in vitro and in vivo and were successfully applied to treat rat models of traumatic brain injury, stroke, cancer, rheumatoid arthritis, and multiple sclerosis, and have also been used as drug delivery vehicles to treat a mouse model of glioblastoma. This work presents the results of our multiple in vivo studies as well as future directions for these nanomaterials in the field of nanomedicine. This work also investigates the mechanism of the potent antioxidant activity of the PEG-HCCs using small molecule model systems and various experimental and analytical methods.

COLL 144

Partitioning of organics into surfactant bilayers

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Solute uptake in microstructured soft materials is a reoccurring theme across several fields. In drug design, for example, one may be interested in development of an optimal vehicle to transport a relatively non-polar pharmaceutical compound through an aqueous medium. For personal care or household cleaning formulations, one may be concerned with controlling uptake of additives. Regardless of application, however, several questions arise about the challenge of tuning solute uptake: How does solute uptake affect micellar and mesophase structure? How do these changes vary with the chemical functionality of surfactants and solutes? How does introduction of additional components influence solute uptake and micellar stability? The present work addresses these questions through the use of configurational-bias Monte Carlo simulations in the osmotic Gibbs ensemble that allow for prediction of solute uptake at a given bulk concentration and concomitant change of the micellar structure. Specifically, loading of different solutes of nonpolar and polar additives in a bilayer system containing nonionic surfactants will be discussed. Simulation results are presented for systems represented by coarse-grained and united-atom force fields.

COLL 145

Modified atomic layer deposition of ZnS on CdSe quantum dot thin films

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Quantum dots are semiconductor nanocrystals that absorb energy through electron excitation, emitting energy through fluorescence as a result. Quantum dots may be implemented in LEDs to offer a cheaper alternative to incandescent lighting and easier access to LEDs for medical devices. Using a modified atomic layer deposition method, a layer of ZnS was grown over CdSe quantum dot thin films at room temperature. Building monolayers of inorganic substances, such as ZnS, on top of CdSe nanocrystals on films was used to improve the durability of the CdSe films as well as introduce a method for fabrication of thin film quantum dots at low temperatures. Successful growth of a ZnS monolayer confirms the possibility of growing nanocrystal films by monolayers at room temperature. The fluorescence of the films remained but weakened, showing that the methods used have promise for improving durability after further modification.

COLL 146

Size-tunable interfacial charge transfer with CdSe/CdS nanorod photocatalysts

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CdSe/CdS core/shell nanorods (NR) with rod-in-rod morphology offer a new architecture for engineering highly emissive nanostructures. The interplay between energetically matched semiconductors results in enhanced emission from the CdSe core. In order to further evaluate the synergistic role of these semiconductor materials, the photoinduced charge transfer process between CdSe/CdS core/shell semiconductor NR and methyl viologen (MV^{2+}), an electron acceptor, was investigated. The quenching of the emission by the addition of MV^{2+} as well as the production of electron transfer product $MV^{+\bullet}$ directly correlate to the length of the NR shell. Furthermore, transient absorption measurements show that the presence of MV^{2+} largely influences the bleaching recovery of the CdS shell over that of the CdSe core recovery. This discovery allows for the deconvolution of core/shell dynamic and points out the role of CdS shell as the site for electron transfer further indicating responsibility in determining overall photocatalytic efficiency. Thus, optimization of core/shell aspect ratio plays a crucial role in maximizing the efficiency of this photocatalytic system.

COLL 147

Room temperature growth of CdS monolayers on spherical quantum dots

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Quantum dots are semiconducting nanocrystals with quantum mechanical properties. Current procedures of synthesizing nanocrystals, or quantum dots, involve hot injection methods which result in quantum dots with a wide size distribution. Our efforts focused on developing a method of growing monolayers of Cadmium Sulfide on spherical Cadmium Sulfide core quantum dots at room temperature. In this manner, the quantum dot size distribution is narrowed in a controlled manner with the ultimate goal of improving efficiency in potential nanocrystal applications. Multiple methods of growing CdS monolayers were explored, all of which were based on previous work known as colloidal Atomic Layer Deposition (c-ALD). Such work includes the transfer of nanocrystals, or other molecular precursors, between nonpolar and polar phases in a sequential manner. Moreover, the growth of the quantum dots was monitored by observing shifts in absorbance measurements. After growing a single monolayer, a red shift was observed on the absorbance spectrum. The most successful method developed involved c-ALD in the nonpolar phase while preventing the phase transfer of the nanocrystals. Thus, this method allowed for the successful growth of two CdS monolayers on spherical quantum dots of size 3.28nm and 2.96nm in diameter and six CdS monolayers on spherical quantum dots of size 2.92nm in diameter. (Supported by the Welch Grant U-0047 to St. Mary's University).

COLL 148

Probing nano-bio interactions via a multipronged approach

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The surface area and shape of oxidized multi-walled carbon nanotubes (O-MWCNTs) are physical properties that have led to their proposed use in energy, environmental remediation, biomedicine and electronics. While these materials hold promise to benefit society, concern is rising about the potential biological consequences that O-MWCNTs could have upon direct or indirect exposure to biological and environmental systems. Therefore, the possible interactions CNTs on biological systems warrant investigation. Here, we use synthetic supported lipid bilayers (SLBs) composed of 1,2-dimyristoyl-*sn*-glycero-3-phosphatidylcholine (DMPC) as an idealized model system to study interactions between O-MWCNTs and cellular membranes using second harmonic generation (SHG), sum frequency generation (SFG), fluorescence microscopy and mass measurements using quartz crystal microbalance with dissipation (QCM-D). Ultraviolet-visible spectroscopy (UV-Vis) and dynamic light scattering (DLS) were used to study O-MWCNT aggregation as a function of ionic strength and time. SHG data showed increases in signal intensity, which suggests that the O-MWCNTs are interacting with the DMPC bilayer. SHG data also indicate that the degree of adsorption to the model cellular membrane depends on ionic strength with more adsorption at higher ionic strengths. SFG data suggests if particles are present, they do not alter the local structure of the DMPC bilayer. SHG, SFG and QCM-D results are presented to assess the reversibility of O-MWCNT-SLB interactions, and fluorescence microscopy indicates lipid-O-MWCNT accretion. UV-Vis and DLS indicate that despite initial aggregation, O-MWCNTs will largely remain suspended under our experimental conditions. Our results allow us to explore the mechanism through which O-MWCNTs interact with DMPC, our model cell membrane.

COLL 149

Characterizing the aggregation of chromonic dyes in the isotropic phase via prodan, an extrinsic fluorophore

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A key feature of amphiphilic surfactants is their ability to undergo self-assembly in water, a process in which a complex hierarchical structure is established without external intervention. The aggregation process to form spherical micelles is markedly cooperative such that the onset of micelle formation effectively takes place in a quite narrow concentration range characterized by a critical micelle concentration (cmc). In contrast to conventional amphiphiles, chromonic molecules are aromatic structures with hydrophilic solubilizing groups positioned either on the periphery of a polyaromatic central core or as linking groups between aromatic rings. With increasing concentration in aqueous solution, these systems typically show isodesmic aggregation without a critical aggregation concentration whereby stepwise growth occurs at all concentrations to yield a distribution in aggregate size. However, there is recent evidence of some chromonic molecules exhibiting multiple aggregation steps. Our research focuses on a careful re-examination of the isotropic phase of chromonic molecules to explore the relationship of molecular structure to the aggregate structure and nature of the aggregation process.

Measuring the level of aggregation of aqueous chromonic dyes is limited using traditional methods at all but low concentrations. Alternatively, our study uses fluorescence spectroscopic measurements based on the powerful spectral sensitivity of the fluorophore prodan (6-propionyl-2-(dimethylamino)-naphthalene) to its environment. Prodan's maximum emission wavelength depends on both the polarity/polarizability and hydrogen-bonding capacity of the solvent. Variations in aggregate type or size influence the characteristic shape and/or peak wavelength of the prodan fluorescence emission spectrum, allowing for differentiation of the aggregates. We have characterized the aggregation of a variety of chromonic dyes in the isotropic phase including sunset yellow FCF, acid red, benzopurpurin 4B, and methyl orange. Each dye exhibits shifts in prodan emission wavelength upon aggregation, although the concentration dependence of the emission wavelength varies with dye structure and the cross-sectional diameter of the aggregate. Our investigations of dye aggregation as a function of temperature reveal that dye aggregation is both enthalpy- and entropy-driven.

COLL 150

Synthesis of unusually large magnetic nanospheres and their novel applications in protein detection

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Magnetite microspheres and nanospheres are widely used for labeling biomolecules to study ligand-receptor interactions and to achieve molecule-specific detections. However, commonly used commercial magnetic particles have relatively weak magnetic properties, which limit the signal amplitude for detection. This presentation describes the synthesis of magnetite nanospheres (sub-micron sizes) having stronger magnetic properties than the commercial ones and their subsequent applications in probing

protein-protein interactions. Three different sizes of the magnetic nanospheres (i.e., diameter 100, 400, and 700 nm) were synthesized and functionalized. Their magnetic properties were at least one order of magnitude stronger than the widely used M280 magnetic particles in overall sample. We demonstrate the application of the magnetite spheres for specific protein detection using the exchange-induced remnant magnetization (EXIRM) technique. This technique relies on the exchange reaction of the targeted protein with the protein-functionalized magnetic spheres because of the higher affinity of the former to the surface-immobilized receptors. The exchange is indicated by a reduced magnetic signal because of the removal of the magnetic nanospheres after their dissociation. The application is shown with protein A binding with different subclasses of immunoglobulin IgG. Further refinement of the synthesis and applications will be discussed.

Keywords: Magnetic Particles, Molecule-Specific Detection, Magnetite, Exchange-Induced Remnant Magnetization, Protein Interactions

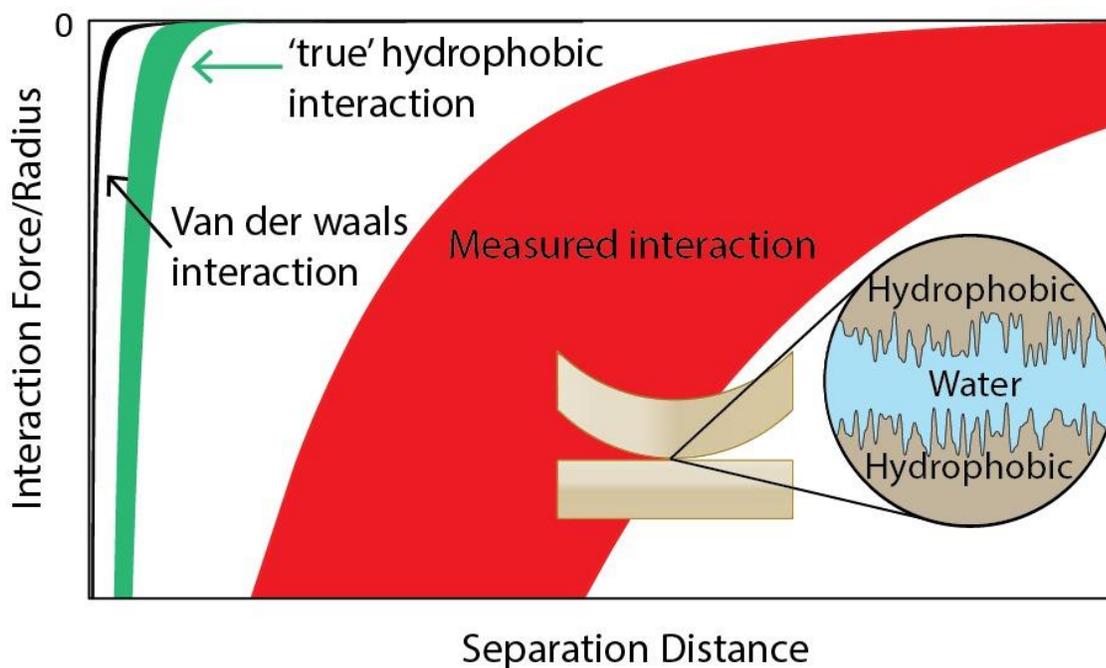
COLL 151

Long-range hydrophobic interaction and contact mechanics between rough polymer films in H₂O, D₂O, and electrolyte solutions

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The interaction and contact mechanics between rough hydrophobic surfaces were measured in degassed H₂O, D₂O and 0.1 M solutions of LiCl and NH₄Cl using the surface force apparatus. The hydrophobic surfaces were composed of polycondensed octyltrichlorosilane (C8OTS) which was vapor deposited on mica substrates to form thin films with nanoscale roughness and advancing and receding contact angles of 107° and 93° respectively. In water, the surfaces were found to exhibit attractive interactions at separation distances greater than 1000 Å placing the interaction in the long-range regime of hydrophobic interactions. Contrary to previously measured long-range hydrophobic interactions, the attraction measured here was not a result of bridging vapor cavities or electrostatic interactions. Although nanoscopic bubbles cannot be ruled out, high resolution interferometry clearly rules out bubbles of sufficient size to account for the attraction. Similarly, the Debye length in 0.1 M electrolyte solution is much too low to account for the attractive range. As a result, the measured attraction is not an effect of any previously suggested artifacts used to explain long range hydrophobic attraction. Moreover, Persson's model for adhesive contact mechanics between rough surfaces was applied to AFM topography measurements of the polymer to deduce the true surface energy (in the absence of roughness) of the films. When modeled with a surface energy expected for smooth hydrophobic surfaces, agreement between the model and measurement was excellent, however the agreement is not conclusive due to modeling the system as purely elastic (without adhesion hysteresis)

and with a spatially constant elastic modulus. Nonetheless, these measurements provide compelling evidence for conditions to obtain ultra-long range hydrophobic attraction.



COLL 152

Characterizing divalent metal ion binding sites in graphene oxide with Mn(II) ions

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Graphene oxide (GO) is typically produced by the oxidation of powdered graphite using Hummer's method. This process produces oxygenic defects in the 2-dimensional carbon lattice of graphene in the form of carboxylic acid, ketone, aldehyde, and epoxide groups. These functional groups may cluster to form metal ion binding sites. The focus of this project is to characterize the binding of Mn^{2+} by aqueous GO over a wide range of Mn^{2+} concentrations. Samples of buffered $MnCl_2/GO$ and buffered $MnCl_2$ were analyzed using Electron Paramagnetic Resonance to determine the amount of bound and free Mn^{2+} ions. At low Mn^{2+} concentrations ($10 \mu M$ - $\sim 1000 \mu M$) the binding can be described by a Langmuir isotherm binding model assuming two different types of binding sites, high affinity and low affinity. Both types of binding sites are sparse relative to the number of carbons present in the GO suspension. When higher concentration Mn^{2+} solutions ($\sim 2mM$ - $4mM$) were introduced to GO, it appeared there was deviation from the Langmuir isotherm binding model and instead adherence to the BET multilayer

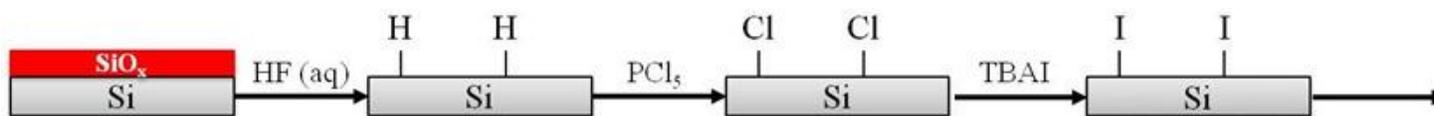
binding model. The results of these studies and current work at higher concentrations of Mn^{2+} will be presented.

COLL 153

Method for attaching thiol groups on a silicon (111) substrate

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Silicon surfaces are promising interfaces because they are mechanically and chemically resilient, able to resist wear in aqueous and organic environments containing, and display good electrical properties. There are a number of methods to conduct a silicon surface thiolation, notably through the attachment of molecules with terminal -SH moieties, which suffers from long reaction times. In present work, we developed an alternative mean for silicon surface thiolation - introducing terminal thiol groups directly onto the silicon surface. We developed two-step, wet chemical process that relies on chlorinating and then surface thiolation, which requires less time for reaction. X-ray Photoelectron Spectroscopy (XPS), Atomic Force Microscopy (AFM) and contact angle measurement were employed for the surface characterization. The thiol group attached silicon substrate can be used for further surface functionalization (for example, UV-induced "thiol-ol" modification).



COLL 154

Fabrication of thermoresponsive PEGMA colloids for controlled drug delivery

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Recently thermoresponsive polymers have been increasingly investigated in nanotechnology and biotechnology applications. Synthetic (macro)molecules exhibiting a lower critical solution temperature (LCST) in water are structures of prime importance in applied polymer research[1]. There has been a great interest on responsive polymeric micelles over the last few decade. Such structures are generally called as smart materials which have stimuli responsive nature. Indeed, these water-soluble polymers precipitate over their LCST[2]. In case of thermoresponsive polymers, temperature can be used as a simple external trigger to change the conformation of the polymer. Poly(N-

isopropyl acrylamide) (PNIPAM) and its copolymers are one of the most frequently used thermoresponsive systems with various accomplished applications[3]. Some literature reports showed that certain cell types can accept thermosensitive PNIPAM containing colloids. However, contradicting toxic behavior of PNIPAM formulations, in particular at the decadent-hydrophobic state was also reported. To improve the antifouling properties of thermosensitive colloids, either incorporating thermosensitive poly(ethylene glycol) containing methacrylate (PEGMA) units or directly usage of PEGMA polymers can be applied as an excellent alternative [4]. Herein, new PEGMA colloids having different LCST values ranging from 32 to 90 °C are successfully synthesized and characterized by using DLS, UV, and FTIR. The thermoresponsive characteristics of all synthesized PEGMA nanoparticles are explored and compared. Controlled drug and fluorescent dye release mechanisms of these PEGMA colloids are investigated under conventional heating or laser ablation (photothermal).

Acknowledgements

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COLL 155

Iron oxide nanocages for medical applications

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Cancer has been one of the most multifaceted and problematic ailments and there has been a need to engineer new ways to combat the disease. Establishing new drug delivery approaches is important and one way to make such delivery system is to utilize nanoparticles as carriers by conjugating drugs and/or anti bodies to these nanoparticles. There has been some success and failure with this method, and our research is grounded in releasing drugs more effectively because it will allow minimizing the usage of drugs while maintaining a large degree of anti-cancer activity. Many nano-drug delivery systems have taken advantage of the nontoxic iron-oxide nanoparticle, and there have been significant progress in their effectiveness. Here we are interested in

whether the shape of these particles is important for drug delivery efficiency. Recently we developed the methodology to fabricate inorganic nanocages whose size was 15 nm or less. When we applied this novel cage approach to the fabricate iron oxide drug delivery system in a diameter of 15 nm capped by stable catechol-dopamine ligands, an anti-cancer drug of Riluzole Hydrochloride showed twice the efficiency to kill osteosarcoma cells as compared to the free drug injection. Due to the stability of the dextran-dopamine capping agent and the unique cage shape of iron oxide *in vitro*, there is an implication of the similar anticancer activity by this hybrid system in circulation *in vivo*.

COLL 156

Adsorption of amphoteric polyacrylamide on silica and cellulose surfaces monitored by QCM

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Amphoteric polyacrylamide (AmPAM), as an dry strength agent and retention agent, is widely used in wet end of papermaking. Its adsorption behaviors was investigated in detail. The influencing factors, including substates (silica and two cellulose films), polymer properties (MW and concentrations) and media properties (pH, ionic strength), were all investigated. The results reveal that type of substrate, media pH, polymer concentration, ionic strength of the solution, had significant effect on the adsorption process, while the parameter of molecular weight played the least important role in the adsorption. The highest adsorption amount was achieved on the conditions of when the solution pH is close to the isoelectric point of AmPAM, the polymer concentration is high, the ionic strength equals to 100 ppm NaCl solution, and the interface has the highest charge density. The discovery offers some information to improve adsorption between amphoteric additives and cellulose fibers. It also shed some light on the mechanism of paper drystrength improvement.

COLL 157

Design of hetero-chemical patterns for controlling frictional behavior at polymer-polymer interfaces

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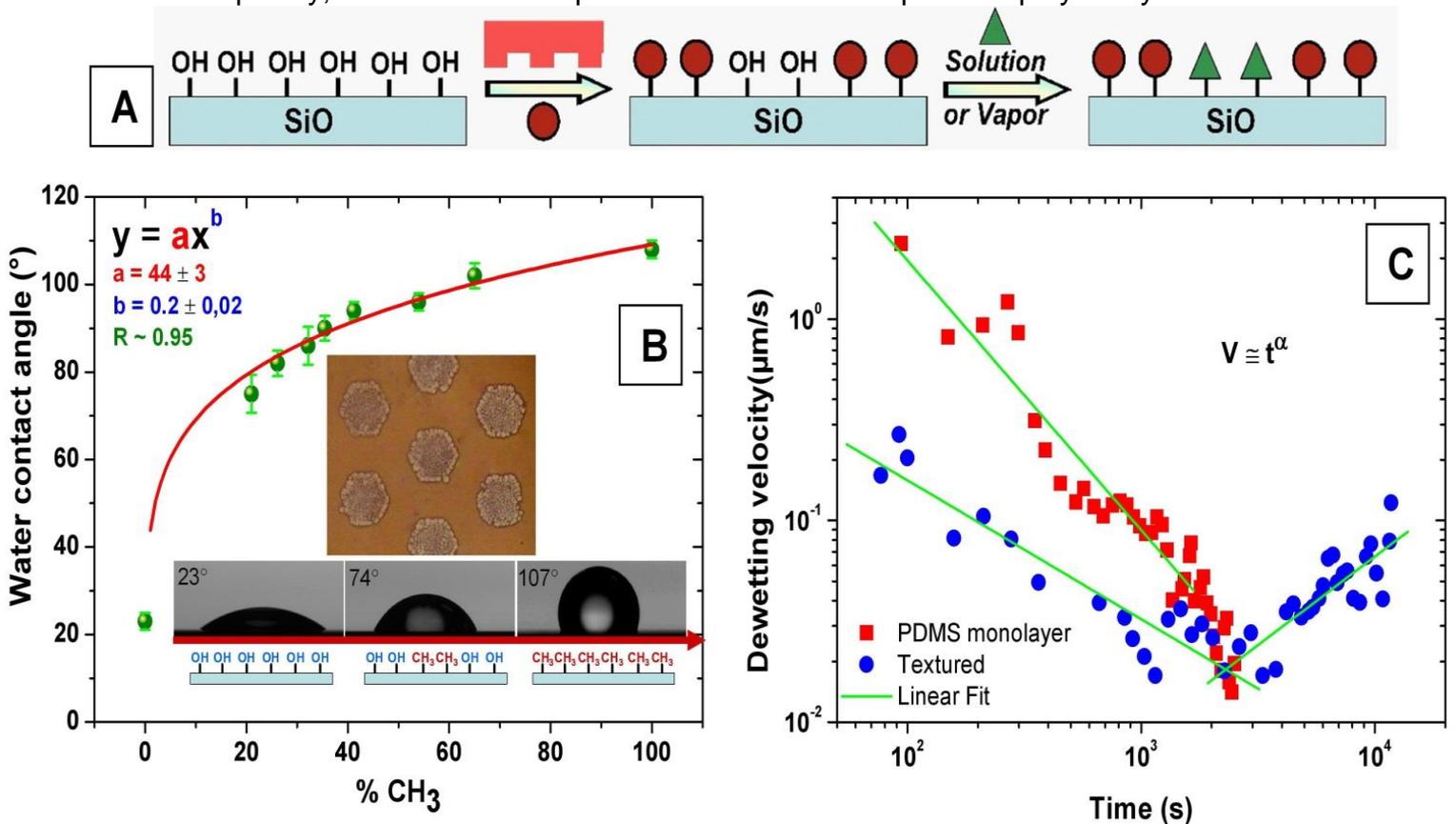
There are many common situations where contact interfaces involving elastomers are used for adhesion and/or friction functions: for example, tire/road contact in the automotive or plunger/syringe contact in the medical industries. For decades, a growing

interest has been developed in controlling friction through surface modification, with the main effort being on topographical features. In our work we are developing a general methodology (Figure 1A) to design well-defined surfaces combining micro-contact printing (μ CP), self-assembled monolayers (SAMs) and polymer grafting techniques not only to control the geometrical and mechanical properties of surface, but also to precisely tune the surface energy using a broad range of functionalities (Figures 1A-B). The frictional behavior on patterned surfaces was investigated:

a- at micro and nano scales by following the dewetting of an ultrathin polymer film (sliding of a polystyrene thin film onto the modified substrate). Figure 1C shows an example of the dewetting of a polystyrene thin film on homogenous and hetero-chemically patterned surfaces.

b- at macro scales by following the evolution of the frictional coefficient at the contact between a rubber sphere and textured substrates.

Consequently, we show that the printed hetero-chemical patterns play a key role in the



rupture properties of contact interfaces.

Figure 1: (A) Schematic representation for designing tailored chemical patterned surfaces combining μ CP and SAMs processes. The red circles and the green triangles are functionalized triethoxy- or trichloro-silane. (B) The evolution of water contact angle with the percentage of

grafted methyl groups. (C) The dewetting velocity on homogenous and hetero-chemically patterned surfaces.

COLL 158

Surface oxidation-reduction of CuOx nanoparticles for the catalytic oxidative reaction

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We establish a continuous catalytic reaction test system using metal oxide nanoparticles. The CO oxidation catalyzed by the CuOx nanoparticles (CuOx-NP) is chosen as the model system. The test system is composed of a fixed-bed catalytic reactor with the in-situ temperature-monitoring of the catalyst bed during the exothermic reaction. For the activity test, the gas chromatography is used as the downstream detector to analyze the compositions of gases after the reaction. In addition, a customized temperature-programmed reduction system (TPR) is developed for evaluating the oxidation-reduction ability of CuOx-NPs. Results show that the decrease in the initial reduction temperature of CuOx-NP results in a decrease in the light-off temperature of CO oxidation, showing an increase in the ability of catalytic oxidation. The results also indicate that the predicted performance by the TPR is consistent with the measured catalytic activity. In comparison to the single-component CuOx-NP, the addition of CeO₂ effectively enhances the oxidation-reduction ability of the existing CuOx-NP catalysts and also reduces the required light-off temperature to CO oxidation. Our work provides a prototype method to optimize the performance of nanocatalysts that can be used to promote the exothermic oxidative reaction, which is of the great interest as a fuel additive to the energy applications.

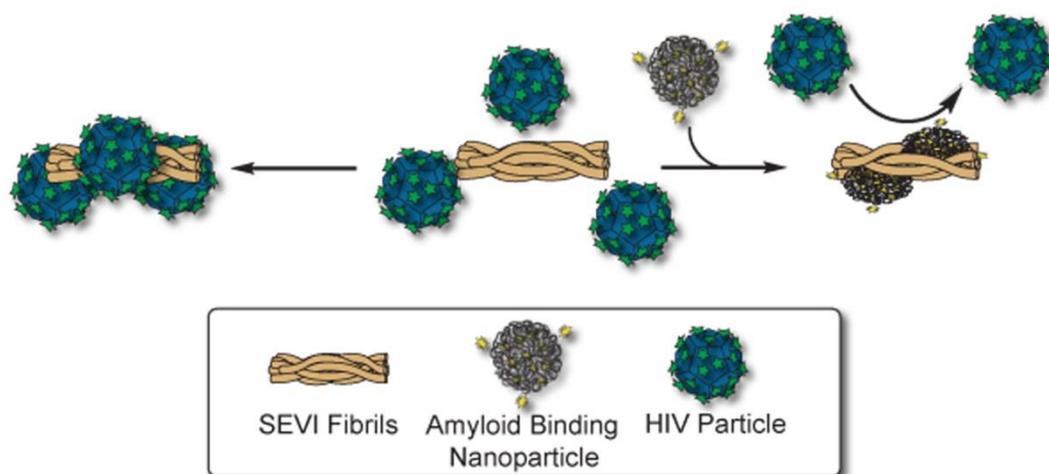
COLL 159

Amyloid targeting polymeric nanoparticles which inhibit the enhancement of HIV infectivity related to binding and internalization of HIV virions by SEVI amyloid fibril-mediated mechanisms

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Semen-derived enhancer of viral infection (SEVI) amyloid fibrils are natural materials found in semen, and have been suggested to increase HIV infectivity by 400,000-fold through facilitating the attachment and internalization of HIV virions in cells. Previous studies from our group have shown that monomeric and oligomeric amyloid-binding molecules can inhibit SEVI-mediated enhancement of HIV infectivity. Though oligomeric molecules exhibited a dramatic increase in binding affinity to the SEVI fibrils when

compared to monomers, this increased binding was only accompanied by a modest improvement in the inhibition of SEVI-mediated infectivity of HIV. In an effort to understand the relationship between binding affinity and activity of SEVI-targeting agents, we designed and synthesized polymers and polymeric nanoparticles of similar size to HIV virions and evaluated steric effects on SEVI-mediated enhancement of HIV infectivity. Our results show that these amyloid-binding polymeric materials maintain binding characteristics similar to previously published small molecules, but they displayed significantly improved inhibition of SEVI-mediated enhancement of HIV infectivity. The results suggest that sterics may be as important of a parameter as binding affinity in the design of novel inhibitors of SEVI-enhanced infection of HIV.



Polymeric nanoparticles inhibit the binding of HIV to the surface of SEVI amyloid fibrils

COLL 160

Zeta potential measurements for the characterization of polymer surfaces with varying amide/amine contents

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Zeta potential measurements are widely utilized for colloidal and fiber systems, in which the colloid stability and fiber hydrophobicity / hydrophilicity can be quantified by the isoelectric point IEP and the zeta potential.¹⁻² However, as of today, only few studies were reported on polymer films employing the 'streaming potential measurement'. In this presentation, the application of zeta potential measurements in the analysis of polymer surfaces is well elucidated by two examples.

The first example utilizes the streaming potential for the determination of the relative curing degree of amine-cured epoxy resins. With higher curing degrees, more amide groups are formed (coherent with the consumption of amine groups), and the content of

functional groups that are capable to be protonated decreases. Correspondingly, the IEPs of the cured epoxy resin surfaces decrease with the cure temperatures, and the surface charging polarity reverses with increasing cure temperatures (Figure 1, left). The other example to be shown focusses on the application of partially hydrolyzed copolymers of poly(2-nonyl-oxazoline) as contact biocides.³ If these copolymers are used as additive in low quantity in polypropylene compounds, the surface energies of the compounds do not alter (compared to 100% polypropylene). Copolymers with higher degrees of hydrolysis have higher IEPs due to the presence of amine groups, which correlates with the different pK_b of amide and amine groups: the compound containing pN₁₀₀ (unhydrolyzed) has a IEP of 8.7, while the IEPs of samples containing pN₅₀A₅₀ and pN₂₅A₇₅ (50% and 75% hydrolysis respectively) are at pH \approx 13.5 (Figure 1, right).

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Figure 1: Left: The surface zeta potential of epoxy resins cured at 60 °C and 150 °C. Right: The surface zeta potential of polypropylene PP as well as compound plates of 95% PP and 5% of poly(2-nonyl-2-oxazoline) or its partially hydrolyzed congeners.

COLL 161

Modeling the effect of varying surface thickness on the photomobilities of Si slabs

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We develop a general computational procedure to compute the photoexcited electronic mobility in semiconductor slabs using a combined density matrix theory and electronic band structure treatment. This method has been applied to 6x4 Si(111):H slabs for varying thickness (from 4-12 layers) both with and without adsorbed silver clusters. Electronic band states were generated for 10 k-points in the $\Gamma \rightarrow X$ direction in an

orthorhombic supercell using density functional theory in a plane wave basis using PBE exchange and correlation density functionals. Steady state reduced density matrix methods including dissipative effects were used to compute the photoexcited populations of each electronic band in response to the absorption of photons in the visible and near visible range. We find that the absorption of small silver clusters to the surface of the Si(111) slab enhances photoexcited electronic mobility by limiting the recombination of photoexcited electrons and holes. With increasing slab thickness this effect is reduced as the states contributed to the bandgap by the silver cluster become delocalized into the silicon slab. Increasing the size of the silver cluster on the thicker slabs appears to restore the effect photoexcited electronic mobility seen in the smaller slabs. This effect is important in the development of future photovoltaic materials where photoexcited electronic populations and photoexcited electronic mobilities both affect the efficiency of conversion of light into electrical energy.

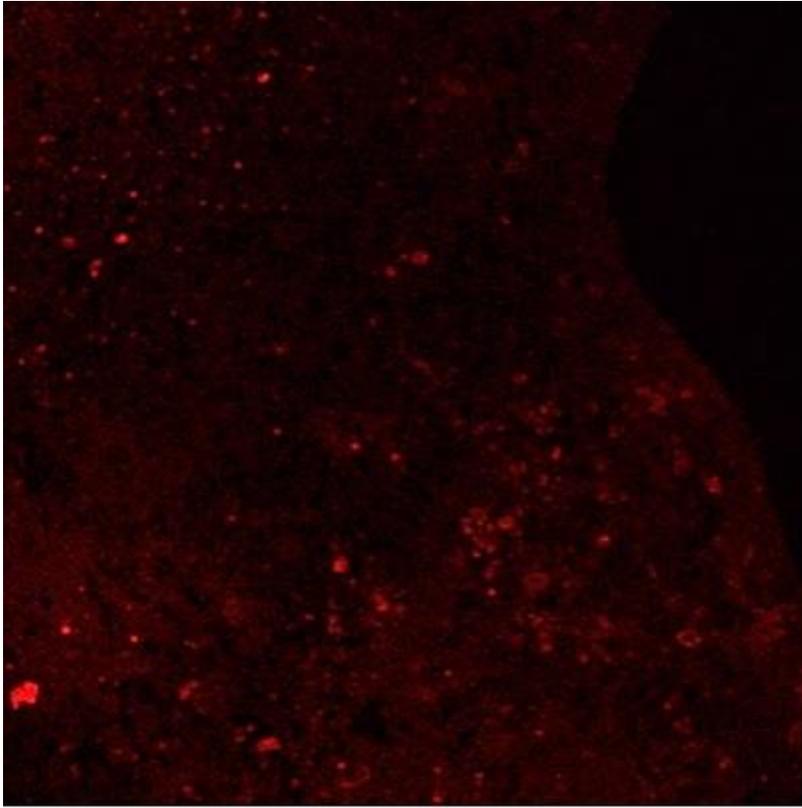
COLL 162

Fluorescently multiplexed proteinase K: Non-mesoporous silica nanoparticle

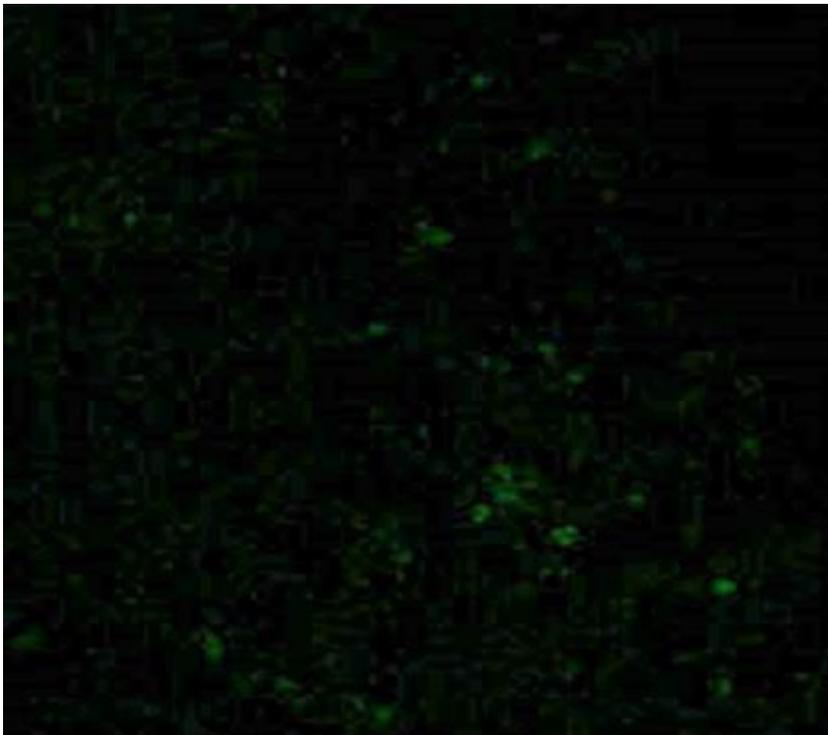
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The objective of this study was to observe the behaviors of a conjugated enzymatically active Proteinase K protein with a silica nanoparticle via a hetero-bifunctional neutral poly-ethylene glycol (PEG) adapter molecule of 20,000 molecular weight with the intent of impeding lateral flow of a protease enzyme. The reactivity of this class of protease enzyme is tremendous that several strategies would have to be employed to hinder, or slow down or retard the movement and digestive compatibility of this enzyme, while retaining enzymatic activity, via detection of free tyrosine residues through use of the Folin-Ciocalteu's phenol reagent.

We attempted to clarify through the use of multiplexing of Fluorescent dyes (one fluorophore attached to the enzyme and another, distinct fluorophore embedded within the structure of the silica nanoparticle) designed for detection via confocal microscopy. The use of confocal microscopy was exploited a technique using a laser light source of an exact wavelength to measure intensity of a fluorophore, and thus demonstrate the conjugation of that particular fluorophore with the its intended target. This technology has previously been performed in a cell biology context, but has yet to be done with applications to verify conjugation of a tethered protein. Flow cytometry was also used to characterize fluorescent nanoparticle silica size distribution. For the detection of a colloidal suspension of such a conjugated biomolecule this is a novel technique as the multiplexing of fluorophores for non-cellular purposes as the use of non mesoporous silica particles has yet to be documented and has widespread application in the pharmaceutical, biomedical device industry, and gene therapy.



Red Fluorophore attached to Proteinase K.



Green Fluorophore embedded in silica.

COLL 163

Targeting the role of tyrosine in amot protein-lipid binding events

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Angiomotins (Amots) are a family of adaptor proteins that have been shown to control cell proliferation and differentiation. Amots can *selectively* bind with high affinity to phosphoinositol containing membranes through the Amot coiled-coil homology (ACCH) domain. This binding event is linked to endocytosis, changes in cellular polarity, and apical membrane sequestration of nuclear transcription factors associated with development of cancerous phenotypes. Although the lipid selectivity of the protein has been well characterized, the mechanisms residues involved in the Amot coiled-coil homology (ACCH) domain binding these membranes are not yet known have not been fully described. Understanding the structure-function relationship may provide pathways to modulate protein sorting and downstream signaling events inducing cellular differentiation, cancer cell proliferation, and migration. The fluorescent properties of the ACCH domain were previously used to characterize the binding event. However, the relative proximity of the five native tyrosines to the membrane may have led to differences in perceived lipid binding affinities based on fluorescence resonance energy transfer with fluorescently tagged lipids. A variety of short peptides correlating to the amino acid sequence of Amot surrounding these tyrosines were assayed and observed in different membrane mimicking environments. This was done to determine if each tyrosine had the ability to bury into the hydrophobic region of the membrane mimicked by the carbon chain lengths (alcohol study), or simply interacted with the hydrophilic head groups of the lipid (liposome study). In addition, the full length Amot80 ACCH domains (wild-type and tyrosine-to-phenylalanine mutants) were screened for trends in the varying environments. Interactions were characterized by shifts in maximum wavelengths for absorbance, excitation and emission peaks. A characterization of these shifts with respect to what is seen with the various tyrosine and phenalanine mutants may further our understanding of whether each tyrosine is buried within the protein or interacts with the head groups of the membrane.

COLL 164

Optimization of bipolar electropolishing for niobium accelerator cavities

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Although effective, the current polishing processes used for niobium accelerator cavities involve dangerous and environmentally hazardous electrolytes. In this project a safer technique, bipolar electropolishing is being investigated for these cavities. Bipolar

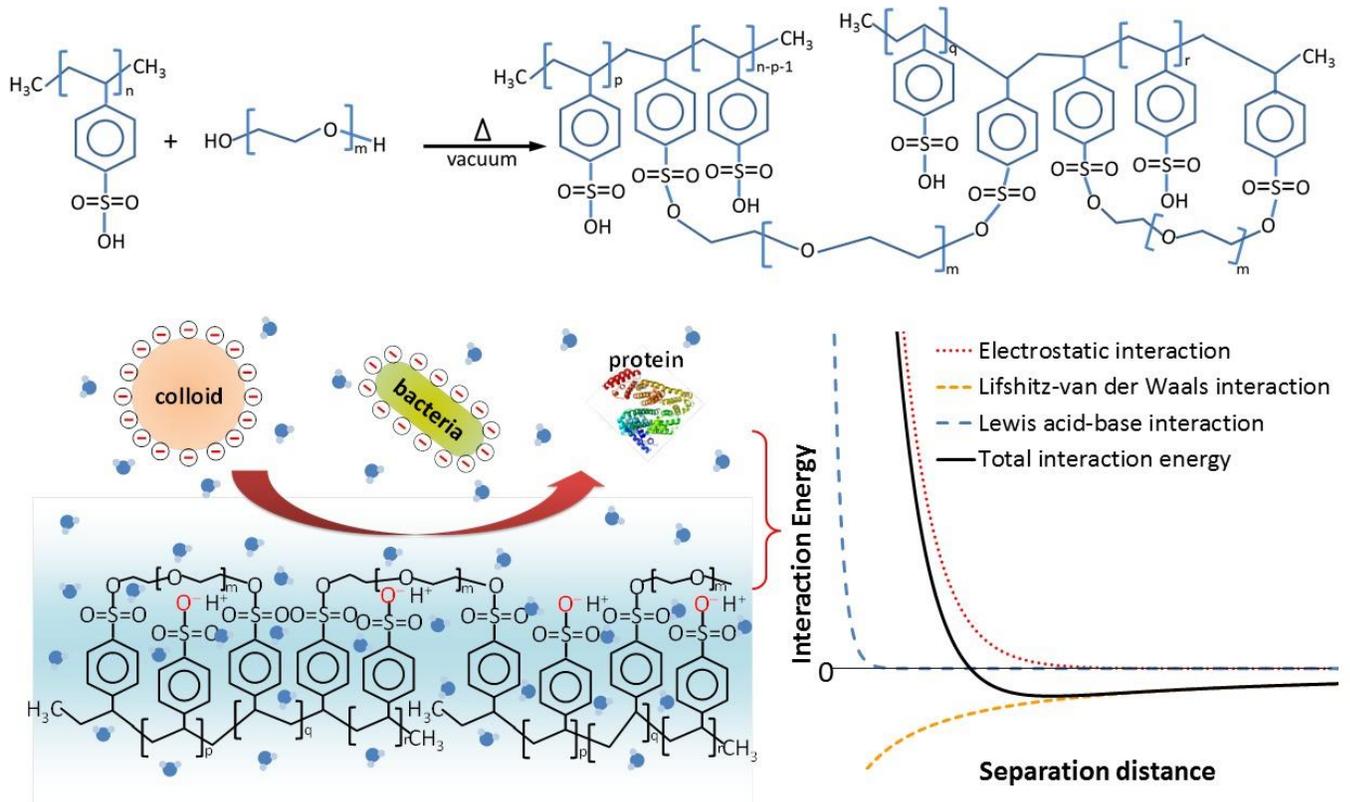
electropolishing involves sending alternating anodic and cathodic pulses with corresponding off times through the niobium sample in a low viscosity HF free electrolyte. The anodic pulse grows a layer of surface oxide, and the cathodic pulse directly or chemically reduces this layer for material removal. The purpose of this project is to test different parameters for bipolar electropolishing of niobium to optimize and gain insight into the mechanism of the process.

COLL 165

Cross-linked polystyrene sulfonic acid and polyethylene glycol as a low-fouling material

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A negatively charged hydrophilic low fouling film was prepared by thermally cross-linking a blend consisting of polystyrene sulfonic acid (PSS) and polyethylene glycol (PEG). The film was found to be stable by dip-washing. The fouling resistance of this material towards bacterial (*Escherichia coli*) and colloidal (polystyrene particles) attachment, non-specific protein (fibronectin) adsorption and cell (3T3 NIH) adhesion was evaluated and was compared with glass slides modified with polyethylene glycol (PEG) brushes, oxidized 3-mercaptopropyltrimethoxysilane (sulfonic acid, SA), and n-octadecyltrichlorosilane (OTS). The extended *Derjaguin-Landau-Verwey-Overbeek* (XDLVO) theory was used to explain the interaction behaviors of *E. coli*/polystyrene particles and substrate interactions, and the thermodynamic models based on surface energy were used to interpret protein and substrate interactions. The cross-linked PSS-PEG film was found to be slightly better than SA and PEG towards resisting non-specific protein adsorption, and showed comparable low attachment results as those of PEG towards particle, bacterial and NIH-3T3 cells adhesion. The low-fouling performance of PSS-PEG, a cross-linked film by a simple thermal curing process, could allow this material to be used for applications in aqueous environments, where most low fouling hydrophilic polymers, such as PSS or PEG, could not be easily retained.



Top row: the condensation reaction between Polystyrene Sulfonic Acid (PSS) and Polyethylene Glycol (PEG) under thermal conditions; Bottom row: the repulsion is enhanced due to negative charges and hydrophilicity of the resulting cured PSS-PEG films towards colloidal particles, bacteria, and proteins.

COLL 166

Development and characterization of surface modified metal oxide nanoparticles

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Metal oxide nanoparticles are interesting candidates as precursors for novel materials in a wide range of electronic devices. However, manufacturing electronic components with nanoparticles often leads to inhomogeneity or the lack of structural control. Surface modification of the metal oxide nanoparticle can increase the suspendability of the particle in solution allowing for their orderly introduction into larger structures. This work details the systematic evaluation of various surface treatments and conditions to optimize suspendability and incorporation into thin film and bulk materials. The formation and uniformity of the surface treatments were analyzed and validated by the introduction of optical probe molecules within the modification layers. The extent of

surface coverage and structural data was determined using contact angles, FTIR, XRD, SEM-EDX, and refractometry.

COLL 167

Gas-phase synthesis of functional nanoparticles for energy applications

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In this study we establish an aerosol-based spray pyrolysis system to generate high purity metal oxide nanoparticles (NPs) with tunable particle size and composition. Copper oxide-based nanoparticle (CuOx-NP) and copper-aluminum oxide nanoparticle (CuAlOx-NP) are chosen as the representative material, and the CO oxidation is used as the model reaction. Differential mobility analysis (DMA) was employed to in-situ monitor the secondary particle size of the synthesized NPs in the gas phase, and the scanning electron microscopy was used for providing the particle imagery of the electrostatically-deposited NPs and the primary size distributions of NPs. Thermo-gravimetric analysis was employed to determine the required temperature of the pyrolysis process, and x-ray diffractometry was used to correlate the crystallite size of NP with the pyrolysis temperature. Temperature-programmed reduction system is employed to measure the ability in the oxidation-reduction of CuOx-NPs and CuAlOx-NP, which can be correlated to the ignition temperature and the conversion rate of catalytic reaction. Result shows that we can successfully synthesize CuOx-NPs and CuAlOx-NP with tunable size and composition with ability of in-situ characterization of physical size in gas phase (i.e., by DMA). By tuning the concentration and the composition of Cu and Al precursor, we can control the particle size and the morphology of nanoparticle. The reduction temperature of CuOx and the corresponding light-off temperature of the CO oxidation reaction can be effectively improved. Addition of Al precursor was found to affect the ability of reduction and catalytic performance. Our work provides a prototype study to fabricate CuOx-NPs and CuAlOx-NP with an optimal performance in catalysis. The results can be used to develop a correlation of material properties versus the oxidation-reduction ability and the catalytic activity, which have shown to be a strong indicator to the performance in the energy release and the ability in catalysis.

COLL 168

Understanding and controlling the magnetic properties of chemically modified graphene oxide flakes using sulfates

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It is essential to understand and develop the ability to tune the magnetic properties of graphene-based materials to pursue prospective applications in nanoelectronics and spintronics. Graphene is known as a unique material that exhibits extraordinary electrical, mechanical, thermal, and optical properties. Even though these properties have been extensively explored, the magnetic properties are poorly defined owing to a lack of information. There are a few theoretical studies; however, studies providing experimental magnetic data are rare. Moreover, most of the available experimental data have dealt with graphene on a substrate rather than in the form of "flakes", either as thermally annealed or adatom graphene oxide (GO) flakes. Therefore, we chose to examine the properties of the flakes of GO before and after their "chemical modification" to systemically investigate the impact of such changes on their magnetic properties. GO flakes chemically functionalized by the covalent grafting of sulfates to their surfaces were examined in this study using two control factors: the absence/presence of the sulfates analyzed using three different reaction temperatures. The GO samples were characterized by Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). The essential magnetic properties were investigated using a physical property measurement system (PPMS) with a vibrating sample magnetometer (VSM) mode.

KEYWORDS: Magnetic Properties, Graphene Oxide Flakes, Sulfates, Functionalization.

COLL 169

Probing the conductivity peak of organic electrolyte gated transistors

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Organic Semiconductors have shown promise for their use in flexible and wide area electronics and biosensing devices. Studies of organic single crystals as semiconductors in Electrolyte Gated Transistors (EGTs) give insight into charge transport properties of organic semiconductors. Electrolyte gating creates an electrical double layer with high charge density at the electrolyte-semiconductor interface. As charge density increases in organic EGTs, carrier mobility decreases dramatically, resulting in a peak in conductivity. The use of surfactants in the electrolyte layer may diminish this mobility loss by increasing the distance between charges in the electrolyte and charge carriers in the semiconductor. The addition of Brij-58 surfactant to [P14][FAP] ionic liquid in a rubrene EGT alters the work function on the electrolyte-semiconductor or electrolyte-gate electrode interface, shifting the conductivity peak and threshold voltage (the gate voltage at which the device turns on) with minimal changes to peak conductivity, suggesting potential tunability of these important voltage levels.

COLL 170

Structural characterization of red light photoreceptors isolated from *Stigmatella aurantiaca* using atomic force microscopy

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Bacteriophytochromes (BphPs) are red-light photoreceptors found in various photosynthetic and non-photosynthetic bacteria. Members of this protein family play a major role in signal transduction pathways that regulate bacterial growth and development. BphPs are composed of a photosensory module that consists of three domains termed PAS, GAF, and PHY along with a signal effector domain, known as histidine kinase (HK). BphPs utilize covalently attached biliverdin chromophore (BV), a linear tetrapyrrole, as an organic pigment to detect light. BV enables photoconversion between red and far-red light-absorbing states, which results in global structural changes within the protein. These structural changes are not well-understood due to lack of crystal structures of intact BphPs which are also too large for analysis by NMR. Therefore, Atomic Force Microscopy (AFM) has been employed to characterize the structure of the photosensory module and the fully intact BphP, which includes HK, in the light-adapted states. Specifically, we focus on the structural analysis of red-light photoreceptor (SaBphP2) from non-photosynthetic myxobacterium *Stigmatella aurantiaca*. PeakForce Quantitative Nanomechanical Property Mapping has been used to gain insight into protein structure and dynamics at physiologically relevant conditions and nanometer resolution. Individual dimers of SaBphP2 have been observed on a mica surface in the presence of red light. The size, orientation, and structure of these red-light photoreceptors have been directly compared to models of intact BphPs generated using PyMOL software and X-ray crystallographic structures of similar BphPs. Cross-sectional analysis and total volume measurements of the SaBphP2 dimers are in close agreement with the models.

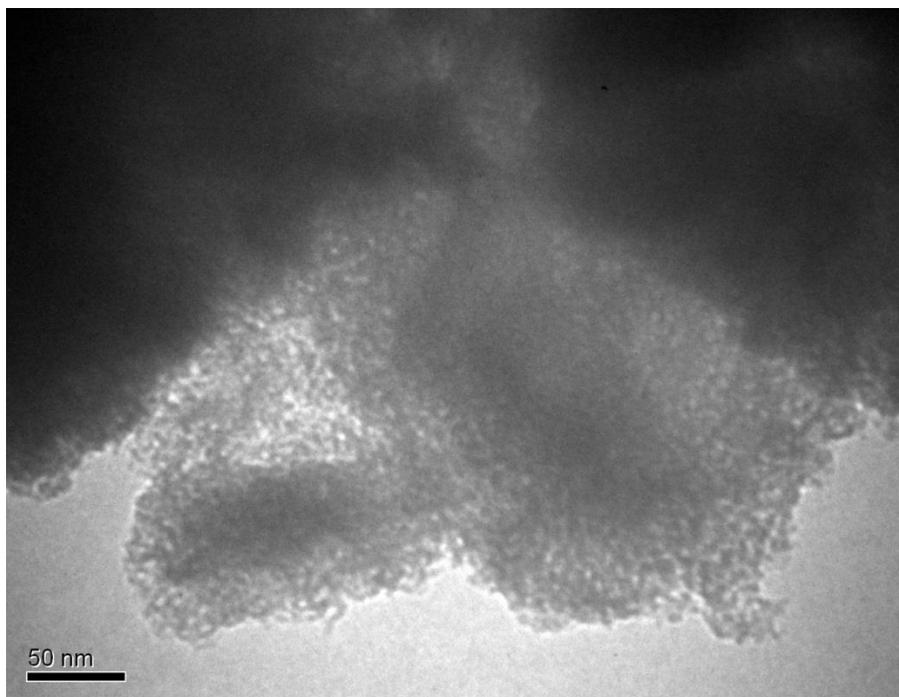
COLL 171

Sol-gel synthesis of modified silica gels containing incorporated heteropolyacids

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The present work reports results of systematic study of mesoporous materials based on silica gels with incorporated heteropolyacids. These materials have unique catalytic and adsorption properties due to presence of strong acidic sites on their surfaces. In particular, they might be used for adsorption of ions of radioactive isotope ¹³⁷Cs from contaminated soils and waters. The materials were synthesized by co-condensation of tetraethoxysilane (TEOS) with phosphotungstic or phosphomolybdic acids using sol-gel technique. Reactions were carried out in acidic media in ethanol/water solution. The following surfactants were used as templates: sodium dodecylsulfate, dodecylamine, trimethylstearylammmonium chloride, and Pluronic P123. The products were obtained at various pH, ratios TEOS/heteropolyacid, temperatures, reaction and aging times.

Effects of various reaction conditions on the yields and structural characteristics of the products were determined. All samples were amorphous with BET surface areas in the range of 400-1100 m²/g. Incorporation of heteropolyacids into silica gel slightly reduced BET surface areas as compared with pure silica gels. The best porous characteristics were achieved at the use of Pluronic P123, which was chosen for further studies. Adsorption properties of the materials and accessibility of adsorption sites were compared in selective adsorption of cesium ions from aqueous solution. Obtained results can be used in development of highly acidic porous catalysts and adsorbents.



TEM image of Mo-containing silica gel

COLL 172

ZnO/TiO₂ bilayer film: Energy storage and photocatalytic properties

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A bilayer film of ZnO and TiO₂ was preliminarily proven to be a possible photocatalyst to be catalytically active when there is no UV illumination. The catalyst was developed based on the principle of p-n junction with TiO₂ as an n-type and ZnO as a p-type semiconductor. The sol-gel method was used to fabricate the bilayer film. The TiO₂ film was first spin coated on a glass plate followed with the ZnO layer. The photocatalytic and energy storage properties were tested using acid orange 7 (AO7) as a model compound. Adsorption of AO7 was allowed before the start of the investigation. A UV

light source was turned on for two hours before off for two hours, followed with another two-hour illumination and two-hour without illumination. Solution was taken at 2nd, 4th, 6th, and 8th hour of the experiment for qualitative analysis. Results showed that even though the TiO₂ film can degrade AO7 with illumination, its photocatalytic activity dropped to virtually zero without illumination. With the addition of ZnO, there was a significant increase in the film activity with illumination. Even more interesting is that the ZnO/TiO₂ bilayer film was able to degrade AO7 when there was no illumination, implying that the film could store energy during illumination and exploit the energy when there was no illumination. During the investigated two cycles, the film activity with and without illumination only slightly dropped from its first cycle.

Preliminary results on photocatalytic activity and energy storage of ZnO/TiO₂ bilayer film prepared with ZnO calcined at 300, 400, and 500 °C (denoted as 300ZnO, 400ZnO, and 500Zn)

	% AO7 degradation			
	Operating time (hr)			
	2	4	6	8
TiO ₂	6.71	0.27	4.55	0.00
300ZnO/TiO ₂	32.90	2.39	28.84	2.11
400ZnO/TiO ₂	41.53	0.65	29.38	0.48
500ZnO/TiO ₂	42.19	1.38	30.82	0.56

COLL 173

Interfacial control of highly absorbent polymers for hemostatic and drug-releasing properties

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In the absence of immediate medical facilities, hemorrhage control, infection prevention, and preserving tissue viability are paramount for a wound dressing material. Our custom designed polymer was tuned to regulate response to thermal and pH stimuli, as well as modulate drug release and exudate absorption kinetics. In an effort to maximize

polymer-wound interfacial action, special attention was given to topography as well as pore size. Rates of exudate absorption were simulated with buffer solutions and coagulation studies performed on whole blood. Drug release kinetics were measured by LC/MS. Relationships between polymer composition and the rates of exudate absorption, drug release, and hemostasis were identified and correlated to interfacial interaction. Results from *in vitro* analysis including blood coagulation assays, zone of inhibition, and dose dependent antimicrobial efficacy are presented. A series of polymer formulations have been synthesized that demonstrate a range of physical robustness, hemostatic capabilities, and drug release kinetics.

COLL 174

Understanding interactions of organophosphates and thioethers with polyoxometalate clusters

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Identification of factors that affect the decomposition of organophosphates and thioethers have been investigated for the future development of applicable materials for air filtration media and self-decontaminating materials. Oxidation reduction reactions and catalysis involving polyoxometalate (POM) clusters have been well documented in the literature for various applications including water splitting and alcohol and alkene oxidations; therefore, an in-depth investigation into the mechanisms and interactions of POM clusters with organophosphate and thioether contaminants has been performed. Herein, a systematic investigation employing a combinatorial approach in which the structural topologies, transition hetero-metal substitutions (Zr, Ni, Fe, Cu) and tailored solubility through cation exchange of POM clusters has enabled an improved understanding of the interactions of POMs with these contaminants. Effects of POM morphologies and hetero-metal selection on reaction rate and by-product generation from reactions with organic contaminant simulants were identified, as well as temperature, illumination, and solvent effects to understand mechanistic interactions.

COLL 175

Thiol-functionalized substrates for protein immobilization

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Thiol-functionalized substrates were fabricated by reacting silicon wafers with either mercaptopropylalkoxysilanes (MPS) or thiol-functionalized polydimethylsiloxanes (SMS). Thiol functional group density is controlled via MPS surface coverage and percentage of thiol content in SMS polymers in the two respective systems. The two

systems differ in hydrophilicity and type of thiol linker: the MPS surfaces are more hydrophilic than the siloxane polymers and the propyl groups are shorter and less flexible than the polymer chains. The two approaches and the reaction variants used within each approach allowed us to prepare thiol-functionalized substrates with a wide range of thiol density, hydrophilicity, and accessibility. In order to ensure smoothness and uniformity of the thiol layers and avoid disulfide aggregates, reducing agents, such as dithiothreitol, were applied either during or subsequent to the modification reactions. Fluorescent tagging of free thiols with tetramethylrhodamine-5-maleimide was used to quantify surface thiol density and accessibility. The thiol-functionalized substrates were then evaluated as platforms for conjugation of biological molecules. Model proteins, such as albumin and lysozyme, were covalently attached to the thiol-functionalized substrates via disulfide bond formation and thiol-disulfide exchange to establish effective conjugation protocols. The substrates were characterized using ellipsometry, contact angle goniometry, and atomic force microscopy before and after each reaction. Immobilization of enzymes and how different reaction systems and variants within affect enzyme activities will also be presented at the conference.

COLL 176

Hydrotreating properties of nickel phosphide on modified oxide supports

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The synthesis, characterization and hydrotreating properties of nickel phosphide (Ni_2P) on phosphorous- and boron-modified alumina (Al_2O_3) supports have been investigated. Past research has shown Ni_2P on Al-containing supports to have disappointing hydrogenitrogenation (HDN) and hydrodesulfurization (HDS) properties compared to Ni_2P on silica (SiO_2) supports. This is due to the strong interaction of impregnated P with Al-containing supports and the formation of AlPO_4 on the supports during catalyst synthesis. A series of modified supports have been synthesized by the deposition of a thin layer of phosphorus or boron, in the form of AlPO_4 and B_2O_3 , respectively, prior to the synthesis of Ni_2P . X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) spectroscopy were used to characterize the P- and B-modified Al_2O_3 supports, while the Ni_2P catalysts were characterized by X-ray diffraction (XRD), BET surface area analysis and CO chemisorption capacity measurements. The HDS and HDN catalytic properties of Ni_2P on the modified supports will also be presented.

COLL 177

Effects of colloidal C_{60} particle size on zeta potential

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Multiple methods are used to synthesize C60 to what is believed to be its most environmentally and biologically relevant form, an aqueous colloidal suspension (nC60). Stability of the suspension is due to a relatively large negative zeta potential that has been shown to develop upon the formation of nC60. Investigations on the spontaneous development of the negative surface charge have provided partial explanations towards the identification of its origin, but a complete mechanism of the origin has yet to be revealed. A relatively uncontrollable variable in nC60 formation, size, is investigated to help elucidate this mechanism. Six different synthesis methods were evaluated to determine the effects, if any, that particle size has on zeta potential. Aqueous suspensions from each method were subjected to a particle-by-particle zeta potential analysis using NanoSight Model NS500HSB. Zeta potential as it relates to particle size will be discussed.

COLL 178

Phosphatidylserine-containing supported lipid bilayer as a separation medium for copper binding compounds

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Many different biological compounds bind copper to varying degrees. These compounds are important in copper trafficking, enzymatic reactions, and cell signaling. We are developing a device that will bind and purify copper binding compounds. To accomplish this, we have fabricated a microfluidic device from glass and PDMS. The device consists of two annealed glass coverslips and a PDMS spacer. The glass supports a lipid bilayer that contains phosphatidylserine, a phospholipid that binds strongly to copper under basic conditions, and under acidic conditions is protonated and releases the copper ions. The supported lipid bilayer is initially saturated with copper ions in a basic solution, then solution containing copper binding compounds and non-copper binding impurities is introduced. The copper binding compounds bind to the bilayer-bound copper ions, and the non-copper binding compounds are rinsed away. Acidic solution is then introduced and the copper and copper binding compounds are released. This technique can also potentially be applied to chromatographic separations, in which compounds with different copper binding constants are eluted at different times based on their binding constant.

COLL 179

Holographic imaging of protein aggregates, slurry agglomerates, and waste water contaminants

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Holographic microscopy is a powerful technology capable of characterizing colloidal microspheres with a high level of precision and accuracy, using Lorenz-Mie theory to determine the size, index of refraction, and 3D position of particles in suspensions. Measurements are made on individual particles enabling the identification and characterization of multiple populations of different particles in the same sample. We will present results demonstrating the capability of the technology for various applications of industrial interest. We will show the detection of sub-visible polystyrene colloidal particles in samples that also contain oil emulsion droplets of a similar size, a capability valuable in waste water analysis. Polishing slurries for applications in the semiconductor industry present a particular challenge for optical techniques because the slurry particles create a turbid background. We will demonstrate the ability of holographic microscopy to detect larger problematic agglomerates in a sea of smaller background slurry particles. Finally, protein aggregates are a problem in the development and manufacture of biological pharmaceuticals. Results will be presented of the detection and analysis of protein aggregates in the critical size range of 200 nm to 20 microns. The size and index of refraction data from these studies demonstrate the ability of this technique to detect subtle changes in the distribution of particles in suspension. These results suggest that holographic characterization could be a valuable tool for monitoring and quality control in a variety of applications of industrial interest.

COLL 180

Effect of molecular topology on hydrocarbon surfactant performance

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In the endeavor to retrieve the remaining oil left after traditional oil extraction methods, CO₂ foam has proved to be an effectual aid. Presently, some of the best-performing surfactants known for water/CO₂ systems are fluorocarbon surfactants, but they are expensive and harmful to the environment, which limits their applicability. In an effort to find alternatives, hydrocarbon analogues have been synthesized, but shown to be less effective than their fluorocarbon counterparts. However, it has been shown that the topology of the tail group is a critical parameter in determining their performance for this system.

Here, we utilize coarse-grained molecular dynamic simulations to explore a greater breadth of tail group structures, in an attempt to gain greater insight into the topological influence of relevant physical properties in CO₂ foam. We chose a Mie potential with parameters taken from the literature fitted to closely match the experimental surface tension and density. We assess the performance of the surfactant based on how much it decreases the surface tension of water/CO₂ interfaces, as well as the critical surface adsorption. These results will be used in later studies to assess the effect of different tail group chemistries on surfactant performance for these systems.

COLL 181

Photothermal lens characterization of Ag nanoparticle colloids and films

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We report on photothermal lens measurements on silver (Ag) nanoparticle water colloids of different concentrations and different particle dimensions. The Ag nanoparticles are prepared through a low temperature reduction method. By rational design of reaction conditions, we demonstrated the correlation between particle size and reaction time and concentration of Ag containing reagents respectively. The nanoparticle size is thus controlled at very high concentrations (larger than 1M) and the particle size distribution is very narrow within each set of conditions. We report Ag nanoparticles with dimensions of 1-3 nm, 3-5 nm, 10-20 nm and 20-50 nm. The UV-Vis absorbance spectra correlate with the particle size and show the typical Ag nanoparticle absorbance ~ 400 nm.

To characterize the photothermal behavior of the Ag nanoparticles, samples in films and solution are utilized, to be able to capture both high and low concentrations. The films are prepared by a spray-printing method to ensure uniform particles density and concentration control. For the photothermal characterization we use a pump-probe mode-mismatched experimental configuration where the pump beam is focused onto the sample generating a thermal lens and a collimated collinearly propagating probe beam of light tests it. Wave-front distortions of the probe wave-front yields a signal that is proportional to the part of the absorbed light degraded into heat. The time evolution of the signal allows determination of thermal diffusivity and other photothermal parameters of the sample. A photothermal lens spectrum is also obtained using as pump source a broadband arc-lamp which light is filtered using interferometric filters. In combination with regular absorbance spectroscopy, the photothermal spectrum provides absorption and scattering quantum yields values of the nanosamples. By comparing the absorbance with the photothermal response, we obtained unique information of Ag nanoparticle scattering, which will be presented.

COLL 182

CRISPR–Cas9 delivery by DNA nanoclews for efficient genome editing

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Statement of Purpose:

The CRISPR-Cas9 system is a promising platform for targeted genome editing. A simplified version of this gene-editing tool consists of only two components: the Cas9 nuclease and a single-guide RNA (sgRNA). Cas9 and sgRNA form a nucleoprotein complex that recognizes target DNA locus adjacent to a protospacer adjacent motif (PAM) using the 20-nucleotide portion of the sgRNA. In spite of the progresses made in improving the efficiency and fidelity of this ribonucleoprotein tool, the lack of an efficient delivery system posed a major challenge to therapeutic translation of these bio-macromolecules¹.

Methods:

A bio-inspired DNA nanoclew (NC) based carrier was tailored for the Cas9/sgRNA complex by utilizing the technique of rolling circle amplification²⁻⁴. The synthesized DNA NC composed of concatenated single stranded DNA (ssDNA) was designed to be complementary to the targeting portion of sgRNA for efficient Cas9/sgRNA loading. A cationic polymer polyethylenimine was coated onto the Cas9/sgRNA/NC complex to help induce endosome escape (Figure 1).

Results:

The DNA NC based carrier delivered the Cas9/sgRNA complex into the nucleus of a model cell line that constitutively expressed a destabilized EGFP. Genome editing occurred at the pre-designed genomic locus as determined from the increase of EGFP-negative cells as well as the Surveyor Assay and Sanger Sequencing. Efficient EGFP disruption was also observed in xenograft tumor model in mice that also expressed the EGFP.

Conclusions:

The DNA NC based delivery system is an efficient and versatile platform for intracellular delivery of the protein/RNA complex, which could be further extended to deliver other DNA associated protein or nucleic acid therapeutics.

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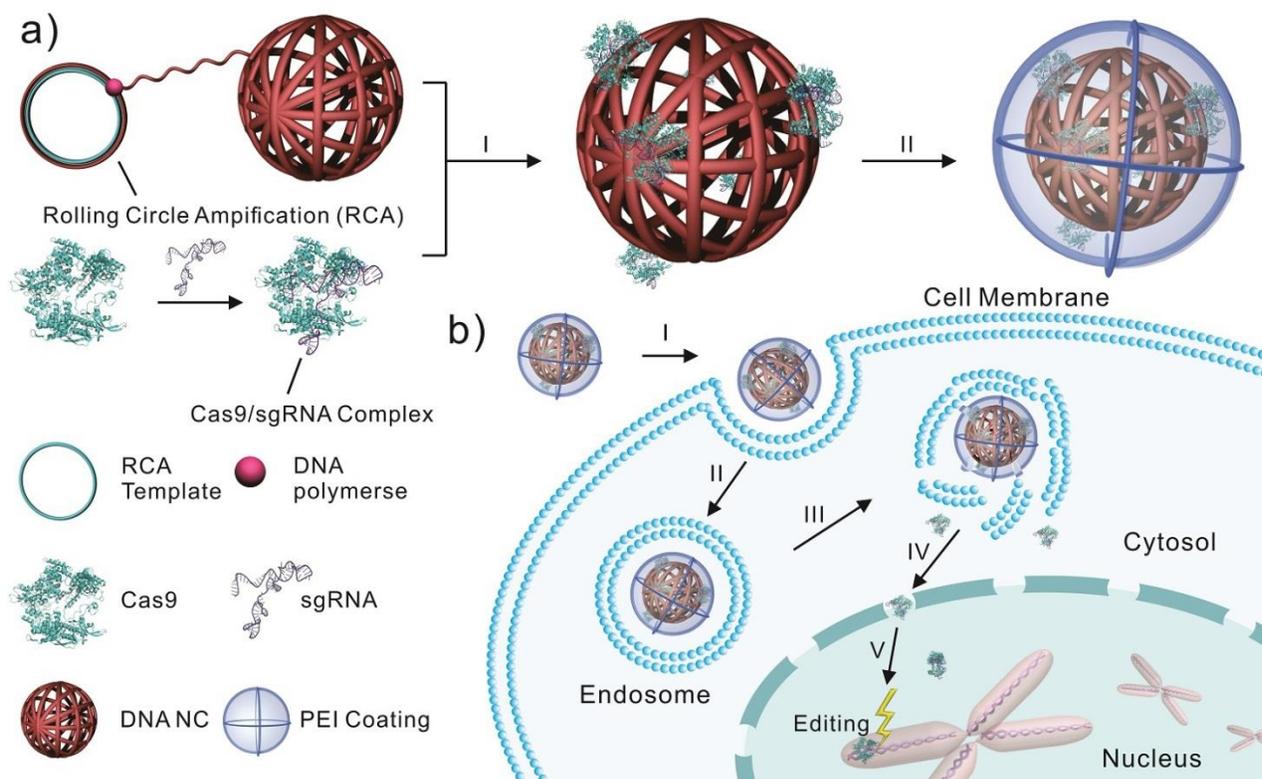


Figure 1. Schematic for CRISPR/Cas9 delivery.

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Size-tunable dendritic nanoparticles through thiol-yne click chemistry

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Robust nanoparticles with well-controlled size are desirable for a variety of applications such as drug delivery, diagnostics and sensing. For further applications of micelle-like assemblies in areas such as drug delivery, where drug carriers made from micelle-like assemblies are injected intravenously (IV), the concentration of drug carrier will dramatically decrease to a level below the CAC of assemblies. To solve this problem, finding a way to stabilize the assemblies is essential for further applications of micelle-like assemblies. To obtain stable assemblies, one strategy that has often been used is to crosslink the aggregates. Crosslinking the assembly will stabilize the aggregate structure and de-crosslinking the aggregate will make the assembly ready for disassembly triggered by stimulus. Adding stimulus will then allow for the release of guest molecules that are encapsulated inside the assemblies. In this project, we utilized the thiol-yne 'Click' chemistry to both stabilize and control the size of the assemblies formed from temperature-sensitive amphiphilic dendron. We have previously reported

that pentaethylene glycol containing facially amphiphilic dendron shows temperature-sensitive property and there is a size change with temperature variation. By taking advantage of this behavior, we were able to achieve different sizes of stably crosslinked micelle-like assemblies by photo-crosslinking the propargyl moieties of a G1 facially amphiphilic dendron with dithiol crosslinker molecules. Assemblies that are crosslinked with pH-responsive crosslinker molecule has been shown to disaggregate in the acidic environment according to the guest release studies. All crosslinked and de-crosslinked assemblies are characterized by dynamic light scattering (DLS) and transmission electron microscopy (TEM).

In this work, we provided a design of preparing robust and size-tunable assemblies with a stimuli-responsive feature.

COLL 184

Layer-by-layer low-temperature passivation of semiconductor nanocrystals with transition metal chalcogenides

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The synthesis of colloidal semiconductor nanocrystals is typically performed via hot-injection routes that suffer from a somewhat limited control over the growth kinetics. This leads to a broad distribution of nanoparticle sizes and poorly defined surface stoichiometries. To address this issue, we have developed an alternative growth strategy that relies on the stepwise, controllable evolution of nanocrystals sizes. As a result, fabricated nanocrystals exhibit well-defined surface morphologies and a small dispersion of particle diameters. By using different metal chalcogenide nanoparticles as a starting material, we are able to fabricate large quantum dots and core/shell nanocomposites utilizing a sequential deposition of fully-saturated cation and anion half-monolayers onto starting “seeds”. The layer-by-layer technique also allows us to deposit a shell material with a precise thickness on each nanoparticle in solution. Besides an expected benefit of the demonstrated synthetic strategy to QD-LED applications, where narrow emission lines are important, the sequential ionic synthesis is expected to be useful in applications employing nanocrystal solids (photovoltaics, transistors), as the reduced dispersion of surface compositions should promote a more cohesive response of nanoparticles in the film to the same chemical treatment. Based on the demonstrated homogeneity of nanocrystal shapes and the simplicity of the synthesis, we expect the present growth strategy to emerge as a viable alternative to traditional hot-injection methods of nanoparticle synthesis.

COLL 185

Fabrication and characterization of germanane as a lithium-ion battery anode

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Germanium is a promising anode material for lithium-ion batteries due to its high theoretical energy density ($\sim 1600 \text{ mAh}\cdot\text{g}^{-1}$) based on an alloying between lithium and germanium (Li_xGe). However, common alloying anode architectures suffer from long-term instability upon repetitive charge-discharge cycles that arise from stress-induced degradation upon lithiation (volume expansion $>300\%$). We describe the use of the two-dimensional nanosheet structure of germanane to mitigate stress from high volume expansion. Stable single- to multi-sheet dispersions of pure germanane were created and assessed for purity and degree of exfoliation with transmission electron microscopy, ultraviolet-visible spectroscopy, Raman spectroscopy, and atomic force microscopy. Representative battery electrodes that were cycled within a voltage range of 0.01 to 2 V vs. Li/Li^+ measured a reversible Li-ion capacity of $575 \text{ mAh}\cdot\text{g}^{-1}$ at a charging time of 5.5 hours. The measured capacity does not yet approach the theoretical limit, which we attribute to the mitigation of volume expansion when germanane electrochemically stores Li ions in two dimensions rather than in the bulk.

COLL 186

Computational modeling in the development of gas hydrate inhibitors

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In the off-shore natural gas fields, the gas is transported to onshore gas plant through pipelines. During winter, the operating condition favors gas hydrate formation, which causes safety, operational and economical concerns. Basically, gas hydrate structures are formed as a result of weak Van der Waal interactions between guest organic molecules, e.g., methane and water. Therefore, investigating such weak interaction is important in understanding the hydrate formation and inhibition. Computational molecular modeling is of great value to get such fundamental understanding, which directly helps in designing efficient inhibitors.

COLL 187

Flash Sintering of solution synthesized Bi_2Te_3 nanoplatelets

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The renewed interest in thermoelectric power generation has largely focused on solid-state engineering of increasingly exotic materials. However, developing scalable syntheses while simplifying material processing has the potential to broaden the impact of wide-spread dissemination for waste/heat conversion. Herein, we describe printable Bi_2Te_3 nanoplatelet and the structure-property evolution of its thin films upon sintering with flash lamp. For this, the physical attributes of Bi_2Te_3 , including robust optical absorbance, low thermal diffusivity and low melting point lends itself particularly well for photonic sintering. Upon flash exposure, we observe evolution from a thin film of discrete nanoplatelet subcomponents to a mesoscale mesh-like network with distinct crystalline regimes. The resultant film, with nanostructures consistent with pronounced melt-and-recrystallization within plane, also exhibit electrical connectivity and Seebeck response comparable to undoped Bi_2Te_3 derived from conventional means. Penultimately, in contrast to previous thermoelectrics assembled from Bi_2Te_3 nanoplatelets and particles, the photonic sintering method obviates the need for bulk-reformation from nanoplatelets via high-pressure arc/plasma-sintering to yield thermoelectric response. Ultimately, the photonic sintering method may provide a scalable solution method (“ink”) for conformal thin thermoelectric coatings on a variety of substrates with arbitrary geometry.

COLL 188

Convenient bio-inspired approach to the synthesis of multifunctional, stable fluorescent silica nanoparticles

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Fluorescent silica nanoparticles have the potential to offer a safer, brighter, and more stable marker for biological materials, such as proteins and antibodies, than organic dyes currently used as bio-labels. We describe the preparation of fluorescent silica nanoparticles via a new, efficient one-step procedure and the quantification of their brightness and stability. We use a branched poly(ethylene imine), PEI, which has a multifunctional purpose: to condense the silica and form nanoparticles, to be labeled and affix the labeled group into the silica matrix, and to be reacted post-functionally to attach surface functionality to the particles. Amine-reactive fluorophores including fluorescein isothiocyanate (FITC), carboxyfluorescein succinimidyl ester (CF), and tetramethylrhodamine isothiocyanate (TRITC) were attached to the PEI, which retained its activity for silica polymerization. The amount of fluorophore was optimized and studied via steady-state and time-resolved fluorescence spectroscopy. The silica matrix serves to protect and stabilize the incorporated fluorophores, allowing them to be used in a wide range of environments for long periods of time. This method can be extended to a variety of fluorescent molecules, spanning the colors (emission wavelengths) currently used in the medical field for imaging, and this may offer a new, bright system

for standard detections. In addition, we show that a portion of the amines is present on the particle surface and is available for further labeling. As a demonstration, gold nanoparticles were attached to the surface to form well-defined heterobifunctional nanostructures.

COLL 189

Fabrication of mesoporous gold-coated polystyrene particles for enzyme immobilization

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In this study, we describe the preparation of mesoporous gold-coated PS (polystyrene) particles, characterized by their controllable pore size, for use as scaffolds to support CPO (chloroperoxidase) enzymes. First, mono-sized PS particles were fabricated in water by soap-free emulsion polymerization with a thermal initiator. Second, the PS particles were functionalized by covering their surface with PAA (polyallylamine) to convert their negative charge to positive in water. Third, mono-sized silica nanoparticles were synthesized by using a sol-gel method in water with L-lysine, which acts as a dispersant and a basic catalyst. Fourth, gold nanoparticles were prepared as seeds for growth of an ultra-thin gold by using 4-mercaptobenzoic acid as a stabilizer. Fifth, the mono-sized silica nanospheres and the gold nanoparticles were electrostatically deposited in isolation on the PAA-PS particles by a pH adjustment. Finally, ultra-thin gold layers were coated on PAA-PS particles, followed by silica etching with sodium hydroxide solution at 80°C. The morphology of the mesoporous particles will be described and their properties as promising enzyme substrates will be analyzed.

COLL 190

Application of soy protein flour as a novel detackifier agent in the recycled pulp

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A series of experiments were conducted on recycled pulp samples for the novel purpose of determining the efficacy of applying soy protein flour to decrease the stickies from the pulp. It was used of two different trials and various conditions for applying the soy proteins under industrial-like papermaking conditions including alkaline versus acidic, different temperature and enzyme level. Number of stickies as well as its size were used for this evaluation and a novel optical method was employed to monitor the change in sticky counts in the paper after being treated with soy flour. Also paper mechanical and optical properties were measured and the results compared with control sample. It wasn't used of any additive for a better elucidation of effect of protein. Results

indicated the addition of soy protein can significantly cause the reduction of stickies and dirt on the sheets especially in alkaline condition. Test of mechanical properties also revealed soy protein can cause a remarkable increase in most of the mechanical strengths, such as tensile, tear, burst and etc. but tensile index was the main criterion for the comparison based on industrial consideration.

COLL 191

Effect of incorporation of lysolipid on the stability of dipalmitoyl phosphatidyl choline bilayer membrane at various temperatures: Molecular dynamics simulation approach

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Drug delivery and its release depend greatly on the ability to control the permeability of the vesicle encapsulating the drug. Liposomes, which are spherical nanoparticles composed of one or more phospholipids, have emerged as a promising delivery system for potent chemotherapeutics. It is well known that the permeability of drug through lipid bilayers exhibits a maximum as the lipid bilayer undergoes the transition from gel to liquid-crystalline phase, which has been studied intensively in order to control the permeability. One of the ways for the controlled drug release is to add lysolipid, which affects the transition properties such as transition temperature.

In this study, we run fully atomistic molecular dynamics (MD) simulations with flat lipid bilayer model comprised of both dipalmitoyl phosphatidyl choline (DPPC) and 0-30% lysolipids of monopalmitoyl phosphatidyl choline (MPPC) at various temperatures with two different distributions of lipid molecules. The stability of the lipid bilayer is investigated by monitoring formation energy, density profile, area per lipid molecule and the lateral diffusion coefficient as a function of simulation temperature. Through this study, we attempt to clarify the most probable distribution of MPPC in the mixed lipid bilayer.

COLL 192

Single-molecule chemical investigations on DNA nanostructures

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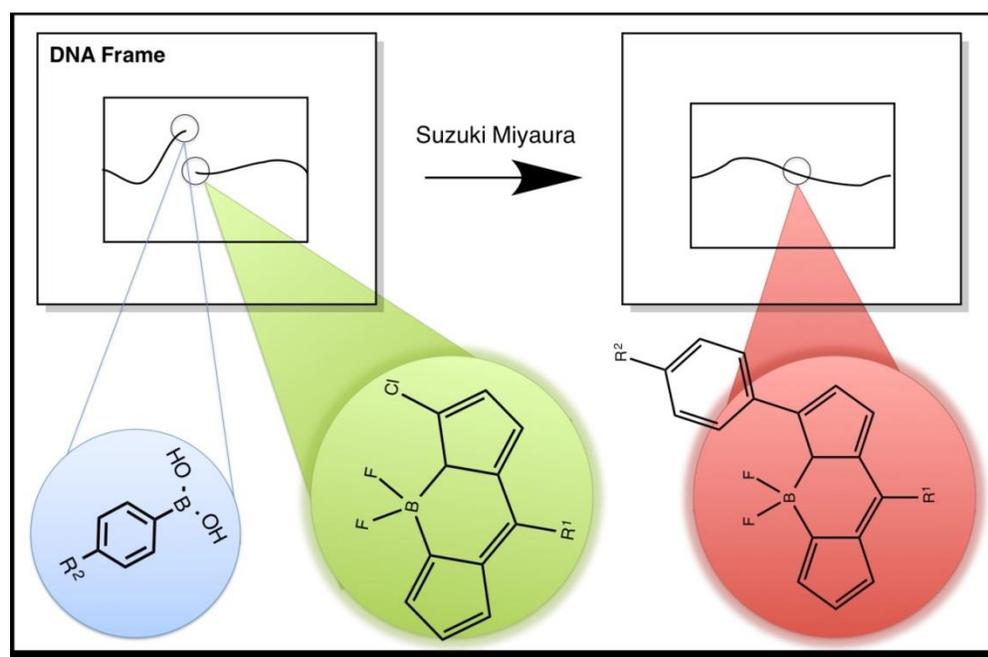
Single-molecule investigations give insight into transient intermediates, alternate chemical pathways, and dynamic behaviour of molecules that cannot be discerned from time-averaged results of the bulk. At the single molecule level complex reaction

pathways can be analysed and understood.

DNA nanostructures are commonly used as a scaffold in single molecule reactions as the predictability of Watson-Crick base pairing allows functional groups and biomolecules to be precisely organized. Single-molecule experiments typically focus on biological problems, and there are many examples of investigations taking advantage of DNA, however, DNA nanostructures are seldom used for single-molecule chemical investigations despite their many benefits.

Here we have designed DNA origami to facilitate the observation of chemical reactions at the single molecule level by monitoring changes in light-emitting functionalities with fluorescence microscopy or by observing a physical change with AFM. Furthermore, by covalently attaching the structures to a surface we can forego the Mg^{2+} , which is typically used to physically bind the DNA structure on a surface, allowing flexibility in reaction conditions.

We envision the use of this platform for a variety of single molecule investigations, particularly regarding chemical catalysis.



Scheme of single-molecule reaction on DNA origami.

COLL 193

Nonlinear optical interactions between silver nanoplatelet surface plasmons and various organic/inorganic excitons

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The tunability of surface resonance frequency in plasmonic metal nanostructures via size and shape control, when coupled with the absorption frequency of various organic

and inorganic excitons, provides a unique nonlinear response. Achieving these nonlinear responses, such as formation of a transparency window, using different organic and inorganic excitons increases future applicability of the technology, which includes sensors, light-harvesting systems, and other optical devices. These transparency windows have been reported in silver nanoplatelet-J-aggregate dye systems and have been observed in silver nanoplatelet-inorganic quantum dot systems. In this work, the coherent plasmon-exciton coupling of silver nanoplatelets with a J-aggregate dye and cadmium telluride/selenide quantum dots is explored. Direct and near direct overlap of absorption spectra of plasmons and excitons are examined to determine Rabi splitting energies and the strength of nonlinear absorption impacts.

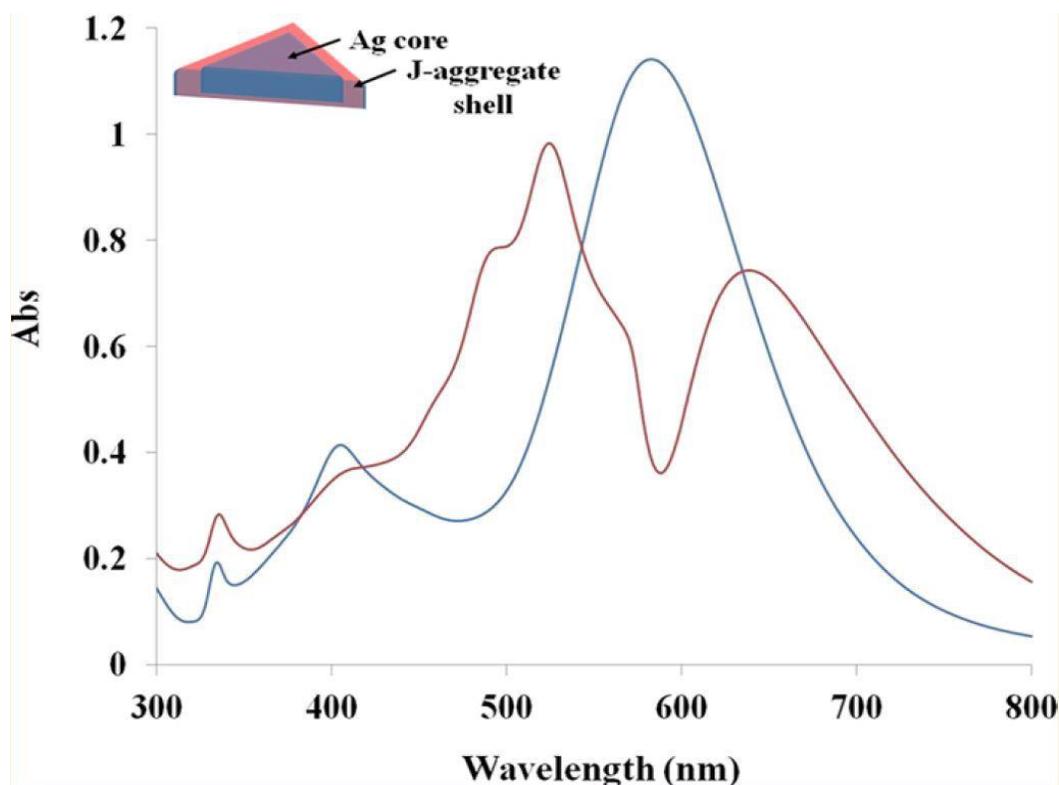


Figure – Absorption spectra of J-aggregate dye on silver nanoplatelets core (red curve), and silver nanoplatelets (purple curve). Diagram provides visual representation of the plasmon-exciton coupling interaction.

COLL 194

Study of mobility of tri-metallic alloyed nanocrystal in a glassy silica nanosphere

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A tri-metallic FeAuPd nanocrystal was generated by coalescence of Fe₃O₄, Au, and PdO grains in thermally stable silica nanosphere through reductive annealing under Ar/4%H₂ atmosphere at 700 °C. During the reductive annealing, The FeAuPd nanocrystal was displaced from the center of the sphere, thereby leaving a void in its trajectory and creating a unique hollow nanostructure, FeAuPd@*h*-SiO₂, which traps the migrating FeAuPd nanocrystal in the middle of the silica nanoshell (Figure 1). The migration degree of the FeAuPd nanocrystal was increased by increasing the annealing time as well as elevating the annealing temperature. To investigate this temperature relation in detail, the thermal properties of the FeAuPd@*h*-SiO₂ were characterized using DSC and thermogravimetric analysis (TGA). Based on the DSC curve, FeAuPd@*h*-SiO₂ has glass transition temperature $T_g = 695$ °C, and TGA detected no change in mass up to 1100 °C. During annealing at 700 °C, the phase of the amorphous silica shell changed to glass-liquid transition phase, which was getting decreased viscosity, so the FeAuPd nanocrystals can move relatively easily outward silica shell through the glassy silica matrix to relieve the high interfacial strain with the unfavorably interacting silica. We observed the migration phenomenon through measuring *in situ* heating TEM.

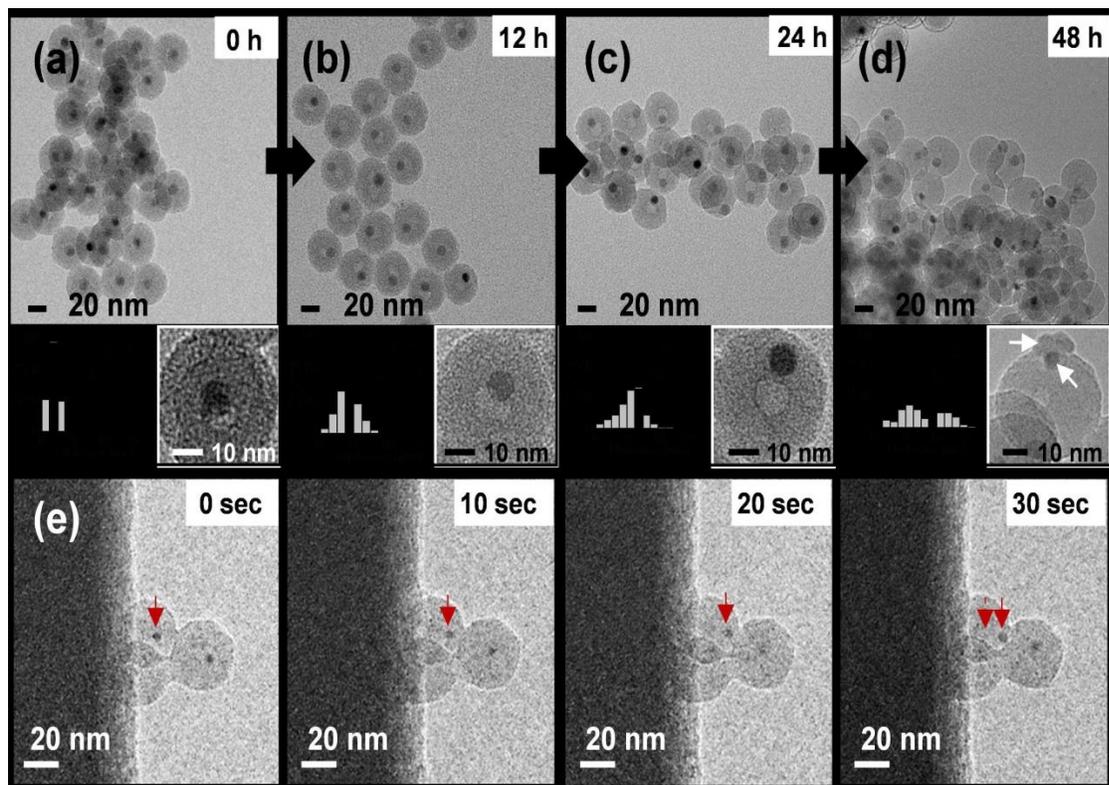


Figure 1. Migration of trimetallic FeAuPd nanocrystal in silica nanosphere (upper) and *in situ* heating TEM of the migration (bottom)

Designing and building an effusive molecular beam doser for methane sticking on vanadium

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Methane is an abundant and efficient fuel source. However, liquid compounds are easier and less expensive to transport safely. The conversion of CH₄ to liquid organics such as methanol and formaldehyde is currently performed through an indirect process involving the water-gas shift reaction to form syngas, CO and H₂, and then a Fisher-Tropsch process to form liquid hydrocarbons. A direct process would be preferred, and identifying an effective catalyst is highly desirable. An effusive molecular beam has been designed and constructed. This heated doser will allow the methane gas temperature to be varied from 300 to 900 K during dissociative chemisorption experiments. Additionally, a microcanonical unimolecular rate theory (MURT) has been used to predict sticking coefficients for CH₄ on V(100) and V(110). These calculations have been informed by previous studies of CH₄ on other transition metal surfaces (e.g., Pt(111) and Ni(100)). MURT predictions suggest optimal conditions for planned methane dissociative sticking experiments, which will be performed in the Abbott-Lyon laboratory beginning in summer 2016. Together, the MURT calculations and sticking experiments will increase our understanding of methane's behavior on early transition metal surfaces.

COLL 196

Wettability and packing structure of partially fluorinated ω -alkylated self-assembled monolayers

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This presentation describes the preparation and characterization of partially fluorinated self-assembled monolayers (FSAMs) on gold that expose hydrocarbon segments of different chain lengths at the FSAM interface. The adsorbates used to form the FSAMs in this study are of the form CH₃(CH₂)_n(CF₂)₆(CH₂)₁₁SH (where n = 0 – 6), in which the interfacial transition dipole (HC–FC) was systematically buried in the film as the alkyl chain was lengthened. The wettabilities of this series of partially fluorinated, progressively alkylated FSAMs were probed using a variety of contacting liquids having varying polarities, with specific attention paid to the influence of cohesive forces within the contacting liquid. In addition, the FSAMs were characterized using X-ray photoelectron spectroscopy, ellipsometry, and polarization-modulation infrared reflection-absorption spectroscopy to obtain insight into the organization and packing of the adsorbates within these unique films.

Keywords: Fluorinated Self-Assembled Monolayers (FSAMs), Wettability, Odd-Even Effects, Inverted Dipoles

COLL 197

Deoxygenation properties of bimetallic phosphide catalysts

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Catalytic deoxygenation is a critical step in the upgrading of bio-oils to renewable biofuels. Transition metal phosphides (Ru_2P , Ni_2P) have shown promise as hydrotreating catalysts, with similar activity and lower tendency towards deactivation than sulfide-based catalysts. Bimetallic phosphides of ruthenium ($\text{M}_x\text{Ru}_{2-x}\text{P}$, $\text{M} = \text{Co}, \text{Ni}$) with a range of metal compositions have been synthesized and characterized by a number of physicochemical techniques. The bimetallic phosphides form solid solutions over a wide range of compositions and catalysts with high dispersions of the phosphide phase on silica have been prepared. The deoxygenation properties of the $\text{M}_x\text{Ru}_{2-x}\text{P}/\text{SiO}_2$ catalysts have been investigated using furan ($\text{C}_4\text{H}_4\text{O}$) and crotonaldehyde ($\text{C}_4\text{H}_4\text{O}$) as model organo-oxygen compounds. The deoxygenation properties (activities, selectivities) show a strong dependence on $\text{M}_x\text{Ru}_{2-x}\text{P}$ composition, which will be discussed in the context of the characterization studies.

COLL 198

Investigating polymer mediated depletion stabilization of gold nanoparticles in nonpolar solvents

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The majority of synthetic approaches for gold nanoparticles rely on polar solvents many of which are aqueous based. However, there is a need to have stable dispersions of gold nanoparticles in common organic solvents for advanced surface chemistries and for compatibility with polymer processing schemes. Recent work from our group has shown that the addition of high molecular weight polymers such as polymethylmethacrylate and polyvinylacetate that do not have a strong interaction with the surface of gold nanoparticles are able to stabilize nanoparticles in nonpolar solvents. This work showed that even though the two polymers are similar in chemical structure they differ significantly in their ability to stabilize the nanoparticles in solution. These results are consistent with a depletion stabilization mechanism that is largely dependent on establishing an entropic equilibrium. The molecular weight dependence of the stabilization is one facet of the stabilization that we are currently exploring and have found that the stabilization behavior follows a significantly different trend at lower

molecular weights when compared to larger molecular weights. Gaining a better understanding of the stable phase space should engender new avenues for subsequent surface modifications in nonpolar organic solvents.

COLL 199

Novel nano-drug carrier based on ginsenoside Rb1

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A large amount of chemosynthetic nano-drug carriers has to be used to administer a needed dose of a drug. However, high doses of these excipients may cause the emergence of toxic potential to the patients. The use of non-toxic materials in pharmaceutical formulations could minimize the adverse effects of pharmaceutical residues entering the body and environment. Ginsenoside is a main bioactive constituent of herb *Panax ginseng*. Here, we show that self-assembly of the ginsenoside Rb1 with anticancer drugs leads to the formation of stable nanoparticles, which have greater anticancer effects *in vitro* and *in vivo* than the free drugs. The obtained nanoparticles possessed appropriate size, high drug loading efficiency, slowly drug release rate, higher blood circulation half-time of free betulinic acid and oleanolic acid. Furthermore, the antitumor effect of the nanoparticles in a mouse tumor xenograft model exhibited much better tumor inhibition efficacy and fewer side effects than that of free drugs, strongly supporting their application as efficient carriers for anticancer therapy.

A large amount of chemosynthetic nano-drug carriers has to be used to administer a needed dose of a drug. However, high doses of these excipients may cause the emergence of toxic potential to the patients. Green chemistry aims to develop green nanoparticles loaded with drugs to reduce the use of toxic and harmful ingredients in the production process and provide the lower-dose prescribing for medical treatments. The use of non-toxic materials in pharmaceutical formulations could minimize the adverse effects of pharmaceutical residues entering the body and environment. Ginsenoside is a main bioactive constituent of herb *Panax ginseng*. Here, we show that self-assembly of the ginsenoside Rb1 with anticancer drugs leads to the formation of stable nanoparticles, which have greater anticancer effects *in vitro* and *in vivo* than the free drugs. The obtained nanoparticles possessed appropriate size, high drug loading efficiency, slowly drug release rate, higher blood circulation half-time of free betulinic acid and oleanolic acid. Furthermore, the antitumor effect of the nanoparticles in a mouse tumor xenograft model exhibited much better tumor inhibition efficacy and fewer side effects than that of free drugs, strongly supporting their application as efficient carriers for anticancer therapy.

COLL 200

Quantum chemical studies on the adsorption of DNA bases on Ge(100)

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We investigated the adsorption characteristics of DNA base molecules on Ge(100) surface using density functional theory (DFT) calculations and scanning tunneling microscopy (STM) observation. Focusing on the multifunctionality of DNA bases, such as guanine molecule, possible reaction pathways through each functional groups were compared. Competitive reactions among different reaction sites in guanine may lead to either mono- or multi-dentate products. Calculation results also revealed that the C=O dative bonded structure following N-H dissociation is one of the most stable adsorption configurations. In addition, the N-H bonding at N1 position was found to be one of the most favorable N-H dissociative reaction sites. Moreover simulated STM features were in good agreement with experimental observations in terms of the electron charge density around the adsorbed guanine molecules and the reacting Ge atoms.

COLL 201

Oils derived from native plants to generate a naturally-derived wound dressing

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In order to maintain a sterile environment and protect patients in a clinical setting from microorganisms can be a challenge. Previous research has been conducted where creating anti-microbial surfaces could minimize the growth of microorganisms like bacteria, fungi, or viruses. Most of the challenges faced throughout the process of creating these surfaces are antimicrobial surfaces can be difficult to industrialize, they are not uniform throughout, and can be wiped off a surface by simply passing over a cloth or a finger. Gelatin B are peptides and proteins produced by partial hydrolysis of collagen extracted from the skin, bones, and connective tissues of animals, its molecular weight affects its viscosity, gel strength and other properties, such as emulsion stabilization. The purpose of using Gelatin B is it contains an alkali treatment that can destroy certain chemical cross linkages present in collagen, the part of the connective tissue that in the skin helps in firmness, suppleness and constant renewal of skin cells. Our goal is to infuse Gelatin B with a variety of plants essentials oils (Sage, Thyme, Neem Seed Oil, Yarrow, Propolis, Black Elderberry, Ginger, and Turmeric. The newly generated surfaces will be tested against gram positive, gram negative bacteria, and fungi. Our aim is to create new antimicrobial surfaces which may be used as a wound dressing which is naturally derived.

COLL 202

Multifunctional coatings created using an antimicrobial polymer as a platform for titania precipitation on cotton

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Titania precipitation on cotton has been achieved utilizing a commercially available antimicrobial polymer, Reputex 20. The cotton swatches precipitated with titania retain antimicrobial activity and we have also shown the ability to encapsulate diisopropylfluorophosphatase (DFPase), an enzyme capable of breaking down organofluorophosphates such as diisopropylfluorophosphate (DFP). Cotton swatches are easily prepared and precipitation occurs at room temperature in aqueous solutions at near neutral pH. Fluoride assays are used to demonstrate enzyme activity and bacterial overlays show zones of clearing against *S. aureus*. Both the antimicrobial properties of Reputex 20 and the hydrolytic activity of the DFPase enzyme are retained after titania precipitation, generating a cotton material exhibiting multifunctional properties. Initial laundering studies will also be presented showing durability of the coating material on the cotton swatch.

COLL 203

Surface assembly of octadecyltrimethoxysilane and 2-[methoxy(polyethyleneoxy)propyl]trichlorosilane nanostructures for the deposition of metal nanoparticles

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Reproducible and practical approaches for the surface fabrication of nanopatterns from organosilanes can be accomplished with particle lithography. Spatially selective surfaces can be designed to isolate and bind nanoparticles. Organosilanes bind to surfaces by covalent bonding to generate robust, stable films and nanostructures. Approaches with particle lithography enable high throughput to generate regularly-shaped nanopatterns with a surface density of approximately 10^9 patterns/cm². The nanopatterns offer excellent model surfaces for fundamental studies of interfacial chemistry, solvent-molecule interactions and self-organization. Using octadecyltrimethoxysilane (OTMS) and 2-[methoxy(polyethyleneoxy)propyl]trichlorosilane (PEG) as a resist, nanopatterns of organosilanes were prepared on glass surfaces using particle lithography. Monodisperse mesospheres of silica or latex were deposited on the substrate for form a surface mask. A heating step was used to temporarily anneal the beads to the surface, to sustain steps of vapor deposition and immersion. When the surface mask was removed, a periodic arrangement of nanoholes was generated, with spacing corresponding to the diameters of the mesosphere mask. The nanoholes contain circular areas of exposed substrate for attaching a second organosilane. After each step of nanofabrication, atomic force microscopy (AFM) was done to visualize the changes in surface morphology. Cursor profiles were used to evaluate the thickness, orientation and density of nanostructures. Planned directions for this research will apply particle

lithography with organosilanes to develop spatially selective surfaces for patterning nanoparticles.

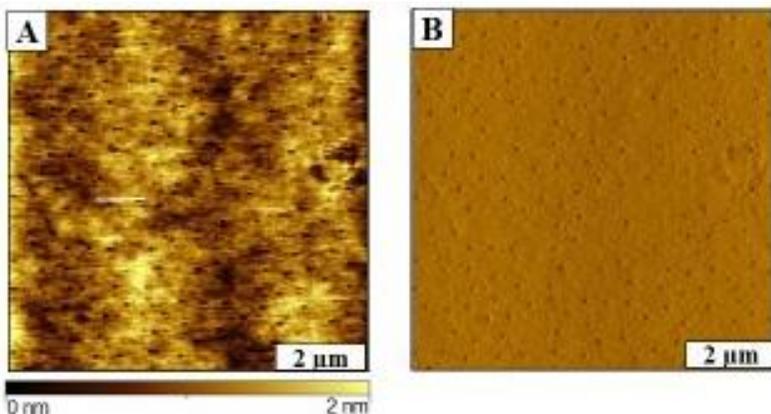


Figure 1) Nanopores of MPTMS produced by steps of vapor deposition and immersion imaged with tapping-mode AFM. (a) Topography, (b) corresponding phase image.

COLL 204

Factors affecting morphologies and hydrophilicity of poly(vinyl alcohol) thin films spin-cast on polydimethylsiloxane substrates

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Physical surface modification of hydrophobic polydimethylsiloxane (PDMS) via adsorption of poly(vinyl alcohol) (PVOH), an amphiphilic, water-soluble and semicrystalline polymer, was evaluated as a method to hydrophilize PDMS surfaces. Specifically, dilute PVOH aqueous solutions were spin-cast onto PDMS substrates, which were prepared by covalently attaching linear PDMS of 2 kDa, 9 kDa, 17 kDa, 49 kDa, and 116 kDa to silicon wafers. PVOH morphologies and surface wettability were studied as a function of PDMS molecular weight, PVOH degree of hydrolysis, and residence (adsorption) time of PVOH solution. It was determined that a residence time of 1 min or longer was necessary to allow PVOH to adsorb at the solution–substrate interface. PVOH degree of hydrolysis as well as PDMS molecular weight play significant roles in the final PVOH film morphologies. In general, as PDMS molecular weight/thickness increases, dewetting of PVOH films becomes increasingly pronounced. With 88%-hydrolyzed PVOH, thin films transition from continuous, to honeycombs, to droplets. Surface hydrophilicity is greatly enhanced when surface coverage of PVOH is high. With 99%-hydrolyzed PVOH, instead of droplets, fractal morphologies were observed on PDMS substrates of high molecular weights. The formation of the fractal morphologies is hypothesized to be driven by PVOH crystallization in the drying process. The results from PVOH spin-cast onto PDMS substrates were congruent with those found via adsorption of PVOH onto PDMS in a

parallel study. The similarities indicate that PVOH adsorption at the solution-substrate interface is the driving force for the attachment of PVOH thin films onto PDMS surfaces. The centrifugal force in the spin-cast process, however, provides directional control on PVOH morphologies. This study establishes that the morphologies and wettability of the PVOH thin films prepared on the PDMS substrates via spin-cast are directly affected by the physical characteristics of PVOH and PDMS.

COLL 205

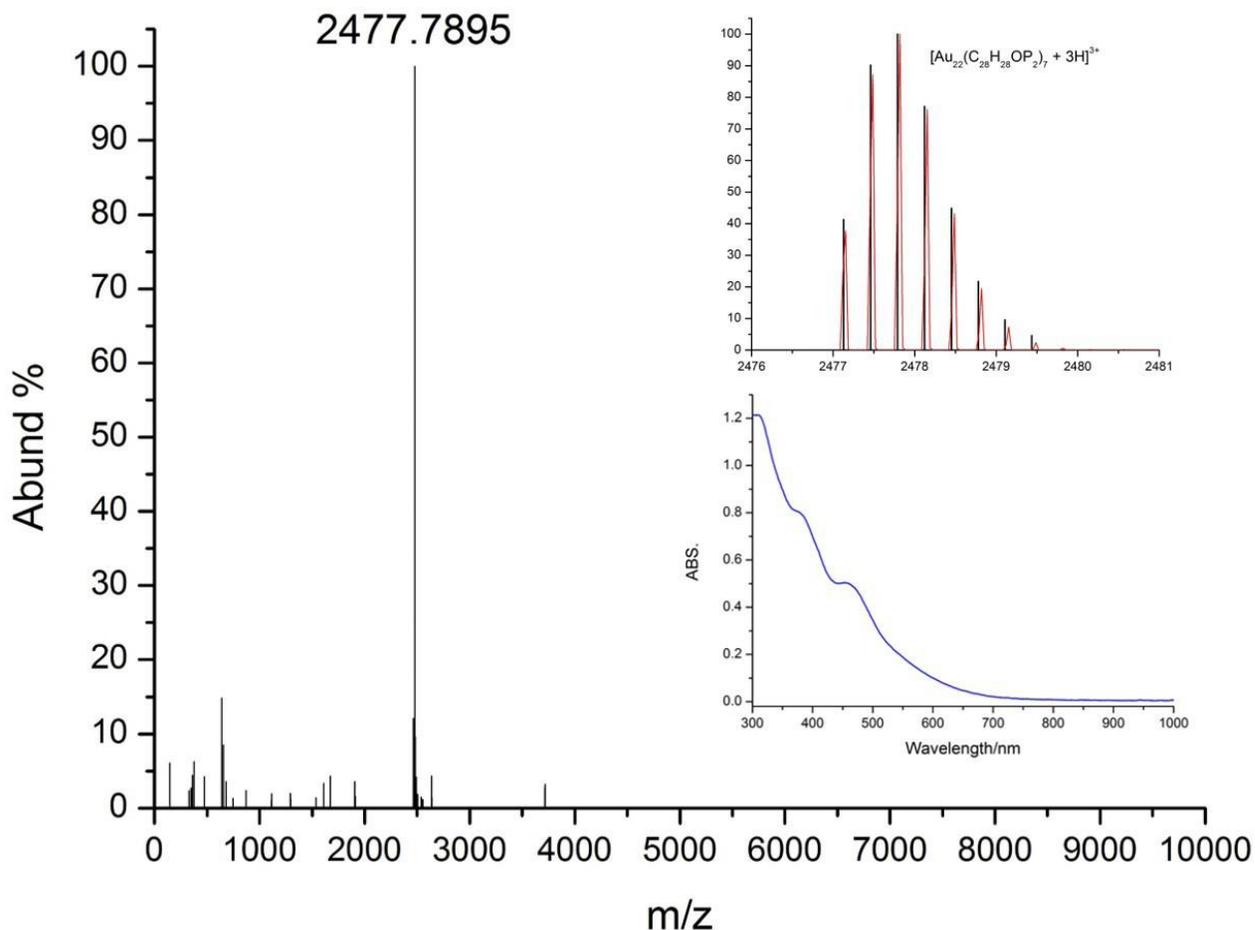
Synthesis of diphosphine-protected Au₂₂(C₂₈H₂₈OP₂)₇ nanocluster

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We are interested in bulk synthesis of the Au₂₀ pyramidal cluster [1] with phosphine ligands. We report the efficient synthesis and separation of a new Au₂₂(C₂₈H₂₈OP₂)₇ nanocluster with 25% yield based on Au. The purity and formula are confirmed by high-resolution electrospray ionization mass spectrometry. UV-Vis-NIR spectroscopy shows absorption peaks at around 315 nm, 385 nm and 465 nm, which is different from the previously reported Au₂₂(C₃₂H₃₆P₂)₆ nanocluster [2]. Collision-induced dissociation further confirms the differences between the two Au₂₂ nanoclusters. The current work will help our understanding of the ligand effects on phosphine-protected gold nanoclusters.

[1] Li, J., Li, X., Zhai, H. J., Wang, L. S. (2003). Au₂₀: A tetrahedral cluster. *Science*, 299(5608), 864-867.

[2] Chen, J., Zhang, Q. F., Bonaccorso, T. A., Williard, P. G., Wang, L. S. (2013). Controlling gold nanoclusters by diphosphine ligands. *Journal of the American Chemical Society*, 136(1), 92-95.



COLL 206

Molecular adsorption and surface coverage effects on the morphology of gold nanoparticle

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Controlling the molecular adsorption has a potential to tailor the green synthesis of gold nanoparticles (AuNPs). Caffeic acid (CA) is known for the strong adsorption on metal or metal oxide surfaces under wet condition. However, many experimental observations have the limitation to explain the detailed adsorption configurations and the effect of functional groups upon the molecular adsorption. In this study, we implemented first-principles calculations to elucidate the adsorption phenomena of CA and its deprotonated forms on Au(100), (110), and (111) surfaces. We examined all possible adsorption configurations with employing the van der Waals interactions to take into consideration the dispersion forces. We found that molecular adsorption is changed by the surface coverage, adsorption structure, and functional groups. We also predicted

AuNP's morphologies on different reaction conditions by examining the adsorption strength at different facets and coverages. Our results provide fundamental information for controlling nanoparticle's morphology by molecular adsorption.

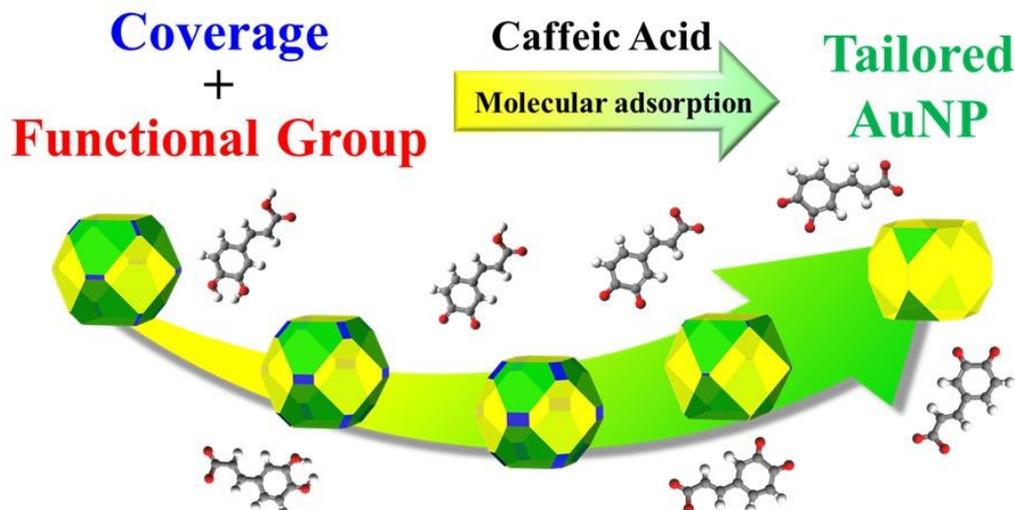


Fig. 1 A schematic of how the morphology of gold nanoparticle is changed by molecular adsorption with various surface coverages.

COLL 207

Graphene quantum dot-Titania composite materials for photocatalytic water splitting and photovoltaic applications

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Titania (TiO_2) is a wide band gap semiconductor that exhibits photocatalytic activity, high resistance to photocorrosion, and stability when exposed to light. The appropriate valence and conduction band energies of TiO_2 are best suited to overcome the thermodynamic and the electrochemical potential required for photoelectrolysis of water. However, TiO_2 as a photo anode material faces some significant challenges such as poor absorption of visible light, high carrier recombination, and limited charge-carrier transport. To overcome these limitations, we propose the synthesis of a composite material using carbon based graphene quantum dots (GQDs) and TiO_2 nano particles. The GQDs are synthesized by an inexpensive wet chemical method using bird charcoal as a precursor. GQD nanostructures exhibit band gap tunability based on their size and has the potential to enhance the photo absorption in TiO_2 . In particular, the hybrid combination of the nano materials is expected to decrease the recombination of charge carriers, increase charge carrier mobility and aids to improve the overall photo-conversion efficiency. The size and surface morphology of the synthesized composite is

studied using scanning electron microscope (SEM) image, atomic force microscope (AFM) and dynamic light scattering (DLS). Electrical/electronic performance of the composite is investigated by photocurrent density measurements. Further, optoelectronic properties are studied using photoluminescence (PL) spectrum and UV-visible transmission spectrum. The use of this combination of nano materials is non-toxic, inexpensive, and novel for photo electrochemical (PEC) water splitting application and has implications for cost effective solar fuel cell developments.

COLL 208

Synthesis, characterization, and cellular uptake of cholesterol-modified poly(ethylene glycol)-poly(D,L-lactic acid) polymeric micelles for effective delivery of curcumin in cancer

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In this study, poly(ethylene glycol)–poly-D,L-lactide (mPEG–PLA) copolymer-based polymeric micelles was prepared for the delivery of a potent hydrophobic anticancer drug, curcumin. As a unique strategy of increasing biodegradability and hydrophobicity, the block co-polymer, mPEG-PLA was modified by cholesteryl chloroformate. Curcumin (CUR) has been reported to be a safe and potent chemotherapeutic drug. However, poor bioavailability and suboptimal pharmacokinetics largely moderated its anti-cancer activity in pre-clinical and clinical models. To improve its applicability in cancer therapy, we encapsulated curcumin in poly(ethylene glycol)–poly-D,L-lactide-cholesteryl chloroformate (CUR-mPEG-PLA-ch) polymeric micelles using the thin-film hydration method. The preparation process was optimized with a central composite design (CCD). These optimized CUR-mPEG-PLA-ch micelles were monodisperse (PDI=0.462 ±0.019) with a mean particle size of 136.2±1.7 nm, an encapsulation efficiency of 93.16±1.15%, and drug loading of 11.90±0.21%. Differential scanning calorimetry (DSC) showed the existence of the drug in a crystalline state inside polymer matrix. The blank micelles exhibited negligible *in vitro* cytotoxicity, yet curcumin-loaded micelles could effectively induce cell death compared to free CUR against murine melanoma cells (B16F10) (Fig 1) and human breast cancer cells (MDA-MB-231). Further, fluorescence microscopy and flow cytometry assay revealed internalization mechanisms for free and curcumin-loaded micelles. These results suggested that mPEG-PLA-ch micelles would be a potential carrier for the delivery of curcumin in cancer improving its bioavailability significantly compared to conventional therapy.

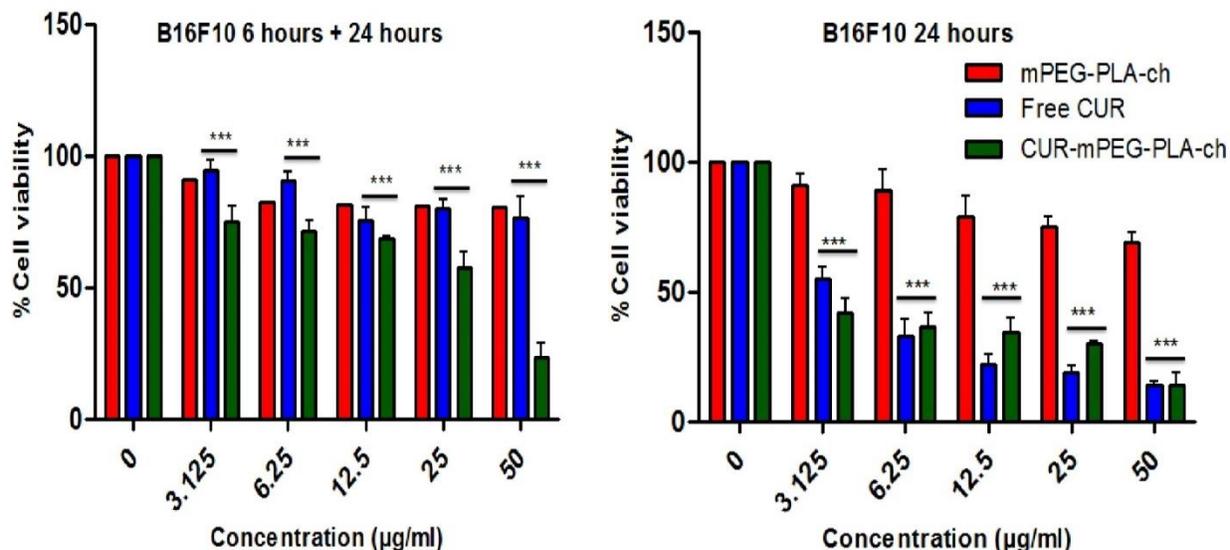


Figure 1: Assessment of cell viability of B16F10 cells treated with Free CUR and CUR-loaded micelles at CUR concentration of 0–50 µg/mL for 6 and 24 h. The significance of difference between the mean was analyzed by Student's t-test, ***, ** indicates $p < 0.001$ and 0.01 , respectively.

COLL 209

Transferrin modified vitamin E: Conjugated lipidic mixed micellar system as nanocarrier for the delivery of curcumin in cancer

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Micelles are self-assembled, nano-sized colloidal particles which could serve as a carrier for small hydrophobic drug molecules with poor pharmacokinetics. In the present study, we have developed a polymeric micellar system, constituted by the self-assembly of an amphiphilic lipid-based co-polymer where hydrophilic block poly(ethylene glycol) is linked to two hydrophobic moieties, phosphatidylethanolamine (PE) and α -tocopherol via an amino acid linkage as shown in Figure 1. The synthesized polymers were characterized by IR and ^1H NMR spectroscopy. Micellar system was loaded with hydrophobic drug, curcumin, and actively targeted to tumor by attaching glycoprotein transferrin on the micellar surface. The transferrin receptor expression on cancer cells can be up to 100-fold higher than the average expression in normal cells owing to their rapid proliferation rate and iron demand, thereby transferrin has been explored as a targeting ligand for nanocarriers to deliver therapeutic agent into cancer cells. The micelles size and surface charge size were measured by Zetasizer. Transferrin modified Vit-E/PEG-5k conjugated polymeric micelles (VPM) and unmodified VPM showed mean hydrodynamic diameter of 114.2 ± 1.82 nm and 110.8 ± 1.82 nm respectively. The tumor-targeted drug-loaded micelles were evaluated for drug loading,

stability and *in vitro* release profile. Cellular uptake study indicated that the Tf-VPMs were taken up by cancer cells with higher efficacy compared to VPM. The therapeutic efficacy of the newly developed curcumin loaded mixed micellar system will be assessed.

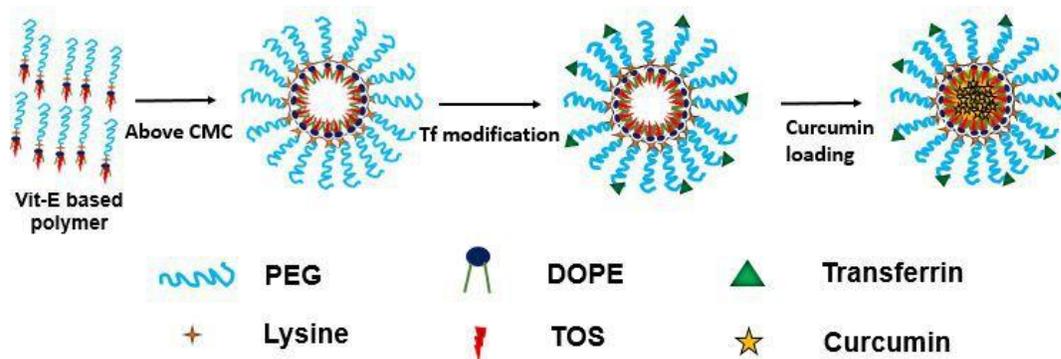


Figure 1. Schematic representation of Tf modified Vitamin E micelles

COLL 210

2-photon fluorescence of quantum dots for investigations of nanoparticle formation and growth

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Quantum dots have been studied intensely in the past years due to their unique fluorescent properties which are controllable by the size of the particle. For online measurements often UV-Vis is used in order to gain access to particle size evolution during quantum dot synthesis. We now want to explore whether the two-photon fluorescence (2-PF) of the quantum dots can be used instead of UV-Vis as fluorescence is expected to be more sensitive to shape, surface termination and defects inside the quantum dot. Compared to one-photon fluorescence (1-PF), 2-PF uses longer wavelengths for excitation, thus reducing scattering losses. In order to determine a possible advantage of 2-PF we investigated the sensitivity of 2-PF in terms of concentration and compared it with UV-Vis and 1-PF sensitivity. We found that for CdS and CdSe quantum dots, the respective 2-PF is still detectable at concentrations which are not accessible with UV-Vis or 1-PF. This can be highly advantageous for detection of earlier stages of particle formation for 2-PF. Preliminary results show that the synthesis of ZnO quantum dots can be followed in situ with 2-PF. To improve spectral resolution the synthesis will be transferred into a t-mixer in order to spatially resolve the different stages of particle formation which then allows for higher integration times at

each stage. For ZnO quantum dots we moreover found that ligand exchange of acetate with catechol takes place within 15 min for UV-Vis and 2 s for 2-PF. This suggests that the two techniques indeed probe different states or sites of the quantum dots.

COLL 211

Effects of defective graphene on the enhanced gas sensing: A density functional theory study

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Graphene has a huge potential as a gas sensor due to the high carrier mobility, large specific surface area, and low electrical noise. Inducing structural defects in graphene lattice has been shown to enhance the capability for sensing gas molecules. However, the mechanism for controlling the sensing of gas molecules on graphene as a function of the type of defects remains unclear. We examined the adsorption of gas molecules (NO_2 and NH_3) on the defective graphene at the atomic-level. Firstly, Density functional theory (DFT) calculations were performed to clarify the defect formation mechanism by comparing the formation energies of various types of defects. Based on these results, we investigated the adsorption of gas molecules on defective graphenes. Among the defects we examine, vacancy defects were considered a contributing factor to gas molecules sensing performance from the optimized geometries, energetics, and charge transfer analysis. Furthermore, the effects of gold cluster on graphene was also studied for controlling the vacancy defects. Developing defects in graphene is important for high-sensitivity gas sensor. Our results will provide an insight into the prospective materials for gas sensor based on the graphene.

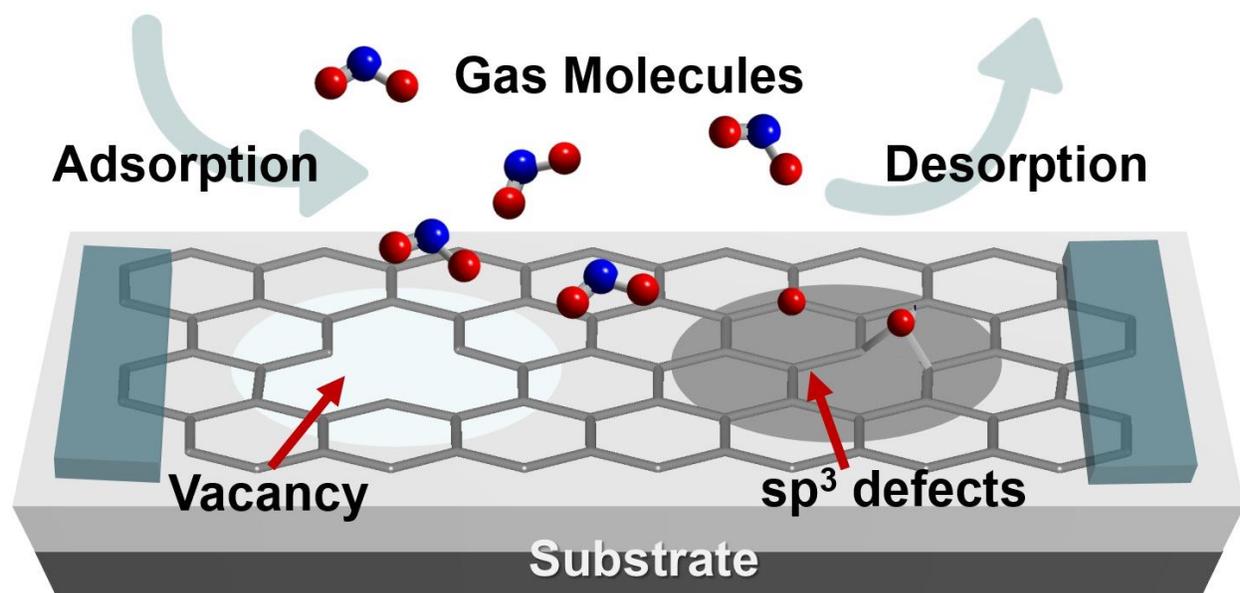


Figure 1. Schematic of sensing mechanism of NO₂ and NH₃ on defective graphene.

COLL 212

Development of a multiplexed point-of-care SERS immunoassay based on antigen mediated aggregation of gold nanoparticles

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Surface-enhanced Raman spectroscopy (SERS) immunoassays have been increasing in popularity in the past several years due to the ability to provide low limits of detection, high sensitivity, and multiplexed detection. While SERS-based assays have led to improvements in the analytical performance of immunoassays relative to conventional assays, e.g., ELISAs, greater efforts are needed to develop convenient and rapid SERS-based assays that are suitable for point-of-need applications. To this end, we show the development of a multiplexed immunoassay utilizing antigen-mediated aggregation of gold nanoparticles (AuNP). We recently developed a SERS-based aggregation immunoassay for one analyte that provided better detection limits and faster analysis when compared to ELISA. This work focuses on the expansion of the assay for multiplexed detection. This aggregation immunoassay is performed using extrinsic Raman labels (ERLs), which consist of a AuNP modified with a mixed monolayer of a Raman dye and an antibody. In order to obtain a multiplexed assay, ERLs were made using unique combinations of Raman dye and antibodies specific for mouse IgG, goat IgG, and rabbit IgG. Several different Raman dyes were systematically studied in order to obtain a unique signal for each antigen that is being studied. Cross reaction and nonspecific aggregation of the ERLs were also evaluated to establish proof-of-principle for the multiplexed SERS assay.

COLL 213

Asymmetric functionalization of gold nanoparticles to produce controlled dimers: A novel approach to aggregation based immunoassays

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Bioanalytical assays based on the aggregation of modified gold nanoparticles (AuNPs) have many attributes critical for point-of-care (POC) tests, including the speed and convenience of a one-step procedure. However, these aggregation based assays are often limited by a narrow dynamic range and low sensitivity. In conventional aggregation based assays, the AuNP surface is fully modified with a single antibody (Ab-AuNP).

Upon the introduction of the target antigen, the Ab-AuNPs undergo uncontrolled aggregation to produce large aggregates of various sizes. The focus of this research is the development of a novel scheme to asymmetrically functionalize the AuNPs and localize the antibody to one confined region on the AuNP surface. These asymmetric functionalized AuNP will facilitate the controlled formation of AuNP dimers in aggregation based assays to increase sensitivity and yield a wider dynamic range. In this work, AuNPs are immobilized onto APTMS modified glass surfaces and incubated with BSA, a stabilizing protein, in which BSA absorbs onto the region of the AuNP that is not in contact with the glass surface. The partially modified AuNPs are released from the glass surface via sonication and antibody is added to absorb only onto the unoccupied region of the AuNP surface. DLS and TEM are utilized to confirm the stability of the asymmetric AuNP in a biological medium and the successful formation of controlled dimers upon the addition of target antigen. An aggregation assay for mouse IgG will be carried out with these novel asymmetric AuNPs, as well as conventional Ab-AuNP, for direct comparison of analytical performance.

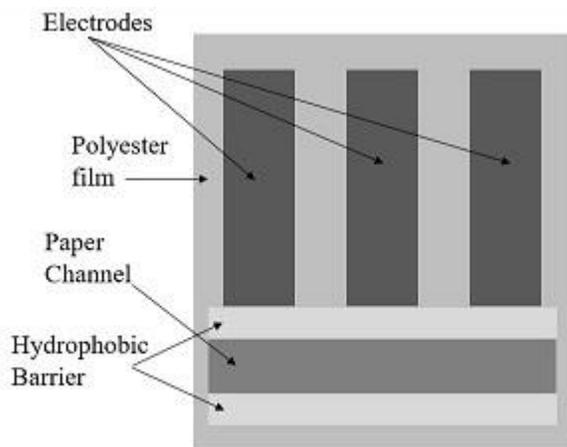
COLL 214

Graphene quantum dots enhanced microfluidics based paper analytical device (μ pads) for glucose detection

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Microfluidics based Paper Analytical Devices, commonly known as μ PADs, have revolutionized the analytical diagnostic platforms towards the development of affordable, portable, and point-of-care diagnostics. Most of them employed colorimetric assay for the detection of biomolecules. The disadvantage with this method is loss of resolution and sensitivity. However, the applications of nanotechnology have improved the performance of these devices. By interfacing with nanoparticle, μ PADs showed the significant improvement in the detection sensitivity and reproducibility. Being electrically conductive and non-toxic, Graphene Quantum Dots (GQDs) are considered to be the suitable candidate to develop nanoparticle enhanced μ PADs for the sensing of biomolecule like glucose. We propose a microfluidics based paper analytical device with GQDs as its working electrode to detect the concentration of glucose in urine sample. GQDs are synthesized from the bird charcoal using the top-down approach. The principle of operation of the device is based on the electrochemical reaction between enzyme, glucose oxidase and the test analyte, glucose. The proposed device has a microfluidic paper channel into which the enzyme is pre-adsorbed and is in conformal contact with the electrodes. Through the introduction of urine sample to the paper channel, sample reacts with enzyme and generates ions through a two-step reaction. These ions are detected by the electrodes and the response is monitored. Depending upon the output response, the glucose level in the urine is estimated. In addition, the current detection methods of glucose involve the usage of blood as the test analyte because the level of glucose in blood is relatively higher than urine. GQDs being

electrically sensitive, meaningful results can be obtained from the urine sample itself. In conclusion, affordable and efficient point of care diagnostics can be developed using paper microfluidics and nanotechnology to detect the level of glucose in urine.



Device schematic showing the arrangement of electrodes and channel.

Device schematic showing the conformal contact of electrodes with the channel.

COLL 215

Structural conformation of methacrylate-based functionalized monomers and polymer thin films at the air interface

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Polymer chemistry involves investigations that focus on synthesis, characterization and examination of macromolecular properties. An important fraction of these studies is extensively focused in understanding their multifunctional and complex structures through different polymerization processes to appeal to a wide variety of applications. Overall, the functional groups present and the approach in which they assemble into a macromolecular structure play a critical role towards understanding a polymeric system. However, the more fundamental question arises on how these complex polymeric structures are assembled from their monomers at the interface leading to the formation of complex structures. In this study, our group aims to provide insights into these processes using femtosecond sum frequency generation (SFG) spectroscopy and other characterization techniques. Our preliminary studies on the substitution of functional groups at the ethyl group of the methacrylate monomers (hydroxy (-OH), chloro (-Cl) and phenoxy (-OPh)) showed that there is a preferential surface ordering of alpha-methyl (α -CH₃), alkene-methylene (alkene-CH₂), and methylene (CH₂) groups toward the air interface. The observation of the alkene-CH₂ at 3000 cm⁻¹ in the SFG spectrum

showed that this specific functional group indicates that a monomer has not undergone radical polymerization. Also, at a monomeric state, the interfacial molecules found their most favorable molecular conformation to satisfy the minimum free energy requirement at the air interface. In comparison, polymer thin films (PTFs) of these selected monomers were also prepared to observe if there are any differences in the spectral profile. For polymers, the alkene-CH₂ group was not observed but revealed that the α-CH₃ group dominated the surface of the poly(2-hydroxyethyl methacrylate) PTFs while for the other two substitutions, α-CH₃ and CH₂ groups segregated at the surface. The functionalization of the ethyl group methacrylate monomers and PTFs has affected the assembly of the interfacial molecules. Orientational analysis and polarization mapping methods are also applied to gain a better interpretation of the molecular conformations of these interfacial molecules.

COLL 216

Detection and identification of negatively-charged gold nanoparticles using pH indicator arrays

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Engineered nanoparticles (NPs) are currently being researched due to the wide varieties of applications they enable, such as microelectronics, next-generation batteries, and Nano therapeutics. Unfortunately, engineered NPs may pose a health risk in both humans and in the environment. Therefore, as nanomaterial-enabled technologies become more common, it will be essential to develop NP sensors that can rapidly detect and quantify the concentration of NPs in the environment. Currently, detecting and identifying engineered NPs requires relatively high-cost and low-throughput characterization techniques (such as electron microscopy). We are investigating a simple NP detector that is low-cost and offers rapid response time (< 30s), composed solely of six commonly available pH indicators. The indicators were exposed to citrate-stabilized, poly allylamine hydrochloride (PAH), and polyacrylate (PAA)-wrapped 12 nm gold nanoparticles (AuNPs). Each indicator is not specific to the NPs, but the overall color change of the indicator array gives a response which is specific to each NP surface chemistry tested. Similar indicator arrays have previously been used to detect a variety of compounds, including volatile organics, metals, and metal oxides. Thus far, we have used the indicator arrays to successfully detect aqueous solutions of 12 nm AuNPs at a particle concentration as low as 1×10^{-10} M.

COLL 217

Layer-by-layer assembly and catalysis from polymer-capped Au nanoparticles

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Layer-by-layer assembled multilayers were fabricated via electrostatic assembly of polyethylenimine- capped gold nanoparticles (PEI- capped Au NPs) and the conducting polymer, poly(3,4-ethylenedioxythiophene):poly(p-styrenesulfonate) [(PEDOT:PSS)^{-Na⁺}]. The multilayer films were characterized by laser ablation inductively coupled plasma mass spectroscopy, atomic force microscopy, ultraviolet-visible spectroscopy, and cyclic voltammetry. The electrocatalytic role of these conductive multilayers is evaluated and includes an investigation into the oxidation of carbon monoxide (CO) and 2-hydroxybenzyl alcohol (2-HBA). Preliminary work for CO electrooxidation revealed the presence of an anodic current associated with the CO oxidation half reaction. Studies include assessing the current density of the anodic peak from CO electrooxidation as a function of multilayer structure such as gold content and bilayer number. In preliminary electrocatalytic work, the oxidation of 2-HBA produced a polymeric film on the surface of electrode. This film is insoluble in water and in most organic solvents and is hypothesized to be a polyphenylene oxide (PPO) derivative. Electrochemical conditions are evaluated and related to the molecular structure of the PPO film as determined by infrared spectroscopy. The role of the PEI-capped Au NPs in the nucleation and growth of the polymeric film relative to blank electrodes will be discussed.

COLL 218

Mechanism and characterization of inorganic mineralization of palladium on virus templates

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In recent years, many virus-inorganic materials have been synthesized as a means to produce high quality nanomaterials. However, the underlying fundamental mechanisms involved in virus coating have not been sufficiently studied to allow for directed synthesis. In our work, the recently discovered, expedient biosynthesis of palladium nanorods known as the hydrothermal synthesis is studied using different virus-palladium systems.

X-ray Absorption Spectroscopy (XAS) was combined with TEM to confirm an autocatalytic reduction mechanism mediated by the TMV1Cys virus surface. This reduction proceeds via two first order regimes which result in two linear growth regimes as spherical palladium nanoparticles are formed. By combining this result with particle growth data, we determined that the first regime is characterized by growth of palladium nanoparticles on the virion while the second regime characterizes a second layer of larger particles which grew sporadically on the first palladium nanoparticle layer. Subsequent aggregation of free solution based spherical particles and metallized nanorods characterize a third and final regime. The use of XAS to simultaneously monitor the kinetics of biotemplated reactions along with growth of metal nanoparticles provides insight into the pertinent reduction and growth mechanisms so that nanorod properties can be controlled through their populating nanoparticles.

In follow up studies, comparative kinetic and adsorption characterization were performed in different virus-metal systems, under various experimental conditions using UV-Vis spectroscopy; In situ SAXS was applied in monitoring nanoparticle growth on the surface of the virus. As a result, pertinent synthetic levers for biomineralization have been identified leading to a more robust understanding of how adsorption and reduction contribute to nanoparticle formation. Such knowledge is critical for scale up and directed synthesis while applying the hydrothermal synthesis .

COLL 219

Elucidating the mechanism behind spin-dependent charge transport through DNA monolayers

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The possibility of selectively filtering electrons with a particular spin by chiral molecules at metal-molecule interfaces without the use of a permanent magnet has stimulated renewed interest in probing spin-dependent phenomena in adsorbed chiral molecules and assemblies. In particular, unprecedented spin-selective electron transmission at room temperature has been observed through self-assembled monolayers of double-stranded DNA. These surprising results demonstrate the unique and exciting potential to utilize a more versatile class of materials to combine the fields of spintronics, bioelectronics, and biomagnetics. However, the mechanism governing electron spin filtering by DNA remains elusive. Thus, we combine advanced surface chemistry with novel electrochemical characterization strategies to deconvolute the relative contributions of molecular, surface, and interface properties to spin-selective electron conduction through DNA monolayers adsorbed on ferromagnetic substrates. We probe molecular structure and substrate parameters that have been theoretically predicted to influence spin polarization such as molecular length and nitrogenous base sequence, heavy-ion incorporation, DNA attachment chemistry, and substrate spin-orbit coupling. Understanding the mechanism responsible for this spin-dependent effect is critical to assessing the viability of implementing DNA assemblies as sources of polarized electrons in organic spintronics devices, and advancing the frontiers of room-temperature spin-dependent transport.

COLL 220

Colloidal self-assembly of multi-fluorescent hybrid silsesquioxane particles

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Nanoscale particles derived from silsesquioxane core structures are important nanomaterials that can be applied in electronic devices. As the surface silsesquioxane core structure can be easily functionalized with various semiconducting organic molecules, there has been a great effort to use them as emissive layers for optoelectronic devices. However, There has been a significant challenge assembling nanoscale to microscale particles into a well ordered microstructures. Here we describe a novel method to assemble microparticles into three-dimensional micro-colloids using organic-inorganic hybrid particles through strong H-bonding interactions. To do this, a series of reactive group functionalized silsesquioxane microparticles were prepared by direct hydrolysis and co-condensation of their respective silane precursors. Particle sizes were controlled upon adjusting the molar ratios of organotrialkoxy silane to the base concentrations. These resulting microparticles with reactive amine groups and benzyl chlorides groups are found to be more advantageous for the self-assembly in a variety of polymer matrices due to the formation of strong H-bonding interaction of amine group with active sites of the polymer substrate.

COLL 221

Lithium fluoride nanoparticles injected with hyaluronic acid for management of osteoarthritis pain

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Osteoarthritis affects nearly 27 million adults and is one of the five leading causes of disability according to the CDC. This disease is characterized by the continuing degradation of cartilage and underlying bone changes in joints. Treatments of osteoarthritis include hyaluronic acid, which is injected directly into the joint and leads to a reduction in pain over 1-6 months. However, 3-5 weekly injections are required which can result in increased inflammation and higher chances of infection. Recently, lithium has been shown, in vitro and in vivo, to display cartilage-protective abilities by downregulating inflammatory cytokines TNF- α and IL-1. Yet, this lithium treatment is injected as an aqueous solution and may extravasate before the full dosage can be used by the cells in the joint. We have synthesized lithium fluoride nanoparticles using a simple and easily scalable method in polyethylene glycol. It was found that these particles, when dispersed in a hyaluronic acid gel, can gradually release lithium when exposed to extracellular calcium. We investigated the effect of lithium fluoride nanoparticles mixed with hyaluronic acid in intra-articular knee injections and assessed the combination's ability to match the pain relief and mobility enhancement of multiple injections of hyaluronic acid.

COLL 222

Four criteria demonstrating cross-linking of ultras-small superparamagnetic iron oxide (USPIO) nanoparticles

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Justification. Treatment of dextran coated USPIOs with epichlorohydrin is widely cited in the literature as a method for stabilizing the dextran coating through chemical cross-linking. A search of the literature fails to reveal any citations demonstrating the achievement of crosslinking or stating a set of criteria that can be used to establish that cross-linking has been obtained (see citations in reference 1). Both the cross-linking chemistry and operational process are deceptively simple. In fact the chemistry and process are both complex and difficult to reproduce from one laboratory to another. Criteria are needed to define and standardize the cross-linking process.

Results. We present a set of four criteria to demonstrate cross-linking, to serve as a starting point to control reaction reproducibility and to allow routine quality control of the cross-linking process. The first three criteria are based on altered biochemical, chemical, and biological properties between the parent USPIO and its cross-linked child.

- 1.The cross-linked USPIO should show an increased resistance to degradation by enzymes, e.g., dextranase, in comparison to the starting USPIO.
- 2.The cross-linked USPIO should show an increased resistance to degradation by chemicals, e.g., periodate oxidation, in comparison to the starting USPIO.
- 3.The cross-linked USPIO should show a diminished binding by lectins for the cross-linked iron oxide nanoparticle in comparison to the starting USPIO.
- 4.The fourth criterion requires generation of a new material, a USPIO ghost (first described in reference 2), consisting of the cross-linked dextran minus its iron oxide core. The parent USPIO and its ghost have a similar size and charge.

In addition to providing the fourth criterion for crosslinking, USPIO ghosts allow for simpler analytical measurements of conjugated USPIOs free of optical and chemical interferences associated with the nanoparticle's iron oxide. Among their many potential applications, USPIO ghosts provide new materials for drug delivery development, cell labeling/tracking and gadolinium chelated-T1 agents.

Examples of the four criteria will be presented in our presentation.

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COLL 223

Emulsion properties depend on the equilibrium phase behavior and structure encountered during the emulsification process

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In order to improve our understanding of the effects that the equilibrium phase behavior and structure of amphiphilic molecules (e.g., surfactants, lipids, block copolymers) have on the emulsification process and the properties of emulsions stabilized by these amphiphiles, we have exploited the known phase behavior of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) amphiphilic block copolymers (Pluronics or Poloxamers) [1] in the presence of two immiscible solvents. Specifically, we considered ternary systems consisting of Pluronic F38 [2], L64 [3], P84 [4], P104 [5], or L121 [2] with water and p-xylene which exhibit a very rich phase behavior, including a variety of water-continuous and oil-continuous lyotropic liquid crystalline (LLC) phases. We prepared emulsions having the same (final) compositions but through different emulsification paths, and evaluated the emulsions on the basis of homogeneity and droplet size. We found finer and more homogenous emulsions to result when oil-in-lamellar structures (as revealed by small-angle X-ray scattering) were formed during the emulsification process, or when the emulsification path traversed the lamellar LLC phase [6]. This can be attributed to the favorable properties of the lamellar structure: high oil solubilization capacity with concurrent facile dispersibility in water, relatively low interfacial tension, and relatively low viscosity. The findings reported here are relevant to the preparation of emulsions for diverse applications such as skin-care products, pharmaceuticals, food products, coatings, inks, agrochemicals, oil dispersants, and nanomaterials synthesis.

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COLL 224

Tracking and aiding the survival of stem cells by indocyanine green- and insulin growth factor-loaded mesoporous cellular foam

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Increasing stem cell survival and engraftment efficacy is critical for the field of regenerative medicine. Here, we report theranostic mesoporous cellular foam (MCF, **Fig. 1a, b**) that has photoacoustic and acoustic signals for real time cell tracking to improve engraftment efficiency. This same material is a slow release reservoir of insulin-like growth factor-like (IGF) to improve cell survival. The loading efficiency and loading capacity of MCF for cargos varies as a function of loading concentration (**Fig. 1c**) when using indocyanine green (ICG) as a model cargo. MCF can load about 169 μg ICG when the ICG loading concentration is 10 mg/ml . At the same concentration of 8 mg/ml , the average grey values of IGF loaded MCF (ICG@MCF) and bare MCF are 166 and 182 respectively, so the acoustic signal of ICG@MCF is 8.8% lower than bare MCF ($n=20$, $p<0.001$) (**Figure 1d**). While shown in **Figure 1e**, the photoacoustic signal (red signal in the figure) of ICG@MCF 0.93, is about 5.5-fold higher than MCF alone which is 0.17 ($n=20$, $p<0.001$). At an IGF protein concentration of 158 $\mu\text{g/ml}$, the loading efficiency and loading capacity of IGF to ICG@MCF is 53.1 % and 8.4 $\mu\text{g/mg}$ respectively. The in vitro release result indicates that only 7.2% IGF was released within one hour and 27% was released after one week (**Figure 1f**).

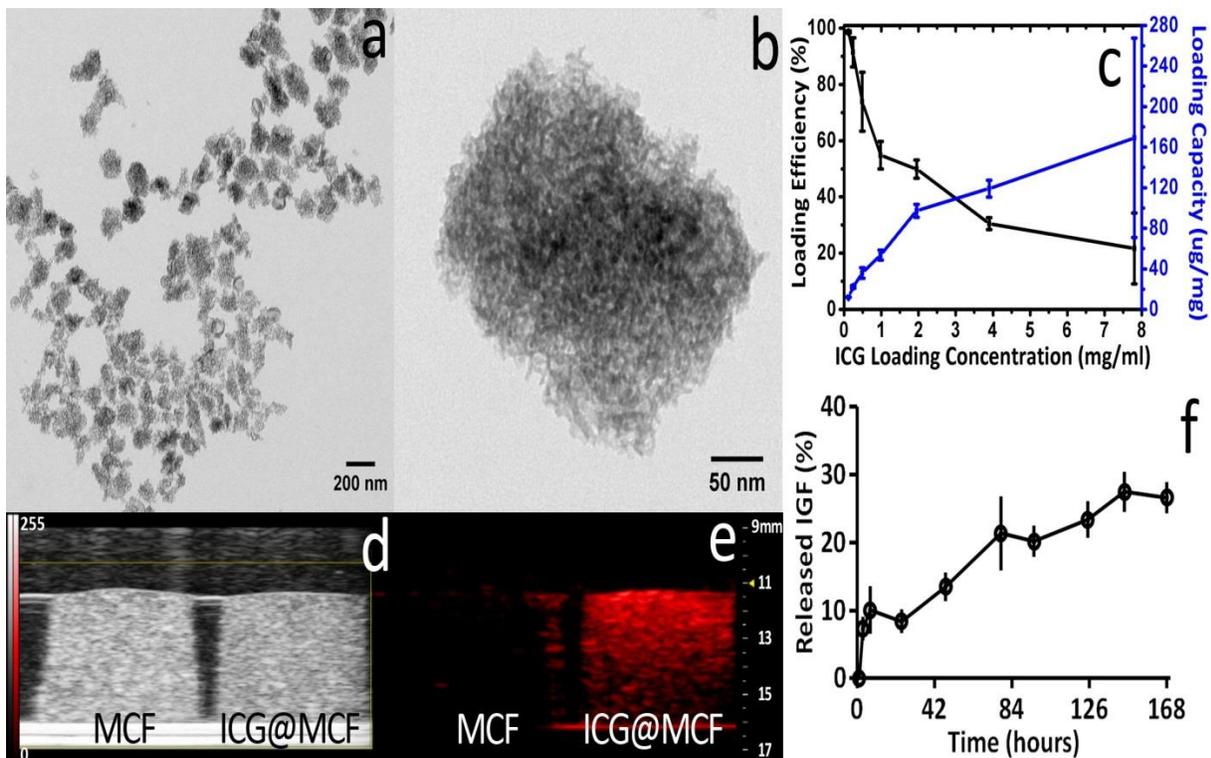


Figure 1 (a, b) TEM images of mesoporous cellular foam (MCF). (c) Loading efficiency and capacity of ICG into MCF. (d) Ultrasound and (e) photoacoustic images of MCF and ICG loaded MCF (ICG@MCF). (f) In vitro release of IGF@MCF in PBS at 37°C.

COLL 225

Nanoporous materials genome center: Methods and software to optimize gas storage, separation, and catalysis

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The Nanoporous Materials Genome Center (NMGC) discovers and explores microporous and mesoporous materials, including metal-organic frameworks, zeolites, and porous polymer networks. These materials find use as storage and separation media and catalysts in many energy-relevant processes and their next-generation computational design offers a high-payoff opportunity. Towards that end, the NMGC develops state-of-the-art predictive modeling tools, databases, and web-based repositories, and employs them to increase the pace of materials discovery. This poster will provide an overview on the NMGC activities.

COLL 226

Solvent and ligand effect on ultrafast and temperature-dependent optical properties of bi-icosahedral Au₂₅ clusters

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Gold clusters smaller than 2 nm exhibit unique quantum size effects with discrete electronic energy levels, and possess both semiconducting and molecule-like characteristics. Exciting optical, electrochemical and catalytic properties are observed in gold clusters because of their discrete electronic transitions. In recent work, we have shown unique optical transitions in the gold-clusters using ultrafast luminescence and temperature-dependent absorption measurements. In the present work, measurements are aimed at understanding of both ligand and solvent effects on the optical transitions. Here we used bi-icosahedral Au₂₅ clusters ([Au₂₅(PPh₃)₁₀(X)5Cl₂]²⁺; X- thiolated ligands) as the systems to investigate both ligand and solvent mediated effects. These Au₂₅ clusters were synthesized using five different thiolated ligands to investigate how the ligand affects optical properties and four different solvents used to investigate the solvent mediated properties of the clusters. Temperature-dependent absorption measurements of bi-Au₂₅ in aprotic (toluene) and protic (ethanol, TFE and 2-butanol) were carried out to understand the influence of solvent hydrogen bonding on the low energy absorption. In toluene, both low and high energy absorption bands shift to higher energies consistent with electron-phonon relaxation. However in protic solvents of ethanol, TFE and 2-butanol, the low energy absorption shows zig-zag trend with high to low high energy shifts with a decrease in temperature.

COLL 227

Microdroplet traps for the investigation of nanocrystal interactions in small volumes

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Substantial progress in the colloidal synthesis of metallic and semiconducting nanocrystals has enabled precise control of their composition, size, and morphology and thus their physical properties (e.g., optical, electrical, and catalytic). This synthetic control makes nanocrystals attractive materials for numerous technologies. Despite this progress, relatively little has been done to investigate how nanocrystals nucleate, ripen, and interact when they are confined to microenvironments, such as micro-droplets or vesicles, like those encountered in biomineralization. We aimed to develop an effective method of studying nanocrystals within synthetic microenvironments by creating microfluidic systems which could transport aqueous micro-droplets for indefinite periods of time. We could then load the droplets with colloidal nanocrystals (and relevant precursors). In this demonstration, we fabricated a microchannel system, trapped droplets containing gold nanocrystals within it, and monitored the droplets via videography. We tracked the changes in droplet volume and trajectory over time and followed nanocrystal aggregation and ripening by following shifts in the plasmonic band using image processing. The approach we report provides an experimental framework for investigating nanocrystals in microenvironments with tunable chemistry and volume.

COLL 228

Novel polymeric silsesquioxane nanocolloids and their assembly

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Assembly and fabrication of colloidal structures have attracted much attention as next generation devices such as biochips, sensors, and ultrahigh-density optical and magnetic recording media. A number of methods have been introduced to obtain 2-D and 3-D colloidal assemblies including spin-coating, solvent evaporation, interface self-assembly, micro-contact printing, and electrostatic assembly technologies. Patterning ordered structures of colloidal crystals is also promising for creating multifunctional inversed photonic crystals with full band gaps. Despite the potential importance for variety of applications, the primary requirement for the success of such applications relies on the capability of fabricating colloidal structures with quality and controlled geometries.

Here we introduce a novel covalent synthesis method to make colloidal assemblies with controlled long -range order of nanocolloids. Two polymeric systems derived from

anthracene derivatives were assembled into different morphologies after base-catalyzed hydrolysis and co-condensation of their functionalized dialkoxy silane precursors in an aqueous medium. This in-situ polymerization followed by self-assemble process is a unique approach to make colloidal nanostructures from variety of ligands functionalized alkoxy silanes.

COLL 229

Chiral ceramic nanoparticles

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Plenty of researches about chiral noble metals Au and Ag and some of chiral II-VI semiconductors like CdS, CdSe, CdTe and PbTe have been reported and paid attentions. While no ceramic NPs have been reported till now in terms of the chiral property, which have favorable applications in catalysis, optical properties and biomedical science. Here we are the first to report chiral ceramic NPs with interesting near infrared (NIR) chiroptical activities. Chiral capping ligands L/D-aspartic acid introduced chirality in achiral tungsten oxide nanoparticles with oxygen vacancy (WO_{3-x} NPs), a kind of ceramic NPs. As-prepared WO_{3-x} NPs exhibit a broad NIR absorption and circular dichroism (CD) spectra (800-1200nm). Interestingly, it showed enhanced absorption and CD signal simultaneously with adding water or exposed in air. The appropriate amount of water (0.04V/V%--0.20 V/V% water in sample) or humidity of air can cause coloration and enhancement of absorption and CD signal. The as-prepared chiral WO_{3-x} open up the possibility of effective medicine delivery acting as a carrier to cancer cells and subsequent laser photothermal therapy to kill tumor as WO_{3-x} can absorb NIR light and transfer to heat effectively.

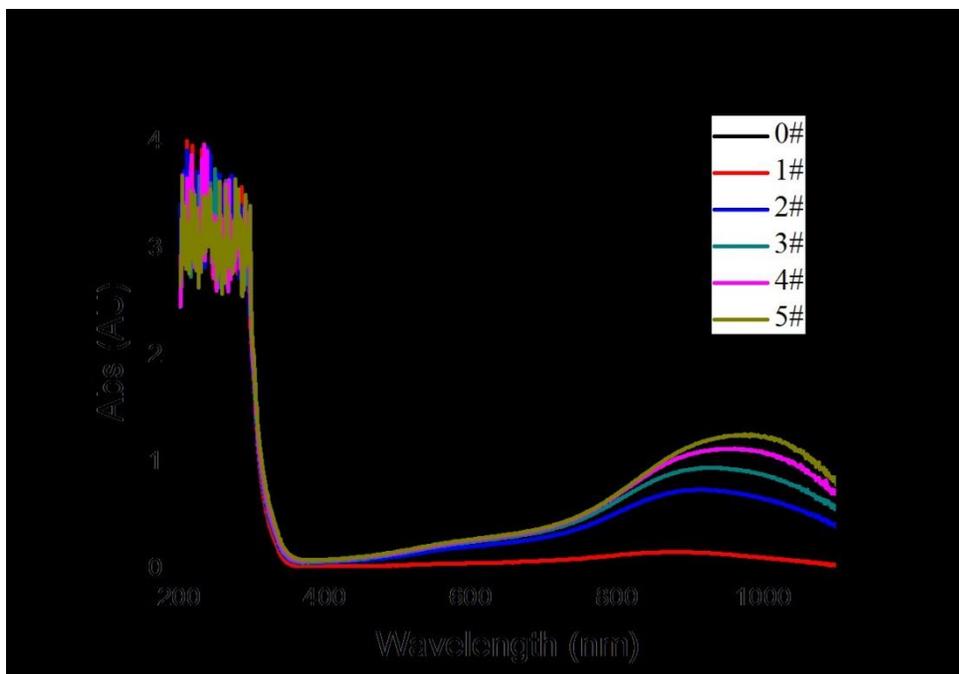


Fig 1. Absorption spectra after adding water to original samples. 0#--5# adding 0-5 μ L water into 2.5 mL L/D- aspartic acid-WO_{3-x} samples respectively.

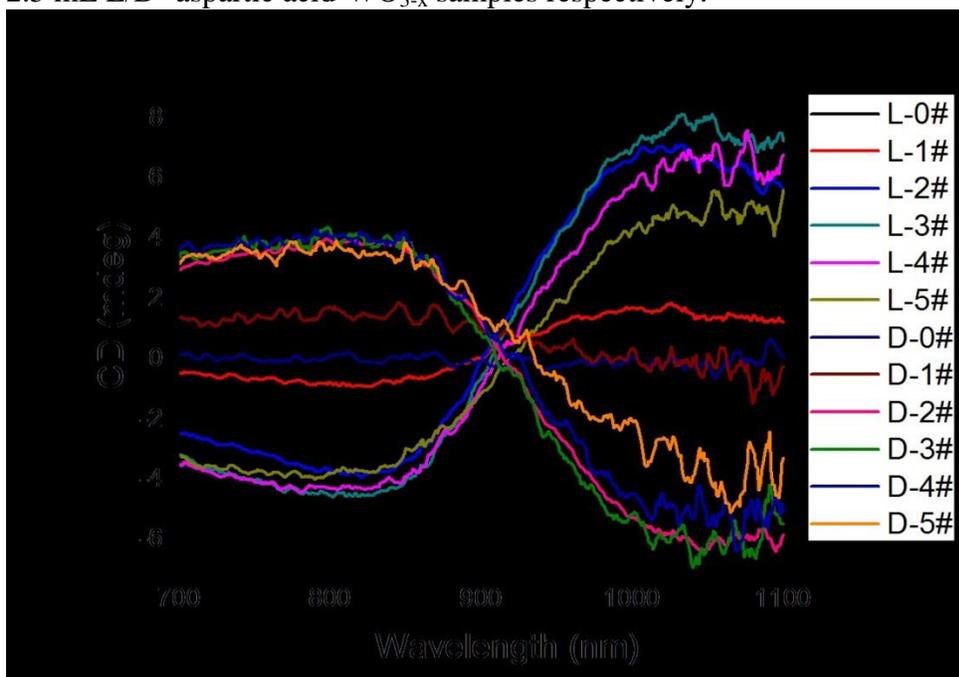


Fig 2. CD spectra after adding water to original samples. L-0#--L-5# adding 0-5 μ L water into 2.5 mL L-aspartic acid-WO_{3-x} samples, and D-0#--D-5# adding 0-5 μ L water into 2.5 mL D-aspartic acid-WO_{3-x} samples respectively.

Interferences in reflected infrared extinction spectra from a gold-coated periodic particle array

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The infrared extinction spectra of molecules adsorbed to gold films over periodic particle arrays in the infrared have the potential to show enhanced extinction at wavelengths that are resonant both with vibrations of adsorbed molecules, and with the localized surface plasmon. A third type of resonance that can contribute to such extinction spectra are diffractive resonances. An experiment was carried out in which four distinct hexagonally packed arrays of polystyrene spheres, having diameters of 3, 4, 5 and 6 microns respectively, were prepared on calcium fluoride windows and coated with gold. FTIR microscopy was used to obtain spectra of each gold-coated array. In these spectra the envelope of the gas phase CO₂ absorption at ~2350 cm⁻¹ undergoes characteristic changes in shape associated with interference of multiple resonances. The interferences are not observed in the water vapor bands nor in the 670 cm⁻¹ CO₂ band. The interference effects were reproduced with a second set of arrays that were independently produced and analyzed. The periodicity of the interferences appears to scale with the sphere diameter, as the spectral line-shape at ~2350 cm⁻¹ from the three micron arrays is replicated in the spectra from the six micron arrays. We present a preliminary model of the spectra that incorporates the infrared absorption of molecular carbon dioxide, as well as the localized surface plasmon resonance (LSPR), and diffractive resonance of the gold-coated film over microsphere array.

COLL 231

Silver nanoparticles synthesis as SERS substrates for ketoconazole determination

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In this work, silver nanoparticles were prepared by reduction procedure. They were then characterized using various characterization techniques; scanning electron microscope, energy dispersive X-ray spectroscopy, thermogravimetric analyzer, X-ray diffractometer, Fourier transformed infrared spectroscopy, Raman spectroscopy and high-resolution transmission electron microscope. The silver nanoparticles were of around 40 nm average size. The UV spectroscopy showed a maximum absorbance of silver nanoparticles at about 400 nm. Raman spectra showed multi sharp peaks can be assigned for Ketoconazole molecule as peaks at (790 cm⁻¹) for C-Cl stretching vibration, (1050 cm⁻¹) for C-O vibration, peak present at (1388 cm⁻¹) for C-H bend, C=C (aromatic) stretching vibration present at (1610 cm⁻¹), and stretching vibration C=O detect at (1707 cm⁻¹). The intensity of C-O peak, increase with increase the concentration of KCZ

solution. Raman spectra of Ketoconazole on Ag showed interaction between Ketoconazole and Ag lead to highly SERS enhance peak of KCZ at (1050cm⁻¹), and slightly enhance a peak of C-Cl at (785cm⁻¹). The peak intensity of KCZ at (1050cm⁻¹) with Ag is stronger than without Ag/NPs, due to the excitation of surface Plasmon resonance on substrates as a result from the strong interaction between KCZ and Ag/NPs. These substrates are promising for SERS applications in other drugs characterization.

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COLL 232

Localization of porphyrins to spatially confined sites of self-polymerized 4-(chloromethyl)phenyltrichlorosilane studied with atomic force microscopy

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Particle lithography was applied to successfully to create complex heterostructures at the nanoscale. Experiments with atomic force microscopy demonstrate capabilities to reproducibly generate surface platforms with spatial selectivity for the attachment of multicomponent nanopillars. Images of the main steps of the surface reactions were captured *ex situ* with AFM to reveal changes in the growth and morphology of the nanopillars. A protocol was developed to confine and pattern the growth of porphyrins to specific sites of designed nanopillars of 4-chloromethylphenyltrichlorosilane (CMPS). Steps of immersion particle lithography were developed to selectively passivate a surface of Si(111) with octadecyltrichlorosilane (OTS) to prepare a test platform of nanoholes. The exposed sites within the nanoholes were used direct and confine the surface assembly of CMPS nanopillars. Silica mesospheres were used as a surface mask to prepare nanoholes within a passivated OTS matrix. Areas surrounding the CMPS nanopillars were passivated with the methyl-terminated organosilane to prevent nonspecific binding of CMPS. After OTS nanopores were generated and subsequently characterized via AFM, the samples were immersed in a solution of CMPS prepared with toluene. By controlling the concentration, solvent, temperature and time, nanopillars of defined height and morphology were generated within the exposed nanoholes. The CMPS nanopillars were characterized with tapping-mode AFM. The samples were then refluxed in a porphyrin solution to facilitate the attachment of porphyrins. The attachment of porphyrins to CMPS nanopillars was evaluated by measuring changes in the height and width of nanopillars. Through each step of the surface reactions, the surrounding OTS matrix revealed minimal nonspecific adsorption. An increase in the average height of nanopillars was observed after addition of the porphyrin, which corresponds to multilayers of porphyrin macrocycles being attached. Porphyrins have practical applications in dye-sensitized solar cells, flat screen displays and as commercial dyes.

COLL 233

One-step and one-pot preparation of ampicillin-functionalized antibacterial gold and silver nanoparticles

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The emergence of multidrug resistant bacteria (MDR) has necessitated the development of novel antibacterial agents that efficiently block or weaken bacterial growth. As the nanotechnology era emerges, the nano-sized materials are considered to be an effective platform for antibacterial agents. In particular, gold nanoparticles (AuNPs) and silver nanoparticles (AgNPs) have shown promise as bactericidal agents for MDR bacteria. Researchers have reported that the functionalization of AuNPs and AgNPs with ampicillin destroyed MDR bacteria. They applied a two-step process; (1) preparing citrate-stabilized NPs using NaBH₄ and (2) mixing the NPs with ampicillin to generate ampicillin-functionalized NPs. In another report, the enhancement of the antibacterial activity of AgNPs was observed when AgNPs were combined with conventional antibiotics. In previous studies, researchers performed the experiments by a two-step process: (1) preparation of the NPs and (2) functionalization of the NPs with antibiotics. In the current report, facile and simple functionalization of AuNPs and AgNPs with ampicillin was conducted in a one-step and one-pot process. In this synthetic strategy, ampicillin played a role as the reducing agent and as a capping agent. The 2D-/3D-nanostructure, nanotopography and dispersion state were investigated by spectroscopic and microscopic techniques. Remarkably, the newly-prepared AgNPs and AuNPs show excellent and specific antibacterial activities against *Streptococcus pyogenes*. The current system enables the facile functionalization of AuNPs and AgNPs with ampicillin using a one-step process.

COLL 234

Optical and structural characterization of stoichiometric and indium-rich CuInS₂/ZnS colloidal quantum dots

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Ternary I-III-VI colloidal quantum dots (QDs) such as CuInS₂ have recently been considered as a good candidate to replace binary Cd-based II-VI QDs in environmental and biological applications. However, in comparison with binary Cd-based QDs, the structure and optical properties of ternary QDs are less well studied. In this study,

CuInS₂ is synthesized with different Cu:In molar ratios and shows that the quantum yield (QY) of In-rich CuInS₂ QDs (Cu:In = 1:4) is three times higher than stoichiometric CuInS₂ QDs (Cu:In = 1:1), 12% compared to 4% respectively. When ZnS is then coated onto these CuInS₂ QDs, there is an increase in QY results, with those using a Cu:In ratio of 1:4 showing QYs of 40%.

We characterize the ensemble and single particle properties of core CuInS₂ and CuInS₂/ZnS QDs using time-resolved fluorescence, high-resolution transmission electron microscopy (HR-TEM), X-ray diffraction (XRD), and inductively coupled plasma mass spectroscopy (ICP-MS) to connect the elemental and structural parameters to the exciton decay dynamics to better understand the basis for these quantum yield changes.

COLL 235

Ultrasmall metal nanoclusters as electrocatalysts for hydrogen evolution reaction

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The next generation energy, hydrogen, has been received great attention owing to its possibility for efficient energy production and solving problems for the depletion of fossil fuel. Hydrogen evolution reaction (HER) has been studied with various catalysts such as Pt, transition metals and metal complexes. However, these catalysts suffer from their high cost, limited supply and low stability. In this poster, we report that remarkably efficient HER catalysis can be achieved by using ultrasmall Au₂₅ nanoclusters exhibiting unique redox properties and high stability. The redox potentials of Au₂₅ nanoclusters were tuned by doping with foreign metals, such as Pt, Pd, Cu and Ag. Interestingly, Pt-doped nanoclusters displayed reduction potentials that match closely with the proton reduction potential. The Pt-doped nanoclusters showed outstanding HER activity with exceptionally high turnover frequency. Furthermore, ultrasmall Au₂₅ nanoclusters were found to exhibit excellent catalytic activity for oxygen reduction reaction (ORR). The origin of the catalytic activities of these metal nanoclusters is discussed along with reaction mechanisms.

COLL 236

Effects of antifreeze polypeptides on calcium carbonate crystallization

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The formation of sparingly soluble and insoluble inorganic salts (i.e., scale deposits) is a major problem in an industrial and domestic setting. To control scale deposits, chemical scale inhibitors are commonly used. Commercial antiscaling agents include polyelectrolytes that dissociate phosphonates, carboxylates, and sulfonates anionic

groups. However, it is imperative to identify highly efficient polymeric inhibitors and environmentally friendly antiscalants, in particular, to replace phosphonate inhibitors due to their environmental risks. Certain polypeptides with charged groups have been extracted from organisms and found to efficiently control the nucleation and crystallization of minerals. Their structures are attractive models for better understanding the inhibitor-mineral interactions and designing next generation antiscalants. Antifreeze polypeptides (AFPs) from cold-adapted organisms (e.g., fish, insects, and plants) can inhibit the nucleation and crystallization of ice and some non-ice like compounds. Calcium carbonate (CaCO_3), a common scale deposit, is a scalent of interest in this study. We investigate the effects of AFPs on the inhibition of calcium carbonate formation via adsorption to the compound's surface, thus controlling nucleation and crystal growth of the calcium carbonate scale deposits. Two beetle AFPs from *Dendroides canadensis* (DAFP) and *Tenebrio molitor* (TmAFP) are prepared and studied here. These AFPs are repeat proteins having regular spaced charged residues on their surfaces and show their effects on the formation of calcium carbonate. We correlate the charge and molecular properties of the polyelectrolytes with their efficiencies in inhibiting the scale crystal formation. Our results provide better understanding for scale control as well as new designs for green antiscalants.

Acknowledgements

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COLL 237

Green silver nanoparticles synthesized by *Caesalpinia sappan* extract and their antibacterial activities against methicillin-resistant *Staphylococcus aureus*

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Nanoantibiotics that use nanomaterials or nanocomposites for the delivery of antimicrobials represent a new model for treating infectious diseases, especially antibiotic-resistant strains. Silver nanoparticles (AgNPs) have been known to be effective antibacterial agents against methicillin-resistant *Staphylococcus aureus* (MRSA). Currently, green chemistry has been applied to the synthesis of AgNPs, in which natural products or biological compounds have replaced toxic chemicals to reduce silver ions to AgNPs. Among many natural products, a variety of plant extracts are widely used as green reducing agents for the synthesis of AgNPs. Green synthetic

approaches are beneficial due to the simple and environmentally benign processing. In the present study, *Caesalpinia sappan* extract was used as a reducing agent to convert silver ions to AgNPs. Seven surfactants and polymers were added as stabilizers to improve the antibacterial activity of the AgNPs. The as-prepared AgNPs were characterized using UV-Visible spectrophotometry, atomic force microscopy, high-resolution transmission electron microscopy, field-emission scanning electron microscopy and high-resolution X-ray diffraction. Observation of the shapes of the AgNPs was mostly spherical and amorphous. The estimated diameters were in the range of 30.2 to 47.5 nm. AgNPs prepared in the presence of a cationic surfactant, cetyltrimethylammonium bromide (CTAB), exhibited the highest antibacterial activity against 19 strains of MRSA. In contrast, anionic surfactants, sodium dodecyl sulfate and sodium dodecylbenzene sulfonate, did not exhibit any significant antibacterial activity. Based on the results, we were able to conclude that novel nanoantibiotics composed of AgNPs, CTAB and plant extracts are promising candidates for the treatment of MRSA.

COLL 238

Catechin-capped gold nanoparticles: Eco-friendly synthesis and catalytic activity toward 4-nitrophenol reduction

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Gold nanoparticles (AuNPs) are the most stable NPs with diverse applications including catalysts, vehicles for drug/gene delivery, biosensors, and imaging and visualization agents. The AuNPs have been found to demonstrate the improved catalytic performance compared with that of their bulk counterparts. In the current report, catechin was utilized as a reducing and capping agent for the eco-friendly synthesis of the catechin-capped AuNPs. The reaction was carried out at ambient temperature (26°C) within 1 hr. The particles size was estimated to be 16.6 nm by using the Debye-Scherrer equation from high-resolution X-ray diffraction data. Various shapes of catechin-capped AuNPs were observed by microscopic techniques including high resolution transmission electron microscopy, atomic force microscopy, and field emission scanning electron microscopy. The organic thin layer of catechin capped the freshly synthesized AuNPs which provided the colloidal stability of AuNPs. Strong peaks in the X-ray diffraction pattern of the catechin-capped AuNPs confirmed face-centered cubic structure of Au. The catalytic activity of the catechin-capped AuNPs was assessed in the reduction of 4-nitrophenol to 4-aminophenol in the presence of NaBH₄. The results propose that the catechin-capped AuNPs have potential uses in catalysis.

COLL 239

Green gold nanoparticles synthesized with earthworm extracts and their enhancement on anticoagulant activities of heparin

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The common reaction procedure for the preparation of gold nanoparticles (AuNPs) employs noxious chemicals as reducing agents that convert gold ions into AuNPs. The significance of sustainability initiatives has increased the use of biological entities as reducing agents in the synthesis of green AuNPs to replace noxious chemicals. Many researchers have extensively reported the synthesis of green AuNPs using diverse biological entities. Examples of these diverse biological entities include plant extracts, bacteria, fungi, yeasts, polysaccharides, proteins, polypeptides, primarily and secondary plant metabolites. In the present report, aqueous earthworm (*Eisenia andrei*) extracts were used as a reducing agent to obtain green AuNPs without any additional reducing or capping agents. Earthworm extracts reportedly have fibrinolytic, anticoagulant and antithrombotic activities. The newly-prepared AuNPs had an average diameter of 6.13 ± 2.13 nm and were characterized by using UV-visible spectrophotometry, X-ray diffraction, atomic force microscopy, field emission scanning electron microscopy, inductively coupled plasma mass spectrometry, high resolution transmission electron microscopy and Fourier transform infrared spectroscopy. The activated partial thromboplastin time was measured to assess the anticoagulant activity of the newly-prepared AuNPs. The results showed that the combination of the newly-prepared AuNPs with heparin enhanced the heparin's anticoagulant activity suggesting that AuNPs are involved in the blood coagulation cascade.

COLL 240

Resveratrol-capped gold and silver nanoparticles and their antibacterial activity against *Streptococcus pneumoniae*

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The present report focuses on the preparation of resveratrol-mediated green synthesis of metallic nanoparticles (gold and silver) and the evaluation of their *in vitro* antibacterial activities. During the green-synthetic steps, resveratrol was used as a reducing agent to convert gold and silver ions to the corresponding metallic nanoparticles. The newly-prepared gold nanoparticles (Res-AuNPs) and silver nanoparticles (Res-AgNPs) were observed to be spherical-shaped with a characteristic surface plasmon resonance peak at 547 nm for Res-AuNPs and at 412~417 nm for Res-AgNPs, confirming the successful synthesis of both NPs. X-ray diffraction analysis also confirmed the face-centered cubic structure of the Res-AuNPs. The functional groups of resveratrol, the hydroxyl groups and C=C in the aromatic ring, were most likely involved in the reduction reaction which was indicated by Fourier-transform infrared spectra. The average

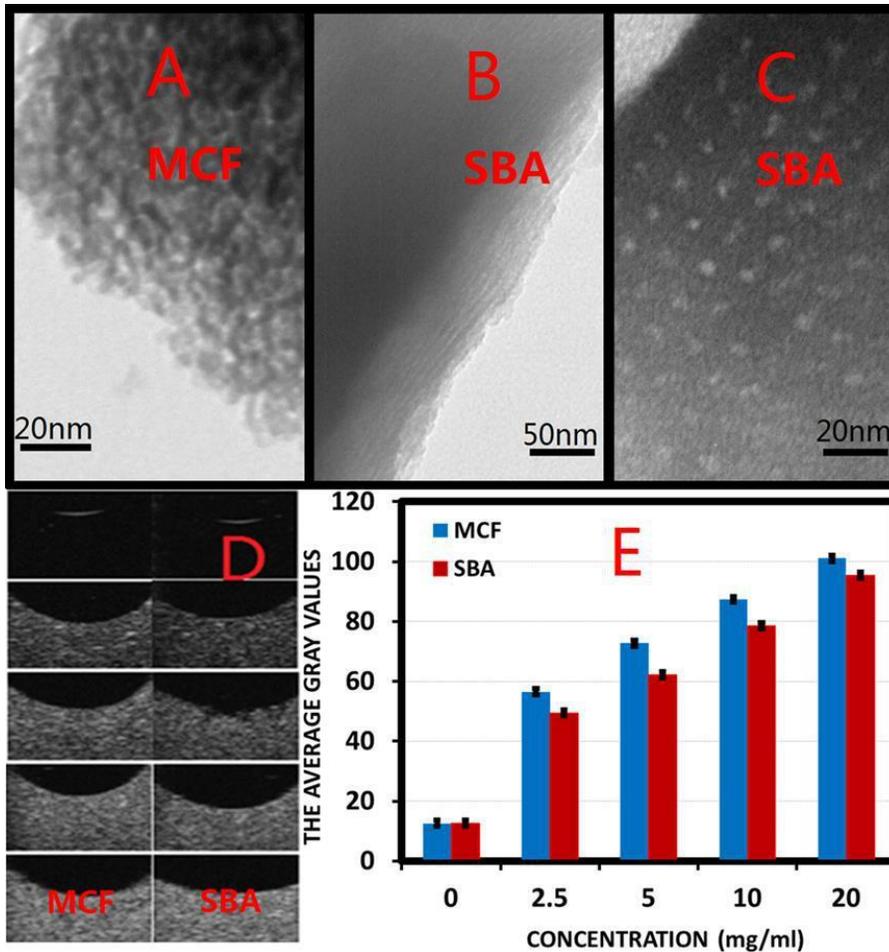
diameter ranged from 8.32 to 21.84 nm, as determined by high-resolution transmission electron microscopy. When the antibacterial activity was screened against Gram-positive and Gram-negative bacteria, Res-AuNPs and Res-AgNPs showed higher antibacterial activity than that of resveratrol alone. The highest antibacterial activity of Res-AuNPs was observed against *Streptococcus pneumoniae*. Interestingly, the addition of sodium dodecyl sulfate during the synthetic steps of Res-AgNPs slightly increased antibacterial activity.

COLL 241

Ultrasound signal of mesocellular foam and mesoporous nanoparticles

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Silica-based mesoporous materials have widespread applications in drug delivery and imaging. Thus far, the most commonly used drug carrier is the MCM and SBA series, and the nanoparticle pore size has important effects on drug loading and release. However, the impact on pore size has not yet been studied for effects on imaging including ultrasound signal. Herein, we synthesized MCF with 10 nm pore sizes (**Fig. A**) and SBA-15 (**Fig. B, C**) with 4 nm pore size followed by ultrasound imaging at 40 MHz (**Fig. D**). The average gray-scale values of MCF nanoparticles at the same weight concentrations of 2.5, 5, 10, 20 mg/ml offer 1.14, 1.17, 1.11, 1.06-fold better signal than SBA-15, respectively (**Fig. E**). The limit of detection is 0.61mg/mL for SBA and 0.44mg/mL for MCF. Future work will optimize MCF nanoparticles' morphology and pore size to load therapeutic proteins for combined therapy and imaging.



COLL 242

Gold nanostructures stabilized with peptide self-assembly for chemical and biological applications

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Peptide molecules have been studied as one of most promising self-assembly materials because they are not only composed of over tens of natural or non-natural amino acids, but also have limitless and designable sequence combinations of amino acids for the various self-assembled nanostructures. It is commonly known that main driving forces for self-assembly of biomolecules are non-covalent bonding such as Van der Waals force, electrostatic interaction, hydrophobic interaction, hydrogen bonding, π - π interaction, etc. and their harmonic combinations. Meanwhile, awful discovery of catalytic properties of novel metal nanoparticles expanded their biomedical applicability as an artificial enzyme. Nanocrystals of Au, Pt, Pd, etc. can replace the representative redox enzymes such as peroxidase, oxidase, reductase, etc. and they have been

mainly applied to the various types of biosensor platforms. In this study, we introduce the peptide self-assembled nanostructures coupled with gold nanocrystals and their intrinsic catalytic performances. The peptide for self-assembly is one of tyrosine-rich peptide (TRP) composed of 7 amino acids, which readily transforms to the variety of self-assembled nanostructures induced by metal ion, representatively gold ion under specific temperature and buffer conditions. Besides, gold nanocrystals are well-known as the peroxidase-like nanocatalyst as well as the nanocatalyst that can facilitate chemical reducing agents. We can expect that the coupling of gold nanocrystal with self-assembly of TRP accomplish the proton-coupled electron transfer (PECT) effect related with improving kinetics and lowering the activation energy. To evaluate catalytic activity of peptide self-assembled nanostructures coupled with gold nanocrystals, they were applied to the reduction of p-nitrophenol as the chemical catalyst and TMB oxidation instead of any peroxidase as the novel biocatalyst for the biosensors.

COLL 243

Electrocatalytic behaviors of metal nanoparticles for CO₂ reduction

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The electrocatalytic conversion of CO₂ into useful chemicals is an attractive alternative to reduce the greenhouse gas. However it is difficult to find proper catalysts for CO₂ reduction as CO₂ conversion typically requires high energy input. In this presentation, we report efficient and selective electrocatalytic conversions of CO₂ based on atomically precise metal nanoparticles. Au-based metal nanoparticles, such as Au₂₅(SR)₁₈ and PtAu₂₄(SR)₁₈ where SR is hexanethiolate, were synthesized and cast on glassy carbon electrode. Electrocatalytic conversion of CO₂ was examined in the potential range between -0.3 and -1.2 V vs RHE in an H-type cell. Product analysis using gas chromatography mass spectrometer (GC-MS) showed CO₂ was converted to CO selectively with a faradaic efficiency greater than 90 % at the overpotential of 0.5 V. PtAu₂₄(SR)₁₈ nanoparticles showed drastically different product distribution in which hydrogen was the major product (>90%). The origin of the vastly different selectivity observed with these two catalysts is presented.

COLL 244

Charge anisotropy of gold nanorods

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The origin of unique optical properties of gold nanorods such as distinctive extinction bands in the upper visible or near-infrared region is surface plasmon (SP) oscillation of free electrons. To understand how these collective electrons interact with optical waves, we should be aware of their electrostatic properties. By implementing various high resolution electron microscopic techniques, we visualized spatial electrostatic potential of single AuNR. AuNR has anisotropic charge accumulation on their surface, which can be defined as a polarized surface charge density. We believe that this anisotropic potential of AuNR is derived by non-uniformly distributed surfactants on its surface, which also has been successfully visualized. Computation of electrostatic potential of gold nanorod considering this charge distribution from surfactant is well matched with the experimental result. More importantly, we demonstrate that this asymmetry of potential in AuNR could be one of the origins of nonlinear optical response of AuNR. Although there are existing theories such as retardation effect, defects, and local environment, this finding could let us another approach to understand nonlinear optical response of various centrosymmetric metal nanoparticles.

COLL 245

Bio-activity of a series of novel multi-functional bio-compatible polymers

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Biological activity and compatibility is one of the most important characteristics inherent in the production and characterization of synthetic polymer materials that interface with biological systems. Such polymers have recently been researched for use in a variety of medical applications, including, but not limited to, drug delivery, hemostasis, and tissue engineering. Herein we report the biocompatible properties of parallel series of novel highly absorbent PNIPAM-based polyacrylate gels and PEG-based polyurethane hydrogel foams, each independently developed to serve as separate components of a composite wound dressing concept. These materials exhibit the ability to efficiently bind platelets and fibrinogen to initiate blood clotting. Secondly, we demonstrate the ability to easily load and effectively deliver a variety of anti-microbial drugs. Finally, these polymers represent a passive surface for the binding and proliferation of a variety of eukaryotic cell types, indicating that these materials are an ideal candidate for tissue engineering scaffolds.

COLL 246

Few-layered 2D nanosheets generated by green liquid-phase exfoliation methods

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Two-dimensional (2-D) materials such as graphene and molybdenum disulfide (MoS_2) have drawn tremendous attentions because of their unique physical properties and broad applications. Typically, these 2-D layered materials are held together by a large number of weak van der Waals interactions which must be overcome in order to produce stable single- or few-layer nanosheets. Various methods have been employed to achieve successful exfoliation from the bulk material, however, these methods are largely inefficient and incapable of mass production of dispersed materials for widespread application. An aim of our research is to improve upon the scalability and reproducibility of 2-D materials via advanced liquid-phase exfoliation approaches that avoid unwanted oxidation and aggregation. We report on these green approaches to liquid exfoliation alongside characterization of the dispersed nanosheets using a host of tools (e.g., scanning electron microscopy, transmission electron microscopy, Raman spectroscopy, UV-Vis spectroscopy) to gauge the crystallinity, thickness, layer number, and surface morphology. These nanosheets are important materials within supercapacitors, hydrogen evolution reaction (HER) catalysts, batteries, and dye-sensitized solar cells.

COLL 247

Plasmonic coupling in nanoparticle cluster and random arrays

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In this work, the plasmonic coupling in silver nanosphere trimers as well as random gold nanoparticle arrays was studied. Silver nanocubes were synthesized using a polyol method, and then etched using ferric nitrate to obtain highly uniform silver nanospheres. The nanospheres assembled into dimers and trimers induced by the electrolytes in solution during synthesis, as well as from the hydrophobic effect. Individual nanosphere trimers were studied using correlated dark field scattering and scanning electron microscopy (SEM). The trimers exhibit polarization-dependent scattering spectra. In contrast to the experimental results, the theoretical studies using the T-matrix method showed that a triangular silver trimer consisted of perfectly spherical particles will have a scattering spectra that is independent of the polarization of light. Discrete dipole approximation method was used to show that slight variation in the geometry of the nanoparticle (not even obvious in SEM) will affect the plasmonic interaction, leading to polarization dependent scattering. The gold nanoparticles used in the random array were synthesized by sodium citrate reduction of HAuCl_4 and then grown to 120nm using a seed mediated method. They were then immobilized into a random array by self-assembly onto a silanized glass slide and the extinction was studied using localized surface plasmon resonance. In the gold nanoparticle random array, the extinction spectra blue shifts from that of both the solution and the single gold nanoparticles on glass, but it is polarization independent. Simulations using the T-matrix method show that this blue-shift is due to long-range dipole coupling. Small nanoparticle trimers show

polarization dependence because of small shape differences but show polarization independence in larger random nanoparticle arrays due to long-range dipole coupling.

COLL 248

Nano-confinement induced phase transitions of dithiol monolayers with applications in directing the assembly of electro-active porphyrin molecules

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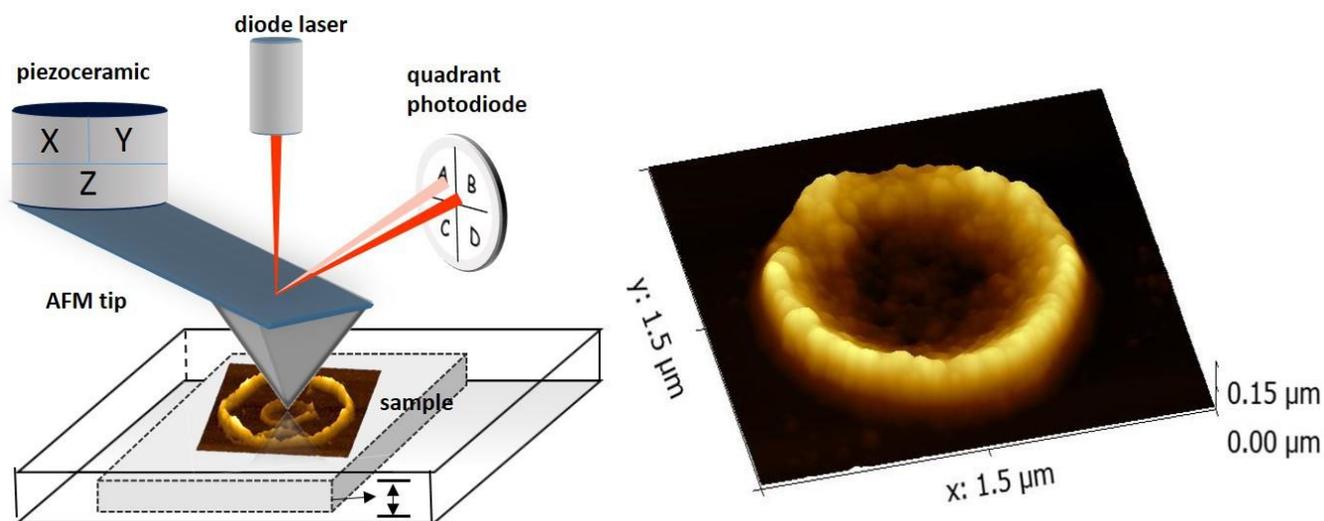
Molecular electronic devices necessitate control over the configuration of molecules, in terms of nearest neighbor interactions and assembly size, on the electrode surface to produce specific and consistent functionalities. However, it is challenging to direct the assembly of molecules into deliberate architectures with selectivity to fabricate integrated electronic circuits. In this work, we investigate a method to direct the assembly of electrically-active molecules with specificity while controlling their internal organization. This method consists of two sequential surface reactions. First, pentanedithiol domains are assembled into a monolayer of passive dodecanethiol on an Au (111) surface. Second, porphyrin derivatives selectively react via 'click chemistry' with the pentanedithiol domains. Pentanedithiol was assembled by phase segregation and nanografting into ca. 5 nm, ca. 40 nm, ca. 50 nm, and ca. 120 nm sized domains. Atomic Force Microscopy (AFM) displayed that these domains formed a standing-up phase. Furthermore, Scanning Tunneling Microscopy (STM) illustrated that the internal-molecular organization is dependent on the size of the domain. The domains undergo a nano-confinement induced phase transition from the densely packed ($\sqrt{3}\times\sqrt{3}$) R30°, to a more sparse (2x2), and finally to a disordered phase with increasing domain size. This results from the variable degree of van der Waals interaction and geometric confinement caused by the neighboring dodecanethiol to sustain the standing-up phase of the pentanedithiol. Such molecular level comprehension of the organization of dithiol monolayers is imperative for their use as a reactive surface template to bind electrically-active molecular head groups. As a demonstration of this purpose, porphyrin derivatives containing a pentafluorophenyl ring were selectively bound to the pentanedithiol domains by 'clicking' the exposed thiol on the surface with the pentafluorophenyl ring. AFM and STM showed that some porphyrins were bound directly to the pentanedithiol domains and others intercalated to pi-stack in-between.

COLL 249

Surface patterns of inorganic nanoparticles characterized with force modulation atomic force microscopy

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Ring-shaped patterns of nanoparticles were prepared as surface test platforms for force modulation measurements. Using particle lithography, a suspension of monodisperse latex mesospheres was deposited on a Si(111) substrate and dried to form a surface mask. The crystalline arrangement of the surface mask provided a structural template to guide the deposition of inorganic nanoparticles. A drop of nanoparticles in solution was placed on the masked substrate and dried. The surface mask was removed using adhesive tape without steps of rinsing or sonication. The nanoparticles persist on the surface to form ring nanopatterns. The nanopatterns were characterized by force modulation microscopy (FMM). Among the modes of atomic force microscopy (AFM), the FMM mode is commonly used to acquire mechanical properties of samples along with topographical information. At resonant frequencies, FMM has demonstrated capabilities for acquiring high-resolution images. To configure a scanning probe microscope for FMM, the scanner is operated in contact-mode while the sample stage is driven to vibrate in the z-direction. Information of the topography, elastic response and surface adhesion can be acquired simultaneously. High-resolution images can be achieved by careful selection of the modulation frequency and strength of the modulation. Studies of the nanopatterns of nanoparticles will be presented with FMM measurements. Chemical assembly of nanoscale materials to generate nanostructures on surfaces offers potential opportunities for fabricating miniaturized biosensors, electronics and data storage devices.



COLL 250

Dynamic surface on gold nanorods for reversible Raman enhancement

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Surface-enhanced Raman scattering of molecules near gold nanorods (GNRs) is a distance-dependent phenomenon. In this work, we aim to build up dynamic surface coatings on GNRs that change their thicknesses reversibly in response to specific outside stimuli. Poly (N-isopropylacrylamide), with lower critical solution temperature around 32 °C in water, was chosen as the thermal response coating on GNRs. The dynamic surface on the GNRs could be achieved by a simple graft-to functionalization step and showed reversible enhancement of the Raman signal of surrounding bipyridine ethylene (BPE) molecules in solution. We also investigated polymer graft-from the GNR surface in situ so that the grafting density and polymer composition can be fine-tuned for further applications.

COLL 251

Langmuir monolayer and AFM analysis of a collagen/phospholipid/titanium model membrane system for the investigation of osteoblast affinity to titanium rods

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Langmuir-Blodgett Monolayers of collagen and phospholipids on titanium substrates are being used as a model system for the affinity of osteoblasts to titanium rods. 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. Langmuir monolayers of collagen are 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, transfer ratio data of collagen monolayers to silicon (SiO₂) substrates increased in the presence of DPPC or DPPE indicating that this may be a good model system for this investigation. In preparation for near future experiments involving Atomic Force Microscopy analysis of collagen/phospholipid monolayers transferred to titanium nitride foil using dipalmitoylphosphatidylglycerol (DPPG) as the lipid because of its impact on bacterial resistance in the bone cell model membrane, we have determined that we can use the ezAFM for analysis of transferred multilayers of arachidic acid.

COLL 252

Using AFM to study transcription factor binding

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This research aims to determine the characteristics of transcription factor binding to DNA using Atomic Force Microscopy (AFM). CRP, a transcription factor found in *E.coli*, is used in this study. To this end, the CRP protein was overexpressed from a pET14b plasmid and was isolated using His tag purification method. Two different segments of DNA that contain the promoter region for CRP were amplified from chromosomal DNA of *E.coli* bacteria strain W3110. These DNA segments were deposited onto mica surfaces and were imaged using an ezAFM instrument. The images show the correct predicted length for the DNA segments. Future experiments will focus on attaching the CRP protein to a surface and imaging the protein with and without DNA bound. The ultimate goal of this study is to examine the strength of the interactions between the DNA and the CRP protein.

COLL 253

Synthesis and AFM characterization of designed nanostructures of transition metal-doped-ceria

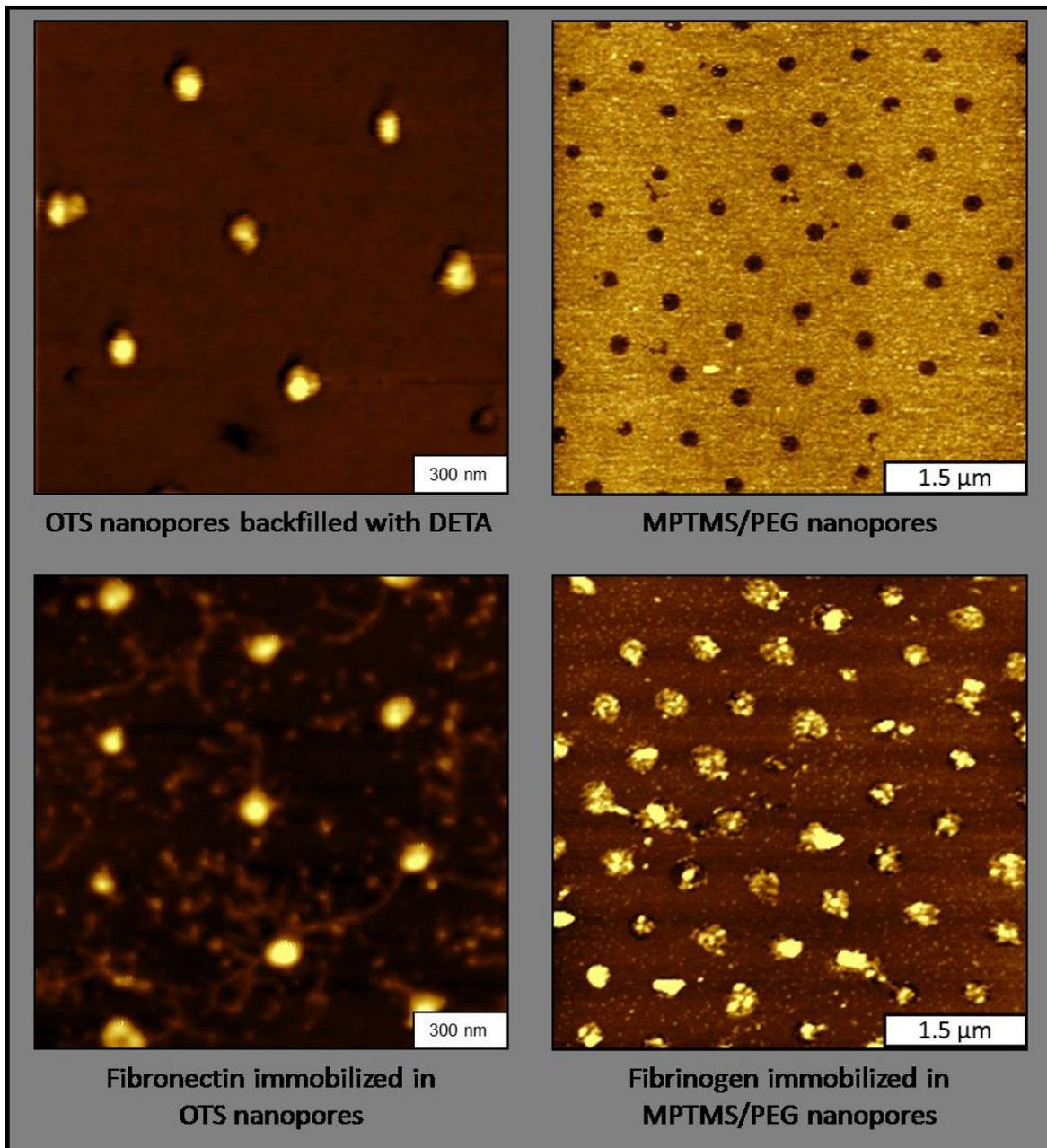
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Test platforms of patterned gold-doped cerium oxide nanoparticles were examined to evaluate catalytic properties as a function of particle size using Kelvin probe force microscopy (KPFM). Gold-doped cerium oxide nanoparticles were synthesized through a urea co-precipitation method. Cerium oxide nanoparticles exhibit catalytic properties with an emphasis on their high surface-to-volume ratio. High throughput patterning of cerium oxide materials were attained using particle lithography followed by calcination of the material at temperatures up to 800 C. Particle lithography was used to generate a surface test platform of nanopatterns of the cerium oxide nanoparticles. A surface mask of 500 nm silica mesospheres was prepared to define the arrangement of nanoparticles. The AFM mode of KPFM is capable of obtaining measurements with high spatial resolution and is commonly applied to characterize the work function and surface potential of samples. Information regarding the electrical and catalytic properties of the sample can be obtained with KPFM, while simultaneously obtaining detailed images of the surface topography. Phase and amplitude images were acquired simultaneously with topographs. Topography frames sensitively disclose fine details of the surface morphology. Studies with KPFM enabled measurements of potential energy differences with nanoscale resolution, tracking differences in the oxidation state of the material. Our goals were to apply scanning probe characterizations of nanoparticle test platforms to investigate catalytic and electrical properties at the level of individual cerium oxide nanoparticles.

Patterning proteins at the nanoscale using spatially selective surfaces prepared by particle lithography

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Surfaces with films of protein are a key component of most biosensor designs. An inherent problem with preparing the sensing element is the self-aggregation of proteins, to form multilayers and aggregates. Our strategy for preparing sensor surfaces uses the selectivity of nanopatterned organosilanes to control the deposition of proteins such as fibronectin and fibrinogen. Nanopatterns of organosilanes can be produced using particle lithography as spatially selective substrates for binding proteins. Two strategies were tested for protein patterning. Monodispersed silica mesospheres were used as a surface mask to accomplish particle lithography. Nanoholes were prepared within a film of octadecyltrichlorosilane (OTS) and filled with (3-trimethoxysilylpropyl)diethylenetriamine (DETA). The methyl headgroups of OTS provide a resist to prevent nonspecific binding of protein. Nanodots of DETA were treated with EDC/NHS to react with carboxylic acids on the fibronectin to form an amide bond with the primary amine of the protein (fibronectin). Fibronectin has numerous functions in processes such as cell adhesion, growth, migration, and differentiation. Fibrinogen is a glycoprotein that helps in forming blood clots. It has a rod-like shape with dimensions of 9 × 48 × 6 nm. A second strategy used nanopatterns of (3-mercaptopropyl)trimethoxysilane (MPTMS) to bind protein with sulfo-SMCC (4-(sulfosuccinimidyl-4-[N-maleimidomethyl]cyclohexane-1-carboxylate), which is a water-soluble heterobifunctional protein crosslinker. The sulfo-SMCC reagent can conjugate glycoproteins, such as fibrinogen. The organosilane and protein nanopatterns were characterized with tapping-mode atomic force microscopy (AFM).



COLL 255

Designed synthesis of lanthanide doped core-shell nanoparticles with excitation at a benign wavelength

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The ability of upconverting nanoparticles (UCNPs) to emit visible upconverted luminescence upon excitation by near-infrared light (NIR) has made UCNPs hold great promise as probes for various biological applications including imaging and sensing. Ytterbium, Yb^{3+} , ions are commonly doped as sensitizers in upconverting (UC) rare earth sodium fluoride nanocrystals. However, the Yb^{3+} -sensitized UC process suffers from 980 nm absorption overlap with water, the most abundant NIR absorber in the body. Substitution of Neodymium, Nd^{3+} , for Yb^{3+} ions allows for the utilization of 808 nm absorption that minimizes signal attenuation in biological tissue and reduces overheating observed at 980 nm. Previous reports have attempted to integrate Nd^{3+} either by direct doping into the core or introducing a core-shell structure; however, these designs were limited to 1-20 mol % Nd [1][2].

Herein we report the synthesis of $\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ @ $\text{NaLuF}_4:\text{Nd}^{3+}$ nanocrystals via thermal decomposition and self-focusing by Ostwald ripening. The previously described tunable layer-by-layer epitaxial shell growth overcomes the limitations of conventional shell growth techniques thus allowing for larger shell thicknesses that ensures spatially confined doping of Nd^{3+} ions within a concentric shell [3] [4]. More importantly, the Nd^{3+} sensitized core-shell design enabled higher concentration doping of Nd^{3+} in the shell than previously reported and thus, significantly enhanced UC emission from the emitter, Er. With the new ability to grow shells in a highly controlled manner, we were able to tune the thickness and Nd^{3+} concentration of the shell to achieve maximum UC efficiency.

[1] Wang, Y.F. et. al., ACS Nano (2013); [2] Xie, X. et. al., JACS (2013); [3] Johnson, N. et. al., JACS (2012); [4] Johnson, N. et. al., ACS Nano (2014);

COLL 256

Adsorption of methanol on ZIF-8 thin films under low temperature and low pressure conditions

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Due to the large porosity and excellent gas selection properties, metal organic frameworks (MOFs) have shown potential for gas sensing, separation, storage and catalysis. Zeolitic imidazolate framework-8 (ZIF-8), a sub-category of MOFs, exhibits selective adsorption of certain alcohols. Much of the work to this point has focused on ambient to high pressure conditions and investigation of the alcohol/water separation

efficiency by microcrystalline ZIFs. In this study, we focus on methanol adsorption by nanoporous ZIF-8 thin films supported on an Au substrate. The study of such films in ultra high vacuum conditions can provide fundamental insight into adsorption and reaction mechanisms. We investigated the adsorption of the simplest alcohol (methanol) by ZIF-8 thin films using temperature programmed desorption (TPD) spectroscopy. In addition, we used X-ray photoelectron spectroscopy (XPS) to identify surface-terminating groups before and after adsorption. Under low-temperature, low-pressure conditions, methanol does penetrate ZIF-8 pores to some extent, which confirms its structural flexibility. Additionally, we found the pore penetration of methanol can be enhanced by increasing the exposure temperature. In our previous studies, we found that CO₂ enters pore structure, while water stays primarily on the outer surface of ZIF-8 thin films. By comparing to the adsorption of methanol to that of CO₂ and water, this work reveals methanol occupies the pores with increasing dosing amount, indicating ZIF-8 is flexible even at low temperature and low pressure conditions. Since the kinetic diameter of methanol (4.7 Å) is larger than the entrance of ZIF-8 pore (3.4 Å), this is the first work confirming the gate-opening effect happen under such low pressure/temperature conditions and demonstrating exposure temperature can be used as a handle to control pore adsorption for certain larger guest molecules. We believe that our work will increase the understanding of gas interactions with supported nanoporous materials in ultra-high vacuum, and open the door to understanding reaction mechanisms in MOFs under ambient conditions.

COLL 257

Influence of surface chemistry on gold nanoparticle biostability

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The stability of nanoparticles (NPs) against aggregation in biological systems is an important research area, because it informs the design of nanotherapeutics for medicinal applications and the study of nanotoxicology. For instance aggregation of NPs has been shown to alter the uptake of NPs by cells compared to well dispersed particles. While there has been detailed research on how size affects NP stability in various biological systems, more research is still needed to find how the surface chemistry (particularly surface charge and ligand density) of NPs may affect the stability of the particles in different biological tissues and media.

For most *in vivo* applications of nanoparticles, NPs will generally pass through the blood stream first (where they will be exposed to serum proteins). Once the NPs encounter a cell the NPs will then generally enter the cytosol *via* endocytosis (encased in a lysosome). As a result, we were particularly interested in the effect of NP surface chemistry on NP stability in serum and in lysosomal fluid. Because it is very difficult to recover or characterize NPs once they enter the cell, we attempted to simulate the conditions of these biological environments, and investigate the effect of these conditions on NP stability.

In this study, we investigated the stability of several negatively-charged gold nanoparticles (AuNPs) in simulated serum and lysosomal fluids. We synthesized 12.0 nm AuNPs stabilized with citrate, and then further functionalized these NPs by wrapping them with a negatively-charged polymer (polyacrylate), or by ligand exchange with negatively-charged thiols. We investigated AuNP stability against aggregation using a combination of UV-vis absorbance spectroscopy, dynamic light scattering, and ζ -potential analysis. Despite the fact that the surface charges of all the AuNPs tested are similar, we find that different types of ligand attachment (e.g.- monolayer ligand shells vs polymer wrappings) influence the rate of NP aggregation in artificial lysosomal fluid. However, prior incubation in fetal bovine serum decreases the rate of AuNP aggregation in ALF, likely because the resulting protein corona provides additional stability against aggregation.

COLL 258

Characterization of nanofoam collapse in response to exposure to volatile organic compounds

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Nanofoams are porous grafted polymer film layers that exhibit the performance of shape-memory polymer materials (SMPs). The surface of silicon wafers were used as a substrate and poly(glycidyl methacrylate) (PGMA) was employed as an anchoring polymer layer via dip coating followed by the sequential attachment of the polymers polystyrene (PS) and poly(2-vinyl pyridine) (P2VP) respectively, leading to the formation of a three component polymer nanofoam. The nanofoam was obtained by freeze-drying where polymer films are swollen in chloroform and cooled under vacuum pressure (20-50 mTorr) to sublime the solvent. The thickness of the nanofoam layers were analyzed using refractive index values collected from a home-built scanning reflectometer before and after nanofoam exposure to one of three volatile organic compounds, including toluene, methanol and acetone, for 40 minutes in a controlled environment. The initial results showed a statistically significant correlation between collapse upon exposure to a particular solvent and its composition. However, external factors that influence collapse of nanofoam with given composition in a specified solvent are yet to be identified. Results of nanofoam collapse upon specific exposure events will lead to future use in industry as sensors to detect chemical warfare agents. This work was supported by the National Science Foundation's REU program under grant number 1460863, the Clemson University Department of Materials Science and Engineering, and the Defense Threat Reduction Agency (projects HDTRA1-10-1-0101 and HDTRA1-13-1-0001).

COLL 259

Examination of 4',6-diamidino-2-phenylindole in silica gels through surface-enhanced Raman spectroscopy and fluorometry

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Silica sol-gels synthesized through hydrolysis and condensation reactions via acid- and base-catalyzed procedures containing 4',6-diamidino-2-phenylindole (DAPI) have been examined using surface-enhanced Raman (SERS) and fluorescence spectroscopy. DAPI is a Raman-active and fluorescent molecule that has traditionally been used in biosensors as a target molecule and a fluorescent stain known to bind strongly to the A-T rich regions of DNA. Sol-gels containing various concentrations of DAPI and silver nanoparticles for Raman-enhancement purposes were dried conventionally to form xerogels or supercritically to form aerogels and then analyzed using SERS and fluorescence spectroscopy to determine the effect of varying the silver to DAPI ratios.

COLL 260

Adsorption and surface reactivity of $Zn_xCe_{1-x}O_{2-y}$ nanoparticles

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A series of zinc-ceria solid solution nanoparticles ($Zn_xCe_{1-x}O_{2-y}$) has been synthesized via a microwave-precipitation method and the adsorption and surface reactivity properties are reported as a function of zinc content. Powdered x-ray diffraction (PXRD) of the approximately 3.0 nanometer materials shows that the lattice parameter decreases linearly with increasing zinc concentration, in agreement with Vegard's Law, with no phase separation occurring up to 30% zinc ($Zn_{0.3}Ce_{0.7}O_{2-y}$). BET measurements show high surface area (> 200 m²/g) for the $Zn_xCe_{1-x}O_{2-y}$ nanoparticles, although the surface area decreases with increasing zinc composition. The activity of the series was evaluated through the catalytic oxidation of carbon monoxide to carbon dioxide, and direct correlation is made between zinc concentration and a lowering of the 50% conversion temperature over pure ceria, with the largest effects occurring at high zinc concentration. X-ray photoelectron spectroscopy (XPS) is used to probe the zinc surface concentration, as well as the local zinc and cerium chemical environments.

COLL 261

Characterization of the interfacial packing structure of progressively fluorinated alkanethiolate self-assembled monolayers

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This presentation details the preparation and characterization of progressively fluorinated self-assembled monolayers (FSAMs), including their lattice spacing on Au(111). The adsorbates used to form the FSAMs in this study are of the formula $\text{CF}_3(\text{CF}_2)_n(\text{CH}_2)_{11}\text{SH}$ (where $n = 0 - 5$). This project seeks to determine the differences in lattice spacing that occur among the FSAMs in this series, and investigate possible causes for those differences. For this report, the monolayers were characterized using the acoustic mode (i.e., tapping mode) of an atomic force microscope (AFM) to produce images of the FSAM interfaces with a minimal degree of disruption of the ordering of the exposed adsorbate chains. Furthermore, the FSAMS were characterized using ellipsometry, polarization modulation infrared reflection-absorption spectroscopy, and contact angle goniometry.

Keywords: Fluorinated Self-Assembled Monolayers (FSAMs), AFM, Acoustic Mode, Lattice Spacing

COLL 262

Fabrication of superhydrophobic wood surfaces with micro-/nano-composite particles

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A composite wooden material with superhydrophobicity was obtained by applying various inorganic particles with micro/nano structures on the wood surfaces. The surface energy of the treated wooded materials were dramatically changed. Owing to the virtue of the coupling agent, which plays an important part in bonding the inorganic particles and the wood surfaces, the structure of the superhydrophobic thin film on the wood surface is extremely stable. The microstructure of superhydrophobic wood was characterized by scanning electron microscopy (SEM), the images showed that the modified wood was covered with a uniform layer of inorganic particles, generating a rough structure on the wood surface. The superhydrophobic performance of the modified wood was characterized by water contact angle measurements. The measurements showed that the wettability of modified wood samples transformed from hydrophilicity to superhydrophobicity with the water contact angles of $153 \pm 1^\circ$. This method can be applied to various wooden materials for broad applications.

COLL 263

Reduction of CO₂ on Cu and Au/W electrode surfaces: A study by differential electrochemical mass spectrometry

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This work describes results from an attempt to employ differential electrochemical mass spectrometry (DEMS) of *selectively pre-adsorbed* reactants and (postulated) intermediates as a *supplementary* experimental approach in the study of the reaction mechanism of the Cu-catalyzed electrochemical reduction of CO₂. The results prompt the following empirical inferences: (i) CO is the first product of CO₂ reduction, as well as the first intermediate in more advanced reactions that include formation of pure and oxygenated hydrocarbons; this is in conformity with the (almost) unanimously held view. (ii) HCHO is not a precursor for C=C double-bond formation. (iii) HCHO is an intermediate for the production of methane and ethanol. (iv) The generation of CH₄ and CH₃CH₂OH from adsorbed CO occurs via two pathways: one requires a theoretically postulated surface species, CO protonated on the C atom, and the other involves adsorbed HCHO, constituted after the rate-limiting protonation step. (v) The generation of CH₄ and CH₃CH₂OH from CO has a much higher activation barrier than conversions from HCHO; not unexpected since the reactions transpire after the slow Cu–OCH⁺ formation and, consequently, are not highly activated.

This work also presents results from an experimental study based on DEMS that tested the theoretical prediction that suggested the viability of a bimetallic near-surface alloy (NSA) electrode made up of Au and W as a CO₂-reduction electrocatalyst selective towards the formation of CH₃OH as a product, away from methane, ethylene or ethanol. At an overlayer NSA that consisted of *n* monolayers (ML) of Au on a polycrystalline W electrode, W(pc)-*n*[(1×1)-Au], no methane, ethylene or ethanol were detected, when the coverage of Au was at submonolayer (*n* = 0.5) or multilayer (*n* ≥ 2) coverage. However, when the overlayer contained only 1 ML of Au, methanol was generated *exclusively*. The anticipated CH₃OH-product-selectivity of the W(pc)-(1×1)-Au NSA has thus been (qualitatively) confirmed. The CH₃OH-selective activity was 52 μA cm⁻² for a Faradaic efficiency of 0.50%; the bulk of the current was expended towards H₂ evolution and, since the topmost layer was Au, most likely in the production of CO and formates that are undetectable by DEMS.

COLL 264

Synthesis and characterization of magnetic Fe and Fe-Co polypyrrole-encapsulated nanoparticles

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Magnetic nanoparticles are multifunctional having therapeutic applications in developing cancer treatment by nano-imaging for early detection of the disease and as a carrier for drug delivery. Studies in magnetic particles for such purposes bring about stimuli responsive release capability's with increased dosage control reducing toxicity. In this

report, we describe the synthesis and characterization of magnetic Fe and Fe-Co nanoparticles encapsulated in polypyrrole. These systems were chosen for their properties as biodegradable metals in hopes of vivo delivery of cancer curing drugs. Also, we are interested in testing and comparing the chemical and magnetic properties of monometallic Fe and bimetallic Fe-Co (with different metal ratios) systems. Preliminary data showed the formation of magnetic nanoparticles with sizes starting from 1.9 nm, according to Transmission Electron Microscopy (TEM) analyses.

COLL 265

Elucidating the structure and assembly of amino acids on silica nanoparticles

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One of the most notable developments in nanotechnology has been its application in the biomedical world. Nanoparticles are now common agents for drug delivery and cancer therapy as well as noninvasive sensors and detectors, and surface coatings that have direct contact with biological systems. However, molecular level detail regarding how amino acids, peptides and proteins are structured and organize on nanoparticles remains poorly understood. One thrust in our research group is elucidating the interface between nanoparticles and amino acids so that we can better understand and predict how a given peptide or protein will bind and organize on a nanoparticle. Solid-state nuclear magnetic resonance (SSNMR), thermogravimetric analysis (TGA), and molecular modeling have been used to probe the interface between L-histidine (His) and fumed silica nanoparticles. Various loading levels of isotopically enriched (¹³C/¹⁵N) His were analyzed with one (1D) and two-dimensional (2D) magic angle spinning (MAS) SSNMR techniques. Homonuclear and heteronuclear (HETCOR) correlation experiments as well as proton-detection methods were employed to elucidate the binding mechanism. Experimental isotropic chemical shifts are compared with computational density functional theory (DFT) values to optimize structural models. Analysis of L-Histidine monochloride monohydrate was also compared to determine if the presence of salt impacts binding. TGA results illustrate the formation of peptide bonds through condensation reactions and are being further analyzed to determine how His binds and behaves on the silica surface. His is one of the most ubiquitous amino acids in known silica binding peptides and it is anticipated that these results will aid other researchers in determining how peptides and proteins bind silica surfaces and advance our understanding of the nano-bio interface.

COLL 266

Tethering of lipids leads to increased resistance to membrane leakage at elevated temperature

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Archaeal organisms, one of the three domains of life, have evolved mechanically and chemically robust membrane compositions that allow survival in hostile living conditions (high temperatures, high osmotic pressure and low pH). The lipids of eukaryotes are structurally different from Archaea, with one major difference being the presence of tetraether membrane-spanning lipids in Archaeal membranes. However, the relationship between lipid structures and membrane integrity is poorly understood. To provide some insight into this question, we synthesized a set of bioinspired lipids to systematically test the effect of tethering on membrane leakage over a broad range of temperature. We will present results from leakage experiments and molecular dynamics simulations to help provide new insight into the relationship between temperature-dependent permeation and lipid structure. Our study shows that mimicking certain structural features of natural Archaea lipids results in an improvement of membrane thermostability, which may help overcome limitations of many current lipid-based technologies.

COLL 267

Characterization of CdSSe and CdSTe quantum dots prepared via microwave assisted synthesis

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Quantum dots (QDs) are semiconductor nanocrystals that display impressive optical properties. Due to their size, these particles possess highly tunable properties such as the band gap, emission spectrum, and absorption spectrum. These crystals have recently gained attention in applications such as bio-imaging, LEDs and photovoltaic cells. In this project, CdSSe and CdSTe QDs were prepared in a MARS 6 microwave assisted system. For the synthesis, thioglycolic acid, cadmium nitrate, reduced selenium (by sodium sulphite reducing agent) and reduced tellurium (by NaBH₄ reducing agent) were used as precursors. The solution was placed in a reaction vessel and irradiated during two steps: pre-heating step and reaction step (180°C). The samples were analyzed by photoluminescence, UV-Vis spectrophotometry and Infrared analyses. The

CdSSe QDs presented an emission wavelength of 560nm and an absorption wavelength of 450nm. The CdSTe QDs had an emission wavelength of 640nm and an absorption wavelength of 385nm. FT-IR spectrums showed the presence of thiol residues. The QDs characterized will be used in future photodegradation experiments of common environmental pollutants.

COLL 268

Polarization mapping sum frequency generation vibrational spectroscopy of methacrylate based functional polymer thin film on dielectric substrate

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Second order nonlinear optical spectroscopic technique of vibrational Sum Frequency Generation (SFG) has been used to selectively probe interfacial molecules of polymer thin films. The SFG spectra of polymer films collected with regular polarization combinations generally contain convoluted peaks making the assignment of peaks difficult. We applied the technique of polarization mapping method (PMM) to resolve the broad peaks into possibly separate vibrational modes. Mapping of sum frequency signal allowed us to resolve and obtain a more accurate assignment of the vibrational modes responsible for convoluted peaks. In this study, broadband Sum frequency spectroscopy, with fixed visible (795nm) and broadband mid-IR beams, is used to study the molecular organization of functional groups at solid/air interface. First, the PM method was applied to octadecyltrichlorosilane (OTS) self-assembled monolayer (SAM) on quartz. This serves as a model system of a well-ordered SAMs on dielectric substrate. Concurrently, by reducing the assembly time of these OTS molecules on quartz, a monolayer was purposely prepared with several gauche defects. Next, SFG spectra of these two systems were obtained by different polarization combinations and PM method which were analyzed to obtain the molecular conformation at the interface. For example, the SFG spectrum of a “not so well-ordered monolayer” acquired at 30°, 5 peaks were observed at approximately 2855, 2875, 2918, 2943 and 2980 cm^{-1} and assigned as methylene(CH_2) symmetric stretch(SS), methyl (CH_3) SS, CH_2 asymmetric stretch (AS), Fermi resonance, and as CH_3 AS, respectively. Also, methacrylate- based functionalized polymer thin films on the dielectric substrates were prepared and also studied with the PM method.

COLL 269

Modifying lipid bilayer permeability with inorganic nanoparticles

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Liposomes are spherical vesicles formed by phospholipid bilayers and comprise the foremost structure of any biological membrane. Applications of liposomes span from drug delivery to cosmetics. Recently, tremendous attention has been focused on studying the interactions of inorganic nanoparticles with liposomes which is an ideal model system for investigating nanoparticle/membrane interactions and designing novel self-assemblies. It is hypothesized that the size and surface chemistry of the metallic nanoparticles can be tailored to substantially impact the rigidity of the phospholipid vesicle assemblies. For hydrophilic surface-modified nanoparticles, the nanoparticles attached to the charged headgroups of the phospholipid membrane, which can impact the structure and rigidity of the vesicle assembly. Hydrophobic surface modified small nanoparticles are preferentially encapsulated within the phospholipid membrane bilayer. Scanning calorimetry (DSC) results for dodecanethiol capped silver nanoparticles (AgNPs) and oleic acid capped Fe_3O_4 nanoparticles (5 nm diameter) encapsulated within the phospholipid membrane bilayers indicate the impact of encapsulated nanoparticles on the phase behavior of liposomes. The dipalmitoylphosphatidylcholine (DPPC, zwitterionic) / dipalmitoylphosphatidylglycerol (DPPG, anionic) 85/15 vesicles have a gel to fluid transition at 41 °C and the phase transition temperature for AgNPs encapsulated liposomes decreased significantly. However, the phase transition temperature for oleic acid capped Fe_3O_4 nanoparticle encapsulated liposomes increased. The nanoparticle-lipid bilayer interactions that are reflected by lipid bilayer permeability, were studied using spectrofluorometry by measuring the efflux of encapsulated fluorescein the probe dye from the small unilamellar vesicles in the presence of the surface functionalized AuNPs and AgNPs. The extent of change in fluorescence signal in the form of relative fluorescence of the fluorescein dye was used to determine the change in membrane permeability. Fluorescein leakage results have indicated that 11-mercaptoundecanoic acid and citrate functionalized hydrophilic AuNPs significantly impact the lipid bilayer permeability. The nanoparticle size effect on the lipid bilayer permeability has been studied with citrate functionalized 5, 13, and 30 nm diameter AuNPs.

COLL 270

Computational study of lumazine assembly around single-walled carbon nanotubes

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Recent studies have shown that organization of special surfactants around single walled carbon nanotubes allows individualization of single-walled carbon nanotubes (SWNTs) that exploit their unique opto-electronic properties. These surfactants adapt different organizational patterns from random to tubular. Our group has shown that flavin mononucleotide (FMN) and its aliphatic (dodecyl) analog FC12 self-organize in a helical pattern that forms a tubular assembly around SWNTs. Such helical wrapping originates

from four sets of H-bonds that “stitch” the neighboring FMN moieties into a continuous helical ribbon, and the π - π interaction of the isoalloxazine ring with the underlying graphene sidewalls. Understanding of molecular motifs and relative interactions involved in their formation may allow us to enhance the organization complexity of these assemblies. Along these lines we investigated a smaller analogue of FC12, i.e. lumazine (LC10) where the terminal phenyl ring of flavin has been removed, resulting in a bicyclic, rather than a tricyclic, moiety. Using Molecular Mechanics simulations the aim of this study is to elucidate the organizational pattern of lumazine (LC10) in comparison to that of FC12. In addition, this contribution intends to address whether the shorter lumazine repeat introduces a gap between helical repeats, which can be studied via spectroscopic techniques.

COLL 271

Morphology-tunable synthesis, growth and optimization of copper nanowires

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Effects of temperature, precursor and capping agent concentrations in synthesis of copper nanostructures are reported. Scanning electron microscopy (SEM) studies revealed that by changing the concentration of the reducing agent, hydrazine, the nanowire morphology transformed from a tapered to a uniform diameter structure. When the synthesis temperature was raised from 60°C to 80°C baseball bat shaped nanowires were observed instead of uniform diameter nanowires. With increasing the copper precursor concentration, caterpillar like hierarchical nanostructures appeared at 60°C. Such rarely reported complex morphological features were made up of tiny self-assembled nanoparticles of copper on comparatively thick nanowires. Thus, the growth mechanism of these nanowires structures appears to be different from the screw dislocation mediated growth model observed by other workers.

COLL 272

Controlling void development in phenolic composites

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Phenol formaldehyde (PF) resin is a ubiquitous element used in manufacturing high temperature components. In composites, the PF resin is typically applied to a fiberglass fabric from a dispersed colloidal polymer state. The polymerization cure stress that develops during the thermoforming of composite panels is responsible for macroscopic geometric distortion or warping often leading to the rejection of experimental and

industrial parts. The relative void content of the PF-fiberglass composite face-sheets in laminates is quantified by Scanning Electron Microscopy. A correlation between the void content and the warpage value is made. The solvent conditions of the PF resin are varied and used to program for voids in the PF matrix of the composites. Monitoring of the polymerization / crosslinking in the PF fiberglass composites was done using Thermogravimetric Fourier Transform Infrared Spectroscopy. The solvent definition of the PF formulation and residual solvents established by the thermal history of samples is linked to voids content; in turn these voids act to relieve cure stress. The control of the resin chemistry, solvency, fiberglass infiltration, and cure conditions permit the fabrication of composites that have relatively low amounts of geometric distortion or warping.

COLL 273

Solution phase investigation of free charge carriers in single-walled carbon nanotubes

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Single-walled carbon nanotubes (SWCNTs) possess attractive features for use in solar energy conversion. SWCNTs have many different structures, each with different properties with respect to the solar-to-electrical conversion process. This is promising because SWCNTs can produce a photovoltaic cell that is tuned to maximize the efficiency of the solar-to-electrical conversion. To achieve this efficiency the SWCNT properties, with respect to the solar-to-electrical conversion process, must be understood. Previous research by scientist at the National Renewable Energy Laboratory (NREL) has confirmed charges are produced from solar energy in SWCNTs. Now, our research is focused on further understanding how modifications to the SWCNTs can impact efficiency. Our first objective seeks to understand the properties of a single structure type. The second objective seeks to understand how SWCNT length, a controllable factor, impacts the conversion process. The understanding from these combined goals will allow for the production of photovoltaics that are efficiently tuned to solar energy.

At NREL, my research focused on obtaining solutions of a one SWCNT structure type, and of various lengths. To achieve this we use an established polymer wrapping process, which with high selectivity produces single chirality suspensions of SWCNTs. We can then use advanced time resolved spectroscopy techniques to elucidate our question.

COLL 274

Colloidal nanocrystals for self-assembled optical nanoantenna

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Engineered nanostructures can support tunable localized surface plasmon resonances (LSPRs), which enables vibrational spectroscopy with single-molecule sensitivity. When these nanostructures are localized to a scanning probe tip, they can also enable nanometer spectroscopic resolution. Colloidal noble metal nanoparticles are ideal building blocks because they exhibit LSPRs in the visible spectrum. In addition, the LSPR is highly tunable with nanoparticle size, shape, and assembly. By carefully selecting nanoparticles and self-assembling them onto an AFM tip, we can engineer an optical nanoantenna with a tunable near-field response. We demonstrate this with Ag nanocrystal coated AFM tips coupled to a metal substrate, these nanoantenna generate a strong optical cavity capable of achieving Raman enhancements of 10^9 and providing chemical spectra with < 50 nm spatial resolution.

COLL 275

Preparation of (Cu-ZnO)@C core- and yolk-shell nanoparticles

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Size-controllable (Cu-ZnO)@C core-shell nanoparticles having diameters of 7-20 nm were prepared by carbonization of Cu²⁺- and Zn²⁺-CD (Cu/Zn ratio=0.1-1) at 573 K for 2 h. By XRD, the major compounds in the (Cu-ZnO)@C core-shell nanoparticles are metallic copper (Cu) and ZnO. Cu₂O is not observed. The TEM images indicate that the core Cu in the (Cu-ZnO)@C core-shell nanoparticles has crystalline sizes of 7-20 nm, which are similar to the observations by *in situ* synchrotron small angle X-ray scattering spectroscopy. After the etching of Cu from (Cu-ZnO)@C, the diameters of Cu are decreased to 3-14 nm. X-ray absorption near edge structure spectra of Cu in the (Cu-ZnO)@C core-shell and yolk-shell nanoparticles indicate the existence of Cu and ZnO. These yolk-shell nanoparticles possessing the function of nanoreactors can be used in, for example, photocatalytic reduction of CO₂ and H₂O.

COLL 276

Use of attenuated total reflectance Fourier transform infrared spectroscopy to monitor the structural dependence of the protein alpha hemolysin in a DMPC bilayer on cholesterol

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Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was used to monitor the secondary structure of the protein alpha hemolysin (AHL) in a dimyristoylphosphatidylcholine (DMPC) bilayer with varying amounts of cholesterol. As protein function is influenced by its structure, there is a need to investigate protein structural changes with membrane composition to better understand the dependence of protein function on membrane composition. AHL was incorporated into DMPC vesicles with various amounts of cholesterol and deposited the germanium ATR surface where they ruptured to form a bilayer. AHL was chosen because it is a transmembrane protein that extends on to only one side of the cell membrane. To elucidate the effects of membrane composition on protein structure, the amide I band of AHL in the IR spectra was deconvolved to represent different protein secondary structures depending on peak position. It was found that the secondary structure of the transmembrane domains of the protein changed with cholesterol concentration demonstrating the dependence of protein structure on membrane composition.

COLL 277

Robust hybrid membrane-coated nanoparticles for targeting tumors

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Despite rapid advances in early diagnostics and treatments, cancer remains one of the most deadly diseases killing over 1500 Americans each day. This is the driving force for new cancer therapies and early diagnostics to enhance the clinical outcome of cancer patients. Of significant interest are image-guided drug delivery (IGDD) agents that probe tumor-drug interactions as well as track the delivery and distribution of drugs and imaging agents. IGDD agents would replace chemotherapies whose administration affects the whole body systematically leading to toxicity. Recent nanotechnology advances have led to the development of nanocarriers/nanoimaging agents for tracking site-directed drug delivery and therapeutic response. For example, the most frequently used, studied, and promising drug delivery platforms are lipid-based nanoparticles because they carry large amounts of cancer therapeutics and imaging agents. Furthermore, their composition is similar to natural cell membranes providing them with “stealth-like” character. However, their formulations are susceptible to rearrangement reducing their stability and there is uncontrolled release of drugs limiting their efficacy as well as blood circulation times. Consequently, there is a critical need for alternative approaches to improve their stability, biocompatibility, and cellular uptake. We have prepared a new class of robust and biocompatible multi-functional IGDD agents comprised of hybrid lipid-coated metal nanoparticles to improve site-directed delivery and biodistribution while minimizing toxicity to normal cells. The design strategy used to improve the robustness of the drug delivery agents and evidence for their unique

stability will be presented. We expect that these stable IGDD platforms will have a significant impact in cancer therapy and bioimaging applications.

COLL 278

Detection of hemoglobing through molecular imprinting technic

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We propose the use of a potentiometric biosensor that incorporates the efficient and specific molecular imprinting (MI) method with a self-assembled monolayer (SAM). We first tested the biosensor using hemoglobin and fibrinogen. No change in detection efficiency was observed when detection was performed in the presence of 100% serum albumin, indicating that the sensor is able to discriminate for the template analyte even in concentrated solution of similar substances. Computer simulations of the protein structure were performed in order to estimate the changes in morphology and determine the sensitivity of the biosensor to conformational changes in the proteins. We found that even small changes in PH can generate rotation of the surface functional groups, without significant change in the morphology. Yet, the results show that only when the detection and imprinting conditions are similar, robust signals occurs. Hence we concluded that both morphology and surface chemistry play a role in the recognition. The sensitiity of the biosensor to the molecular structure was further probed using fibrinogen where variant mutant forms were available. In this case misfolding of the proteins were known to occur as well as conjugation with other molecules such as IGg. In each case the imprinted biosensor was able to clearly detect the presence of the imprinted species. Hence this technique is valuable not only for detecting purified proteins, but also in identifying protein complexes.

COLL 279

ROS-responsive nanoparticles to extend the lifetime of anti-angiogenic drug

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Purpose

Treatment of macular degeneration and proliferative diabetic retinopathy with anti-angiogenic drugs currently requires repeated injections. As the pathophysiology of these diseases involves oxidative stress (ROS), we are examining whether delivering VEGF-Trap in nanoparticles that degrade and release cargo in response to reactive oxygen species lengthen its lifetime in the eye. This approach should tailor the amount

of drug released to the progression of the disease.

Methods

The efficacy and pharmacokinetics of VEGF-Trap in the following formulations are being compared in mice with oxygen-induced retinopathy (OIR) and with laser-induced choroidal neovascularization (CNV): in ROS-responsive particles (composed of a polyester bearing boronic ester groups), in slowly-degrading particles (poly(lactic-co-glycolic acid) (PLGA)), and free drug. Efficacy is measured by lectin staining and fluorescein angiography. To assess lifetime, we examine whether VEGF-Trap delivered up to three months prior to laser induction protects against CNV.

Results

ROS-responsive particles are compatible with intravitreal administration, as they have no effect on electroretinography, intraocular pressure, or expression of inflammatory cytokines. VEGF-Trap is effective in preventing neovascularization in OIR when administered as a free drug (40 μ g) or in ROS-responsive particles, but not in PLGA. ROS-responsive particles are also effectively releasing VEGF-Trap that inhibits choroidal neovascularization in animals injected three months prior to the insult.

Conclusions

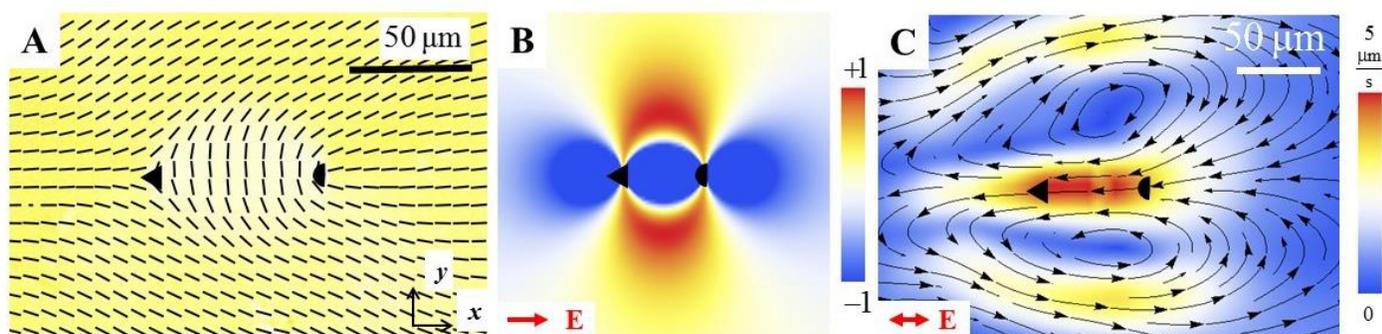
VEGF-Trap retains activity upon formulation in particles by nanoemulsion. ROS-responsive particles allow greater release of VEGF-Trap in eyes affected by neovascularization than PLGA particles, suggesting potential for use in formulation of anti-angiogenics.

COLL 280

Dynamics of colloidal particles in liquid crystals

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Dynamics of colloidal particles in fluids have fascinated scientists for centuries. Phenomena such as Brownian motion, sedimentation, and electrophoresis continue to inspire cutting-edge research and innovation. The fluid in which the colloids move is typically isotropic. Recently, our group started to explore dynamics of particles in anisotropic fluids, such as a nematic liquid crystal. The liquid crystal changes dramatically the dynamic behavior, leading to levitation of particles, anomalous Brownian motion and new mechanisms of electrokinetics. Liquid crystals with predesigned patterns of molecular orientation represent an active electrolytic medium that transports particles of any type (fluid, solid, gaseous), lifting limitations on their electric nature (charge and polarizability). The principle of liquid crystal-enabled electro-osmosis is illustrated in the figure that shows a pre-patterned molecular orientation (director) field with two topological defects (A), charge separation assisted by an external electric field (B), and ensuing electroosmotic flows powered by an AC field (C); the electro-osmotic velocities grow with the square of the electric field. The new phenomena are rooted in anisotropy of liquid crystal properties, such as surface tension, elasticity, permittivity, and electric conductivity. The work is supported by NSF grants DMR-1121288, DMR-1507637 and DMS-1434185.



COLL 281

Engineering interfaces and particles through the assembly of metal–phenolic networks

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The development of rapid and versatile coating strategies for interface and particle engineering is of immense scientific interest. Recently, we reported the rapid formation of thin films comprised of metal–phenolic networks (MPNs) on various substrates by simply mixing natural polyphenols and metal ions. This coating technique is substrate independent (covering organic, inorganic and biological substrates) and has been used for the assembly of capsules by coating particles and then removing the coated templates. It will be shown that a range of polyphenols and a library of metal ions are suitable in forming MPNs for film and capsule engineering. The MPN films and capsules are stable at physiological pH but degrade at acidic pH, making them of interest for intracellular release of therapeutics. By altering the metal ions, different functions can be incorporated in the MPN materials, ranging from fluorescence to MRI and catalytic capabilities. Furthermore, synthetic polymer-phenol conjugates have been used as building materials for control over the biofouling properties of the MPN materials. The ease and scalability of the assembly process, combined with pH responsiveness, negligible cytotoxicity and tunable properties, provides a new avenue for functional interface engineering, and makes these MPNs potential candidates for biomedical and environmental applications.

COLL 282

Spontaneous vs. on-demand degrafting of polymer brushes and organosilane monolayers from silica surfaces

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We discuss spontaneous degrafting of polyelectrolyte brushes and on-demand degrafting of polymer grafts and organosilane monolayers from silica surfaces. We show that spontaneous degrafting occurs in strong and weak polyelectrolyte brushes via hydrolysis of ester or amide linkers in the initiator molecule due to mechanical tension in the grafted chains. Sources of tension include high grafting density of polymer brushes on the surface (σ) as well as swelling and electrostatic repulsion associated with increasing degree of deprotonation (α) of repeat units in weakly charged polyelectrolyte brushes. We also present a method for on-demand degrafting of polymer grafts and small molecules by using tetrabutyl ammonium fluoride (TBAF). We employ this technique to determine the molecular weight distribution of polymer grafts prepared by surface-initiated controlled radical polymerization on flat silica supports. We also demonstrate the application of TBAF for creating spatial degrafting patterns of polymers and organosilane modifiers on silica substrates. Desired in-plane patterns in polymer brush layers in millimeter scale are created by using a microcontact printing TBAF with a stamp made of agarose gel. Position-dependent gradients of the degrafted areas are formed by dipping substrates featuring homogeneous coatings into TBAF solution. The use of TBAF for degrafting is appealing because it cleaves selectively Si-O bonds, does not alter chemically the structure of the degrafted moieties, and activates hydroxyl groups on silicon surfaces to enable deposition of organosilane-based initiators for growth of fresh polymer brush layers and organosilane monolayers. The reusability of the substrate allows us to create a diblock copolymer brushes on selected portions of the substrate not exposed to TBAF while decorating the TBAF-treated sections of the substrate with homopolymer brushes.

COLL 283

Stimuli responsive materials from lipids: Applications into drug delivery systems and diagnostics

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Stimuli responsive systems hold great promise in drug delivery and diagnostics, and while polymers have received much attention in this regard, self assembled lipid systems offer an alternative biocompatible material with which to control either drug release, or interaction of the drug delivery system with target tissues. While liposomes have been proposed as responsive systems in drug delivery and diagnostics for many years, they do not provide reversible control over drug release. Switching between other thermodynamically stable modes of self assembly, such as between bicontinuous cubic and inverse hexagonal or inverse micellar structures enables switching of release of drug or signalling molecules on and off, providing multiple pulses of drug with the same stimulus. We have been taking new approaches to such systems into in vivo

applications, where materials are responsive to heat, light, pH, enzymes among other triggers for new treatments of diseases such as macular degeneration.

COLL 284

Layer-by-layer assembled polyelectrolyte films as porous biomolecular delivery systems

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Biomaterials capable of delivering controlled quantities of bioactive agents, while maintaining mechanical integrity, are needed for a variety of cell contacting applications. We describe here two strategies toward porous, polyelectrolyte-based thin films capable of controlled biomolecular loading and release. In one approach, termed "nanoparticle templating," films are formed via the layer-by-layer assembly of charged polymers and nanoparticles (NP), then chemically cross-linked to increase mechanical rigidity and stability, and finally exposed to tetrahydrofuran to dissolve the NP and create an intra-film porous network. In another approach, termed "solution shock," films are subjected briefly to an extreme acidic environment following LbL assembly, causing expansion and ultimately a spinodal-like breakup of the film into a porous structure. We report here on film structure and mechanics, on biomolecular agent loading and release, and on the behavior of cells cultured on these films. While both strategies yield mechanics and biomolecular agent loading that are suitable for applications such as tissue engineering, the solution shock method offers advantages in simplicity and controllability.

COLL 285

Amphiphilic polymer self-assembly and disassembly

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Amphiphilic polymers, encompassing synthetic block and graft copolymers and polymers of biological origin such as polysaccharides and proteins, exhibit an innate ability to organize from the nanoscale across to the mesoscale. Structure leads to function, and thus amphiphilic polymers find diverse applications that range from drug delivery carriers to membranes for separations to electrolytes for batteries. In the "dry" state, amphiphilic polymers can attain intramolecular organization via crystallization or hydrogen bonding, supramolecular organization via segregation of domains that differ in chemistry or conformation, and mesoscale organization such as spherulites and fibrils. The addition of selective solvents may disrupt certain types of organization but can promote others. The solvents can also affect dramatically molecular mobility and the dynamics of structural transitions. The presentation will utilize research findings from our group to highlight structural transformations that amphiphilic polymers

(poly(ethylene oxide)-poly(propylene oxide) and cellulose) undergo in response to changes in solvent quality/quantity and to external stimuli such as temperature and shear. The evolution of nanostructure is relevant to the design of processes for formulation of actives, synthesis of nanoparticles, and dissolution of difficult-to-dissolve polymers.

COLL 286

Molecular packing and self-assembly

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The concept of molecular packing coupled to geometry has been used to rationalize successfully the self-assembly process of simple surfactant molecules in aqueous solutions. In the forty years since the introduction of the molecular packing model, the self-assembly phenomenon has been studied in a variety of systems such as block copolymers, polymer-DNA conjugates, peptide amphiphiles, polymer-protein conjugates, giant amphiphiles with inorganic or polymetallic head groups, dendritic amphiphiles, nanoparticles bound to alkyl chains or to polymers and Janus like nanoparticles. We will examine to what extent the molecular packing model evolved from simple surfactant science has been able to represent the observed self-assembly behavior of these multiple kinds of new amphiphilic systems. The ability to rationalize observed morphology in terms of molecule packing considerations will provide a powerful tool for designing and manipulating desired self-assembled structures from this variety of complex molecular architectures.

COLL 287

Simple routes to all-polymeric corrals, flow-channels and traps for studies of lipid and protein diffusion in supported lipid bilayers

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We describe simple routes to the fabrication of corrals, channels, traps and other structures for the fabrication of spatially organized lipid bilayers and membrane proteins. These utilize photochemistry and polymer brushes. In the first approach, UV exposure of films of (chloromethylphenyl)trichlorosilane (CMPTS) causes dehalogenation of the surface creating carboxylic acid groups to create hydrophilic, anionic regions, in which lipid mobilities are observed that are similar to those observed on glass surfaces. In masked regions, the halogen remains intact, and is used to grow poly(oligoethyleneglycol methacrylate) (POEGMA) brushes by atom-transfer radical

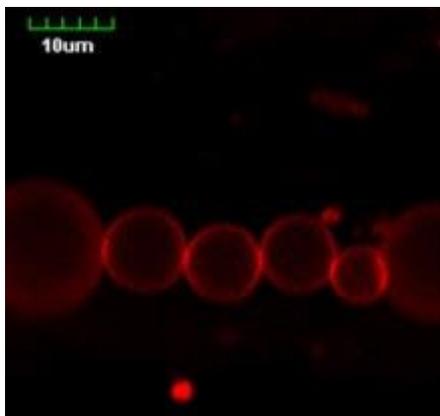
polymerization (ATRP), defining lipid-free walls within which SLBs may be formed by vesicle fusion. Two-component structures are fabricated by using an aminosilane film in which the amine group is protected by a photoremovable nitrophenyl group. Selective exposure, through a mask or using a Lloyd's mirror interferometer, causes patterned deprotection of the film leading to patterned brush growth by ATRP. Poly(Cysteine methacrylate) (PCysMA) is a new, highly biocompatible, stimulus-responsive zwitterionic polymer that forms thick brushes when grown from surfaces by atom transfer radical polymerization (ATRP). Lipid mobility similar to that observed on glass is observed on PCysMA brushes. Measurements of membrane protein diffusion have been made using ac trap structures. After lithographic definition of corrals, channels and other structures, PCysMA is end-capped and the remainder of the surface deprotected; POEGMA brushes are grown by ATRP, enclosing the PCysMA structures. Using interferometric lithography, arrays of close-packed gold nanostructures may be defined on the substrate. These are strongly coupled to photosynthetic membrane proteins, yielding intense extinction spectra. These gold nanostructures are incorporated into brush corrals and other structures, with polymer brushes grown to the same height as the gold nanostructures, enabling the formation of a continuous SLB with integral plasmonic reporters for membrane protein activity.

COLL 288

Characterizing the interactions of lipid bilayers with antimicrobial peptides and magnetic fields

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Antimicrobial peptides are involved in the defense system for most of organisms,. These peptides attach onto cell surfaces, and further insert into the membrane, either forming pores or accumulating like a carpet, both of which will cause the cell death. In this study, we report the interaction of alamethicin on POPC vesicles using magnetic fields. Our data shows that the membrane affinity can be disrupted by alamethicin at a critical concentration. This disruption is confirmed by confocal microscope using fluorescent lipids. To better understand the interaction between alamethicin and the lipid membrane, we use a magnetic based assembly method to monitor the interaction between alamethicin and bilayer.



COLL 289

Nanolipoprotein particles: Encapsulated in silica gel or targeted to lipid phases

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Nanolipoprotein Particles (NLPs) are disc-shaped nanometer-sized lipid bilayer patches stabilized by a belt of scaffold proteins. NLPs have an average thickness of 5 nm, with a diameter ranging from 10-25 nm depending on the stoichiometric ratios and types of lipids and scaffold proteins being used. This allows NLPs to be compatible with the pore size (5-50 nm) of mesoporous silica. Therefore, we perform entrapment of NLPs using a quick, simple sol-gel processing technique for TMOS that includes evaporation of the majority of the methanol after the hydrolysis reactions. To ensure proper functioning of silica sol-gel entrapped NLPs, we have investigated the phase behavior of the lipids in addition to the secondary structure, localization, and environmental polarity of the scaffold proteins. Our results indicate that silica gel-entrapped NLPs remain intact, with only slightly altered lipid and scaffold protein structure and dynamics. We will briefly discuss the potential to entrap NLPs containing embedded integral membrane proteins (IMPs) for various applications such as photocatalysis, biosensing, affinity chromatography, high-throughput drug screening, and bio-reaction engineering.

Further, scaffold proteins can bear polyhistadine tags, which are capable of chelating to Cu^{2+} metal ions. Lipid-phase specific, iminodiacetic acid (IDA) functionalized lipids are also capable of chelating Cu^{2+} , providing a mechanism for phase-targeted binding of NLPs. We investigate this binding via fluorescence microscopy and characterize interaction with phase-separated supported bilayers and giant unilamellar vesicles (GUVs). The thermodynamics (energy of lipid mixing and steric pressure of protein crowding) and morphology of binding are also examined. Targeted binding of NLPs bearing functional IMPs and/or other biomolecules to supported lipid bilayers has a variety of applications, including development of nano-array technologies and biosensors.

COLL 290

Designing beta solenoid proteins for nanoscale materials and devices

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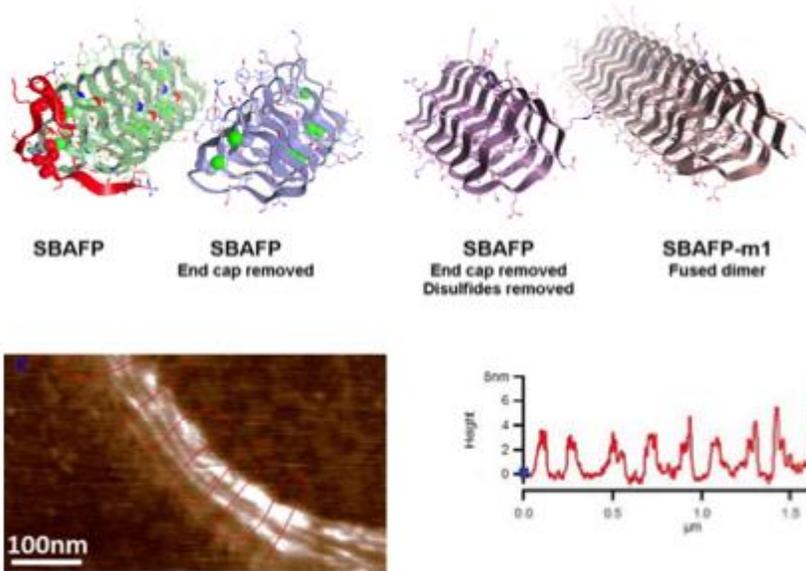
We have modified wild type beta solenoid proteins to undergo longitudinal amyloid aggregation and lateral aggregation through a variety of side chain modification strategies. The native proteins typically have anti-freeze function *in vivo*. The protein aggregates are very stable, can be made flat on a nanoscale level with small binding energy, and can also be designed to co-assemble with other protein complexes in three-dimensional scaffolds. These proteins provide a new approach for developing nanometer precision at the templated growth of ordered heterogeneous nanoparticle or catalytic arrays or co-assembling with other materials such as graphene for device applications. This presentation will overview design principles, synthesis approaches, and materials assembly.

This work was supported by the UC Davis Office of Research RISE program, and by the US National Science Foundation through grants DMR-1207624 and DMR-0844115 (DLC, KR, NRH, AJK, NM, and RRPS).

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Upper: Modifying an antifreeze protein to aggregate. Lower left: Atomic force microscope image of longitudinally and laterally assembled beta solenoid fibrils. Lower right: AFM measured height profile of fibril assembly.

COLL 291

Dissipative and dynamic self-assembly: Spontaneous osmoregulation in giant vesicles

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A fundamental consequence of cellular organization of living systems is that the aqueous milieu, bathing the cells, is also compartmentalized. Although water equilibrates readily across the elastic cellular boundary, passive permeation of solutes is strongly hindered. As a result, gradients of concentrations of ions, salt, and soluble biomolecules are readily established across the cellular boundary, producing osmotic activity of water. To deal with any sudden environmental changes in the amount of dissolved molecules in water, free-living cells have evolved complex molecular machineries and mechanisms (e.g., mechanosensitive channels and compatible solute accumulation), which allows them to dissipate the osmotic stress. But how might primitive cells near the dawn of life on Earth – lacking advanced biochemical or genetic capabilities and composed essentially of simple amphiphiles– have responded to such environmental insults?

Drawing from recent experiments in our labs employing simple models for the cellular chassis (i.e., giant vesicles composed of amphiphilic lipids and polymers), this talk considers how the osmotic activity of water is transduced across cell-like compartments.

It highlights how water activity and accompanying dissipation of osmotic energy couples with the compartmental boundary, mechanically remodeling the membrane shape and spatially reorganizing membrane components - both through a well-orchestrated cooperative dynamics. Comparing these processes as elemental events in the homeostatic working of a living cell, these findings support the idea that water is not a mere solvent for life – a blank canvas on which biomolecules become animated – but an active medium that guides organization and dynamics of biomolecules in complex, subtle and essential ways.

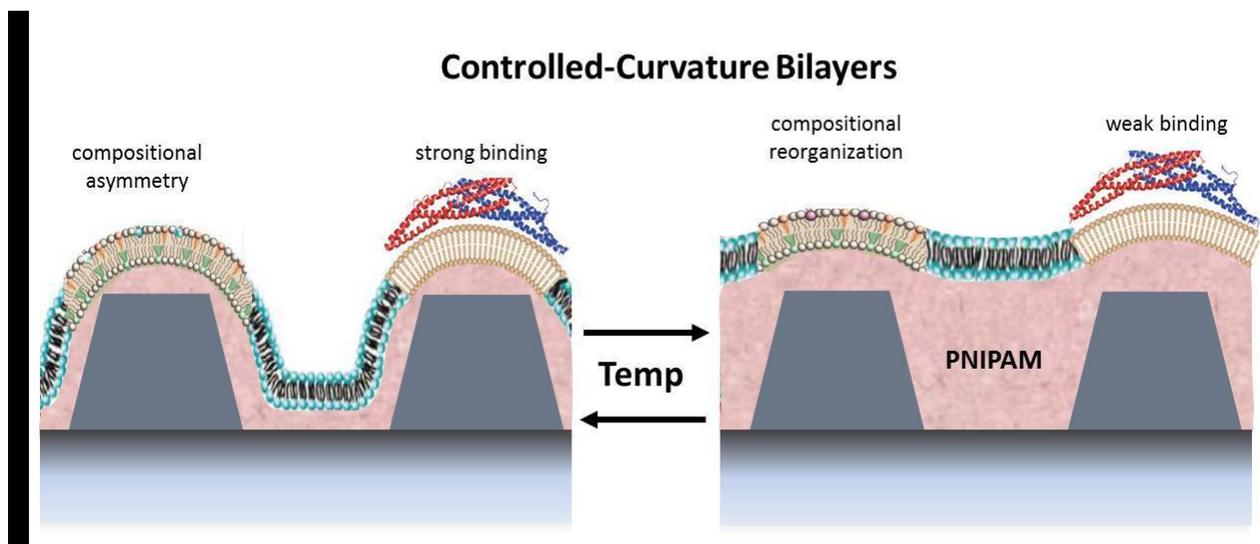
The work is carried out with Doug Gettel, Jeremy Sanborn, Sean Hong, Kamila Oglecka, James Ho, Madhavan Nallani, Rachel Kraut, and Bo Liedberg.

COLL 292

En route to tunable membrane topography: Induced domain reorganization and switchable protein binding

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Curvature-induced membrane phenomena are attracting increasing attention due to their prevalence in critical cell functions and their potential applications in designing therapeutics, regulating protein-membrane binding, and developing advanced biosensing applications. On a fundamental level, nanoscale curvature in multi-component lipid membranes is hypothesized to induce local compositional changes, such as leaflet-asymmetry and lateral domain reorganization, which are intimately linked to signal transduction, cell trafficking and host-pathogen interactions. A variety of methods have been proposed to induce local curvature in membranes, including lipid substitution and the insertion of scaffolding proteins. However, these approaches involve a disruption of the innate membrane properties by changing the membrane composition or introducing guest molecules, both of which are rather inconvenient for studying the natural response of local membrane composition and protein recruitment to changes in the membrane topography. Alternatively, we utilize soft nanostructured scaffolds of poly(N-isopropylacrylamide) (PNIPAM) coatings atop patterned silicon substrates to physically induce curvature in lipid membranes. The highly hydrous nature of PNIPAM offers a suitable microenvironment that provides a sufficient level of freedom for membrane fluctuation and deformability and allows access to natural membrane behavior without the constraints of rigid solid substrates. Further, the thermoresponsive nature of PNIPAM provides a thermal switch for turning curvature on and off in the scaffold topography. The conformation of lipid bilayers to such scaffolds allows tunable 2D membrane architectures and enables real-time realization of lateral membrane reorganization and peripheral protein binding in response to controllable curvature variation. We envision that such membrane tunability will provide new insights into membrane physiology and will potentially open new avenues to thermally switchable membrane-based biosensors.



curvature-induced membrane phenomena

COLL 293

Colloidal properties of nanoerythrocytes derived from bovine red-blood-cells

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Liposomes are nanoscale containers that are typically synthesized from lipids using a high-shear process such as extrusion or sonication. While liposomes are extensively used in drug delivery, they do suffer from certain problems including limited colloidal stability and short circulation times in the body. As an alternative to liposomes, we explore a class of container structures derived from erythrocytes (red blood cells). The procedure involves emptying the inner contents of these cells (specifically hemoglobin) and resuspending the empty structures in buffer, followed by sonication. The resulting structures are termed nanoerythrocytes (NERs), i.e., they are membrane-covered nanoscale containers, much like liposomes. Cryo-transmission electron microscopy (cryo-TEM) and small-angle neutron scattering (SANS) are employed for the first time to study these NERs. The results reveal that the NERs are discrete spheres (~ 110 nm diameter) with a unilamellar membrane of thickness ~ 4.5 nm. Remarkably, the biconcave disc-like shape of erythrocytes is also exhibited by the NERs under hypertonic conditions. Moreover, unlike typical liposomes, NERs show excellent colloidal stability in both buffer as well as in serum at room temperature, and are also able to withstand freeze-thaw cycling. We have explored the potential for using NERs as colloidal vehicles for targeted delivery. Much like conventional liposomes, NER membranes can be decorated with fluorescent or other markers, solutes can be encapsulated in the cores of the NERs, and NERs can be targeted to specifically bind to mammalian cells. Our study shows that NERs are a promising and versatile class of nanostructures. NERs that are harvested from a patient's own blood and reconfigured

for nanomedicine can potentially offer several benefits including biocompatibility, minimization of immune response, and extended circulation time in the body.

COLL 294

Liposomal spherical nucleic acids: Nanostructures enabling the potential of therapeutic nucleic acids

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Liposomal Spherical Nucleic Acids (LSNAs) represent a nanoscale arrangement of highly oriented oligonucleotides surrounding a spherical liposome as a template. LSNAs are a promising class of structures for enabling the potential of therapeutic nucleic acids. LSNAs show characteristics that are similar to SNAs with Au-nanoparticle cores, and the spherical arrangements of oligonucleotide strands is the key capability of LSNAs to enter multiple types of cells by endocytosis. In particular, the interactions of LSNAs with keratinocytes, tumor tissue, and cells of the immune system suggest two key ways to develop LSNAs as nanotherapeutics – as gene regulatory or immunomodulatory agents. LSNAs offer additional design features, such as those that enable the co-delivery of core-encapsulated or core-embedded drugs. Advanced designs, such as LSNAs featuring TLR-agonist oligonucleotides and co-functionalized with peptide or protein antigens, have shown promising activity as vaccines against cancer and infectious disease.

COLL 295

Chemoradiotherapy with nanoparticle therapeutics: Improving targeting and reducing toxicity

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Chemoradiotherapy, the concurrent administration of chemotherapy and radiotherapy, is a key treatment paradigm in the curative management of many solid tumors, including brain, head and neck, esophageal, lung, gastric, rectal, anal, and cervical cancers. Because of its importance, there has been strong interest in preclinical and clinical cancer research to identify strategies to further improve the therapeutic ratio of chemoradiotherapy. One approach is to preferentially deliver chemotherapy to tumors while avoiding normal tissue. Although this was not possible with traditional drug delivery techniques, the development of nanoparticle drug delivery vehicles provided an unprecedented opportunity. Nanoparticles are known to preferentially accumulate in tumors and have low distribution in normal tissue. Moreover, nanoparticles can release their therapeutic cargo in a prolonged fashion, which can increase the synergy between chemotherapy and radiotherapy. Therefore, we hypothesized that nanoparticle chemotherapeutics can improve the therapeutic index of chemoradiotherapy. To

evaluate this hypothesis, my research group has formulated several novel nanoparticle chemotherapeutics and evaluated them in preclinical models of chemoradiotherapy treatment for cancer. Our results demonstrated that nanoparticle chemotherapeutics are indeed more effective and less toxic than their standard chemotherapy counterparts in chemoradiotherapy. To facilitate the clinical translation of nanoparticle chemotherapeutics in chemoradiotherapy, our group has also conducted preclinical evaluation of nanoparticle drugs that are currently under clinical investigation. We were able to confirm that nanoparticle chemotherapeutics hold high potential in improving the therapeutic index of chemoradiotherapy.

COLL 296

Self-assembly of nanoconjugates on the cell surface triggers apoptosis

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The development of nanotechnology combined with the progress of cell and molecular biology has permitted to investigate the interaction between nanoconstructs and cell surface receptors at molecular level. Herein we present an example of rational nanomedicine design based on structure and function of CD20, one of the most reliable biomarkers for B-cell malignancies. CD20 is a transmembrane glycoprotein; its crosslinking results in activation of tyrosine kinases, release of intracellular stores of calcium ions, and initiation of apoptosis. We designed a new therapeutic system comprising two nanoconjugates: a pretargeting component (anti-CD20 Fab' attached to a morpholino oligonucleotide, MORF1) and a crosslinking component (*N*-(2-hydroxypropyl)methacrylamide (HPMA) copolymer (P) grafted with multiple copies of the complementary oligonucleotide, MORF2). Consecutive treatment with the two nanoconjugates resulted in CD20 clustering on the cell surface and effective eradication of malignant B-cells *in vitro* and *in vivo*. There is no need for toxins or immune effector functions [1]. Cortical actin and cholesterol in the plasma membrane promoted the aggregation of lipid raft associated molecules to form clusters after treatment with nanoconjugates [2]. In addition, the time lag between administration of the pretargeting conjugate (Fab'-MORF1) and the crosslinking conjugate (P-(MORF2)_x) can be optimized based on pharmacokinetics and biodistribution of the first conjugate, in order to achieve maximum tumor/tissue accumulation ratio in individual subjects [3]. This approach enabled more efficient treatment and achieved superior therapeutic outcomes in mice when compared to the immunotherapy using rituximab.

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COLL 297

Hybrid nanoparticles for treating resistant cancers

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By harnessing the power of synthetic inorganic chemistry with that of the latest nanoscience and nanotechnology, the Lin group has developed new hybrid nanomaterials for more effective cancer therapy. These biodegradable nanomaterials provide a nontoxic platform for delivering a wide range of potent anticancer drugs such as cisplatin/oxaliplatin, antifolates, biologics, photosensitizers, and others. The hybrid nanomaterials carry high payloads of therapeutic cargoes and can be selectively and more efficiently delivered to tumors than current therapies, leading to reduced toxicity to normal cells and more potent antitumor efficacy. In this talk, I will discuss our recent efforts on with designing hybrid nanoparticles containing multiple therapeutics or treatment modalities for treating resistant cancers in mouse models. The pros and cons of this new delivery platform will also be compared and contrasted with other established nanoparticle systems.

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Formulation of nanoparticles through controlled chemistry for drug delivery application

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Nanomedicine is a new modality for cancer diagnosis and therapy and may change the landscape of oncology. In this presentation I will mainly present the design and synthesis of size controlled silica nanoconjugates and their applications as drug delivery nanomedicine, and discuss their application in various fundamental studies, such as cellular uptake, biodistribution, tumor tissue penetration, retention and inhibition. I will cover several other topics related to anticancer nanomedicine, such as development of conjugated polymeric particles via drug-initiated polymerization of lactide, recent development of chain-shattering polymeric therapeutics and high loading polymer/drug nanocrystals.

COLL 299

Macrophage recognition of 'self' for nano- and micro- medicine

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The body's immune system exists to identify and destroy 'foreign' cells and materials, whether they are bacteria, viruses, flecks of dirt or splinters. Unfortunately, nanoparticles designed to deliver drugs and implanted devices for controlled delivery are just as foreign and subject to the same response. This response has many cellular components, including macrophages — literally "big eaters" — that find, engulf and destroy invaders. Proteins in blood serum work in tandem with macrophages; they adhere to objects in the blood stream and draw macrophages' attention. Drug delivery systems naturally trigger this response, so earlier attempts to circumvent it involved coating the particles with polymer "brushes" (such as PEG brushes). These brushes are intended to physically block various blood serum proteins from sticking to its surface, but they only slow down eventual recognition by macrophages. We had shown years ago that the human protein CD47, found on all mammalian cell membranes, binds to a macrophage receptor known as SIRPA and tells the macrophage 'Don't eat me'. Computational design of a CD47 polypeptide was followed by production and attachment to nanoparticles that could be used in a variety of in vitro and in vivo experiments. We also attached antibodies that might also be used in targeting, but these antibodies also served to attract the macrophages' attention and ensure the peptide's 'passport' was being checked and approved. The key test of the 'Self' polypeptide's efficacy was in NOD.SCID mice that have macrophages with SIRPA receptors similar in function to human. We injected two kinds of nanoparticles — ones carrying the peptide passport and ones without. A 1-to-1 particle ratio initially became, by 20-30 minutes in circulation, up to 4:1 for particles with the peptide versus control particles with polymer brushes. The additional circulation time allows a few more trips through the macrophage-heavy spleen and liver for nanoparticles to find their targets such as tumors. Additional applications of the peptides will be described, including application to viruses and cell therapies.

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COLL 300

Synergistic photothermal and antibiotic eradication of *S. aureus* biofilms using targeted, drug-loaded nanoparticle

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Resistance to conventional antibiotics is a growing public health concern that is quickly out-pacing the development of new antibiotics. The development of resistance emphasizes the urgent need for alternative therapeutic strategies to combat infections caused by these and other bacterial pathogens. Biofilm formation represents a serious clinical issue that further complicates antimicrobial therapy due to the intrinsic antibiotic resistance it imparts. We used *Staphylococcus aureus* as a proof-of-principle ESKAPE pathogen to demonstrate that an appropriate antibiotic can be incorporated into polydopamine-coated gold nanocages (AuNC@PDA) and that the loaded constructs can be conjugated to antibodies targeting a species-specific surface protein as a means of achieving selective delivery to the bacterial cell surface. Near-infrared laser irradiation, at levels within the current safety standard for use in humans, can be used to achieve both a lethal photothermal effect and controlled release of the antibiotic, thus resulting in a degree of therapeutic synergy capable of eradicating viable bacteria. The system was initially validated using planktonic bacterial cultures. In the context of an established biofilm, neither photothermal treatment nor antibiotic treatment was sufficient to completely eradicate the biofilm. However, without changing the dosing parameters, the targeted, drug-loaded nanoconstruct was shown to completely eradicate viable bacteria, thus indicating that this synergistic approach could be used to resolve intrinsically-resistant biofilm infections.

COLL 301

Kras/P53 targeted RNAi combination nano-therapeutics for treating non-small cell lung cancer

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Non-small cell lung cancer (NSCLC) is the main subtype of lung cancer, a leading cause of cell death. Adenocarcinoma, the most common subtype of NSCLC, is associated with mutation of Kirsten rat sarcoma viral oncogene homolog (KRAS) and loss of p53 function. KRAS mutation is responsible for tumor formation and maintenance while loss of p53 is responsible with tumor cell proliferation, survival, drug resistance, and apoptosis. Due to the complex genetic mutation in tumor cells, cisplatin, the main chemotherapeutics for NSCLC, has limited success in clinical trials.

Combination therapy comprising RNA-based therapeutics to target KRAS mutation and loss of p53 along with cisplatin is a promising approach to treat NSCLC. Herein, we report a nano-therapeutics based on layer-by-layer (LbL) approach, allowing packaging of both RNA therapeutics and cisplatin simultaneously. We showed a high loading of both therapeutics as well as a staged release *in vitro*. To demonstrate the treatment efficacy of the nano-therapeutics, we established an orthotopic lung adenocarcinoma

model in nude mice. Biodistribution studies revealed that the nano-therapeutics accumulated in the lung tumor while no accumulation in lung was seen on healthy mice. Further efficacy studies demonstrated that the combination therapy approach prolonged the survival of mice significantly compared to either cisplatin or RNA therapeutics alone. Immunohistochemistry studies indicated that the synergistic effect of both cisplatin and RNAs lead to an enhanced killing effect of lung tumor thus providing an improved survival. Therefore, the combination nano-therapeutics from LbL can potentially be a targeted approach for NSCLC treatment.

COLL 302

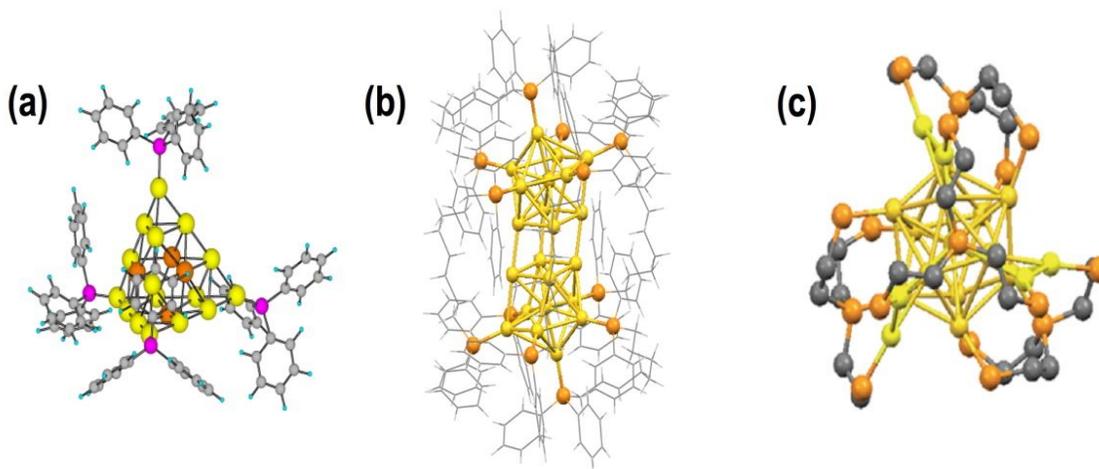
Toward synthesis of the Au₂₀ pyramid and other atom-precise gold nanoclusters using phosphine ligands

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Gas phase studies showed that Au₂₀ possesses a stable pyramidal structure with all 20 gold atoms on the cluster surface [1]. The Au₂₀ pyramid is expected to exhibit interesting catalytic and optical properties, if bulk quantities of samples can be obtained. In this talk, I will report our progress toward the syntheses of the Au₂₀ pyramid using phosphine ligands. Initial effort using triphenylphosphines demonstrated that the Au₂₀ pyramid could be synthesized in solution (a) [2]. Further effort to increase the yield and selectivity using commercially available diphosphine ligands led to the selective synthesis of Au₁₁ [3]. Recent effort using custom-made long-chain diphosphine ligands resulted in the first crystallization of an Au₂₂ cluster (b) [4]. Finally, using a tetraphosphine ligand we were able to synthesize and crystallize an Au₂₀ cluster (c) with high yield [5], except that the gold core has a different structure than the expected pyramid (a). New strategies toward the Au₂₀ pyramid will be discussed.

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COLL 303

Ligand exchange and catalysis on thiolate-protected nanoparticles

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Thiolate-stabilized nanoparticles such as $\text{Au}_{25}(\text{SR})_{18}^-$ and $\text{Au}_{38}(\text{SR})_{24}$ have many useful applications including biotagging and catalysis. These particles have a geometric structure in which a core of gold atoms is surrounded by gold-thiolate oligomeric ligands. Ligand exchange on these nanoparticles is important for functionalization for various applications. In this work, density functional theory studies are employed to predict the most favorable positions for ligand exchange on these nanoparticles. In addition, recent studies on catalysis on these nanoparticles will be presented.

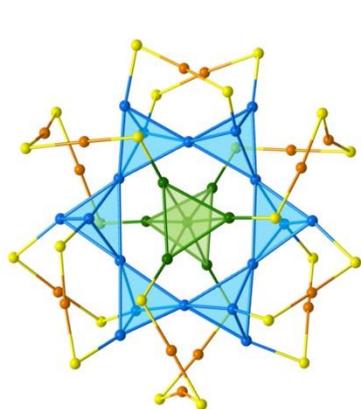
COLL 304

Magic sized gold nanoclusters as supermolecules

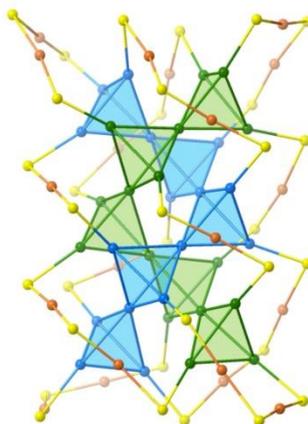
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The origin of magic sizes in nanoclusters is an intriguing issue. In previous research, magic-sized nanoclusters are often regarded as superatoms (i.e. with closed shell electronic structures such as $1\text{S}^21\text{P}^6$). Here, we reveal a supermolecular origin of the stability of magic sized gold nanoclusters, as reflected in the Kekulé-like ring in the $\text{Au}_{40}(\text{SR})_{24}$ cluster and the DNA-like double helix in $\text{Au}_{52}(\text{SR})_{32}$. Both superstructures are composed of Au_4 tetrahedral units and each Au_4 unit can be viewed as a “2-electron

superatom". This supermolecular model is expected to encompass more magic sizes in nanoclusters, just as the fact that an unlimited number of molecules can be assembled from a limited number of atoms.



$\text{Au}_{40}(\text{SR})_{24}$



$\text{Au}_{52}(\text{SR})_{32}$

COLL 305

Tuning the properties of atomically precise silver nanoclusters

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In this presentation I will discuss the latest advances in the synthesis and crystallization of atomically precise ligand-protected silver nanoclusters. These are a special class of homogeneous nanoparticles, with no dispersion in their size or composition, and thus can crystallize into real molecular crystals – unlike typical nanoparticles, which assemble into merely ordered superlattices. Unfortunately, the number of reported nanoclusters still remains limited, while tuning their size and properties continues to be a major challenge. We describe how engineering the cluster's organic ligand shell can lead to direct control over the size of the inorganic core, and how it can be used to introduce anisotropic interactions to the nanocluster akin to valences in molecules. Despite the nascency of those insights, they have already led to the discovery of new silver clusters: a tetravalent $\text{Ag}_{29}(\text{SR})_{12}(\text{TPP})_4$ cluster, and a relatively isotropic $[\text{Ag}_{25}(\text{SR})_{18}]^-$ cluster. The latter is the first metal nanoparticle with an exact analogue in gold, i.e. $[\text{Au}_{25}(\text{SR})_{18}]^-$, hence providing the first model nanoparticle platform to investigate the centuries-old quest for understanding the fundamental differences between the two noble metals. The crystallization of the Ag_{29} and Ag_{25} clusters into single crystals allowed us to determine their full crystal structure and to investigate the optical properties of the nanocluster solids.

We also devised a templated galvanic exchange route to controllably introduce dopants into silver nanoclusters. With this galvanic exchange method we were able to synthesize compositionally uniform $[\text{Ag}_{24}\text{Au}_1(\text{SR})_{18}]^-$ nanoclusters using the pure $[\text{Ag}_{25}(\text{SR})_{18}]^-$ nanoclusters as molecular templates. In contrast, direct synthesis methods of $\text{Ag}_{24}\text{Au}_1$ nanoclusters led to a mixture of $[\text{Ag}_{25-x}\text{Au}_x(\text{SR})_{18}]^-$, $x=1-8$. Mass spectrometry coupled with X-ray crystallography of $[\text{Ag}_{24}\text{Au}_1(\text{SR})_{18}]^-$ nanoclusters explicitly revealed the location of the Au atom and its perturbative effects on the Ag_{25} crystal structure, which are further reflected in the absorption, luminescence, and ambient stability of the particle.

Our work demonstrates a promising path to the modulation of nanoparticle properties at the single-atom level by either ligand engineering or doping.

COLL 306

Molecular silver nanoparticles: Chemical, optical, and structural properties

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An overview of the properties of molecular silver nanoparticles with thiolate ligand shells will be given and compared to those of gold. Silver and gold molecular nanoparticles have distinct differences in their stability, reactivity, structure, and optics. For example, weaker bonding and greater chemical reactivity of silver tends to lead to more rapid evolution of the silver compounds into other species, which enables study of these reactions. This is typically characterized by conversion to smaller sizes, oxides, or larger particles, depending on the conditions of the reaction. The structures of gold and silver compounds are also different. For example, bonding with sulphur differs for the two metals, gold being two-coordinate and silver being three-coordinate, which leads to two distinct sets of structural motifs in the ligand shell and therefore two distinct families of compounds. Finally, although gold and silver are isoelectronic, the d electrons in silver do not interfere with light absorption in the visible part of the spectrum (which gives rise to the difference in color between silver and gold), therefore silver nanoparticles absorb light and emit light more efficiently than gold. Silver nanoparticles also have optical absorption spectra that are significantly more detailed than those of gold, which makes analysis less complex. Clearly silver offers many new opportunities for fundamental studies that will advance our understanding of this class of molecular nanomaterials.

COLL 307

Structure and properties of nanometals from X-ray absorption spectroscopy

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Synchrotron X-ray spectroscopy techniques such as X-ray absorption spectroscopy are useful tools for the element-specific analysis of structural and bonding properties of materials. In this contribution, the application of these techniques in the study of some nanometallic systems will be presented. Materials of particular interest include noble metal nanoclusters, shape-controlled nanocrystals and nanocluster-nanocrystal hybrid systems. It will be demonstrated that the X-ray spectroscopy methods, in association with complementary techniques and quantum simulations, can sensitively probe the structural and property changes induced by the effects such as nanocluster composition, protecting ligands, nanocrystal shape and alloy bonding. The structural information revealed by the X-ray techniques may also be useful in guiding the catalytic and biomedical applications of these materials.

COLL 308

Creation of stable protein films through nanoimprint lithography

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Protein-based materials provide an inherently biocompatible and sustainable platform for the generation of functional materials. Resistance to aqueous degradation of protein films is crucial for most applications such as tissue engineering and controlled drug delivery. Current methods to stabilize protein films use two main strategies: employing the relatively limited variety of naturally self-assembling proteins or using added cross-linkers. While the cross-linking strategy generates functionally diverse structures, unreacted additives retained in cross-linked protein films can adversely affect their final behavior. We demonstrate here a scalable, additive-free nanoimprint lithography (NIL) based method for the fabrication of stable, patterned protein films. This approach is general in terms of protein building block, with the imprinted proteins retaining much of their native structure after the imprinting process. Through parametric variation of temperature and pressure we have determined the conditions necessary to control the stability and biodegradability of purely protein based films. The utility of these films as biomaterials is highlighted through the generation of highly biocompatible non-fouling surfaces and regulation of cellular adhesion through choice of protein precursor.

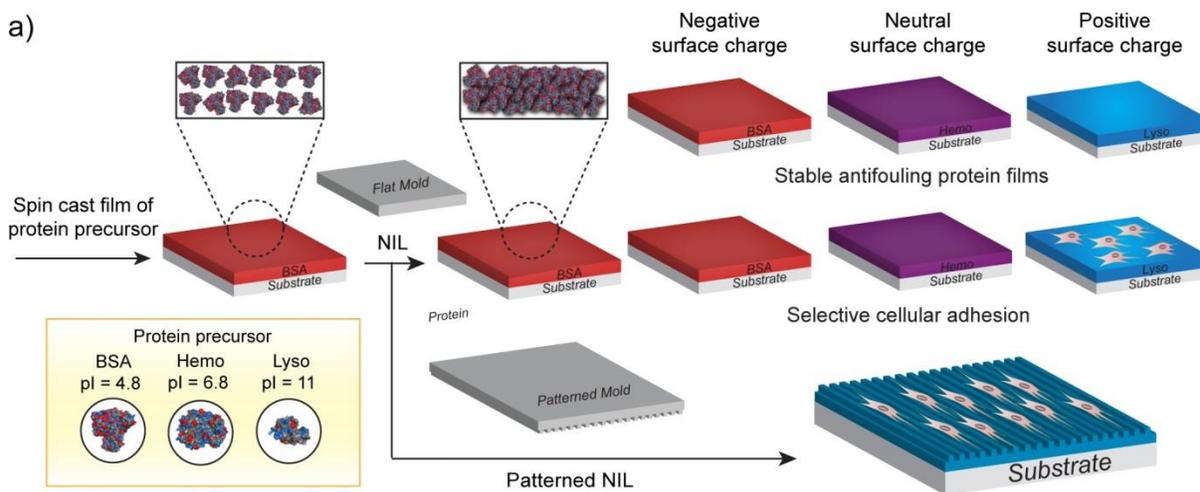


Figure 1. Nanoimprint lithography of protein films for biological applications.

COLL 309

Construction of functional nano protein assembly

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Protein self-assembly into exquisite, complicated yet high-ordered architectures represents the supreme wisdom of nature. However, precisely manipulating protein self-assembling behaviors in vitro is a great challenge. By taking advantage of the cooperation of metal ion chelating interactions, host-guest interaction and non-specific protein-protein interactions, accuracy control of the orientation of protein self-assembly has been achieved. We specify the development of artificial selenoenzymes based on self-assembled nanostructures as scaffolds. Several strategies for enzyme design and protein assembly have been developed based on single molecules, supramolecules and nanoparticles.

For example, we utilized a C2 symmetrical protein, glutathione S-transferase (sjGST-2His), with properly orientated metal chelating sites (2His) on the surface as building block. Under the synergic function of metal-coordination and non-specific protein-protein interactions, sjGST-2His self-assembled in a fixed bending way into highly-ordered protein nanorings. This work provides a de novo design strategy that can be applied in the construction of novel protein superstructures.

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COLL 310

Design of functional nanostructured materials

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We will describe our efforts to interface bioactive molecules with nanomaterials to design functional nanocomposites. We have investigated the structure and function of enzymes when immobilized onto nanomaterials such as carbon nanotubes. We have also been exploring an enzyme-based approach to combat pathogenic bacteria. We will describe an approach that we have recently developed to identify novel bacteriolytic enzymes targeting a variety of bacterial pathogens. We will also discuss the incorporation of these enzymes into antimicrobial nanocomposite films.

COLL 311

Peptide assembly for nanoparticle fabrication in complex shapes and the shape matters for drug delivery efficiency in cancer cells and MR imaging

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It has been a challenge to fabricate nanoparticles less than 15 nm in complex shapes. We developed a new method to fabricate such inorganic nanoparticles by controlling desorption of atoms from seed nanocrystals in peptide self-assemblies. In this compartment, atomic desorption is accelerated from specific crystalline faces of seeds based on the surface energy landscape controlled by the peptide assembly, and this balancing allows one to evolve shape and structure of inorganic nanoparticles into targeted designs. Iron oxide nanocages were succeeded in incorporating drugs inside the cavity and cancer cells were killed more efficiently when the cage-shaped nanoparticles were applied as carriers as compared to spherical and cubic iron oxide nanoparticles. The MRI activity of iron oxide nanocages and the effect of peptide assembly on the nanocage for cell penetration will also be discussed.

COLL 312

Building hybrid architectures for optical sensing and protonic devices with solid binding proteins

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There is growing interest in using combinatorially-selected solid binding peptides (SBPs) to control inorganic growth and morphogenesis and to assemble hybrid architectures across lengthscales. One of the advantages of SBPs is that they can be seamlessly incorporated at defined location of larger protein scaffolds through standard molecular biology techniques. This opens the door to combining the adhesive and/or growth-modifying properties of SBPs with the biological activity of proteins (transport, enzymatic, ligand binding, self-assembly, etc.) to produce new or improved functional architectures and devices. In this presentation, I will illustrate these concepts with two recent examples from our laboratory. The first describes the construction of a variant of green fluorescent protein capable of mineralizing luminescent ZnS:Mn nanocrystals and binding silica microparticles, and its further modification with a DNA aptamer to enable rapid visual detection of UV-absorbing contaminants in water samples. The second focuses on the design of a palladium-binding variant of *H. turkmenista* deltarhodopsin and its integration with palladium hydride contacts to produce a protonic device in which light-activated proton transport to the protode surface and subsequent hydrogen intercalation within its structure correlates with an electrical signal.

COLL 313

Charge effects on the self-assembly of protein block copolymer nanostructures

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Protein-based materials show a great deal of potential as catalysts, sensors, and optoelectronics, where the unique efficiency, selectivity, or activity of enzymes can be captured to improve the performance of these devices. Control over the structure and orientation of the protein in three dimensions is required to improve transport through the devices, increase the density of active sites, and optimize the stability of the protein. The self-assembly of globular protein-polymer conjugates or fusion proteins into nanostructured phases provides a simple method for structural control in biomaterials, where the conjugates or fusions may be envisioned as block copolymers with the globular protein as one block. Self-assembly of the materials in thin films can produce highly functional biocatalysts and materials with potential applications in sensing.

Electrostatics play a major role in the self-assembly of these structures from aqueous solutions. While the specific surface distribution of charge on the protein plays a relatively minor role in self-assembly, large changes in the protein charge (i.e. supercharging) have a large impact on the concentration at which the proteins self-

assemble. While for near-neutral proteins salt screening promotes disassembly and suggests that electrostatic interactions are attractive, proteins with a highly asymmetric charge have repulsive interactions that suppress self-assembly. Using a zwitterionic block in the bioconjugate was also explored as a means to promote self-assembly; however, zwitterionic fusions self-assemble over a narrower range of composition than fusions of any of the nonionic polymers explored. This suggests that dipolar attractions in charge-asymmetric protein-polymer materials play a significant role in the driving force for self-assembly. However, the sensitivity of zwitterionic materials to salt conditions in the buffer also provides a powerful handle for tuning polymer solubility, enabling salt to be used as a method to induce self-assembly.

COLL 314

Atomistic modeling of biologically active nanoparticles and nanomedicines

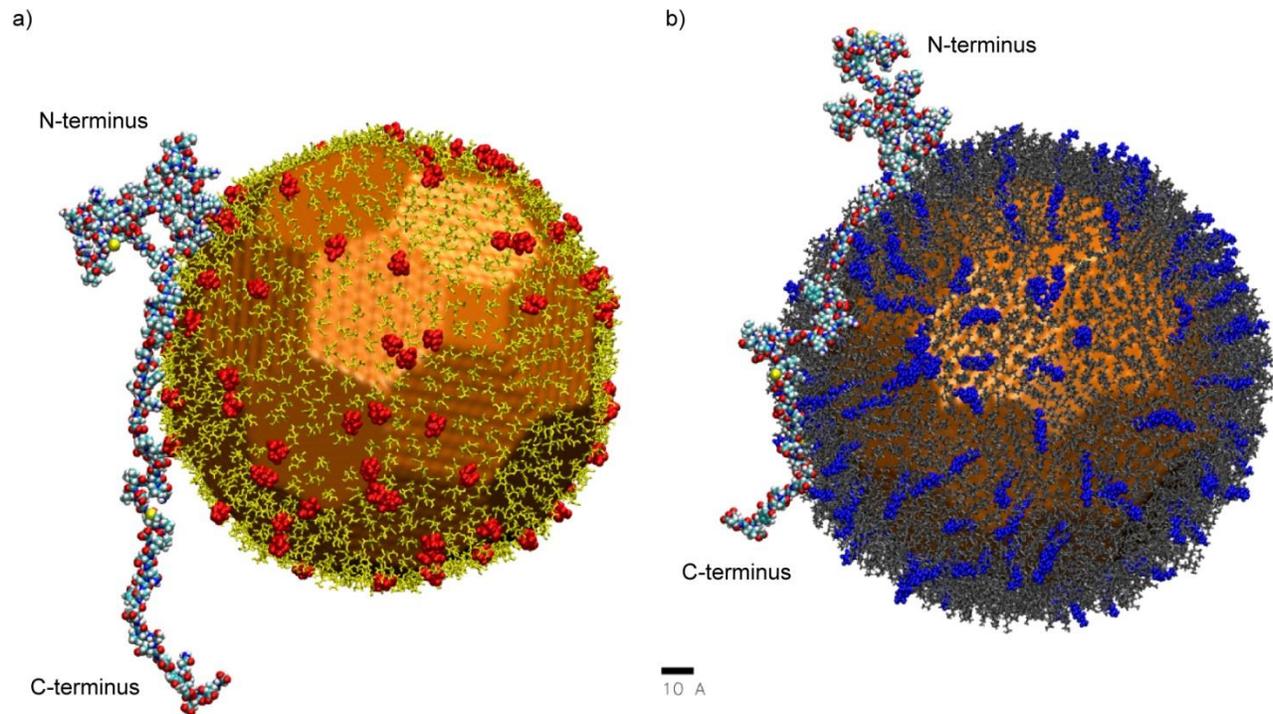
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First, we discuss our collaborative studies of colloidal nanoparticles with bio-active ligands. In our modeling of protein corona, we examine how different types of ligands control the adsorption, configuration and activity of proteins on nanoparticle surfaces [1]. Next, we investigate how nanoparticles couple to and affect the functions of larger cellular and biological units, such as viruses and peptide fibers [2]. In our collaborative modeling of nanomedicines, we discuss the stability of micelles, their ability to carry drugs, and their interaction with membranes and receptors [3]. Many different types of monomeric units are considered and compared in these nanomedicines.

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VMD rendering of α -syn's simulated interaction with individual citrate-capped (a) and MTAB-capped (b) Au NPs, where 10 % of citrate and MTAB ligands are charged [1].

COLL 315

Multifunctional nanoprobes for targeted photoacoustic imaging and photothermal therapy of cancer stem-like cells

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How to prevent gastric cancer occurrence and metastasis is a great challenge. Current study shows that gastric cancer (GC) is one kind of stem cell disease, which has a great influence on tumor initiation and metastatic behavior. Gastric cancer stem cell (CSC)-focused therapy is destined to be one of the most promising paths in anticancer strategies. Herein, we report that branched gold nanostars (GNSs) are chosen as potential photothermal therapy (PTT) agents due to their excellent photothermal conversion efficiency in the near-infrared window and photoacoustic (PA) properties. Anti-CD44-V6 antibody-linked GNSs (GNS-PEG-CD44-V6) were synthesized to target imaging and photothermal ablate CD44 positive GCSCs both in vitro and in vivo. The multifunctional probe could combine with GCSC spheroid clones actively and destroy them completely in an extreme low power density near infrared (NIR) laser treatment (790 nm continuous wave laser, 1.5 W/cm², five minutes). The tumors grown on nude mice could be clearly shown in the fourth to sixth hours by in vivo infrared microscopic and PA imaging. NIR laser irradiation is then applied to the tumors grown on GNS-PEG-CD44v6-injected mice, obtaining an outstanding photothermal therapeutic efficacy.

These results imply that targeting GCSC therapy by the CSC marker modified GNSs is a promising new strategy for GC treatment in the future.

COLL 316

Plasmonic ruler: From cells to detection of micrometastasis in patients

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Here we will discuss how our discovery of the effect of plasmon resonance coupling in imaging of cancer cells using immunotargeted gold nanoparticles has led to development of a new approach toward detection of micrometastases in vivo. In our initial experiments, we showed that labeling of cancer cells using gold nanoparticles targeted to epidermal growth factor receptor (EGFR) is associated with a progressive change in nanoparticle colors from green to red-NIR due to nanoparticle aggregation through the process of cellular endocytosis. We demonstrated in animal models of a metastatic head and neck cancer that this effect in combination with photoacoustic imaging can be used in detection of micrometastasis as small as just ca. 30 cells in vivo. In this talk we will pay close attention to (i) the importance of nanoparticle surface modifications and quality control for in vivo applications, (ii) the connection between technology development and specific unmet clinical need, and (iii) critical aspects of clinical translation.

COLL 317

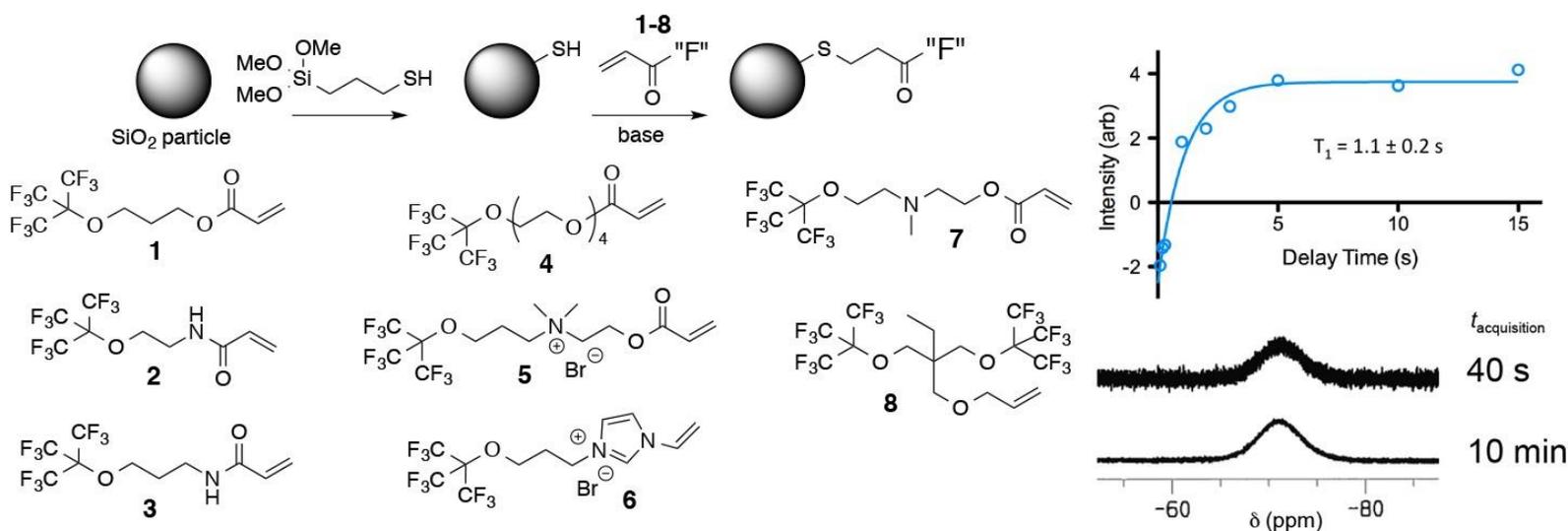
¹⁹F MRI contrast agent based on mesoporous silica nanoparticles

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Novel drug-delivery agents are needed to overcome the limitations of systemic toxicity of traditional chemotherapeutics, and an even more powerful paradigm combines delivery and imaging into one agent. One potential platform for such an agent is nano- or microparticles consisting of mesoporous silica, a well-characterized material with minimal toxicity and with great flexibility for chemical functionalization. Much progress has been made using porous silica particles as multifunctional drug-delivery agents, enabling combined delivery and imaging by incorporating contrast agents for optical detection, PET, and proton MRI. One imaging modality not yet combined with porous particles is ¹⁹F MRI.

Here, we present efforts to prepare multifunctional silica nanoparticles that incorporate

fluorine atoms for detection by ^{19}F MRI. We have synthesized a library of molecules that contain multiple chemically-equivalent fluorine atoms in the form of trifluoromethyl groups. Importantly, the linkers contain a variety of hydrophilic moieties to promote solvation of the fluorine atoms. Also, the fluorinated molecules contain electrophilic groups for facile conjugation to thiol-modified nanoparticles. We have subsequently immobilized these groups to the pores of mesoporous silica nanoparticles that were PEGylated on their exterior surfaces to promote biocompatibility and water-dispersibility. Lastly, we used ^{19}F NMR spectroscopy to detect these immobilized fluorine atoms and measure their magnetic relaxation properties in aqueous systems, demonstrating proof-of-principle that ^{19}F MRI could be used to detect and image these materials.



COLL 318

New approach to achieve enhanced MRI signal using ^{19}F -containing polymeric tracer

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MRI, magnetic resonance imaging, is an extremely versatile and non-invasive anatomical imaging technique that helps to provide early detection and diagnosis of various diseases. Although anatomical resolution of this technique is quite strong, often times intravenous injection of contrast agent (CA) is necessary and toxic. Introducing “second color” to the MRI image using heteronuclear atom such as fluorine (^{19}F) can provide additional anatomical information with the distinct color without using CA. As a result of extensive research, various types of tracer molecules are developed including

small molecules, polymers and hyperbranched structures. However, inadequate sensitivity of ^{19}F -MRI still persists and holds up its application in clinics.

In this study, we designed a multifunctionalized stimuli-responsive amphiphilic polymer that is able to self-assemble in the aqueous environment and well solubilize the highly hydrophobic ^{19}F probe. Tracer contains several magnetically equivalent ^{19}F atoms in order to achieve high signal intensity. In addition to ^{19}F probe, targeted polymer is decorated with stimuli-responsive cleavable moiety that can be removed and improve the segmental mobility of fluorine atoms thus increase the T2 relaxation time. Generally, having shorter T1 (~ 400 ms) and longer T2 (50ms – 200 ms) relaxation time yields better contrast image in MRI. It is previously shown that polymeric tracers have sufficiently short T1, but also quite short T2. Here our main goal is to achieve longer T2 relaxation time by incorporating stimuli responsive moiety into the polymer structure. After mild crosslinking of the polymer in aqueous medium, cleavable moiety is expected to be released when there is an environmental change. Once nanogel forms, morphology of the assembly is locked thus the removal of degradable unit from the assembly interior is expected to improve the segmental mobility of ^{19}F atoms, which eventually leads to longer T2 relaxation time.

We were able to optimize the appropriate ratio of degradable functional group and ^{19}F probe for multifunctionalized polymer, which gives the best signal intensity by using NMR spectroscopy. We observed enhanced T2 relaxation times from 125 ms to 150 ms depending on the ratio of responsive unit and ^{19}F unit. The polymeric tracer has been functionalized with specific targeting group and cell studies has been performed in order to show the imaging capability in-vivo.

COLL 319

Layer-by-layer assembled theranostics in the second near-infrared window for Non-invasive monitoring of ovarian cancer treatment

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Fluorescence imaging in the second near-infrared window (NIR-II) provides anatomical information as NIR-II light (1,000 – 1,700 nm) features deep tissue penetration, reduced tissue scattering, and diminishing tissue autofluorescence. Here, NIR-II fluorescence imaging probes; including down-conversion nanoparticles, quantum dots, single-walled carbon nanotubes, and organic dyes, are constructed into biocompatible nanoparticles (NPs) using the layer-by-layer (LbL) platform due to its modular and versatile design. The layer-by-layer platform has been demonstrated to enable incorporation of diagnostic agents, drugs, and nucleic acids such as siRNA, while providing enhanced blood plasma half-life and tumor targeting. This work carries out head-to-head comparisons of currently available NIR-II materials with identical LbL coatings with regards to their biodistribution, pharmacokinetics, and toxicity. Overall, down-conversion

nanoparticles showed optimal biological and optical performance, and were evaluated as a diagnostic for high-grade serous ovarian cancer. Successful detection of orthotopic ovarian tumors was achieved by *in vivo* NIR-II imaging and confirmed by *ex vivo* microscopic imaging. Furthermore, we constructed a theranostic platform comprising of down-conversion nanoparticles for diagnosis and cisplatin/paclitaxel combination for tumor suppression. We successfully monitored the orthotopic ovarian tumor regression in the non-invasive manner. Therefore, based on NIR - II probes, we have firstly established a versatile and modular theranostic platform for disease treatment and diagnosis.

COLL 320

Hydrophobic mesoporous silica nanoparticles as fluorocarbon-free nanoscale ultrasound contrast agents

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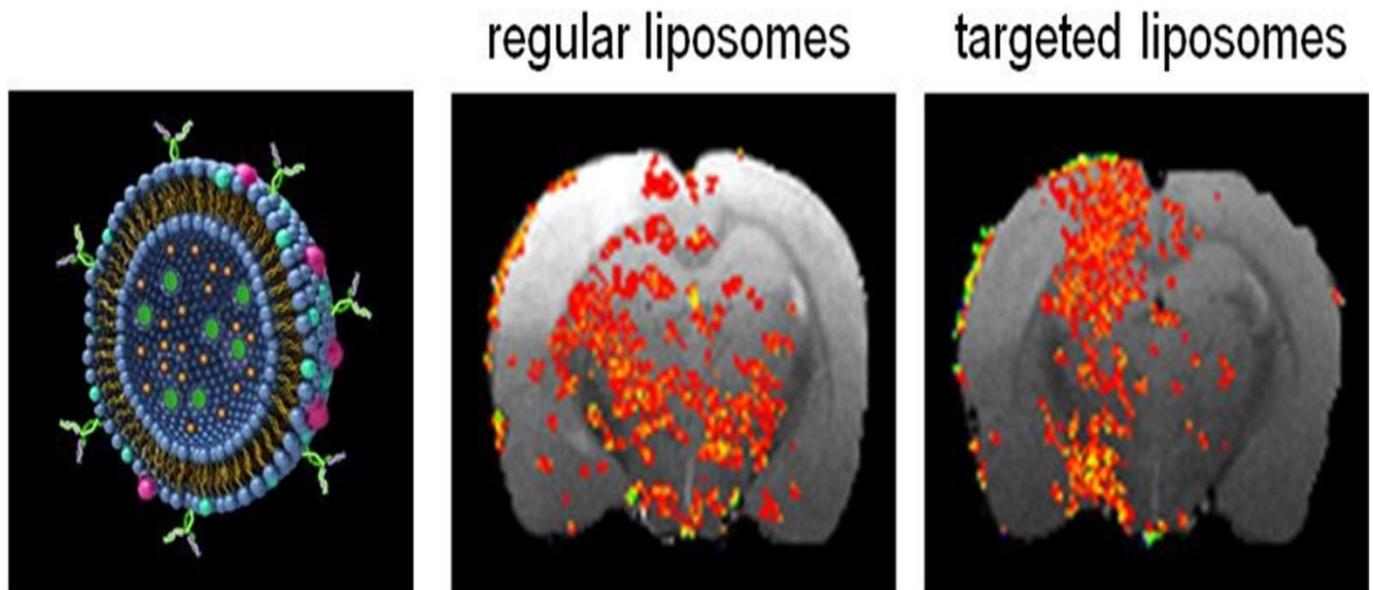
Ultrasound imaging, with its substantial tissue penetration depth, safety, low cost and real-time imaging capability, is a widely-used imaging technique. However, poor contrast of soft tissues results in a low spatial resolution in the ultrasound images and decreases the diagnostic precision of this method. The gas-filled microbubbles can remarkably enhance the signal-to-noise ratio of the ultrasound images; however, microbubbles suffer from short circulation lifetimes and poor extravasation from the blood due to their large size. While better extravasation and pharmaceutical properties can be achieved by utilizing sub-micron sized contrast agents, these approaches provide limited contrast enhancement due to the lower acoustic scattering cross-sections. Here, we describe a distinct nanoscale ultrasound contrast platform using air-containing mesoporous nanoparticles (~100 nm diameter) with hydrophobic (octyl) functionalization. After suspension with Pluronic F127, the particles were stable in buffer and serum. While ordinarily mesoporous silica is hydrophilic, functionalization of the silica surface with octyl groups created pores that remained filled with air. When exposed to high intensity focused ultrasound (HIFU), these particles produced an observable ultrasound response, down to a particle concentration of 6×10^9 particles mL^{-1} , with no background signal and imaging could be sustained continuously for at least 20 minutes. Both the presence of the mesopores and their hydrophobic functionalization were found to be essential for obtaining contrast, but addition of only 0.5 v/v% ethanol quenched the ultrasound contrast dramatically. These studies supported the hypothesis that entrapped air could be pulled into bubble nuclei, which could then act as scatterers for ultrasound imaging. Finally, the particles could be lyophilized and reconstituted with no loss in contrast, and the particles showed very little hemolysis in whole blood, indicating their potential for blood pool imaging.

COLL 321

Magneto-liposomes for magnetic resonance imaging theranostics

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The use of liposomes and other colloidal nanostructures for theranostic (therapeutic plus diagnostic) applications has become very popular in recent years. The possibility to introduce imaging probes of different nature in their structure, particularly MRI contrast agents, allows the multimodal *in vivo* tracking of the fate of these molecules in the living organisms, providing very important information of their biological properties and the mechanisms of disease in which they are involved. The possibility to simultaneously load the particles with therapeutic agents, for their transport and controlled release, and their labeling for targeting specific organs, tissues or cell types, is boosting the field of nanomedicine. In this work we will discuss about the advantages and disadvantages of the use of magneto-liposomes and other colloidal structures in the field of theranostics through practical examples, with particular emphasis in cerebrovascular and cardiovascular diseases.



COLL 322

Multifunctional silica nanoparticles for MR imaging and high intensity ultrasound ablation

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High intensity focused ultrasound is an effective ultrasonic ablative technique that can be used as a minimally invasive surgical tool for benign prostate hyperplasia or prostatic cancer, which are otherwise difficult to treat with current methods. Transurethral incision is highly invasive, while microwave therapy and needle ablation techniques cannot be precisely controlled due to thermal deposition across the tissue. 500 nm silica nanoparticles infused with Gd or Mn have been developed as an ultrasound sensitizer for transurethral high intensity ultrasound ablation. The silica nanoparticles lower the ultrasonic ablative threshold towards a safer range and localize the ablative region to where the nanoparticles are injected. The presence of gadolinium or manganese infused in the silica shell imparts the additional function as a contrast agent for magnetic resonance imaging (MRI) and magnetic resonance thermometry. Electron energy loss spectroscopy and inductively coupled plasma optical emission spectroscopy have been used to quantify the Gd/Mn deposition on the silica nanoshells. *Ex vivo* liver injected with Gd/Mn silica nanoparticles have been used to study ablation area with different high intensity ultrasound powers and duty cycles. The MRI signal intensities have been corresponded to the Gd/Mn deposition concentration on the silica nanoparticles. With the presence of Gd/Mn silica nanoparticles, ultrasonic based thermal ablation can be monitored in real time with MRI and MR thermometry to control the area of tissue thermal gradient.

COLL 323

Ultrasound activated film for *in vivo* biomedical marker

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Bio-imaging of medical devices or surgical retain items in human body is always a challenge. We developed an ultrasound responsive thin film which could be attached to the surface of diversity materials such metal, plastic and glass. The film contains silica hollow shells and poly(cyanoacrylate) matrix. The polymer cross links the particles and bonds the film on medical devices such as surgical tools, medical catheters and other artificial implants. The polymer also blocks the pores in silica shells and keeps air in the hollow space as ultrasound contrast agent. Electric microscope found a domain of polymer and a domain mainly containing hollow shells in the film which indicates a macrophase separation happens during the polymerization. This ultrasound activated film gives strong color Doppler signals with widely used clinic ultrasound equipment. Devices coated with the film can be easily identified in human tissues and organs. The

ultrasound signals have good persistence which means they can be located after several hours in tissues.

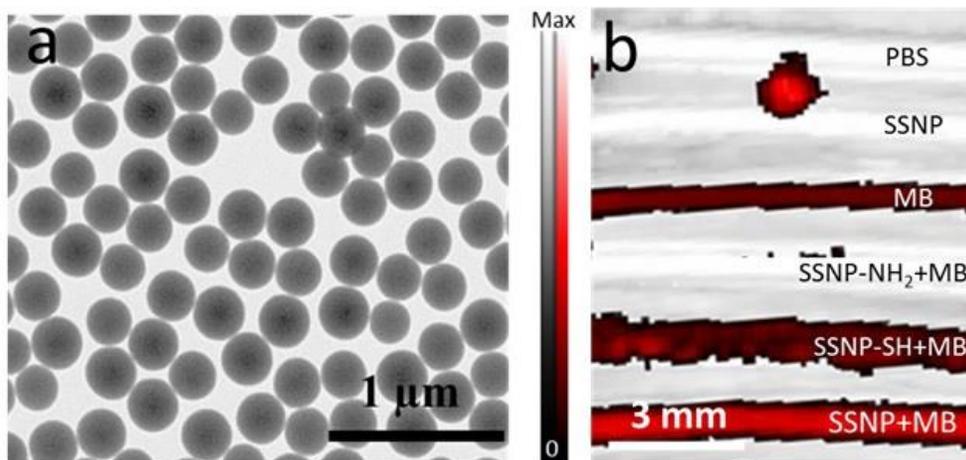
This technology provides a safe, low cost and fast method to locate the biomedical devices in vivo compared to other detection methods such as X-ray, MRI and CT. It has potential applications on small medical device tracking, biopsy marker locating and other implants identification.

COLL 324

Stöber silica nanoparticles can concentrate methylene blue for a charge-tunable photoacoustic imaging agent

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Stöber silica nanoparticle (SSNP) can concentrate methylene blue (MB), an FDA-approved dye for photoacoustic (PA) imaging, for cancer and cell tracking application. However, its negative surface charge reduces their uptake by cells whose membranes are also negative charged. Here, we demonstrate a SSNP that has both a modulated surface potential and a high concentration of MB dye. The size (263 ± 18 nm) and uniformity of SSNP were measured under transmission electron microscope (**Figure a**). The surface potential of SSNP, originally -41 mV, changed to 24 mV and -31 mV by coupling with (3-aminopropyl)triethoxysilane (APTES) and (3-mercaptopropyl)trimethoxysilane (MPTMS), respectively (i.e. SSNP-NH₂ and SSNP-SH). Unmodified SSNP offers 48-fold and 2-fold better loading efficiency than SSNP-NH₂ and SSNP-SH, respectively. All three samples were incubated in 0.8 mM MB overnight and washed 3 times (i.e. SSNP-NH₂+MB, SSNP-SH+MB, SSNP+MB). Vis-NIR spectra showed that 1 mg/ml SSNP can capture at least 3 nM MB, and all SSNPs showed stable and only negligible MB release (<12 %) after the third wash. The SSNPs were prepared in small tubing placed in parallel for ultrasound and PA scanning, respectively. **Figure b** shows the ultrasound (grey) and PA (red) signal. The PA signal of SSNP+MB is 2.5 times and 1000 times higher than SSNP-NH₂+MB and SSNP-SH, respectively.



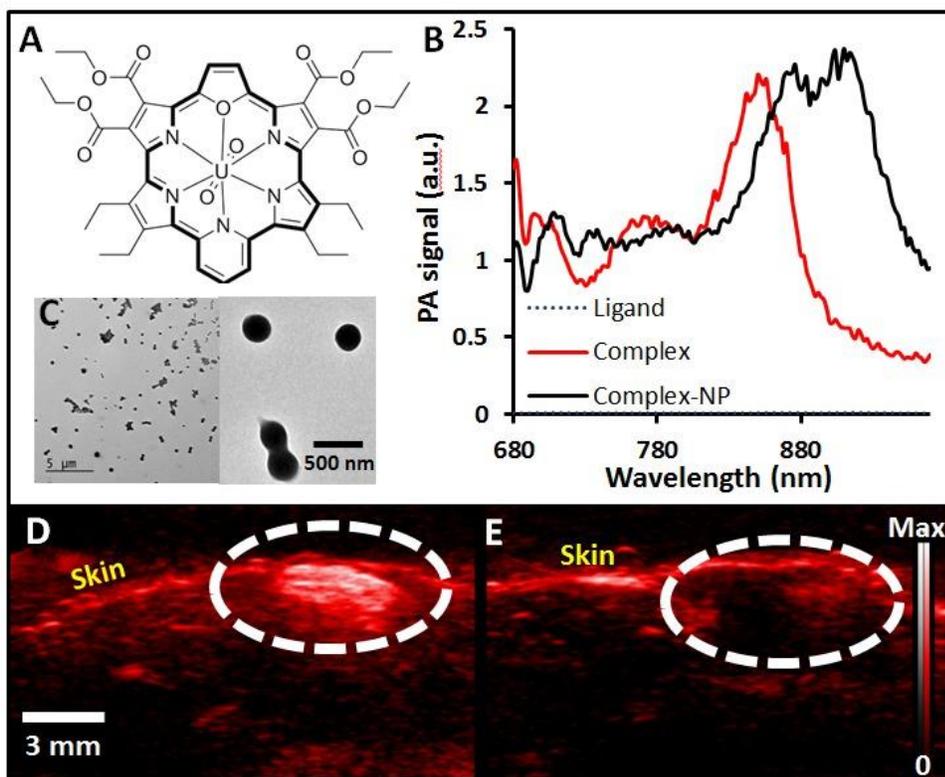
COLL 325

***In vivo*, ppb uranium detection via a porphyrinoid-containing nanoparticle and *in vivo* photoacoustic imaging**

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Defense agencies need chemical tools that can identify, sequester, and quantitate dangerous radioisotopes. Here, we report a hybrid macrocycle, cyclo[1]furan[1]pyridine[4]pyrrole and its uranyl analogue (**Fig. 1A**) that can measure uranium via photoacoustic imaging. The photoacoustic spectra of the ligand- and uranium complex-containing porphyrin analogues (in organic phase) are shown in **Figure 1B** and highlight the 65-fold signal amplification in the uranium containing system. To use these chemical sensors *in vivo*, we encapsulated both the empty and uranium complexed macrocycle in PLGA (**Fig. 1C**). The nanoparticles were 256 nm, as inferred from dynamic light scattering with a poly-dispersity index of 0.166. They contained approximately 29,000 uranyl cations per nanoparticle in the activated sample. The nanoparticles offered a dose-dependent photoacoustic signal with an *in vitro* detection limit of 57 ppb uranium. The *in vivo* sensitivity was tested by implanting 100 μ L boluses of uranium complexed nanoparticles into healthy mice ($n=3$) with a 50% matrigel carrier and imaging with 910 nm excitation and a 21 MHz center frequency transducer (**Fig. 1D**). The lowest concentration detectable versus sham injection was 570 ppb uranium (0.076 nM nanoparticles). The *in vivo* imaging data was validated with inductively coupled plasma-mass spectrometry, which showed that the bolus of uranium complex NPs had 800-fold more uranium than the bolus with empty macrocycle also implanted *in vivo* (**Fig. 1E**). This is the first example of specific molecular-level information via porphyrinoids and photoacoustic imaging.

Ref: Ho et al. *Analyst*, 2015. DOI: 10.1039/C5AN00207A



COLL 326

Multifunctional catalysis for low temperature upgrade of biomass

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C-O bond hydrogenolysis as a means to reduce oxygen content is ubiquitous in biomass upgrade. Yet, general strategies for achieving this transformation are lacking. Recently, we have developed a low-temperature, moderate-pressure, liquid-phase catalytic transfer hydrogenolysis process (CTH) process to convert furfural to 2-methyl furan (2-MF) with a yield of ~80%, utilizing secondary alcohols as hydrogen donors over a Ru/RuO₂ catalyst. 2-MF is a renewable platform chemical that can be used as a drop-in fuel or can be further converted to jet fuels, lubricants, and aromatics.

In this talk we unravel the mechanism and the functionalities of hydrogenolysis in metal/oxide catalysts by combining density functional theory, microkinetic modeling, and isotopic labeling experiments. We find that furfural undergoes Meerwein-Ponndorf-Verley (MPV) reduction over RuO₂ Lewis acid sites to form furfuryl alcohol (FA). In the subsequent FA hydrogenolysis to 2-MF, we elucidate the role of RuO₂ oxygen vacancies. A radical mechanism of C-O bond hydrogenolysis is exposed in agreement with deuterium distribution, obtained in our H/D labeling experiments. Crystal Orbital

Hamilton Population, Born-Haber, and spin density analyses are employed to identify key factors responsible for high hydrogenolysis activity over metal/metal oxide catalysts. The insights are used to propose suitable catalytic materials for these transformations.

COLL 327

Atomic-scale observations of heterogeneous catalyst reactions at up to atmospheric pressure

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Observation of heterogeneous catalysts at operating pressure and temperature is important for studying the dynamics of catalyst restructuring, catalyst sintering and the role of morphology on reactivity. Impressive advances in our understanding of catalysts were made possible through the use of Environmental Transmission Electron Microscopy (ETEM). However, the ETEM approach required a differentially pumped TEM and the introduction of gas into the microscope column, limiting the operating pressure to a few Torr. There are many applications, such as automotive exhaust catalysis, where some of the phenomena do not occur at low pressures, and operation at atmospheric pressure is essential. In our studies we have used a Protochips AtmosphereTM closed-cell holder that confines the gas within a very thin (~5 μm) path between a Protochips AduroTM MEMS-based heater device and a thin amorphous SiN window. The catalyst is dispersed onto the Aduro heater, and can be heated to 1000 °C at up to atmospheric pressure, with closed-loop control independent of gas composition and pressure. Using this approach we are studying Pt and Pt-Pd/alumina diesel oxidation catalysts under “realistic” conditions, obtaining atomic-level STEM images in a JEOL 2200FS aberration-corrected STEM/TEM. In this presentation we will describe a study of the role of Pd in enhancing the stability of Pt-Pd diesel oxidation catalysts.

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COLL 328

Understanding the activity of Pt-Re bimetallic catalysts

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The Pt-Re bimetallic catalysts are known to exhibit superior catalytic activity compared to Pt alone; the Pt-Re system has been used for decades in industrial reforming reactions, and more recently Pt-Re catalysts have demonstrated enhanced activity for the water gas shift (WGS) reaction and aqueous phase reforming of polyols. In order to understand this improved activity of Pt upon addition of Re, it is necessary to control bimetallic cluster composition, cluster sizes and oxidation states of the Re, as well as to probe Re oxidation states under reactions conditions. We have prepared and characterized Pt-Re bimetallic clusters on titania, which most active support for WGS, in ultrahigh vacuum. The activity of these model surfaces were then studied by temperature programmed desorption as well as in a microreactor coupled to an ultrahigh vacuum chamber so that Re oxidation states can be probed before and after reaction without exposure to air. Activities of the supported Pt-Re clusters are also compared with Pt-Re alloys and Re thin films grown on Pt(111) in order to the separate the influence of cluster size effects and cluster-support interactions from Pt-Re interactions.

COLL 329

Improving the accuracy of DFT modeling of electrochemistry

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Density functional theory (DFT) has since long established itself as the standard theory to calculate many properties of matter from first principles, and to give insight and rationalize experimental results. The popularity of DFT is mostly due to its Kohn-Sham approximation method that occupies a "sweet spot" at the intersection of accuracy and computational cost.

As a first approximation, one can model any charge transfer process as a modification of the occupation of Kohn-Sham orbitals in a static point of view. Indeed, following this idea, the calculated electronic properties of thiol-protected gold clusters have been successfully used to model charge transfer processes in electrochemistry [1,2]. However, when more complex systems and processes are involved, or when higher accuracy and level of prediction is required, one needs to devise a strategy that identifies the shortcomings and strengths of every available method and optimizes the accuracy/CPU time ratio by combining different approaches.

Motivated by the study of amorphous carbon (a-C) electrodes to measure concentrations of neurotransmitters in the human brain, we performed simulations aiming at understanding the charge transfer process between the a-C electrode and the biomolecule using an efficient combination of Kohn-Sham DFT, hybrid-functional DFT and classical molecular dynamics, among other approaches. This ranges from generating the a-C network that makes up the electrode material [3], to describing the

water/electrode interface [4], to predicting redox potentials for the molecules of interest.

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COLL 330

Analyzing the case for bifunctional catalysis

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Computational screening based on scaling relations has proven highly successful in rationalizing, why efficient catalysts are often found within only a narrow range of binding energies that allow the dissociation of reactants without hindering the formation of products [1]. It has been suggested that these severe limitations in material space could be overcome by bifunctional catalysts, which couple two active sites, each catalyzing a particular reaction step. Using global optimization techniques and microkinetic modeling in the mean-field (MF) approximation, we explore the theoretical limits for such a bifunctional gain for a wide range of model reactions. This analysis suggests that bifunctional catalysts made from two active sites of similar type, i.e. controlled by similar scaling relations, will generally only lead to negligible bifunctional gain. We correspondingly aim to quantify how "different" the two active sites must be in order for the idea of bifunctionality to work.

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COLL 331

Nickel-gold single and multiple atom alloys; understanding the relationship between atomic geometry and chemical reactivity

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Hydrogenation and dehydrogenation reactions are central to the petrochemical, fine chemical, pharmaceutical, and food industries and are of increasing interest in energy production and storage technologies. Typical heterogeneous catalysts often involve noble metals and alloys based on platinum, palladium, rhodium and ruthenium. While these metals are active at modest temperature and pressure, they are not always completely selective and are expensive. We have previously demonstrated that single palladium or platinum atoms can convert the otherwise catalytically inert surface of an inexpensive metal into a highly selective and cost effective catalyst. In this talk I will describe our recent results that provide a direct link between the active site composition of NiAu alloys and their ability to activate and dehydrogenate alcohols. We used high resolution imaging to characterize the active sites and temperature programmed reaction spectroscopy to probe the chemistry. These studies benefit from our benchmarking work measuring the CO binding strength as well as the energy landscape for the interaction of hydrogen and oxygen on the alloys.

COLL 332

Active gold on active oxides

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Gold nanoclusters, dispersed on well-defined metal-oxide films or doped bulk oxides, are interesting model systems to study many basic catalytic reactions involving electron transfer between the metal and reactants. These systems are also amenable to high-level atomistic ab initio studies. Here we discuss recent density-functional theory computations that demonstrate how gold reacts with ambient oxygen and can activate CO₂

COLL 333

Epitaxially controlled self-assembly of lumazine derivatives on SWNTs

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In order to harness the unique quantum-confined properties of single-walled carbon nanotubes (SWNTs), one needs to reduce bundling while providing them with a uniform physicochemical environment. The sharpness of the SWNT electronics transitions

comes from the homogeneity of the surrounding environment. The larger linewidths of solution-suspended SWNTs typically arise from light aggregation as well as a variety of defects in the coverage of physisorbed surfactants that wrap around SWNTs. Moreover, the susceptibility of exposed SWNT regions to differential doping by H^+/O_2 and other reagents (*i.e.* amines, conjugated molecules, nanoparticles, *etc.*) further enlarge linewidth broadening. Tubular surfactant assemblies such as flavin mononucleotide (FMN) and single-stranded (ss)-DNA are good surfactant candidates since their helical repeat approaches the SWNT exciton Bohr radius, self-organizing on top of the graphene sidewalls to anneal out vacancies that expose the bare nanotube to entities like O_2 . Since tubular organization implies the need for surfactant cooperativity, elucidation of factors that affect such assembly holds great promise towards involving SWNTs in increasingly complex architectures. A C12 aliphatic analog of FMN (FC12) was already shown to possess the narrowest linewidth currently reported. In the case of FC12, the π - π stacking with lateral electrostatic and H-bonding interactions facilitates the formation of ordered helical assemblies that exhibit quasi-epitaxial recognition to the underlying (n,m)-cylindrical graphene lattice, resulting extremely tight FC12 assembly around SWNTs that prevents nanotube bundling through surfactant dissociation as well as leaves no room for O_2 to diffuse through the helix. Hence in this contribution, our target is to show high self-assembled surfactant order with the introduction of controlled defect within the Bohr radius of SWNT exciton or in other word, introduction of ribbon of defect within the ribbon of self-assembled surfactants. For this purpose, we designed a Flavin analogue (Lumazine derivatives) that while wraps the carbon nanotubes in the same way, it exposes well-defined portion of pristine-SWNT that are amenable to physicochemical interactions with the surrounding environment as the wrapping remains intact.

COLL 334

Polymer substituted vertically aligned carbon nanotube membranes for protection against warfare agents

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Current research efforts are aimed at developing hybrid polymer-vertically aligned carbon nanotube (CNT) membranes that are breathable in their native state but become blocked upon exposure to low levels of chemical warfare agents (CWA). Our approach utilizes polymers formed by ring opening metathesis polymerization (ROMP) that have a highly non-planar structure in their neutral resting state to retain the high moisture vapor transport rate of the CNT membranes. Upon reacting with CWAs, these polymers can ionize and planarize, assuming a cationic, aromatic structure. This π -stacking drives a gel collapse that will block the CNT pores. These types of polymers have been grafted from the membrane using surface initiated ROMP (SI-ROMP) on norbornene-substituted surfaces. The characterization of these responsive polymer substituted surfaces and their utility as protective membranes will be discussed. Additionally, the

grafting of polymers from other surfaces and materials and related applications will be presented.

COLL 335

Solution processable molecular transport junctions employing carbon nanoelectrodes

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One of the ultimate goals in nanotechnology is the ability to produce efficient devices based on individual molecules and nanostructures. Despite the many potential benefits envisioned for single-molecule technology (in electronics and biotechnology) the strategies employed to date suffer from various limitations. Among these limitations are the poor control over the molecular assembly and the lack of suitable technologies for the establishment of electrical contact between molecules and electrodes. This results in devices with poor performance, low yield and limited versatility.

Building on our novel bottom-up assembly strategy for the formation of (chemically and geometrically) versatile carbon nanotube (CNTs) junctions,^[1] we present a universal approach for the generation of multifunctional nanomaterials that employ molecular building blocks assembled between CNT electrodes. We will demonstrate single-molecule control in the formation of molecular transport junctions in 1-dimensional configurations via the in-solution assembly of a series of oligophenyls to DNA wrapped CNTs.

We have linked separate metallic single-walled CNTs (SWCNTs) with different conjugated molecular linkers. The so formed CNT-based molecular junctions were interfaced to gold electrodes, and Conductive Atomic Force Microscopy measurements were performed at different locations along the SWCNT junction. This allowed us to measure not only the resistance of DNA-wrapped CNTs but most importantly the molecular conductance of a variety of conjugated molecular wires bridging the nanotubes^[2]. We will further illustrate advances in the controlled assembly of DNA wrapped CNTs into 2-dimensional architectures. In-solution processes allow for the formation of side-by-side configurations rather than 1-dimensional assembly. 2-dimensional assembly has been achieved with single and multi-walled CNTs via multiple linkers, illustrating a versatile technique.

The advantages and novelty of our strategies are: i) single-molecule control over the molecule-nanoelectrode interface, ii) the low-cost/simplicity via assembly in solution rather than through a top-down approach, iii) the versatility of junction formation and iv)

the formation of 1- and 2-dimensional architectures. Because of current limits in the assembly of nanoscale devices, we believe the knowledge developed makes a significant contribution towards the facile fabrication of solution processable systems for single-molecule investigations.

COLL 336

Photoluminescence quenching of single-walled carbon nanotubes through C₆₀: Functionalized flavin helices

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Attaining solution processability together with elevated SWNT concentrations and high degree of individualization presents one of the greatest challenges in nanotubes Photovoltaics. While covalent functionalization can ultimately prevent phase separation, the interruption in the extended π -conjugation of SWNTs dramatically reduces both carrier mobility and uniformity of pristine SWNTs. Consequently, substantial effort has been directed towards non-covalent functionalization methods. Since these surfactants are difficult, if not impossible, to be removed from SWNT bulk heterojunctions, considerable engineering has gone to outfit them with exciton dissociation capabilities as well. Conjugated polymers are a classic example for such surfactants, whose multi-dentate attachment inhibits SWNT/surfactant dissociation. On the other hand, SWNT dispersion involving C₆₀ and its derivatives were proven more challenging due to their single, as opposed to multi-dentate attraction, with SWNTs. Engineering multi-dentate capabilities to C₆₀ acceptors can, in principle, address this challenge; so long that purity and band-uniformity are equally tackled.

To this effect, the supramolecular organizations of flavin mononucleotide (FMN) around single walled carbon nanotubes (SWNTs) was shown to provide effective nanotube dispersions and the ability to impart selective enrichment of *sem*-SWNTs by recognizing the underlying nanotube helical pattern.

In this work, we report the synthesis of a C₆₀-functionalized flavin (FC₆₀), where a PCBM moiety is attached to an isoalloxazine ring *via* a terminal C-12 aliphatic spacer. Unlike physical mixtures of FC12 and PCBM, their covalent coupling induces an effective photoluminescence (PL) quenching for FC₆₀ in dilute solutions *via* a bended conformation that allows the C₆₀ moiety to form charge-transfer (CT) interactions with the isoalloxazine ring. The equally strong CT interaction with the graphene sidewalls affords only a few percent FC₆₀ incorporation within FC12-dispersed nanotubes. The incorporation of as much as 1% FC₆₀, causes effective SWNT photo-induced CT quenching as indicated by both steady state and transient spectroscopic technique. In addition, the minimal broadening in SWNT E_{ij}^S transitions by the incorporation of few percent of FC₆₀ suggests that such a system could ultimately yield a variety of optoelectronic and electro-optic devices with spectrally sharp response in the visible and NIR.

COLL 337

Keeping graphene clean: Prevention of airborne contamination using water

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Graphitic surfaces undergo rapid contamination in air due to adsorption of airborne hydrocarbons. Although a clean graphitic surface is mildly hydrophilic, such contamination makes it appear to be hydrophobic. For many applications, it is desirable to prevent such contamination. We show that airborne contamination can be substantially reduced by coating a graphitic surface with a monolayer amount of water. The graphitic surface remains hydrophilic for several days after such treatment and maintains its intrinsic electrochemical activity.

COLL 338

Synthesis and characterization of meso-graphene oxide roses for cancer applications

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The geometry and conformation of biological materials are known to determine their correct function in highly selective biological environments. As the tissues for targeted therapies are commonly accessed through the blood capillaries, understanding the correlation between the geometry and flow properties of biomaterials in such confined conduits could provide important insight about their efficacy as both drug delivery vectors and therapeutic modalities. Carbon nanomaterials (CNMs) are emerging as materials of interest in biological applications such as, drug delivery, and tissue imaging, and particularly with respect to their toxicity in cancer tissues. Selective uptake of CNMs had been observed in cancer tissue, and can be utilized for multi-fold applications, such as drug delivery and ablation therapy via localized increases in tissue temperature. Graphene oxide-based CNMs possess notable geometrical variants, such as flat sheets, tubes, scrolls and spheres, and form stable and easily-processed aqueous solutions. In this light, we have developed a synthesis protocol for crumpled graphene oxide assemblies (GO roses) of various sizes comprised of agglomerated graphene oxide sheets. This work provides a platform to investigate the geometry-dependence and the size-dependence of the flow behavior of CNM-based colloids for cancer remediation applications. Water-in-oil emulsions (W/O emulsion), used to fabricate the GO roses, were obtained using a homogenizer. The aqueous phase of the W/O emulsion was rapidly removed from the system via evaporation due to emulsification in hot oil. The evaporation yielded spherical, crumpled meso-structures, ranging from sub-micron to several microns in size. Characterization techniques, such as electron

microscopy and dynamic light scattering, were used to study the morphologies and the size distribution of the as prepared GO roses. A decrease in the average particle size was observed as a function of an increasing homogenizer rotor speed.

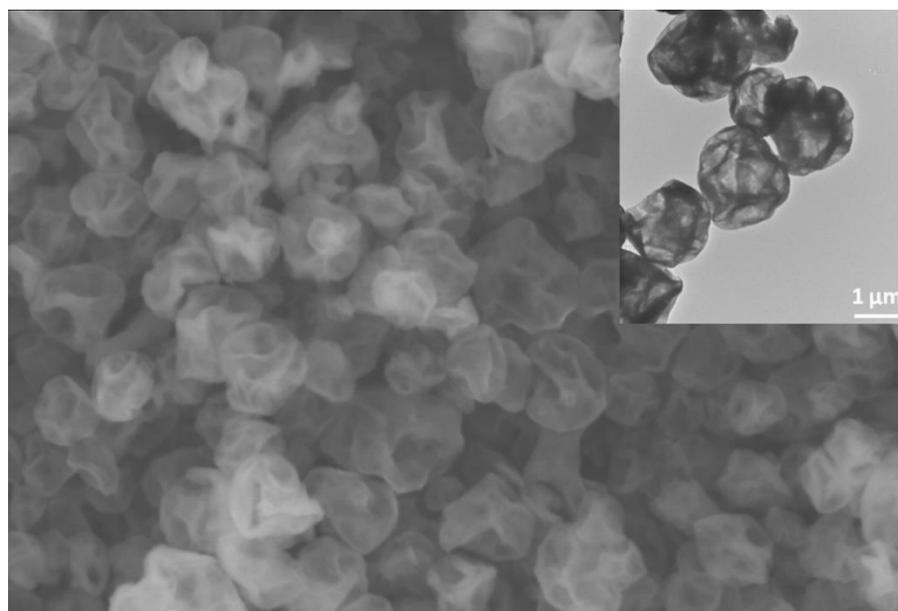
COLL 339

Crumpling of graphene nanosheets for 3D networks preparation

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In this work, aqueous dispersions of pristine graphene nanosheets were prepared using pyrene derivatives as dispersants. Controllable crumpling of these nanosheets was achieved by rapid evaporation of the dispersions in an industrially scalable spray dryer. Morphological transition of 2D nanosheets to 3D crumpled particles was directly observed by sample collection within the spray dryer. Crumpling mechanism depends on parameters such as nanosheets elasticity and surface chemistry and as observed in HRTEM images, it is different for pristine graphene and graphene oxide nanosheets. The particle size and morphology of the products can be tuned by altering the spray drying parameters such as temperature and pressure. Also, the unfolding of the crumpled particles upon rewetting depends on the nanosheet type and the solvent choice.

Furthermore, 3D networks of highly crumpled graphene oxide were prepared using a low-temperature sol-gel technique. These networks display a remarkable homogenous porous structure. The electrical conductivity of these samples is comparable to conductivity values reported for the networks prepared from 2D graphene nanosheets.



Self-assembling of few-layer graphene (FLG) into a fractal-like conductive network, induced by solvent evaporation

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The transcription of properties from low- to higher dimensions in an efficient and simple way by the appropriate design of devices is a challenge. In 2D or 3D systems (films, polymers, composites) containing conductive nano(micro)carbons, the electrical properties of the carbon components are barely propagated through the surface or bulk due to the high percolation threshold, which is related to an insufficient carbon loading, weak contact between individual components (morphological and chemical identity-dependent interactions) and/or their disordered, random arrangement.¹

Here, a self-assembling of FLG into a fractal-like branched conductive patterns at the macrosurface is proposed as a way to achieve percolation at reduced carbon content and lower surface coverage, compared to the random arrangement (Figure 1, below).² The “self-assembling” phenomenon is induced by evaporation of the solvents and the final pattern face depends on the applied conditions. Preliminary studies including few patterns are presented together with the measurements of their electrical conductivity.

This interesting finding recalls the natural tendency of Matter to self-organize into functional systems. The fractal like, branched structures are commonly observed in numerous natural systems being in charge of transport function, such as river beds, trees or neural system.

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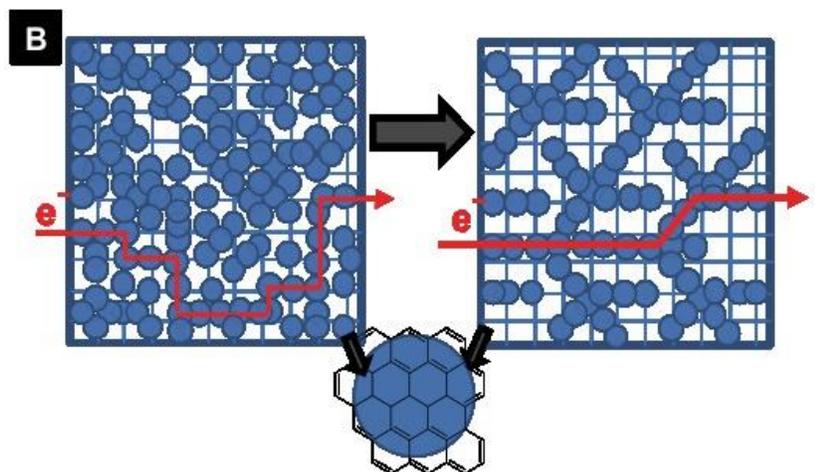
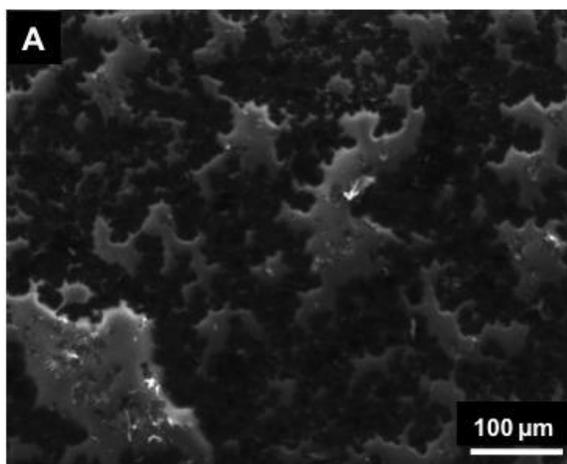


Figure 1. A) Self-assembled branched FLG conductive pattern by SEM, B) The conductive path improvement, from randomly to self-assembled FLG flakes (exemplary path).

COLL 341

Reversible near-infrared fluorescence quenching of flavin suspended single-walled carbon nanotubes

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One of the interesting characteristics of Single-walled carbon nanotubes (SWNTs) is their stable and strong fluorescence at near-infrared (NIR) region. Their fluorescence is highly responsive to their physical and chemical environment, making SWNTs a highly sensitive platform for biological and chemical sensing applications. Particularly, the non-photobleaching, NIR fluorescence of SWNTs provides unique advantages in biological environments over conventional fluorophores, which typically photobleach and emit fluorescence at visible wavelengths, because biological tissues are optically transparent and minimally auto fluorescent at NIR wavelengths. Because the direct covalent attachment of receptors to the nanotube surface invariably extinguishes fluorescent emission from SWNTs, noncovalent and indirect methods of functionalization are required for this purpose. Boronic acids have attracted attention as an alternative receptor to enzymes for saccharide detection. The reversible complexation of saccharides with aromatic boronic acids creates a fluctuation in the electronic properties of aromatic boronic acids which make them a basic scheme for various boronic-acid-based saccharide sensing approaches, including electrochemical, fluorescence and colorimetric measurements. The likely complexation of saccharides with aromatic boronic acids conjugated on the surface of SWNTs, through π - π interactions between the graphene side-wall of SWNTs and the aromatic moiety of the boronic acids, could modulate the SWNT fluorescence signal in response to binding of saccharides. Dispersion of SWNTs by flavin molecules in both aqueous and organic solutions has been already reported. A covalently linked aromatic boronic acid to the flavin molecules wrapped on the graphene side-wall of SWNTs is in proper proximity of SWNTs to establish an efficient photo-induced charge transfer interactions. In this work, we report synthesis of Boronic Acid-functionalized flavin to disperse SWNTs in water to create SWNT-based fluorescent probe for saccharides. Interaction of boronic acid moiety with SWNTs quenches their fluorescence which later would be recovered by addition of saccharide. SWNTs dispersed by boronic acid functionalized flavins can be separated and re-dispersed to get rid of any extra boronic acid in the solution and to substantially increase the detection rate.

COLL 342

Characterizing the differences in adsorbed surfactant and hydration layers around single wall carbon nanotubes using analytical ultracentrifugation

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Over the past decade, numerous methods have emerged for the dispersion and liquid phase purification of single wall carbon nanotubes (SWCNTs). The success and efficiency of the dispersion and purification methods are believed to be strongly dependent on the characteristics of the bound layer of dispersant (such as small molecule surfactant(s) or DNA) both in the amount of bound dispersant as well as the specific structure it forms at the nanotube surface. However, only limited direct measurements of the differences in the bound layers on well-resolved SWCNT populations have been reported. Thus, it is important to elucidate the structure of the adsorbed surfactant and hydration shells around different single species SWCNTs and surfactant-SWCNT complexes, respectively, to quantitatively address the differences in structure that drive differential separation. To study the structure of the adsorbed surfactant layer, we utilize analytical ultracentrifugation (AUC) to resolve the density and radial distribution of adsorbed bile salt surfactants (sodium deoxycholate, sodium cholate) and sodium dodecyl sulfate on different species of SWCNTs at various solution conditions. AUC is a powerful technique which allows for simultaneous sampling of the entire population distribution of a solute (e.g. proteins, DNA, particles). In our experiments, we use single wall carbon nanotubes which have been both chirality and length sorted, giving us a population of particles which not only have a narrow length and diameter distribution, but also unique optical transitions and unique interactions with surfactants. We measure and compare the anhydrous and buoyant radii around multiple semiconducting and metallic SWCNT species dispersed in sodium deoxycholate and provide direct measurements of the effects of adding co-surfactant to the observed sedimentation behavior in the AUC. Such results not only push the current limits of nanoscale metrology but also improve our understanding of contemporary nanotube separation and purification processes on a broader scale by contributing knowledge pertaining to interactions between SWCNTs of different electronic properties with various types of amphiphilic molecules.

COLL 343

Precise chemical, physical, and electronic nanoscale contacts

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The chemical, physical, and electronic connections that materials make to one another and to the outside world are critical. Just as the properties and applications of conventional semiconductor devices depend on these contacts, so do nanomaterials, many nanoscale measurements, and devices of the future. We discuss the important role that chemistry can play in making and optimizing precise contacts that preserve key transport and other properties. Initial nanoscale connections and measurements guide the path to future opportunities and challenges ahead. Band alignment and minimally

disruptive connections are both targets and can be characterized in both experiment and theory.

COLL 344

Nanoparticles interactions

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Interactions between inorganic nanoparticles are central to a wide spectrum of physical, chemical, and biological phenomena. Their understanding is essential for technological implementation of successes of nanoscale synthesis, engineering of self-organized nanoparticle superstructures with various dimensionalities, collective properties at nanoscale, and predictive biological responses to nanoparticles. Recent studies indicate that seemingly small forces can result in large changes in patterns of nanoparticle assemblies. The quantitative description of forces between nanoparticles encounters, however, many difficulties not present, or not as severe, for micro-sized particles. They are revealed in numerous experimental observations that, are, unfortunately, often ignored. Inconsistencies in accounting of nanoparticle interactions are observed across all materials platforms that include ceramic, semiconductor, and metallic nanoparticles, crystalline and amorphous nanoparticles, dispersions of inorganic, organic, and biological nanomaterials. Such systematic deviations of predictions from reality point to the generality of such phenomena for nanoscale matter. In this talk, the analysis of the sources of these inconsistencies and heuristic rules emerging from experimental studies will be presented. Directions for future research that might overcome these inconsistencies will also be discussed.

COLL 345

Responsive polymeric nanoassemblies

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Molecular designs that afford tunable supramolecular assemblies are of interest in a variety of applications, including catalysis, sensing, drug delivery, tissue engineering and diagnostics. When these assemblies are nanoscopic in size and are responsive to specific stimulus, then the interests in these nanoscale scaffolds are even higher. We have developed macromolecule-based amphiphilic supramolecular assemblies, which not only exhibit these features, but also can bind guest molecules efficiently. We have also shown that these non-covalently bound guest molecules can be released in response to specific triggers. The molecular design principle is versatile enough to be adapted for physical, chemical, or biological stimuli. From a fundamental perspective, we divulge the structural factors that underlie the stimuli-responsive behavior of

supramolecular assemblies. From an application perspective, the implications are numerous.

COLL 346

Design rules for thermally reversible bioadhesive thin films

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Environmentally responsive polymer coatings have enormous potential uses in biotechnology, with applications ranging from self-cleaning surfaces to tissue engineering. Several high profile examples demonstrate the utility of thermally reversible Poly(N-isopropyl acrylamide) (PNIPAM) coatings in tissue engineering, because the polymer solubility transition (LCST) of 32°C is close to physiological temperature. However, we postulated that the inability to reproducibly fabricate efficient, thermally reversible bioadsorbant PNIPAM films was due to the limited knowledge of mechanism(s) underlying temperature sensitive bio-adsorption and its relationship to the polymer properties. This talk presents new findings that challenge a widely assumed model of protein (and cell) adhesion to PNIPAM films. These results identified the likely mechanism underlying rapid, reversible, temperature-dependent protein (and cell adsorption) to these polymer coatings. Our findings further inspired the establishment of new design criteria for temperature responsive PNIPAM thin films that reproducibly switch bioadhesion.

COLL 347

Star polymer adsorption and surface forces

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Nanoparticulate polymer brushes, including polymer-grafted nanoparticles and multi-arm star polymers, have unique interfacial properties that make them interesting materials for surface engineering applications. In the context of adsorption at liquid/liquid interfaces, they are demonstrated to be highly efficient emulsifiers. At solid/liquid interfaces, they have demonstrated potential as boundary lubrication agents. Compared to individual polymer chains in solution, these materials are expected to have decreased entropic penalties for adsorption and are thus able to adsorb under a greater variety of solvent quality or surface attraction conditions than would be expected for individual chains. Yet, in the case of polyelectrolyte brushes, where strong lateral repulsions may hinder adsorption under strong brush charging conditions, it remains a challenge to achieve high extents of adsorption under conditions that also favor good solvency and strong (electro)steric repulsive forces between opposing layers. This presentation will compare the interfacial properties of pH-responsive polymer-grafted

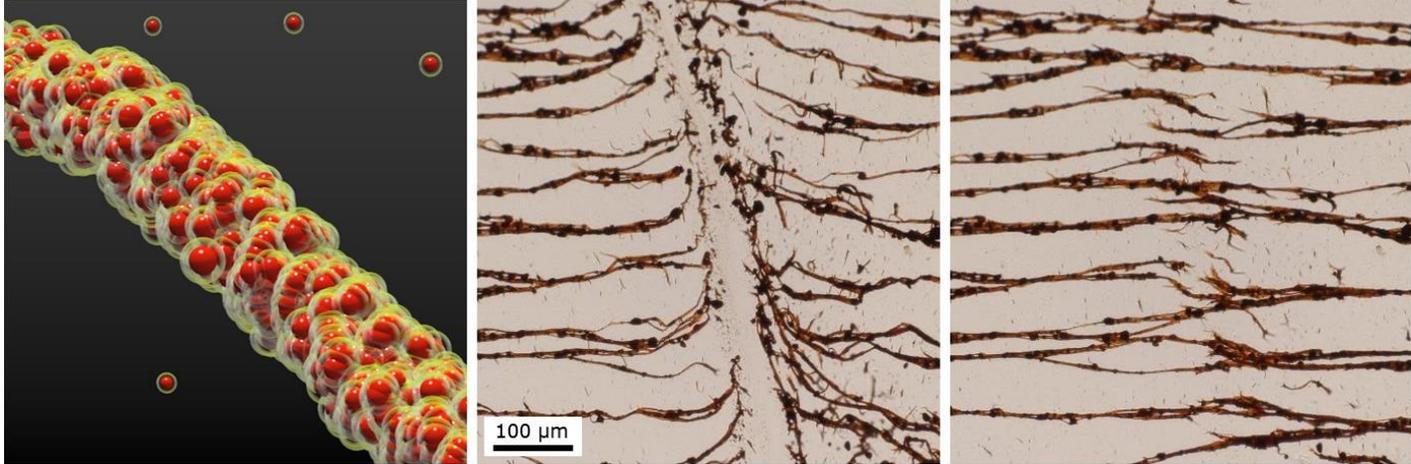
nanoparticles and compact star polymers. The effects of polymer composition and architecture on adsorption and the resulting effects on normal and frictional forces between opposing adsorbed layers will be discussed. Sequential layer processing strategies that exploit the persistence of non-equilibrium adsorption states to maximize adsorption will be discussed as well.

COLL 348

Design of new classes of responsive soft matter by embedding nanoparticle structures in Pickering foams and multiphasic gels

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The properties of multiphase colloidal systems such as foams and emulsions are critically dependent on capillary effects at interfaces and stability of thin liquid films. We will discuss how embedding magnetic field-responsive particles in such systems allows making novel responsive classes of soft matter, including smart foams, emulsions and gels. In the first part of the talk we will present the design and characterization of magnetically responsive Pickering foams that remain stable at ambient conditions, but can be rapidly destroyed upon exposure to a gradient of magnetic field. These foams are stabilized by particles from hydrophobically modified cellulose with magnetic responsiveness imparted through incorporation of carbonyl iron particles into the films. We will also discuss how these systems can be made photo- as well as thermally sensitive, to make new photo-thermo-magneto responsive foams (*Chem. Sci.* 4:3874, 2013). In the second part of the talk, we will describe a new smart gel system containing ultraflexible chains of magnetically responsive nanoparticles formed in multiphase water-oil systems. Liquid lipid shells condensed on the nanoparticles lead to directed assembly of microfilaments and networks via nanocapillary bridges. These liquid bridges allow for particle rolling and sliding, and the resulting chain flexibility was measured to be orders of magnitude higher than any other linear structures reported to date (*Nature Mater.* 14:1104 2015). The physical properties of filaments and gel structures formed by the nanocapillary binding of particles depend on the bridge fluidity, type and lipid composition. The nanoparticles' binding through soft, "snappable" capillary forces provides a facile means of creating self-repairing networks (illustrated below). The nanocapillary bridging could be applied as a tool for multiscale assembly of temperature-responsive and self-repairing gels, complex lattices from Janus and patchy particles, and new types of responsive multiphase composites.



COLL 349

Non-equilibrium colloidal assembly pathways via synergistic dipolar, depletion, and hydrodynamic interactions

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The ability to assemble nano- and micro- colloidal particles into ordered materials and controllable devices provides the basis for emerging technologies. However, current capabilities for manipulating colloidal assembly are limited by the degree of order, time to generate/reconfigure structures, and scalability to large areas. These limitations are due to fundamental problems with designing, controlling, and optimizing the thermodynamics and kinetics of colloidal assembly processes rather than a shortage of available actuators or complex colloidal components. Our approach is to provide viable non-equilibrium kinetic pathways for rapid assembly of defect free colloidal crystals using serial and parallel combinations of magnetic field mediated assembly (to control transport, structural evolution, annealing) and depletion mediated assembly (to produce stable equilibrium crystals). Results include video microscopy experiments and Stokesian Dynamic computer simulations to measure and model superparamagnetic colloidal particles experiencing depletion attraction in time varying magnetic fields. Findings show multi-body hydrodynamic interactions and magnetic dipole relaxation mechanisms are essential to capture assembly and annealing of attractive colloidal crystals. With the ability to measure, model and tune colloidal interactions and dynamics, we demonstrate the use of time varying fields to manipulate non-equilibrium pathways for the assembly, disassembly, and repair of colloidal microstructures.

COLL 350

Specificity and mechanism of an aminophospholipid flippase

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Phospholipid organization in cell membranes is non-random; the choline-containing phospholipids (phosphatidylcholine and sphingomyelin) are enriched in the outer monolayer of the plasma membrane and topologically equivalent luminal surface of internal organelles, while the primary amine-containing phospholipids (phosphatidylserine (PS) and phosphatidylethanolamine) are enriched on the cytoplasmic side of these membranes. This lipid distribution is generated and maintained by asymmetric biosynthesis and the action of several families of selective, and non-selective, lipid transporters. One of these transporters, the PS flippase, transports and concentrates this lipid on the cytofacial side of the membrane at the cost of ATP consumption. Transport demonstrates a unique structural specificity for PS, including a stereospecific interaction with the glycerol moiety. PS flippase activity has been associated with some members of the P₄-ATPase superfamily.

Using the baculovirus-insect cell system, we have expressed, purified and characterized a mammalian member of this family (ATP8A1). ATPase activity of this enzyme displays a specificity for PS that is reminiscent of PS flippase activity in human erythrocytes. However, when purified and reconstituted into proteoliposomes, murine ATP8A1 alone is incapable of recapitulating PS transport. Evidence from other P₄-ATPase family members (ATP8A2 and the yeast enzyme Drs2) suggests that flippase transport activity requires the presence of both the P₄-ATPase and a partner protein of the CDC50 family. Co-expression of ATP8A1 and its cognate CDC50 protein (CDC50A) enhances ATPase activity, however, the mechanism by which CDC50A regulates the activity of ATP8A1 remains unresolved. Using homology modeling and site-directed mutagenesis, we explore proposed pathways for lipid transport by ATP8A1 and potential interaction sites with CDC50A.

COLL 351

Probing cellular mechanosensitivity using cadherin-functionalized polymer-tethered lipid bilayer architectures

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Previous analysis of cell migration on artificial polymeric substrates of adjustable substrate stiffness suggests that external mechanical cues may have a profound influence on cellular fate and function of anchorage-dependent cells in an extracellular matrix environment. In contrast, less is known about how cells may respond to mechanical signals from neighboring cells, considered to be important in processes, such as epithelial-mesenchymal transition and vascular leakage during inflammation. To address this uncertainty, here we explore properties of C2C12 myoblasts on cadherin-functionalized polymer-tethered lipid membrane systems of adjustable substrate stiffness. These biomembrane-mimicking cell substrates allow the free assembly of

linkers into linker clusters at cellular adhesions without impairing cell migration, thus better replicating the dynamics at cell-cell-junctions than polymeric substrates with polymer-conjugated linkers. Moreover, polymer-tethered lipid membrane systems are well suited to examine cellular mechanosensitivity because substrate stiffness can be controlled either by the number of bilayers in a polymer-tethered multi-bilayer stack or by adjustment of lipopolymer concentration in the membrane system. The latter approach is attractive because polymer-tethered membranes with a lateral gradient in lipopolymer concentration can be built. Results from myoblasts are presented, which illustrate the functionality of these cell-cell-mimicking artificial cell substrates.

COLL 352

Fully automated, parallel lipid bilayer platform for specific nucleic acid detection

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We have developed a mechanical approach for lipid bilayer formation based on droplet interface bilayers which uses simple consumables and is parallelizable, automatable, and requires no expertise or training. The platform allows for the repeated formation and measurement of bilayer arrays, which we demonstrate through the parallel formation and simultaneous measurement of 32 bilayers. The consumable is compatible with SBS standard 96 well plates and is easily scalable to higher densities for high throughput automated bilayer formation and measurement. We characterized the bilayer characteristics and yield of our platform and validated it through the simultaneous measurement of the protein nanopore α -Hemolysin over the array plate. We have automated this platform by processing this consumable plate with a motion control robot integrated with a fluid handling station and multichannel electrophysiological amplifier. The platform is capable of running completely unattended, repetitively cycling through plate acquisition, solution dispensation, electrical measurement, and plate disposal, while executing a variety of easily modified assays or experimental protocols. As a proof-of-concept demonstration of our system, we show fully automated measurement of α -hemolysin and its use to quantitatively detect microRNA.

COLL 353

Consequences of lipid oxidation on bilayer structural and mechanical properties

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Processes that produce reactive oxygen species (ROS) are ubiquitous in biology. Unsaturated lipids in cell membranes represent a major target for reaction with ROS. Oxidation of these lipid species has consequences for the structure and properties of membranes, and has significant implications related to the dysfunction of cellular

processes resulting from oxidative damage.

In membranes containing polyunsaturated lipids, oxidative processes can lead to tail group cleavage. This produces two molecular products: a larger species with the headgroup and a single intact tail, and a smaller species derived from the cleaved tail. Our studies have shown that upon replacing less than 3% of the unsaturated lipids in a synthetic bilayer with the larger of these species, the permeability of the membrane to small molecules increases by an order of magnitude. However, if the smaller tailgroup-derived species are included, the membrane barrier properties are significantly recovered.

Oxidation of unsaturated lipids can also lead to a series of changes in area per lipid in a bilayer. As area per lipid changes, membrane tension is altered. We have shown that the oxidative alteration of membrane tension can be treated as a two-step process. In the first step, oxidated lipid tails are modified with hydrophilic groups, leading to an increase in area per lipid and a decrease in membrane tension. As oxidation continues, the tail groups are cleaved completely, reducing area per lipid and increasing membrane tension. Simultaneous with this increase in surface tension is a decrease in lipid line tension. These two effects synergistically lead to the formation of micron-scale pores in synthetic bilayers.

Finally, our recent work has shown that oxidation can radically alter the phase behavior of phosphatidylethanolamine (PE) lipids. In biological systems, these lipids facilitate the formation of high-curvature membrane structures necessary for cell function. This high curvature is reflected in the inverse hexagonal phase that the lipids take on in water. We have shown that upon oxidation, PE lipids undergo molecular changes that allow them to take on a lamellar phase in water. Interestingly, at moderate water concentrations, these oxidized PE lipids also form previously unobserved micron-scale cubic structures.

COLL 354

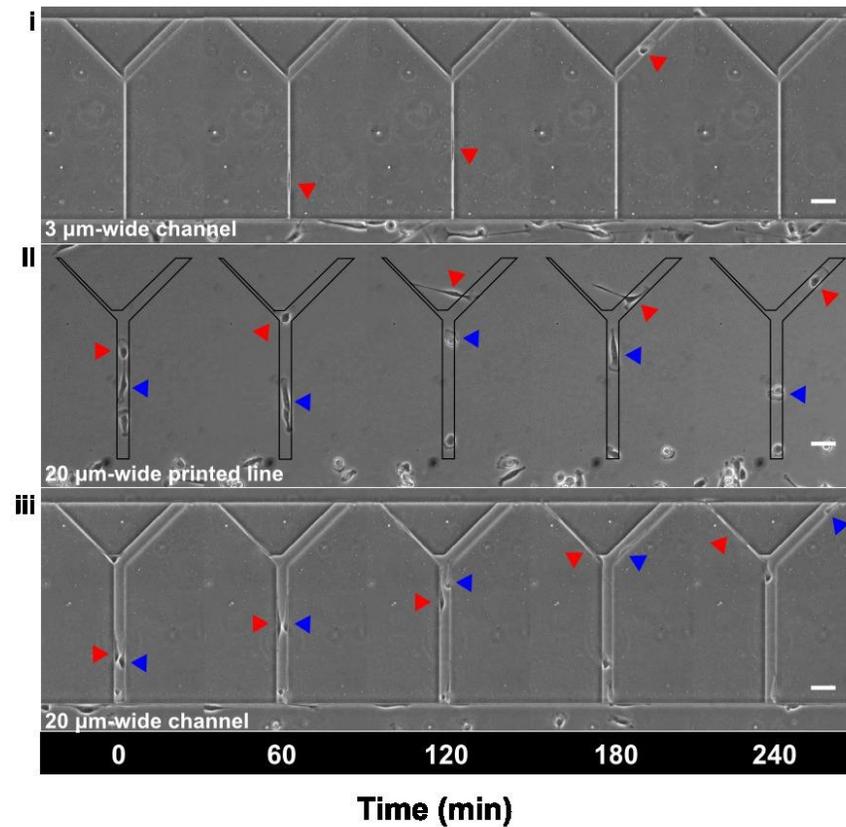
Interplay of the physical microenvironment, contact guidance and cell signaling in cell decision making

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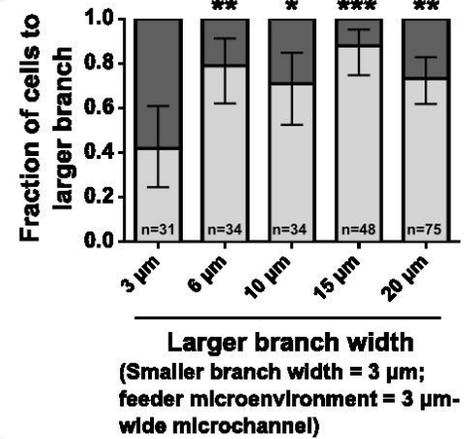
The peritumoral physical microenvironment consists of complex topographies that influence cell migration. The decision making of cells upon encountering anisotropic, physiologically-relevant physical cues has yet to be elucidated. By integrating microfabrication with cell and molecular biology techniques, we provide a quantitative and mechanistic analysis of cell decision making in a variety of well-defined physical microenvironments. Cell decision making following lateral confinement on 2D microcontact printed lines is governed by the branch width at bifurcations. Cells

confined in narrow feeder microchannels also preferentially enter wider branches at bifurcations. In contrast, in feeder channels wider than the cell body, cells elongate along one channel side wall and are contact guided to the contiguous branch channel independently of branch channel width. This contact guidance-mediated decision is regulated by the lateral and axial length scales of the feeder channels. Knockdown of $\beta 1$ -integrins or inhibition of cellular contractility suppresses contact guidance. Concurrent, but not individual, knockdown of non-muscle myosin isoforms IIA and IIB decreases contact guidance, suggesting the existence of a compensatory mechanism between MIIA and MIIB. Conversely, knockdown or inhibition of Cdc42 promotes contact guidance-mediated decision making. Taken together, the dimensionality, length scales of the physical microenvironment and intrinsic cell signaling regulate cell decision making at intersections

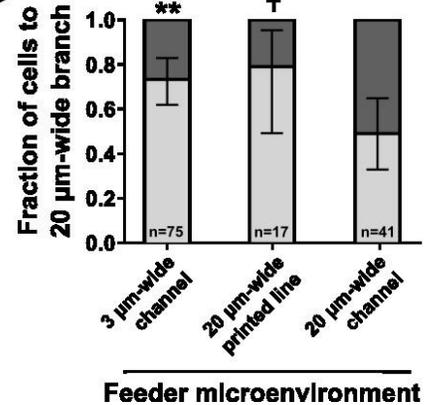
A Cell decision making from various feeder microenvironments



B



C



COLL 355

Evaluation of drug-mediated changes in cardiomyocytes by AFM

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Drug-induced cardiotoxicity is one of the major reasons a compound can experience late-stage attrition during development due to its common association with potentially fatal Torsades de Pointes arrhythmias. These adverse effects can be detected by prolongation of the QT interval, which is mostly human Ether-à-go-go-Related Gene (hERG) channel connected. In this presentation, we investigate the possibility of using known hERG blockers, E-4031 and Sotalol, to induce irregular beating patterns in the mouse and human induced pluripotent stem cell derived (miPSC and hiPSC) cardiomyocyte model systems, which can be rescued back to normal beating patterns by subsequent opening of the hERG channel using the enhancer compound Nicorandil. All experiments were carried out using an AFM-based approach to precisely monitor the beating interval of cardiomyocytes, and therefore verification was implemented using three individual cardiovascular compounds with comparison to previously reported methods. This represents that AFM can serve as a sensible pre-screening tool for use during drug development.

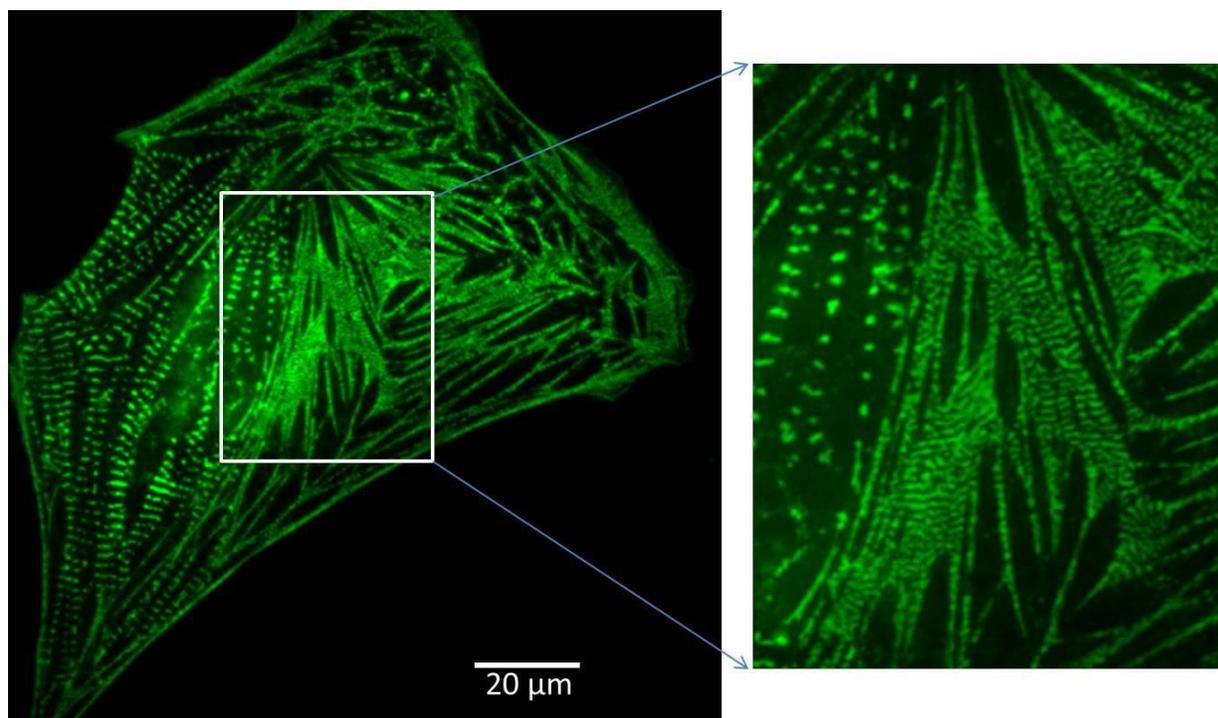


Figure 1. Fluorescence images of human induced pluripotent stem cell derived cardiomyocytes. Green: Alexa 488 conjugated secondary antibody.

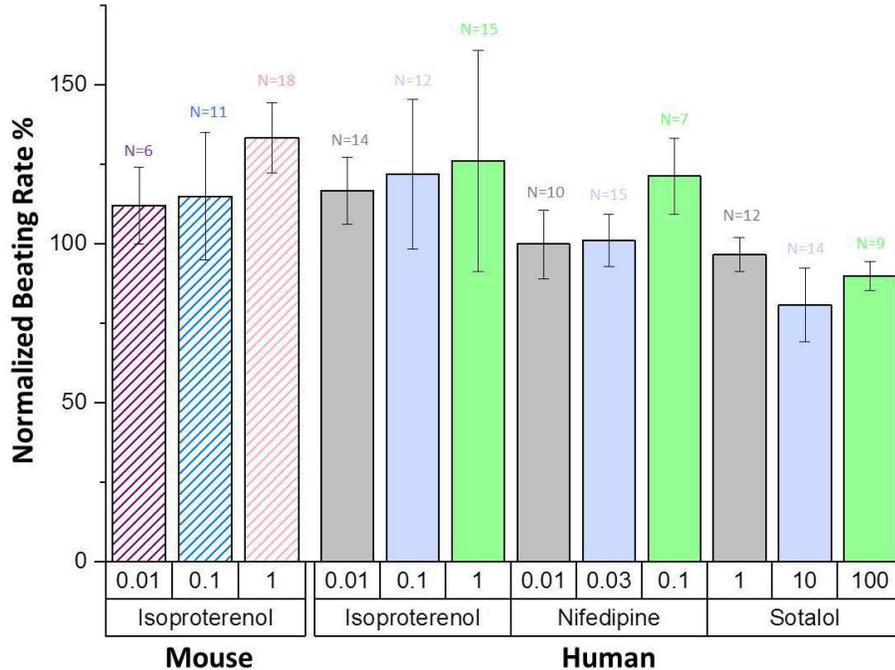


Figure 2. Bar graph of individual drug-induced effects on beating rate (mean \pm standard deviation as percent change from control) of murine and human cardiomyocytes at increasing concentrations, at 36-37°C. Brackets with asterisks show significant difference from one another ($p < 0.05$) by unpaired student's t-test. (N=number of cells analyzed).

COLL 356

Nanomechanical properties of the stratum corneum and its interaction with a single hair fiber

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The mechanical resistance of the stratum corneum, the outermost layer of skin, to deformation has been evaluated at different length scales using atomic force microscopy. Nanomechanical surface mapping revealed that Young's modulus of the stratum corneum varied over the surface with a mean value of about 0.4 GPa. Force indentation measurements showed permanent deformation of the skin surface only at high applied loads (above 4 μ N). Force measurements utilizing the single hair fiber probe supported the nanoindentation results of the stratum corneum being highly elastic at the nanoscale, but revealed that the lateral scale of the deformation determines the effective elastic modulus. This result resolves the fact that the reported values in the

literature vary greatly and will help to understand the biophysics of the interaction of razor cut hairs that curl back during growth and interact with the skin.

COLL 357

Smart pH-activated nanoparticles for targeting the tumor microenvironments

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One of the most challenging and clinically important goals in nanomedicine is to deliver imaging and therapeutic agents to solid tumors. Here we report the design and development of stimuli-responsive smart nanoparticles for targeting the the acidic microenvironments of solid tumors. By targeting the broad tumor habitats rather than tumor-specific receptors, this strategy has the potential to overcome the tumor heterogeneity problem and could be used to design diagnostic and therapeutic nanoparticles for a broad range of tumors.

COLL 358

Renally excreted ultrasmall silica nanoparticles as clinically translated multimodal cancer-targeted platforms for nanomedicine

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Despite recent advances in imaging probe development for nanomedicine, the translation of targeted diagnostic platforms remains challenging. Renally excreted (~6- to 7-nm) hybrid inorganic (silica) particles, termed Cornell dots (C dots), were labeled with ¹²⁴I for positron emission tomography (PET) imaging and modified with cRGDY peptides for molecular cancer imaging. ¹²⁴I-cRGDY-PEG-C dot particles are inherently fluorescent, containing deep red/NIR dyes for lesion detection, cancer staging, and treatment management in humans. However, the translation of such particle probes has not kept pace with the accelerated growth in minimally invasive surgical tools that rely on optical imaging agents. Tumor-targeted C dots exhibit hallmarks of an optimal diagnostic probe, as they selectively target disease while exhibiting bulk renal clearance, in integrin-expressing human melanoma xenografts and spontaneous melanoma miniswine models. Bulk renal clearance was achieved by tuning particle sizes below that of the effective renal glomerular filtration size cutoff of 10 nm; this minimized nonspecific uptake in the reticuloendothelial system (RES), and thus

abrogated potential off-target toxicities. In small and larger-animal models, both pre-operative PET and intraoperative optical imaging demonstrated high tumor-to-background ratios and favorable pharmacokinetic and clearance profiles. In miniswine, higher sensitivity and specificity of the particle tracer was observed relative to ^{18}F -fluorodeoxyglucose (^{18}F -FDG) used to stage melanoma. Preclinical findings were confirmed in a first-in-human clinical trial in metastatic melanoma patients. The particle tracer was found to be safe, well-tolerated, and exhibited in vivo stability and distinct, reproducible pharmacokinetic signatures defined by renal excretion. Preferential uptake and localization of the probe at sites of integrin-expressing lesions, including those within the central nervous system, suggest the potential utility of these targeted C dots in cancer diagnostics. The use of these methods to accurately estimate the fraction of the injected particle load that accumulates at sites of brain tumors, and the monitoring of time-dependent changes in particle uptake, can be extended to treatment management settings for estimating particle dosing requirements in the context of therapeutic interventions.

COLL 359

Renally cleared contrast agents for tissue-specific targeting

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Two fundamental and unsolved problems facing biophotonics and nanomedicine are nonspecific uptake of intravenously administered diagnostic and/or therapeutic agents by normal tissues and organs, and incomplete elimination of unbound targeted agents from the body. To solve these problems, we have synthesized a series of indocyanine near-infrared (NIR) fluorophores that varied systematically in net charge, conformational shape, hydrophilicity/lipophilicity, and charge distribution. Using 3D molecular modeling and optical fluorescence imaging, we have defined the relationship among the key independent variables that dictate biodistribution and tissue-specific targeting such as lung and sentinel lymph nodes (*Nat Biotechnol.* 2010), human prostate cancers (*Nat Nanotechnol.* 2010), and human melanomas (*Nat Biotechnol.* 2013). Recently, we have developed new pharmacophore design strategy “structure-inherent targeting,” where tissue- and/or organ-specific targeting is engineered directly into the non-resonant structure of a NIR fluorophore, thus creating the most compact possible optical contrast agent for bioimaging and nanomedicine (*Nat Med.* 2015). The biodistribution and targeting of these compounds vary with dependence on their unique physicochemical descriptors and cellular receptors, which permit 1) selective binding to the target tissue/organ, 2) visualization of the target specifically and selectively, and 3) provide curing options such as image-guided surgery or photo dynamic therapy. Our study solves two fundamental problems associated with fluorescence image-guided surgery and lays the foundation for additional targeted agents with optimal optical and *in vivo* performance.

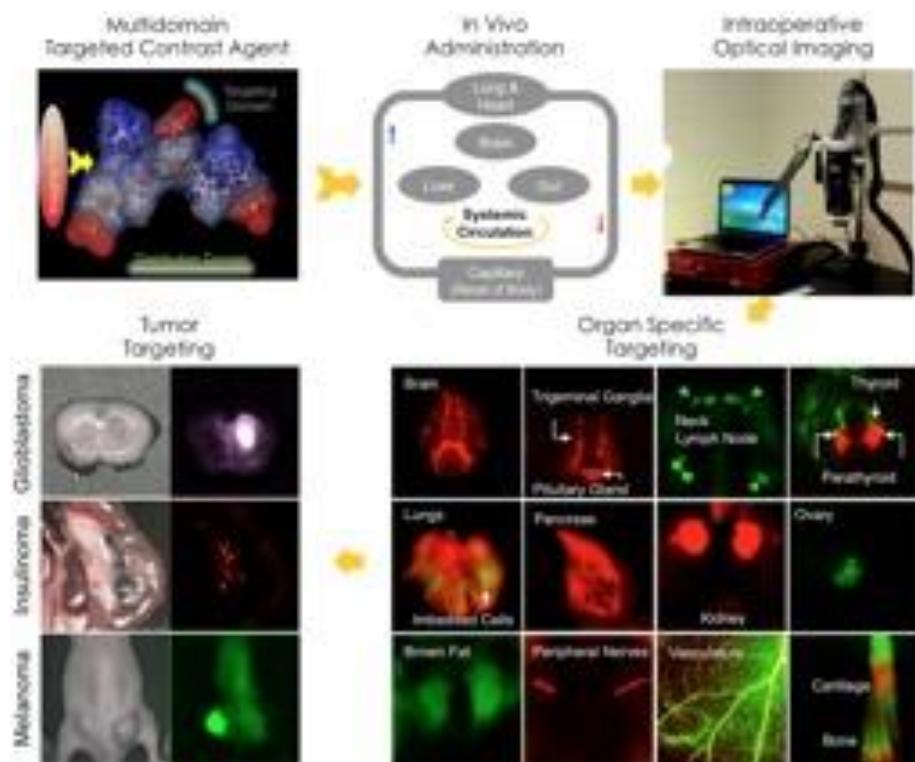


Figure 1. Development of tissue- and organ-specific nanoprobe for bioimaging and nanomedicine.

COLL 360

What may happen to hybrid nanoparticles once they are administered *in vitro* or *in vivo*

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Quite frequently inorganic nanoparticles (NPs) are engineered with a firmly grafted organic surface coating to improve their physicochemical properties and applicability. While stability of such NPs typically is assayed in simple *in vitro* tests, their stability in a mammalian organism remains to be demonstrated. In this study NPs composed out of a 4.8 nm monodisperse, radioactively labelled gold core (^{198}Au), engineered with a radioactively labelled polymer shell (^{111}In), possessing high colloidal stability, were synthesized. NP suspensions were intravenously injected into rats. Quantitative biodistribution analyses were performed independently for ^{198}Au and ^{111}In , demonstrating that *in vivo* the polymer shell comes at least partially off the NP core. While ^{198}Au accumulates mainly in liver, as typical for NP biodistribution, ^{111}In shows a non-particulate biodistribution similar to that of intravenously injected ionic ^{111}In . This demonstrates that even NPs with high colloidal stability can radically change their physico-chemical properties *in vivo*. Additional “in test tube” and *in vitro* data suggest

that degradation of the polymer shell is caused by proteolytic enzymes in the liver. This demonstrate that in vitro and in vivo besides the corona of adsorbed proteins to the surface of NPs, also their inorganic surface coating can be enzymatically degraded.

COLL 361

Near IR nanobiophotonics for nanomedicine: From targeting, to theranostics, to clearance

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Nanobiophotonics taps on nanoscale manipulation of optical interactions, control of light propagation and energy flow on nanoscale to produce a major advancement in Nanomedicine¹⁻³. It provides a nanoplatforms with the ability to guide targeting, activate multiple therapy, and study clearance, thus yielding valuable information on pharmacokinetics and pharmacodynamics. Its ability to sense therapeutic efficacy in real time, enables nanoplatforms a “see, treat and see” approach, now referred to as theranostics

A major limitation of nanobiophotonics is the issue of light penetration in tissues. We are developing up-converting rare-earth ion doped optical nanotransformers in a core-multiple shell design using nanochemistry . These nanotransformers convert tissue penetrating Near IR (NIR) light from an external source, in situ and on demand, to a wavelength needed for deep tissue imaging as well as for a specific diagnostic or therapeutic application. Using these nanoparticles as imaging probes, we have also demonstrated NIR high contrast 3D imaging *in vivo*. We have used them for studying biodistribution to ascertain targeting, and eventually follow clearance . We have used in-situ photon conversion for photodynamic therapy and drug release . We are also developing light-guided/activated gene/siRNA delivery nanoplatforms and opto-genetics which benefit major health care issues such as cancer, infectious diseases (e.g. swine flu, Ebola, HIV, TB, Malaria), aging, neurological problems, brain diseases, drug addiction, chronic pain, depression and obesity.

We have also demonstrated remote and noninvasive actuation of optogenetics using near IR absorbing optical nanotransformers that can provide an effective intervention /augmentation strategy to enhance the cognitive state and lead to a foundation for futuristic vision of super human capabilities .

This talk will conclude with a discussion of new opportunities.

COLL 362

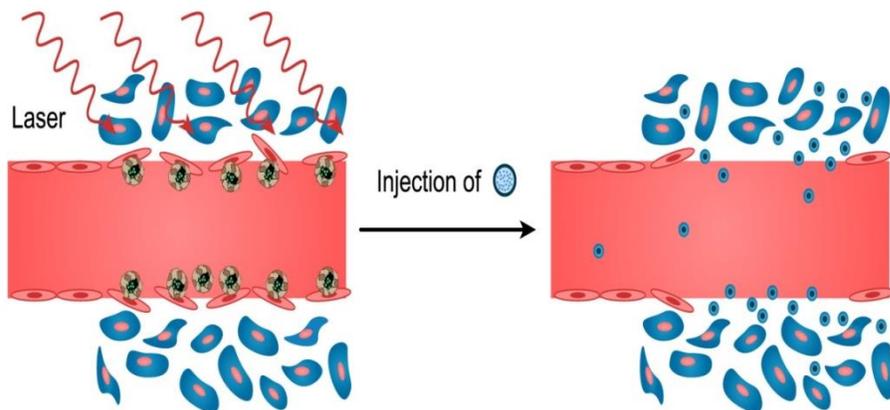
Surface engineered ferritins for drug delivery and photodynamic therapy

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Ferritins are a family of iron storage proteins with ubiquitous distribution among almost all life forms. Ferritins feature a cage-like structure, with an outer diameter of approximately 12 nm and an inner cavity of 7–8 nm. While natural ferritins are always filled with a ferric oxhydroxy core, E coli made artificial ferritins have an empty cavity at the center. Ferritins are decomposed into the 24 subunits when the pH is decreased to 2~3; when the pH is tuned back to neutral, however, the subunits can reconstitute into a nanocage, and in a nearly intact fashion. Such pH-mediated disassembly-and-reassembly provides a facile means to load molecules into ferritins. For instance, we recently reported that chemotherapeutics like doxorubicin can be into ferritins with high efficiency. Moreover, we found that fluorinated zinc phthalocyanine or $ZnF_{16}Pc$, a potent photosensitizer, can be loaded into ferritins by up to 60wt%. Meanwhile, the surface of ferritins can be modified, through either chemical conjugation or genetic engineering, to present tumor targeting ligands. These features of ferritins, along with their intrinsic biocompatibility and biodegradability, suggest great potential of the platform as a novel delivery system. More recently, we found that $ZnF_{16}Pc$ -loaded and RGD4C presenting ferritins can home to tumor endothelium; with photo-irradiation at relatively low fluences, the resulting PDT treatment leads permeabilized tumor vasculatures (Fig. 1). As a result, macromolecules or nanoparticles administered afterwards are able to extravasate and accumulate more efficiently at the tumor sites. This methodology can artificially enhance the EPR effect of tumors so as to improve nanoparticle delivery to tumors.

**VASCULAR TARGETING PDT
MEDIATED BY P-RFRTS**

**ENHANCED EPR FOR
IMPROVED DRUG DELIVERY**



COLL 363

Cell membrane-camouflaged nanomotors for biodetoxification and drug delivery

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Attempts to apply artificial micro-/nanomotors for diverse biomedical applications have inspired a variety of strategies for designing motors with diverse propulsion mechanisms and functions. However, existing artificial motors are made exclusively of synthetic materials, which are subject to serious immune attack and clearance upon entering the bloodstream. Herein we present a platform by using red blood cell as camouflage coating for micro-/nanomotors. As the first example, a red blood cell membrane-camouflaged nanowire that can serve as new generation of biomimetic motor sponge is described. The biomimetic motor sponge is constructed by the fusion of biocompatible gold nanowire motors and RBC nanovesicles. The motor sponge possesses a high coverage of RBC vesicles, which remain totally functional due to its exclusively oriented extracellular functional portion on the surfaces of motor sponge. These biomimetic motors display efficient acoustical propulsion, including controlled movement in undiluted whole blood. The RBC vesicles on the motor sponge remain highly stable during the propulsion process, conferring thus the ability to absorb membrane-damaging toxins and allowing the motor sponge to be used as efficient toxin decoys. The efficient propulsion of the motor sponges under an ultrasound field results in accelerated neutralization of the membrane-damaging toxins. Such motor sponges connect artificial nanomotors with biological entities and hold great promise for treating a variety of injuries and diseases caused by membrane-damaging toxins. Furthermore, we also demonstrated an elegant approach that directly turns natural red blood cells (RBCs) into functional micromotors with the aid of ultrasound propulsion and magnetic guidance. Since the RBC motors preserve the biological and structural features of regular RBCs, these motors possess a wide range of antigenic, transport, and mechanical properties that common synthetic motors cannot achieve and thus hold considerable promise for a number of practical biomedical uses.

Refs:

1. Advanced Functional Materials, 2015, DOI: 10.1002/adfm.201501050.
1. ACS Nano, 2014, 8 (12), 12041–12048.

COLL 364

Stability of gold nanoaggregates affects biological fate

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(2) Irell & Manella Graduate School of Biological Sciences, Monrovia, California, United States

Gold nanoparticles (AuNPs) have been widely investigated for a variety of biological applications, including drug delivery and targeting for cancer therapy. However, although AuNPs can be used to target the tumor via the EPR effect, AuNPs of this size range (50-200nm) also show high accumulation and persistence in the liver and spleen. On the other hand, NPs that can be renally cleared from the body (<5nm) show poor tumor targeting. Thus, using these NPs for cancer therapy faces the challenge of needing opposing size ranges, which cannot be met using only one type of NP.

One strategy is to use AuNP aggregates that can be controllably disassembled into their renally-clearable components. We have previously reported a method for the controlled synthesis of AuNP aggregates using a crosslinker that can be easily and systematically modified. Here we investigate the relationship between chemical modifications of the crosslinker and the resulting changes in aggregate morphology and behavior under different biologically-relevant conditions. We demonstrate that our method is able to synthesize uniform, 100nm spherical AuNP aggregates using crosslinkers of varying valencies. We show that changing linker valency can modulate aggregate stability, which affects the cellular fate of the aggregates.

COLL 365

Molecular mimicking self-assembly: Precise positioning of nanoparticles using non-biological molecules

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Realizing the enormous potential of nanoparticles (NPs) in such as energy, biomedical, and optoelectronic fields requires the organization of these particles into larger or hierarchically ordered structures with defined macroscopic properties. Great progress has been achieved in the precise assembly and positioning of nanoparticles in space using molecules. One of the most striking examples is DNA-programmed assembly of NPs as molecular equivalents. This method can be used to program the organization of NPs into astonishing structures with remarkable complexity and precision, such as chiral arrays of plasmonic NPs, and superlattices that resemble atomic or molecular crystals. However, this method shows limitations such as limited processability and poor scalability at low cost. Nevertheless, unmet challenges still remain at the frontier of precise organization of NPs.

Recently, we have developed a novel molecular mimicking strategy for assembling multiple types of NPs with extraordinary precision in space using non-biological polymers. This robust method does not require the use of asymmetric surface functionalization of NPs, as often used by conventional approaches. By using this strategy, a variety of supracolloidal molecules with defined valence can be produced at

high yield. The localized chemistry on the surface of the supracolloidal molecules can be readily controlled. The supracolloidal molecules can further assemble potentially into a wide range of hierarchical structures. In this talk, I will present this new strategy of developing NPs that can mimic conventional molecules for precise self-assembly, as well as the similarity and differences between these NPs and molecules.

COLL 366

Controlled synthesis of nanostructured metal catalysts

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Catalysis is critically important to energy production and to meeting the environmental quality mission of promoting the development and utilization of clean, efficient, and reliable energy resources. It is essential to understand the relationships between the atomic and nanoscale structure of metal nanoparticles and catalyst supports and the crucial role these play in promoting or altering catalytic pathways. The key focus of this talk lies in the controlled synthesis of metallic Au catalysts with unique metal-support interactions and nanostructured nonmetallic catalysts for heterogeneous catalysis. Critical issues and emerging science and technology in heterogeneous catalysis will be discussed in context of controlled synthesis.

COLL 367

Microscopic insights into the synthesis of discrete and hybrid colloidal metal nanoparticles

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Colloidal metal nanoparticles are ubiquitous in applications such as catalysis and plasmonics, including as discrete nanoparticles and also combined with other materials in hybrid constructs. Many aspects of colloidal metal nanoparticle synthesis are now mature, well understood, and widely implemented, but many knowledge gaps still exist. In this talk, we will present and discuss a series of high-resolution transmission electron microscopy studies (HRTEM, HAADF-STEM, STEM-EDS element maps) that probe the early stages of metal nanoparticle nucleation and growth. For example, in the polyol synthesis of colloidal Rh nanoparticles, we observe the early formation of ~1 nm Rh seeds, which can be isolated and used as a stable stock solution of embryonic seeds. Different ligands added to the embryonic seeds determine their eventual fate, e.g. the shapes into which they will ultimately evolve. Additionally, microscopic studies of the early stages of Ag nucleation and growth on Pt-Fe₃O₄ heterodimer nanoparticle seeds reveal indiscriminate nucleation on all surfaces, followed by surface diffusion and coalescence to ultimately form a Ag-Pt-Fe₃O₄ heterotrimer nanoparticle product. Using

this knowledge, we can interrupt this process and instead generate Pt-Fe₃O₄-Ag, a distinct configurational isomer. Collectively, these and additional microscopic insights offer important new guidelines for the synthesis of discrete and hybrid colloidal metal nanoparticles with precisely targeted morphologies and properties.

COLL 368

Computational design of nanoparticles and nanowires for electrocatalysis

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Core/shell nanoparticles (NP) represent a promising class of catalysts in energy conversions. We have proposed a multiscale computational strategy to design core/shell NPs for electrocatalysis. A universal relation between surface strain and oxygen adsorption energy on NPs is established based on which one can computationally screen and design core/shell NP catalysts for superior ORR activities. This strategy is first applied to Pt-based core/shell NPs, and Fe-Pd, Co-Pd, and Ni-Pd alloys are predicted as promising candidates for the core materials. We have systematically examined the effect of particle shape, size, thickness and chemical composition on ORR activities for Pd-based core/shell NPs. The NPs possess under-coordinated facets and elastic strains, both are beneficial to ORR activities. Based on the same principle, we propose penta-twinned Cu nanowires (NWs) as excellent candidates for CO₂ electroreduction. The penta-twinned NWs possess a combination of ultrahigh mechanical strength, large surface-to-volume ratios and an abundance of under-coordinated adsorption sites, all desirable for CO₂ electroreduction. In particular, we show that the NWs can withstand elastic strains orders of magnitude higher than their conventional counterpart, and as a result their CO₂ electroreduction activities can be significantly enhanced by elastic tensile strains. With a moderate tensile strain, the bias potential for methane production at a decent current density can be reduced by 50%.

COLL 369

Designed chemical synthesis and assembly of uniform-sized nanoparticles for medical and energy applications

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Recently our group has been focused on medical applications of various uniform-sized nanoparticles. Using 3 nm-sized iron oxide nanoparticles, new non-toxic MRI contrast agent was realized for high resolution MRI of blood vessels down to 0.2 mm.¹ We fabricated tumor pH-sensitive magnetic nanogrenades composed of self-assembled iron oxide nanoparticles and pH-responsive ligands for theranostic application, enabling the

visualization of small tumors of < 3 mm via pH-responsive T1 MRI and fluorescence imaging and superior photodynamic therapeutic efficacy in highly drug-resistant heterogeneous tumors.²

We reported large-scale synthesis of magnetite nanocrystals imbedded in a carbon matrix. We demonstrated galvanic replacement reactions in metal oxide nanocrystals. When Mn₃O₄ nanocrystals were reacted with iron(II) perchlorate, hollow box-shaped nanocrystals of Mn₃O₄/γ-Fe₂O₃ were produced.³ These iron oxide-based nanomaterials exhibited very high specific capacity and good cyclability for lithium ion battery anodes. We report a simple synthetic method of carbon-based hybrid cellular nanosheets loaded with SnO₂ nanoparticles. The resulting SnO₂-carbon nanosheets exhibit specific capacity of 914 mAh g⁻¹ with the retention of 97.0% during 300 cycles, and the reversible capacity is decreased by only 20% as the current density is increased from 200 mA g⁻¹ to 3000 mA g⁻¹.⁴

1. "Large-scale Synthesis of Uniform and Extremely Small-sized Iron Oxide Nanoparticles for High-resolution T1 MRI Contrast Agents," *J. Am. Chem. Soc.* **2011**, 133, 12624.
2. "Multifunctional Tumor pH-Sensitive Self-Assembled Nanoparticles for Bimodal Imaging and Treatment of Resistant Heterogeneous Tumors," *J. Am. Chem. Soc.* **2014**, 136, 5647.
3. "Galvanic Replacement Reactions in Metal Oxide Nanocrystals," *Science* **2013**, 340, 964.
4. "Hybrid Cellular Nanosheets for High-Performance Lithium Ion Battery Anodes," *J. Am. Chem. Soc.* **2015**, 137, ASAP.

COLL 370

Crystal phase-controlled synthesis of novel noble metal nanomaterials

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In this talk, I will summarize the recent research on the crystal phase-controlled synthesis of novel noble metal nanomaterials in my group. It includes the first-time synthesis of hexagonal-close packed (*hcp*) Au nanosheets (AuSSs) on graphene oxide [*Nat. Commun.* **2011**, 2, 292], surface-induced phase transformation of AuSSs from *hcp* to face-centered cubic (*fcc*) structures [*Nat. Commun.*, **2015**, 6, 6571], alternating *hcp/fcc* Au square-like plates from AuSSs [*Angew. Chem. Int. Ed.* **2011**, 50, 12245], ultrathin Au nanowires containing *hcp* phase [*Adv. Mater.* **2012**, 24, 979], synthesis of ultrathin *fcc* Au@Pt and Au@Pd rhombic nanoplates through the epitaxial growth of Pt and Pd on the *hcp* AuSSs, respectively [*Angew. Chem. Int. Ed.*, **2015**, 54, 5672], the first-time synthesis of 4H hexagonal phase Au nanoribbons (NRBs) and their phase transformation to *fcc* Au RNBs as well as the epitaxial growth of Ag, Pt and Pd on 4H Au NRBs to form the 4H/*fcc* Au@Ag, Au@Pt and Au@Pd core-shell NRBs [*Nat. Commun.*, **2015**, 6, 7684], and the synthesis of 4H/*fcc*-Au@metal sulfide core-shell NRB heterostructures [*J. Am. Chem. Soc.*, **2015**, 137, 10910]. In addition, the concept

of crystal-phase noble metal heterostructures is proposed [ACS Nano, 2015, DOI: 10.1021/acsnano.5b05040].

COLL 371

Heterostructures of two-dimensional materials and their potential applications

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The development of two-dimensional (2D) layered materials is driven both by fundamental interest and their potential applications. Atomically thin 2D Transition metal dichalcogenide (TMD) materials provide a wide range of basic building blocks with unique electrical, optical, and thermal properties which do not exist in their bulk counterparts. Our recent demonstration in vapor phase growth of TMD monolayer [1] has stimulated the research in growth and applications [2]. In this presentation, I would start with the discussion on the synthesis and characterizations of crystalline MoS₂ and WSe₂ monolayers. These layer materials can be transferred to desired substrates, making them suitable building blocks for constructing multilayer stacks for various applications [3].

The interlayer interaction based on van der Waals force enables the possibility to assemble different 2D materials into arbitrarily and vertically stacked heterostructures. Heterostructures of 2d materials formed by vertical stacking have been realized recently via transfer of their exfoliated flakes, where their properties are dominated by the stacking orientation and strength of interlayer coupling. The method to determine valence band and conduction band alignment for various TMD materials is proposed [4]. Another very attractive structure is the lateral heterostructure, where the junction is atomically sharp and the active region can be as narrow as few strings of atoms at the junction areas. This structure offers much easier band offset tuning since materials are spatially separated. The direct growth of such lateral heterostructures will be presented [5]. These unique 2D heterostructures have abundant implications for many potential applications. Preliminary results and perspectives on monolayer electronics shall be discussed.

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COLL 372

Fluorescent, edible protein nanoparticles for pH sensing, small molecule sensing, and cellular imaging

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We have synthesized a number of different nanoparticulates from a variety of proteins (GlowDots) where the size, absorption, emission, net charge, and other characteristics of the particles are under complete chemical synthesis control. Particle sizes are uniformly 35 nm in diameter, as evidenced from dynamic light scattering, gel electrophoresis, and transmission electron microscopy. The color and emission properties of the GlowDots are controlled as desired to produce indigo, blue, yellow, green, orange, or red emitting GlowDots as well as other colors, including white light emitting particles which can be tuned for different excitation wavelengths. Particles are taken up by several different cancerous cell lines. The samples are water-soluble, stable under ambient conditions for extended periods of time and are being examined for a variety of practical applications which include but are not limited to cellular imaging, pH and small molecule sensing, solar antennas, and diagnostics.

COLL 373

Formation of protein fibers around gold nanoparticles: Fiber formation more likely for hydrophilic proteins at low concentrations

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We have recently shown that protein-templated synthesis of gold nanoparticles (AuNPs) can lead to the formation of protein fibers that encapsulate the NPs. Upon studying the protein-properties that control the formation of AuNPs and AuNP fibers, we observe that aromatic amino acids and gold ligating amino acids play a role in these processes, as might be expected. Surprisingly, we also observe that AuNP fiber formation is observed, not for hydrophobic proteins, but for hydrophilic proteins instead. Coupled with the observation that AuNP fiber formation is more likely at low protein concentrations, our experiments show a system in which the presumed optimal conditions for protein fiber formation (high concentration of hydrophobic proteins) are not adhered to. We will discuss these observations within the framework of polymer-induced liquid-precursor phases in non-classical nucleation. We will also discuss some potential uses for this novel material.

COLL 374

Proton conduction in a cephalopod structural protein

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Proton conducting materials play a central role in a diverse array of renewable energy and bioelectronics technologies. Thus, a great deal of research effort has been expended to develop improved artificial proton conducting materials, including ceramic oxides, solid acids, porous solids, polymers, and metal-organic frameworks. Within this context, proton conductors from naturally occurring proteins have received relatively little scientific attention, despite advantages that include intrinsic biocompatibility, structural modularity, tunable physical properties, ease and specificity of functionalization, and generalized expression/purification protocols. We have recently characterized the cephalopod structural protein reflectin with a diverse array of electrical and electrochemical techniques and found that this material is an effective proton conductor, with figures of merit that compare favorably to those of artificial analogues. Our findings may hold implications for the development of the next generation of biologically-inspired proton conducting materials.

COLL 375

Crystalline silk nanodiscs: One material many applications

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We report the fabrication of Crystalline Silk Nanodiscs (CSNs) from silk fibroin of wild variety by removing the amorphous bulky/polar amino acids by acid hydrolysis¹, followed by homogenization and ultrasonication. CSNs are responsible for the strength for which silk is known for. CSNs are highly crystalline (~93%) β -sheeted materials which are super hydrophobic (130°). This is the first time where we report silk nanocrystals with well-defined nano-disc having dia. from 20nm to 150 nm with thickness of disc ~5nm. The amino acid makeup of these SNCs is about ~84% Alanine. The density is about ~1.26 g/cm³ which provides them highly favourable conditions when used as a filler for polymer nanocomposite applications. The elemental analysis shows presence carbon, nitrogen, oxygen and hydrogen. CSNS have carboxyl and amino functionalities allowing easy chemical and mechanical modification making them easy to use natural materials.² They are obtained from nature, thus are low cost, easily available and renewable. Preliminary cytotoxicity studies show that they are non-toxic to human cell lines making them bio-compatible allowing their use as biomaterials. The thermal degradation onset for this material is ~200 °C, which is roughly the processing temperature of most polymers, making it processible for industry based applications. Authors have tried to suggest few possible areas of applications for this material, but with all above mentioned properties there could be numerous applications for this novel material. These silk nanocrystals may be used as a filler for polymer nanobiocomposites to be used for packaging applications.³ With high crystallinity and hydrophobic nature the composite will have superior barrier and mechanical properties (unpublished data). CSNs can act as drug carriers, binding the drug to the CSN can enable the easy entry of drug into the cellular matrix.⁴ Cross-linked silk nanocrystals can be used in the fields

of materials science having applications in bio templates and biocatalysts, biosensors, chromatographic analysis.

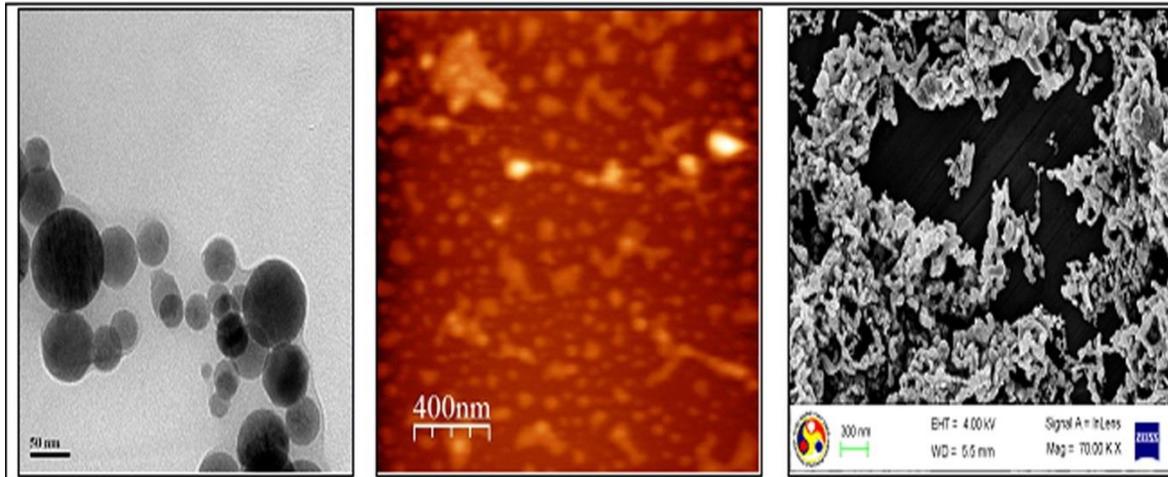


Figure 1: Crystalline silk Nano discs (CSN) as observed from the a. Transmission Electron Microscopy (TEM), b. Atomic Force Microscopy (AFM), c. Scanning Electron Microscopy (SEM).

COLL 376

Self-assembly of nanodiscs by apolipoprotein C-III

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Apolipoproteins together with phospholipids assemble into lipoproteins, nm to μm sized particles responsible for the transport of cholesterol and triglycerides throughout the body. Remodeling phospholipid membranes by apolipoproteins *in vitro* can result in so-called nanodiscs which are structurally similar to high-density lipoprotein (HDL) particles. Although nanodiscs hold tremendous potential to enable future biotechnologies, their structures and mechanisms of assembly are not well understood. Apolipoprotein C-III (ApoC-III) is a protein component of HDL and can remodel both unilamellar and multilamellar membranes composed of 1,2-dimyristoyl-*sn*-glycero-3-phosphocholine (DMPC) into nanodiscs through spontaneous self-assembly. They are monodisperse as characterized by dynamic light scattering and have a particle size of 13 ± 2 nm as visualized by electron microscopy. Using three single-Trp-containing variants of ApoC-III, specific lipid-interactions in nanodiscs were studied at positions 42, 54, and 65. Using circular dichroism spectroscopy, it was confirmed that ApoCIII adopts a highly helical conformation upon nanodisc formation. Steady-state and time-resolved fluorescence measurements reveal distinct residue-specific behaviors with W54 experiencing the most hydrophobic environment, which is similar to that observed for unilamellar vesicles. All three mutants behaved similarly near the transition temperature of DMPC at 28 °C. In contrast, the ability of each mutant to form nanodiscs was greatly altered at physiological temperature as revealed by optical turbidity measurements.

While W42 is nearly indistinguishable from the wild-type protein, kinetics for W54 is slowed and, remarkably, nanodisc formation by W65 is fully suppressed at 37 °C. Our data would suggest that despite the modest mutations of Trp to Phe at two of the three native sites, the N-terminal aromatic sidechains, especially W42, are important for lipid binding and nanodisc assembly. This observation may be biologically meaningful as only W42 is invariant across species.

COLL 377

Profiling the dielectric constant at the membrane-peptide interface of silica-nanoparticle-supported lipid bilayer using ionizable EPR probes

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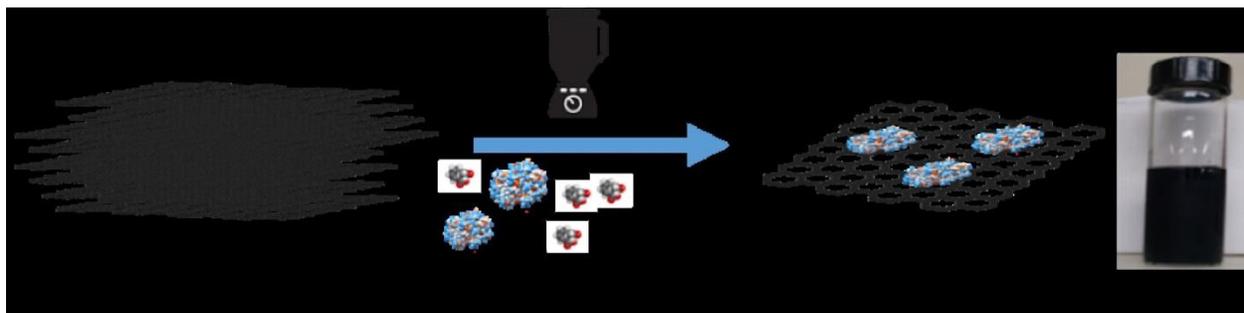
Substrate-supported lipid bilayers attract an interest as models of cell membranes as well as self-assembled hybrid nanostructures for various biotechnological applications. Despite extensive ongoing efforts, incorporation of membrane proteins into such hybrid lipid-based systems remains largely problematic. We hypothesize that nano-confinement and solid support of lipid membranes can alter lipid or membrane protein dynamics as well as physico-chemical characteristics of the membrane-lipid interface. In this work we report on employing pH-sensitive ionizable EPR labels to profile a heterogeneous dielectric environment along the α -helix of a transmembrane WALP peptide integrated into lipid bilayers formed on the surface of silica microbeads. Nitroxide EPR spin labels were attached to two cysteine residues positioned equidistant from the center of the peptide, thus, ensuring symmetric location of the labels with respect to the bilayer center. Spin-labeled WALP was incorporated into large unilamellar vesicles and substrate-supported lipid bilayers were prepared via a spontaneous fusion upon mixing of liposomes containing spin labeled WALP and an aqueous suspension of silica beads. The change in the protonation state of the nitroxide was directly observed by EPR. Q-band (35 GHz) double electron-electron resonance (DEER) experiments were carried out to determine the distance between spin labels when embedded in lipid bilayers to provide information about the label location. Two pH sensitive spin labels, S-4-(4-(dimethylamino)-2-ethyl-5,5-dimethyl-1-oxyl-2,5-dihydro-1H-imidazol-2-yl) benzylmethanethiosulfonate (IKMTSL) and methanethiosulfonic acid S-(1-oxyl-2,2,3,5,5-pentamethyl-imidazolidin-4-ylmethyl) ester (IMTSL), were used to expand the pH range of the titration experiments. We have observed a systematic shift in the depth profile of the effective pK_a of the EPR probe at the WALP-lipid interface for silica-supported system as compared to data obtained for WALP incorporated in large unilamellar lipid vesicles. We have shown that *i*) negative charges on the silica surface stabilize the protonated form of the EPR probe and *ii*) altering pH conditions is required for protonation of the ionisable protein side chains at the membrane-lipid interface. In addition, water penetration at the peptide-membrane interface was assessed by a hyperfine sublevel correlation spectroscopy (HYSCORE) experiment. Supported by NSF- 1508607 to TIS.

COLL 378

Edible chemistry 101: Direct exfoliation of graphite to graphene in serum

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We present a scalable method to produce high quality graphene in biological media via direct exfoliation of graphite in a kitchen blender, in serum. Graphene is a wonder material but a major bottleneck in developing its applications is the large-scale production, under biologically relevant conditions. We report here a scalable method to produce graphene in biological media, while producing a very high quality, nearly defect-free graphene. Surfactants are usually used as stabilizers for graphene dispersions in water, but the use of certain surfactants may not be appropriate for biological applications. This challenge is addressed by using biomolecules as exfoliation/stabilizing agents in the current work, and graphene is produced from graphite at a high rate of $\sim 3 \text{ mg mL}^{-1} \text{ h}^{-1}$ in 10 % aqueous bovine serum at pH 7.4. Current method opens up a simple, green, sustainable, inexpensive and top-down approach for graphene production under physiological conditions, using an ordinary kitchen blender, which is accessible to most laboratories. Raman spectroscopy and transmission electron microscopy clearly indicated that the graphene produced is defect free, micron in size and consisted of about <4 layers. The few-layer graphene showed high colloidal stability, stable for months at room or biological temperatures.



High yield production of graphene in serum

COLL 379

Peptides with selective affinity to polymers for harvesting the cell sheet

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Cell sheet technology is a novel approach to prepare and harvest monolayer cell sheets by using poly N-isopropylacrylamide (PNIPAm) or (PNIPAm)-modified surfaces as

thermo-responsive cell culture substrates. As the temperature is lowered from 37°C to 20 °C, the cultured cells detach spontaneously as the surface substrate changes from hydrophobic to hydrophilic. However, evidence showed that the cell metabolic processes were suppressed below 32 °C, which may result in low cell viability of the recovered cell sheet and subsequent inefficient clinical therapies. In this study, we describe a cyclic peptide, which is used as a chemo responsive linker between cells and a PNIPAAm-modified surface. The linker is engineered to have high affinity for cells and for the PNIPAAm-modified surface. Release of the cells is achieved by a mild chemical process that modifies the cyclic peptide linker, reducing its affinity to the polymer surface. We will describe a process to discover synthetic polymer NPs with affinity and selectivity for a specific peptide sequence. A polymer NP is used as the bait to capture a peptide that is presented by a phage library. Based on our previous work, a lightly crosslinked (2%) synthetic polymer hydrogel NP comprised of N-isopropyl acrylamide (NIPAm) monomers and hydrophobic and carboxylic acid groups, was found to bind with high affinity to the cyclic peptide, KPCISFWQFWFGFCSS (P14C). The interaction between the polymer NP and the cyclic peptide (P14C) is ~ three-fold stronger than with the corresponding linear peptide (P14L). Appending RGD onto the cyclic peptides' N-terminal allows cell capture by the synthetic polymer NP to harvest cell sheets (see figure below). Glutathione (GSH), which is not harmful to cells, is used to cleave the cyclic peptide to linear peptide at 37°C to release the cell sheets. In preliminary results, NPs were coated on a 96 well plate. After addition of P14C-RGD, the cells attached to the wells in the plate. Control wells (blank and BSA coated) had only a few cells attached). The result establishes that P14C-RGD could be used as a linker between cell sheets and PNIPAAm-modified polymer surfaces. Synthetic polymers with high affinity for the RGD modified cyclic peptide will be applied to induce cell sheet formation and harvesting at 37°C.

COLL 380

Stability of proteins in supraparticles

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Self-assembly of proteins and inorganic nanoparticles driven by weak interactions opens the door for engineering organic-inorganic analogs of cellular organelles comprised of diverse components and with integrated functionalities. Such systems are fundamentally and technologically attractive due to their uniformity, versatility and simplicity of preparation. To demonstrate such assemblies, we combine ~3.4 nm FeS₂ nanoparticles with ~5 nm protease protein and observe spontaneous formation of spherical supraparticles with a narrow size distribution containing both components. Assembly was originated from the competition between electrostatic repulsion and non-covalent attractive interactions. Non-covalent interactions between protease and like-charged NPs lead to drastically different self-assembly behavior previously unseen for

each component individually, and which mimics the cooperative assemblies of proteins. We also demonstrate remarkable that the catalytic curve profile has changed, but the catalytic activity is retained in a determinate temperature and pH.

Examination by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) of 1:3 FeS₂ NPs-protease assembly reveals the formation of uniformly sized, spherical SPs with a TEM diameter of 112 ± 13nm which matches the diameter determined from Dynamic light scattering (DLS). Image of individual NP inside a SP can be distinguished by its crystal lattice with periodicity of 0.23nm. Besides the SPs were investigated by tomography 3D and the overall attractive potential between the similarly charged FeS₂ NPs and Protease is investigated by theoretical calculations. Further were examined the effect of ionic strength and temperature of assembly on the diameter of the SPs. Various spectroscopy data were performed which shows the positions of all peaks in the UV-Visible / Circular Dichroism spectra remain unchanged, indicating that the electronic state and conformation of the protease molecules in the SPs are preserved.

Catalytic activity of FeS₂-protease SPs using casein as substrate at pH 11 and at 4°C and 20°C showed a huge catalytic curve profile change, demonstrating that Superstructures display complex internal organization and can incorporate biological component which retains its functionality.

COLL 381

Protein-nanoparticle conjugate scaffolds for versatile biosensing

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The exciting properties of noble metal nanoparticles have made them ideal candidates for a variety of applications including catalysis, imaging, sensing, and drug delivery¹. These noble metal nanoparticles exhibit a phenomena called localized surface plasmon resonance (LSPR) which is a result of the oscillation of the electrons in the conduction band when excited by electromagnetic radiation, and is realized spectroscopically using UV-visible spectroscopy. Integration of proteins and nanoparticles has been a topic of interest in biotechnology and medicine due to the significant physiological relevance of proteins²⁻⁴. Herein, we present versatile protein-nanoparticle conjugates that were developed by binding gold nanoparticles to the surface of the extracellular matrix protein collagen⁵. After the nanoparticles were bound to collagen, cross-linking the collagen fibrils was mediated by glucose and heat. The cross-linking of the collagen-nanoparticle scaffolds were monitored by the ingrowth of an LSPR peak ~640 nm, representing the aggregated species, and the loss of the intensity of the LSPR peak ~525 nm, representing uncrosslinked nanoparticle-bound collagen. This novel assay shows sensitivity to glucose for a wide range of concentrations, 0.1 mM to 50 mM. To demonstrate the versatility of this assay, the protein-nanoparticle scaffolds were tested against the enzyme matrix metalloproteinase 1 (MMP1), which is activated by zinc and calcium ions⁶. Once activated, MMP1 cleaves collagen at specific sites, and results in a peak shift from a reduction of plasmonic coupling yielding an assay specific for either

zinc or calcium.

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COLL 382

Determination of nanocrystal size by analytical ultracentrifugation: Limits of Stokes law

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A key challenge in biomedical imaging with nanocrystals is determination of sparticle size. In general conjugation will lead to an increase in the hydrodynamic size of the nanocrystal. This can be used to separate conjugated nanocrystals and to estimate the number of biomolecules bound to the nanocrystal. Sizing of biological molecules by TEM is generally fraught with difficulty. Consequently, methods which directly measure the hydrodynamic size are preferable.

One of the most promising methods is analytical ultracentrifugation. However, as with many other sizing techniques, the method assumes that the diffusion coefficient determined from sedimentation velocities can be converted into an effective size via Stokes Law. It also requires the exact thickness of the ligands used to colloidally stabilize the nanocrystal to be known or determined. This is an ongoing area of research [1]. In this paper we examine new data on the systematic study of CdSe, Au nanocrystals and fullerene in the presence of different ligands [2,3].

We demonstrate that AUC can resolve differences in size down to $< 1\text{\AA}$ during sedimentation and can resolve different sized ligands. However we find that Stokes' law breaks down for particle sizes $< 4\text{nm}$. The reasons for this relate to increases in the solvent viscosity near the nanocrystal surface, which lower the sedimentation rate. The result is that the predicted particle sizes are larger than experimentally found. A model

to explain these deviations will be presented [4].

We find that calibration curves produced by AUC are as good as those from TEM, are statistically more precise and less prone to operator bias. The method is non-destructive and allows even minor aggregation to be detected. These calibration curves will make it possible to study quantitatively the binding of biological molecules to nanocrystals for medical imaging applications.

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COLL 383

Upconverting nanoparticles as platforms for multimodal imaging and metal-based photochemotherapy

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Rare-earth upconverting nanoparticles (UCNPs) transform near infrared into UV-visible light via multiphotonic processes, and simultaneously display promising magnetic resonance and nuclear imaging capability. Significant research efforts are underway to design innovative theranostic agents, which integrate the attractive diagnostic features of these nanomaterials with light-activation strategies for drug delivery and photodynamic therapy.¹

In this contribution, we will discuss our most recent advances in the development of UCNPs as bone-targeting multimodal imaging probes, and demonstrate their potential for the near infrared photoactivation of antitumor metal-based prodrug candidates.²

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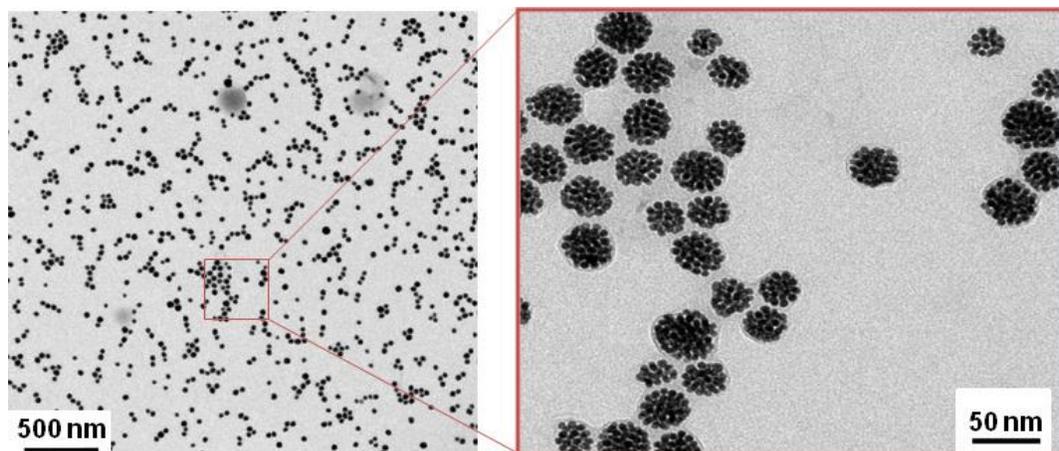
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COLL 384

Controlled assembly of biocompatible metallic nanoaggregates using a small molecule crosslinker

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The controlled assembly of biocompatible nanoparticle aggregates using small molecule crosslinker has been a long standing challenge, likely owing to difficulties in controlling rates of initiation, propagation and termination. Here we demonstrate that adjusting the concentration of the starting nanoparticles or the crosslinker allows for the preparation of relatively homogenous aggregates from metallic nanoparticles of varied composition and size, presumably by controlling the rates of initiation and propagation. Capping reactive thiols on the formed aggregates with PEG-maleimide provides a termination step and renders the aggregates stable and biocompatible. The size of the aggregates can be systematically adjusted. The aggregates are biocompatible and show no toxicity when incubated with cells. The aggregates are highly stable and appear unchanged after uptake by cells. The aggregates are readily labelled and used for PET imaging. It is expected that this straightforward and inexpensive assembly of highly stable nanoparticle aggregates will expand the biological applications of this class of materials. Furthermore, this method for preparing aggregates is highly modular as the crosslinker, the building block nanoparticles and the exterior coating can all be independently varied and the use of alternative crosslinkers and capping agents will enable applications in diverse material applications.



Nanoparticle aggregates can be assembled in a controlled fashion using small molecule crosslinkers. They are biocompatible and can be used for PET imaging.

COLL 385

Characterization of amphiphilic copolymer micelles for drug delivery

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Amphiphilic copolymers with a polyethylene glycol (PEG) backbone and side chains of different molecular weight and hydrophobicity form spherical aggregates (micelles) in aqueous solution. These copolymer aggregates can be used as carriers of hydrophobic drugs and for imaging purposes. Certain types of aggregates are expected to be more suitable for incorporation of small hydrophobic molecules in their core and subsequent release. The aggregates adsorb very sparingly to hydrophilic, negatively charged surfaces because of their outer, PEG-containing region. Atomic force microscopy (AFM) in tapping mode in liquid was used to characterize the adsorbed aggregates to detect the presence of a hydrophobic core and monitor possible size changes when other molecules become incorporated. A good correlation was found between the volume of individual adsorbed aggregates of different copolymers as determined with AFM and light scattering data on the corresponding aggregates in solution.

COLL 386

Imaging gold nanoparticles in and around cells

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Gold nanoparticles scatter visible light very well, and so can readily be imaged by darkfield microscopy. In this talk I will describe how to make these particles resonant with different frequencies of light; what kind of imaging experiments can be done with them, with cells; and finally show more recent work that showcases the surprising result that gold nanoparticles can influence cell behavior, even if the particles are not in the cells.

COLL 387

PEGylated gold nanoparticles: Impact on cell fitness

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Gold nanoparticles (Au NPs) are among the most widely studied materials in the context of bionanotechnology. The interesting optical properties of Au NPs makes them well-suited materials for myriad applications in life science, including photothermal therapy,

optoacoustic imaging, biosensing, etc. Moreover, Au NPs are considered among the safest nanomaterials, mainly because of the inertness of gold, which confers Au NPs with good stability against corrosion in physiological media. Indeed, Au NPs are already being applied in clinical trials as photothermal agents. PEGylation of NPs, i.e., surface modification of NPs with polyethylene glycol (PEG), is among the most widely applied surface modification applied to NPs aimed for biological applications.

The physico-chemical properties of various series of PEGylated gold nanoparticles, varying in the molecular weight of the PEG, size of inorganic core, hydrodynamic size and net charge, are exhaustively described, including stiffness, hydrophobicity and catalytic activity. For a series of PEGylated gold nanoparticles only two parameters, net charge and hydrophobicity were varied, whereas other parameters such as hydrodynamic size, stiffness and catalytic activity were kept constant. The impact on cell fitness of this series of nanoparticles was evaluated, revealing that less negatively charged, more hydrophilic nanoparticles were more effectively uptaken by cells and further, they had a negative impact on membrane health, autophagy and cell area.

COLL 388

Enhanced two-photon photoluminescence with colloidal plasmonic semiconductor nanocrystals

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Two-photon absorbing (TPA) inorganic nanoparticles that are capable of upconverting near-infrared (NIR) light have the potential to enable a wide range of biophotonic applications, ranging from fluorescence imaging in live tissue to photodynamic therapy and clinical diagnostics. The synthesis of bright nanoparticle probes with large two-photon action cross-sections is still a major challenge. One strategy to increase the brightness of TPA nanoparticles is to excite a localized surface plasmon resonance (LSPR) that serves as virtual state for NIR photon absorption. I will present spectroscopic data for CuS nanodisks demonstrating that these colloidal semiconductor nanocrystals that support LSPRs in the NIR to mid-infrared wavelengths have the potential to exhibit extraordinary two-photon action cross-sections. We measure the two-photon action cross-sections for CuS nanodisks whose LSPR wavelengths are tuned on and off the NIR excitation wavelength. We also demonstrate that these TPA properties can be tuned to span a large range operating wavelengths covering the tissue transparency window. Overall, these colloidal semiconductor nanocrystals present a novel “all-in-one” structure for nonlinear optical processes since there is no physicochemical interface between plasmonic and photoluminescent components.

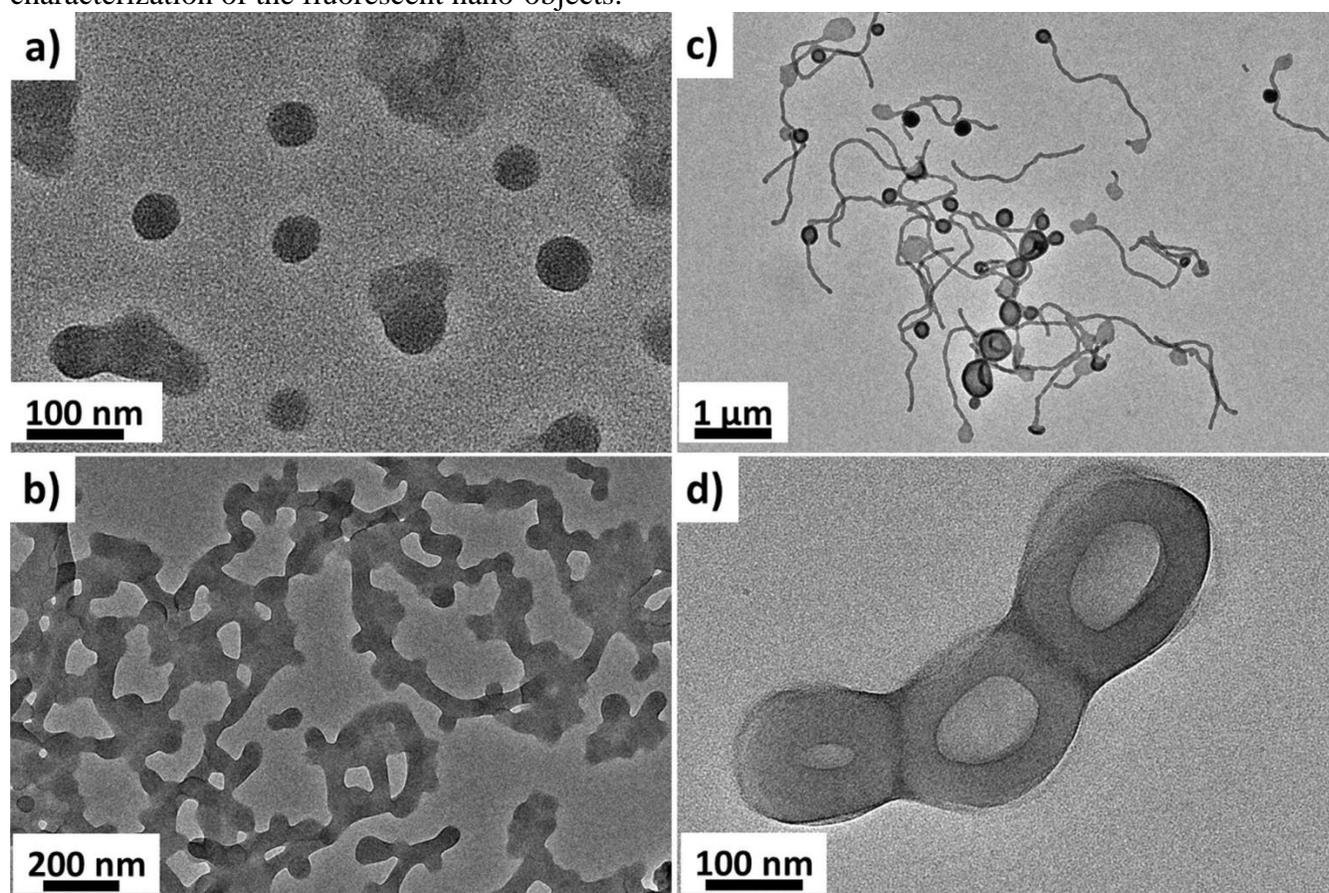
COLL 389

Controlling the morphology: A Facile approach to prepare fluorescent nano-objects via polymerization-induced self-assembly

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Fluorescent nano-objects with controllable sizes and morphologies were prepared using reversible addition-fragmentation transfer alcoholic dispersion polymerization of benzyl methacrylate (BzMA) and 2-(4-vinylphenyl)ethene-1,1,2-triyl)tribenzene (TPE), a polymerizable derivative of the aggregation-induced emission dye. The molar ratio of BzMA to the macromolecular chain-transfer agent poly[2-(dimethylamino)ethyl methacrylate] (PDMAEMA) was set as 160, 220, 320 and 360, respectively, while the ratio of TPE to PDMAEMA was kept constant. After polymerization for 24 h at 70 °C, the resulting colloid was characterized by ^1H NMR, fluorescence spectrum, dynamic laser scattering and transmission electron microscopy. As the ratio of BzMA/PDMAEMA increased, hydrodynamic size of these self-assemblies increased accordingly, and their shape evolved from micelles to worm-like micelles and vesicles. This approach provided a facile way to prepare fluorescent nano-objects with controllable sizes and shapes, which may find applications in studying the shape effect on bio-imaging.

a) Synthetic routes to the fluorescent nano-objects, and b) ^1H NMR, c) fluorescence, and d) DLS characterization of the fluorescent nano-objects.



TEM morphology evolution of the fluorescent nano-objects when setting the ratio of BzMA/PDMAEMA as a) 160, b) 220, c) 320 and d) 360.

COLL 390

Synthesis of bulk mesoporous dilute alloy catalysts

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Unsupported bulk mesoporous dilute alloy catalysts have the potential for major impact on improving the energy- and atom-efficiency of chemical synthesis. These unsupported mesoporous alloy catalysts can be easily prepared by selective corrosion. The process results in the formation of well-defined unsupported bicontinuous architectures with nanoscale ligaments and pores that are mechanical robust and thermally stable, thus eliminating complications from metal-support interactions. The most studied example is nanoporous gold (np-Au), which is actually a Au-rich Ag-Au alloy which, specifically in the $\text{Ag}_{0.03}\text{Au}_{0.97}$ composition, combines high reactivity and selectivity for a wide variety of oxidation reactions, from simple CO oxidation to complex oxygen-assisted coupling reactions. Various techniques have been developed to further tune the alloy composition by doping with small amounts of active metals or metal oxides. Specifically, we will discuss the fabrication and catalytic performance of metal and metal oxide modified np-Au and np-Cu alloy foams. We observed that even small amounts of Ni doping activate nanoporous gold for ethanol dehydrogenation and significantly lower the activation energy for ethanol dehydrogenation on nanoporous copper. One monolayer thick alumina coatings, prepared by atomic layer deposition, further stabilize the nanoscale morphology and thus improve the long-term stability. Finally, we will provide an outlook on the fabrication of micro-architectures with complex deterministic morphologies and compositions that are optimized for catalytic and transport properties by using additive manufacturing techniques such as direct ink printing or projection micro-stereolithography.

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COLL 391

Structure and reactivity of AgAu Alloys

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New catalysts capable of selective conversion under mild conditions could dramatically decrease the energy demands of the chemical industry. Nanoporous Au, a nanostructured material with 2 to 3% Ag, is capable of highly selective (~100% in some cases) oxidation under mild conditions with high stability. The dissociation of O₂ is the most critical step in many oxidation processes on nanoporous Au, yet the active site for O₂ dissociation is unknown. Therefore, we have performed a careful search for structures that can both form under reaction conditions and are able to dissociate O₂.

We predict that the terraces are Au-terminated under reaction conditions, and hence are unlikely to dissociate O₂. However, step sites likely can dissociate O₂: under reaction conditions, Ag is most stable in the rows next to the step sites, and the barrier to O₂ dissociation on these structures is lower than on Ag(110), which can dissociate O₂ at room temperature. The barrier we calculate on these AgAu step sites is in agreement with our experimental results for the barrier on nanoporous Au. Our findings may explain the high activity and high selectivity of nanoporous Au, as these mixed-metal step sites can likely dissociate O₂ (unlike pure Au) but may remain selective for oxidation processes (unlike pure Ag).

COLL 392

Continuous gas phase catalytic production of methyl acrylates by nanoporous gold-mediated cross coupling

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Acrylates and methacrylates are important building blocks of industry. They are produced primarily by acid-catalyzed homogeneous reactions, resulting in energy demands for separation and waste remediation processes. In an effort to reduce this energy demand, there has been considerable attention given to the development of heterogeneous catalysts for the direct oxidative coupling of unsaturated alcohols and/or aldehydes to form esters. Here we report the catalytic production of acrylates in the gas phase at one atmosphere pressure using np(Ag)Au catalysts in the presence of O₂. Model studies on well-defined Au(110) surfaces in ultrahigh vacuum show the selectivity to depend strongly on the gas phase composition., and these effects are mirrored in the steady state catalytic behavior over np(Ag)Au. The findings extend the fundamental principles of selective oxidation coupling on gold surfaces to the production of unsaturated esters..

COLL 393

Catalytic reactions on optically excited plasmonic metal nanoparticles

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It has been recognized for some time that strong interaction of electromagnetic fields (e.g., light) with plasmonic nanomaterials offers opportunities in various technologies that take advantage of photophysical processes amplified by this light-matter interaction. More recently, it has been shown that in addition to photophysical processes, optically excited plasmonic nanoparticles can also activate chemical transformations directly on their surfaces. This potentially offers a number of opportunities in the field of selective chemical synthesis.

I will discuss our findings that plasmonic silver nanoparticles, optically excited with low intensity visible light, exhibit direct photo-catalytic activity. I will discuss underlying mechanisms associated with these phenomena. 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.

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COLL 394

Experimental establishment of scaling relationships for processes on alloy catalysts

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Scaling relationships between fundamental kinetic parameters for catalytic processes and descriptors of catalytic materials have greatly accelerated the use of computational methods such as DFT to screen and identify catalyst materials that are optimal for a given process. For example the barrier to a critical, rate-determining elementary step, ΔE_i^\ddagger , can be correlated with electronic properties such as the *d*-band energy, E_d , thereby allowing E_d , rather than ΔE_i^\ddagger , to be used as the basis for rapid screening of new materials. We have developed the experimental analog to this methodological framework by using high throughput methods to make rapid parallel measurements of catalyst reaction kinetics and catalyst properties across continuous regions of alloy composition space. The kinetics of H₂-D₂ exchange have been measured at 100 compositions of the Pd_xAg_{1-x} alloy with $x = 0 \rightarrow 1$, in order to determine the barriers for dissociative adsorption and recombinative desorption of H₂ as functions of alloy

composition, ΔE_{ads}^\ddagger and ΔE_{des}^\ddagger respectively. A number of catalyst properties have also been measured across alloy composition space: the d -band energy, $E_d(x)$; surface segregation, $\theta_{Ag}(x)$; and the hydrogen adsorption energy, $\Delta E_H(x)$. Using alloy composition, x , as the parametric variable, these then allow the establishment of experiment-based scaling relationships such as $\Delta E_{ads}^\ddagger(E_d)$. In the case of H_2 adsorption these demonstrate the expected monotonic decrease of the ΔE_{ads}^\ddagger with increasing E_d (relative to the Fermi level), but also reveal that the scaling is non-linear. This non-linearity may be a consequence of hydrogen-induced Pd segregation to the alloy surface.

COLL 395

Discovery and optimization of catalysts using high-throughput approaches

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High-throughput experimental (HT) methodologies are uniquely suited to rapidly generate experimental data, and hence represent the key enabling counterpart to bring computational materials design efforts to fruition. The field of catalysis was an early adopter of high-throughput screening technologies. Two examples for employing high-throughput approaches to the discovery and optimization of catalysts from our group will be discussed.

1) The synthesis parameters of catalytic nanostructures for a multi-dimensional parameter space that is often being explored only in small subsections due to experimental constraints. In addition, synthesis metadata are often not connected with the final reaction performance of catalysts. We will show an example where the synthesis of a variety of Cobalt CO oxidation catalysts was systematically explored and synthesis parameters were mapped onto reactivity using high-throughput experimentation.

2) Often, catalyst deactivation is addressed by optimizing composition and particle size of the catalysts and by periodic off-stream regeneration. In Fischer–Tropsch synthesis (FTS), the primary reaction involves the hydrogenation of CO and polymerization of hydrocarbons. Water is produced as a side-product. Metallic Co is the preferred catalyst for FTS, however, the presence of water has made it difficult to implement Co. Thus, tuning the redox reaction to favor reduction of the oxide in situ preserves metallic Co under reaction conditions and constitute a key advance in the field of FTS. Kinetic and spectroscopic data will be presented to demonstrate the concept of such a self-healing catalyst based on Co nanorods.

COLL 396

Modeling energy efficient catalysts from first principles

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The current demand for highly selective and energy-efficient catalysts requires increasingly reliable (accurate and efficient) methods for modeling of complex materials based on quantum-mechanical first principles. The development of such novel approaches based on density-functional theory and many-body dispersion (DFT+MBD) methods for non-covalent interactions will be highlighted in this lecture. The application of DFT+MBD (or approximations thereof) to complex material interfaces reveals several surprising findings: (i) van der Waals interactions determine the selectivity of catalytic reactions on gold surfaces [1], (ii) the stability of aromatic molecules is the same on Cu, Ag, and Au surfaces, despite their very different electronic properties [2], (iii) the dynamical behavior of molecules on realistic stepped surfaces can be significantly more complex than revealed by non-dynamic measurements [3], (iv) "Weak" non-covalent interactions can strongly affect (opto)electronic properties of organic/inorganic interfaces, in agreement with experiments [4]. All these findings, taken together, reveal the surprising qualitative role of presumably "weak" non-covalent interactions in energy-efficient catalysts and other complex material interfaces.

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COLL 397

Understanding the interactions of conjugated oligoelectrolytes in phospholipid membranes for enhanced cross membrane charge transfer

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Many molecules spontaneously incorporate within biological membranes and alter their properties for a wide range of applications including antimicrobial activity, drugs, signaling, and bioelectrochemistry. Despite the numerous applications, the interactions of these additives within phospholipid membranes are often poorly understood due to the complicated and variable properties of phospholipid membranes and challenges associated with characterizing them. Here, we examine the interactions of conjugated oligo-electrolytes (COEs) within phospholipid membranes. COEs readily incorporate bacterial and eukaryotic membranes, where they facilitate charge transport; this has been to enhance the performance of numerous bioelectrochemical devices, including microbial fuel cells and bioelectrochemical synthesis. Electrochemical techniques (e.g.,

cyclic voltammetry) were used to understand how the activity of COEs is modulated by phospholipid membrane properties in model bilayer systems while nanoparticle attachment was used to probe COE behavior in *Shewanella oneidensis*. It is shown that the COEs alter the properties of the surface of *S. oneidensis* in a concentration dependant manner and that furthermore the activity of COEs in phospholipid membranes can be modulated by addition of additives like cholesterol, choline and cholic acid.

COLL 398

Fixed membranes for the study of wildtype α -synuclein's binding to lipid bilayers

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The protein α -synuclein has been heavily implicated in the development of multiple neurodegenerative diseases, notably Parkinson's disease. While its natural function is still unknown, α -synuclein is suspected to be involved with the regulation of neurotransmitter vesicles, due to its well-known behavior for forming α -helical secondary structures upon binding to acidic phospholipid vesicles, as well as its high affinity to these anionic vesicles. However, due to the malleable nature of vesicles and liposomes, it is difficult to ensure the retention of their size, shape, and structure after protein binding. In fact, α -synuclein has been shown previously to possess the ability to deform lipid vesicles into tubular structures. To circumvent this, we functionalized gold nanoparticles with diameters ranging from 12 - 90 nm with a hybrid lipid bilayer in order to "fix" the radius of curvature of the liposome. A gold core in the center of these hybrid liposomes adds useful optical and photothermal properties to these lipid vesicles. The results of this study suggest that wildtype α -synuclein shows high tendencies for forming α -helical structures when bound to lipid nanoparticles with diameters of 12 – 20 nm and 65 – 85 nm; surprisingly, α -synuclein seems to adopt a different protein conformation when bound to lipid nanoparticles with diameters 30 – 45 nm.

COLL 399

Interactions of nano-size antibiotics with biomimetic bacterial cell membranes

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The increasing prevalence of bacterial strains with resistance to conventional antibiotics is a major global healthcare problem. Strategies based on the cellular response of bacteria to antimicrobial agents have been followed to reduce the adaptive pressure on

these bacteria. One of these strategies consists in damaging the bacterial membrane, which leads to leakage of intracellular constituents into the extracellular environment and changes in intracellular pH. Langmuir technique has been used to evaluate the interaction of several antibacterial agents with cell membrane models at the molecular level.

In this work Vancomycin (VAC) - a widely used antibiotic with acquired bacteria resistance – was transformed sonochemically into nanoparticles (NPsVAC) which antibacterial efficiency was further evaluated on biomimetic bacterial membranes. The results indicate a higher membrane-VAC interaction when antibiotic is in nano-form rather than in solution.

On the other hand, nanoparticles (NPs) during circulation in biological fluids are affected by the protein corona phenomenon that consists in the adsorption of biomolecules on the NPs surface altering thereby their targeting and efficiency. Thus, the bacterial membrane-NPsVAC interactions were also studied in corona effect conditions, in order to simulate the real application scenario.

COLL 400

Interaction between triblock copolymer poly (propylene glycol) – poly (ethylene glycol) – poly (propylene glycol) and model lipid membranes

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Lipid nanoparticles composed of model membranes can spontaneously form clusters induced by amphiphilic triblock copolymers through the hydrophobic interaction. Here we investigate the dynamic behavior of such clustering in a unilamellar vesicle (ULV) system composed of 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine (DPPC) and 1,2-dihexanoyl-*sn*-glycero-3-phosphocholine (DHPC) induced by amphiphilic poly (propylene glycol)_m – poly (ethylene glycol)_n – poly (propylene glycol)_m (PO_m - EO_n - PO_m). Time-resolved UV-vis absorption and static light scattering were employed to monitor the aggregation rate. Our results show that the introduction of acyl chain mismatch between DHPC and DPPC is essential to facilitate the formation of clusters through creating ‘active sites’ on the ULV surface. With higher polymer-to-lipid weight ratio (P/L), the apparent UV-vis absorption and radius of gyration always grew faster at the initial clustering stage, while, at the later stage of clustering, the final size of the clusters strongly depends on the hydrophobicity of the polymer. Specifically, the relatively hydrophilic polymer, PO₁₄ – EO₁₄ – PO₂₄ induced larger terminal aggregates at higher P/L ratios, while the more hydrophobic polymers, PO₂₅ – EO₇ – PO₂₅ and PO₂₆ – EO₂₀ – PO₂₆ resulted in smaller terminal clusters at higher P/L ratios. This phenomenon can be explained by the fact that hydrophobic polymers are more stable

when their hydrophobic segments are embedded in the bilayer core, thus presumably consuming the majority of the active sites on the ULV surface at the initial clustering stage, inhibiting further clustering of ULVs when at high P/L ratio. However, the majority of the more hydrophilic polymer remains in water phase, allowing more “active sites” available for larger clusters to form at the later stage at the same P/L ratio. Molecular simulation will be performed to further verify our hypothesis in the future. The fundamental understanding of the polymer-induced ULV clustering mechanism enables our design of instrument-free biosensor as a signal amplifier.

COLL 401

Molecular mechanisms of peptide and protein binding at nanostructured interfaces

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To achieve the overall goal of constructing sensors and devices that incorporate and exploit the physical properties of biomolecules relies on developing a fundamental molecular level understanding of how biomolecules interact and organize at abiotic interfaces, specifically the surfaces of nanomaterials. Recently, researchers have been making considerable headway identifying and studying peptides that bind various nanomaterials with modeling techniques. However, experimental molecular level detail regarding how peptides and proteins are structured at nanoparticle (NP) surfaces is still lacking. A first step is the understanding of how specific amino acids in a given protein sequence bind to nanoparticle surfaces. Our research group is using a combination of solution and solid-state nuclear magnetic resonance (NMR) techniques to probe these interactions and ultimately, determine the structure of biomolecules at the surface of nanostructured materials. We believe a better understanding of the molecular structure and dynamics of peptides and proteins on NP surfaces will help advance the field and bring us closer to building devices that couple the unique properties of biomolecules with NPs. We have been developing and applying NMR methods to probe the conformational structure and molecular interactions (H-bonding) responsible for the assembly of amino acids, peptides, and proteins at the interface of various nanostructured materials. Recent results from our research group on this topic will be discussed.

COLL 402

Semiconductor nanorods functionalization for plasma membrane insertion

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Colloidal semiconductor nanoparticles prepared by hot injection into the high-boiling point organic solvents, e.g., tri-n-octylphosphine oxide (TOPO), are intrinsically hydrophobic. Their utilization for biomedical applications requires surface modification and functionalization that render the nanoparticles biocompatible. Such functionalization is usually achieved either by (i) amphiphilic copolymer encapsulation while keeping the original surface ligand intact; (ii) exchange of the original ligands with new multifunctional ligands. We present a facile surface chemistry that replaces covalently bound surface ligands with cysteine-rich alpha-helical transmembrane polypeptides. This unique chemistry and peptide functionalization is aimed at inserting ~10-12 nm short ZnSe/CdS type II nanorods into the plasma membrane in a vertical orientation by self-assembly. Once stably inserted into the membrane, these nanorods could serve as single particle membrane potential probes via the quantum confined stark effect (QCSE)

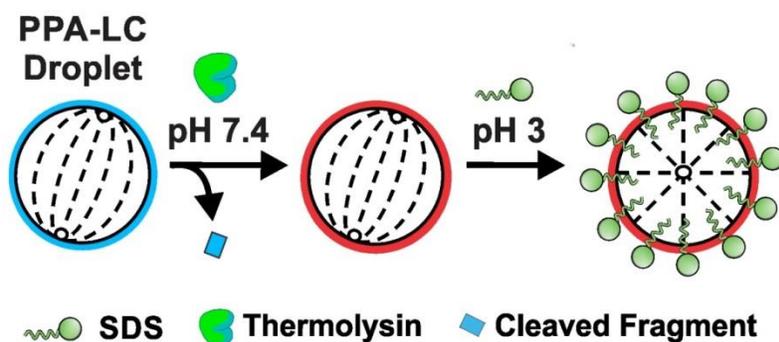
COLL 403

Transforming liquid crystal interfaces with enzyme-responsive polymers and surfactants

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Biological signal cascades found in living systems are highly concerted for performing advanced functions. Attempts to synthetically mimic their complexity are of great interest, though significant challenges in simulating their dynamic nature remain. Notably, amplification of molecular triggers is garnering specific importance for many applications like advanced biosensors and “smart” materials. One example is the use of liquid crystals (LCs), which can be utilized as optical reporters of biological events that occur at aqueous-LC interfaces. Furthermore, LCs can dynamically couple with responsive systems, thus permitting a customizable approach for transmitting nanoscopic or microscopic responses. We have developed biologically active peptide polymer amphiphiles (PPAs), which incorporate biphenyl mesogens capable of organizing within LC phases. Rational design of this system permits the detection of biomolecular events (i.e. enzyme cleavage) due to LC ordering transitions in co-surfactant and PPA-coated LC microdroplets.¹ We note that this work establishes a potentially modular approach for detecting a range of biomolecular events, wherein the composition of PPA and interactions between PPAs and co-surfactants can be tailored to induce changes in LC geometries.

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COLL 404

Aggregation properties of a short antimicrobial peptide in the presence of model membranes

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The cationic antimicrobial peptide CA14 with the sequence CWGEAFSAGVHRLA was found to inhibit the growth of bacteria. The physical stability and secondary structure of CA14 were investigated in the presence of model membranes. The model membranes are composed of 1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC) and 1,2-Dioleoyl-sn-glycero-3-phosphocholine (DOPC). Infrared (IR), dynamic light scattering (DLS), fluorescence, differential scanning calorimetry (DSC), and atomic force microscopy (AFM) techniques were employed. Infrared spectroscopy was used to examine changes in secondary structure content while AFM imaging was used to examine the morphological differences. DLS measurements were performed to monitor the aggregation process. IR spectra indicate that CA14 adopts a major α -helix structure in the absence of model membranes. An increase in β -sheet structure content of CA14 is observed in the presence of model membranes. Interaction of CA14 with model membranes was examined using tryptophan and phenylalanine fluorescences. Upon addition of the model membranes, the initial fluorescence of CA14 is quenched. The decrease in fluorescence is selective for DPPC relative to other neutral phospholipid DOPC. Dynamic light scattering (DLS) data indicate that CA14 peptide has an influence on the size distribution of model membranes. In the presence of increasing amount of CA14, a disappearance of large vesicle aggregates was observed. AFM images show a significant change in the surface roughness level of DPPC and DOPC vesicles in the presence of CA14. DSC data indicate that the incorporation of CA14 greatly modifies the thermal stability of DPPC and DOPC

COLL 405

Enzymatically-crosslinked multilayer antioxidant/nanoantibiotic coatings for prevention of bacterial biofilms

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The increasing emergence of multi-drug resistant bacterial strains is one of the most serious problems in modern medicine. To overcome the action of conventional antibiotics bacteria develop various effective resistance mechanisms including the formation of surface-attached communities of cells enclosed in extracellular polymeric matrix, known as biofilms. Biofilms formed on indwelling medical devices cause life threatening infections and are associated with increased mortality and morbidity in the hospitals. Therefore, novel strategies for prevention and eradication of drug resistant bacterial biofilms have been sought. This work reports the development of antibacterial and antibiofilm coatings on medical devices comprising polyphenols and antibiotic nanocapsules (NCs). The widely used antibiotic gentamicin was first sonochemically processed into NCs improving its antibacterial potential. Afterwards, the nanoantibiotic was combined with the antioxidant tannic acid to build bacteria resistant multilayer coatings on the surface of silicone urinary catheters. To improve the stability of the coatings at physiological conditions, the deposited layers were further crosslinked with laccase enzyme. The antibacterial efficiency of the coatings with nano-gentamicin was significantly enhanced compared to the coatings of non-processed antibiotic. Moreover, the biofilm formation of clinically relevant Gram-negative *Pseudomonas aeruginosa* and Gram-positive *Staphylococcus aureus* was reduced by 40 % in static conditions. The enhanced antibiofilm activity of the nanoantibiotic assemblies was also demonstrated *in vitro* under dynamic conditions using a model of catheterized human bladder. Laccase-assisted crosslinking of the layers resulted in the formation of stable coatings able to counteract biofilm occurrence over seven days of catheterization.

COLL 406

Antibacterial approaches from materials engineering perspective: Enzymes on work

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Nosocomial infections are the infections that patients acquired in hospitals. These infections represent a leading cause of death, increased stay in hospitals and healthcare costs. Here we describe several antimicrobial approaches for biotechnical functionalisation of medical textiles and indwelling devices, and the early diagnosis of infection.

Medical textiles coated with antimicrobial nano-particles (NPs). Current technologies for

antimicrobial NPs coating of medical textiles are characterised by low coating stability and poor uniformity of the coatings, leaching of NPs, energy-consuming coating processes and dark colour of silver – the most widely used antimicrobial agent. Alternatively, sonochemistry can be used as a versatile tool for designing of antimicrobial surfaces. Combined sono-enzymatic coating of fabrics with ZnO improved the NPs uniformity and adhesion, and enhanced their antimicrobial activity. The antibacterial efficiency of the coatings resisted multiple washing cycles at hospital laundering regimes.

Anti-biofilm indwelling medical devices. 80% of all urinary tract infections treated in hospitals are due to biofilm formation on the catheters. Building a dual antimicrobial/antifouling coating on silicone urinary catheters using an enzyme-triggered bottom-up approach efficiently prevented the biofilm formation of both Gram+ and Gram- bacteria. Bacterial cell-to-cell communication, involved in biofilm formation, is regulated through secretion and uptake of extracellular signals called autoinducers (AIs). Coating of urinary catheters with enzymes quenching the AIs and degrading the biofilm matrix provided efficient antibiofilm effect both *in vitro* and *in vivo*. Importantly, the enzymatic quenching of AIs was achieved in the extracellular environment eluding the intrinsic resistance-development mechanisms of bacteria and attenuating bacterial virulence. Moreover, the nano-formulation of these enzymes with clinically relevant antibiotics provided increased bacteria susceptibility at lower antibiotic dosage. Enzymes can be used as biomarkers for wound infection in a diagnostic kit. This kit relies on the detection of overexpressed during infection MMPs, MPO and lysozyme, implementing two complementary strategies to detect bacterial infection - immunochemical quantification of the enzyme proteins, and quantification of the enzymatic activities.

COLL 407

Contrasting the interactions of dental pulp stem cells with 3-D printed vs molded polymer constructs

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Additive manufacturing is increasingly being used to replace standard extrusion methods in engineering polymeric biomedical scaffolds. The principal advantage of this technology is the ability to print directly from a biomedical scan to produce components which are designed for an individual. Hence devices, whose function and utility had previously been demonstrated, can now be potentially manufactured in a simpler and more efficient manner. The question arises whether devices which may be macroscopically similar are in fact identical when interacting with cells. The surface properties of materials determine the nature of the interaction with tissue. Hence, even though the bulk properties may be similar, the surface properties, are far more sensitive to the manufacturing process. Since cells interact with surfaces on multiple length scales, this is a critical question when considering the function of biomedical devices. For this research we used MakerBot printers with PLA filaments. The scaffolds were

sterilized with ETO and dental pulp stem cells were incubated on the scaffolds in alpha-MEM, 10% FBS, and 5% CO₂, for up to 28 days.

Examination of the PLA scaffolds revealed significant differences in roughness between molded and printed surfaces. Molded surfaces were smooth, while printed surfaces had heterogeneous roughness. on multiple length scales. SEM/EDX examination of the sample surfaces after 28 day incubation in the absence of any induction factors revealed much larger quantities of biomineralized deposits on the printed than the molded surfaces, which correlated to up regulation of ALP and OCN on these surfaces. Hence 3D printing induced differentiation in the absence of any soluble inducing agents.

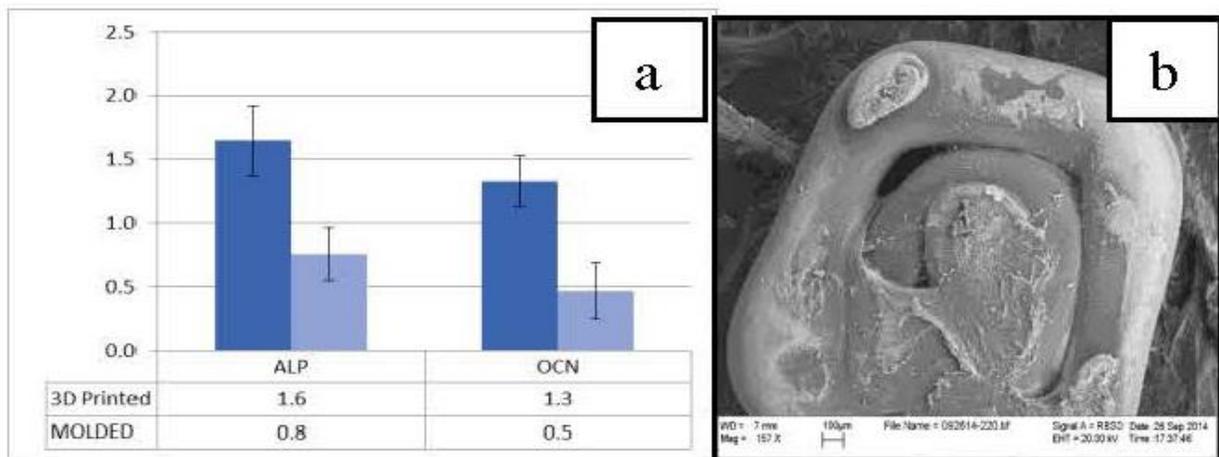


Figure 1. (a) qRT-PCR of DPSC incubated on printed and molded scaffolds for 28 days. (b) SEM image of surface feature of the 3-D printed scaffold.

COLL 408

DNA from mm to nm length scales

Juan J. De Pablo, depablo@uchicago.edu. Institute for Molecular Engineering, University of Chicago, Chicago, Illinois, United States

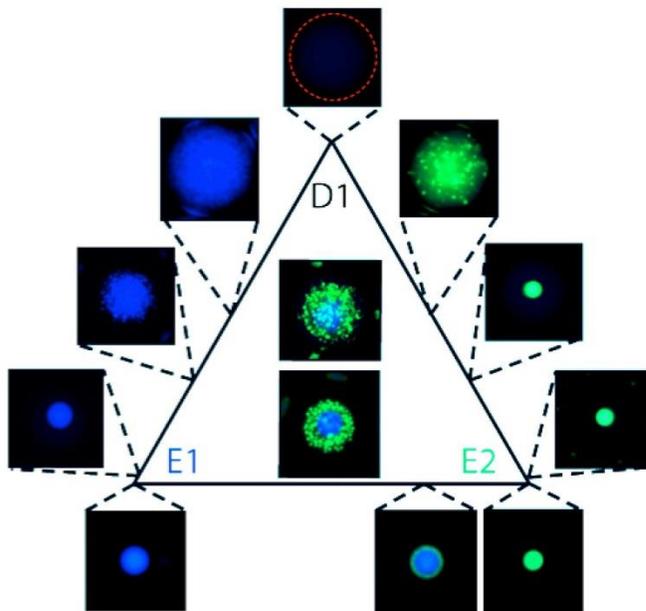
The packaging of DNA in chromatin involves elements of molecular recognition at angstrom length scales, interactions between nucleosomes at nanometer length scales, and fibers at 10's to 100's of nanometer dimensions. In this presentation, a multiscale description of chromatin will be presented in which van der Waals, electrostatic, and hydrodynamic interactions are coupled to arrive at a description that is able to explain a number of intriguing structural and dynamic features of DNA packaging.

COLL 409

Programming molecular self-assembly of intrinsically disordered proteins

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A number of dynamic, protein-rich intracellular structures containing phase separated, unstructured proteins comprising low-complexity amino acid sequences have recently been shown to serve a variety of important cellular functions, including signaling, compartmentalization and stabilization. The understanding of these structures, and the ability to synthesize models of them, has been limited. Here we present simple methods for programming diverse assemblies comprised of a series of elastin-like polypeptides, model intrinsically disordered proteins possessing sequences of low-complexity. By encoding the stimulus-induced phase behavior of proteins at the amino acid sequence level, we demonstrate the reversible formation of a variety of protein-rich structures within microdroplets, ranging from uniform nano-, meso-, and micro-scale puncta (small, distinct particulates) to multilayered, orthogonally-phase-separated, multicomponent granules. The ability to build such protein assemblies can facilitate new insights into (1) the genetic to molecular to microscale relationships of phase separating proteins and their assembly, (2) the role of such granules in cell biology, and (3) engineering protein-based microgels.



Schematic processing diagram illustrating the range of micro- and nanostructures possible by programmable assembly of intrinsically disordered proteins in microdroplets.

COLL 410

Design and assembly of nanostructured polyvalent materials

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This talk will describe our efforts to assemble and organize polyvalent nanostructured materials. Polyvalent molecules presenting multiple copies of ligands, have applications ranging from pathogen inhibition to vaccine design. We will describe our recent efforts to design highly active polyvalent molecules. In particular, we will describe the use of protein engineering methods to control polyvalent display. We will examine the stimulus-responsive formation of polyvalent assemblies. We will also discuss recent biological and biomedical applications of polyvalent molecules.

COLL 411

Tension in phase separated bilayers: From molecular structure to system-scale morphology

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The temperature and composition dependence of phase transitions in phospholipid membranes has been the focus of much research in the past several decades because of the role of phase separated domains (phospholipid rafts) in cell signaling and trafficking. Methods such as NMR and FRET have been instrumental in identifying boundaries in thermodynamic phase space between single and phase-separated regions. An important breakthrough, however, has been the somewhat recent use of fluorescent microscopy to identify conditions where phase separated domains are first visible, connecting this boundaries in thermodynamics space. The ability to visualize phase separated domains, however, revealed intricate patterns and additional detail not previously available. In this talk we demonstrate how membrane tension influences phase separation in multicomponent phospholipid bilayers, with the impact of tension made clear through the use of fluorescence microscopy: Solid domains formed at high tension exhibit selective intercalation of membrane dye. Conversely, the solids formed at the same temperatures but at low tension exclude all tracer dyes, indicating a fundamental difference in molecular order between the two types of solids. This difference turns out to be evident in the phase separation temperature as well, if one looks carefully. Finally, the types of solid domains formed at high versus low tension are fundamentally different in shape: either compact irregular flower and hexagons or long stripes that span the entire membrane over many tension of microns, influencing system-scale connectivity.

COLL 412

Molecular structures of biological molecules at abiotic/biotic interfaces

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Biological molecules such as peptides and proteins have been extensively incorporated into composite materials used in many important applications such as biosensors and biochips. The molecular structures of these biological molecules at the abiotic/biotic interface greatly influence the functions of these composite materials. In this study, sum frequency generation (SFG) vibrational spectroscopy has been applied to study molecular structures of peptides and proteins at abiotic/biotic interfaces, supplemented by attenuated total reflection (ATR) – FTIR spectroscopy and CD spectroscopy. Various peptides and enzymes have been immobilized on self-assembled monolayers as well as polymer surfaces, and their structures were elucidated using SFG, ATR-FTIR, and CD as a function of surface coverage and chemical environment. Molecular interactions between peptides and liquid crystals were also examined, showing that the liquid crystal samples respond differently to interfacial peptides with different secondary structures.

COLL 413

Electron transfer within microheterogeneous domains: Colloidal Au–nucleated cytochrome c superstructures

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Ultraporous, multifunctional nanoarchitectures are fabricated by “nanogluing” appropriate guests into the network of an about-to-gel silica sol [1]. Biofunctionality can also be engineered by nanoglu-capture of a protein superstructure previously self-organized in buffered medium by charge-directed assembly of cytochrome *c* at colloidal gold or silver nanoparticles [2–4]. In buffered medium, the superstructure (containing thousands of proteins) stabilizes the interior proteins, as shown by a shift to higher pK for unfolding, and the ability of the cyt. *c* to persist through the harsh conditions necessary to produce an aerogel, as monitored by the shape and intensity of the Soret band. Within the silica matrix, the protein reversibly binds gas-phase NO and remains in a stable configuration for > 6 weeks at room temperature under ambient humidity [2]. The Au nanoparticle that nucleates the protein superstructure serves as a nanoscopic electron bank whereby hundreds to thousands of electrons are ultimately extracted from the Au nanoparticle in buffered medium to form ferrocyanochrome *c*, while the Au nanoparticle is refreshed by reductive regeneration by trace tannic acid present as a stabilizer in the originating commercial colloidal Au sol. The kinetics signatures for electron transfer support the multi-party electron relay necessary to generate ferrocyanochrome *c* without inducing massive oxidation of the single Au nanoparticle at

the heart of the superstructure. Fluorescence monitoring of guanidinium–induced unfolding verifies that superstructure-associated cyt. *c* is stabilized even after reduction of Fe^{III}-cyt. *c* to form Fe^I-cyt. *c*, indicating that the superstructures remain intact during redox reactions. Such studies provide confirmation that the cytochromes are not static entities within the superstructure and that their ability to undergo redox reactions correlates with the size of the Au nanoparticle and the ionic strength of the buffered medium.

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COLL 414

Self-propelled particles in anisotropic environments: From collective bacterial behavior to urinary tract infections

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This talk describes recent research from our lab on the remarkable behavior of motile rod-shaped bacteria suspended in mechanically anisotropic thin films with liquid crystalline properties. In the first part of the talk, we describe a model system of urinary tract infections caused by the bacterial pathogen *Proteus mirabilis*. In this system, elastic forces placed on suspended cells due to the liquid crystalline structure of their environment force them into close physical contact aligned pole-to-pole, the locomotion of cells propels them forward along the far-field director, and the orientation of cells (arranged pole-to-pole) inhibits the flagella from 'reversing' and forming motility structures at both ends of the cell. In these environmental constraints, cells are locked into 1-dimensional, rectified movement over very long distances (centimeters). We discuss parallels to the urinary tract. In the second part, we describe how *P. mirabilis* cells moving collectively on polymer surfaces at high density (e.g., high volume fraction) maximize cell-cell interactions for their mobility. As these cells have large aspect ratios that can be >100, they have adapted to solve the 'packing problem' to maximize cell-cell interactions by altering the composition of their cell walls and to reduce their stiffness. The resulting cells are remarkably pliable (Young's modulus ~100x lower than wildtype

cells), which enables them to bend and be compliant, pack at high density, and move collectively and rapidly across polymer surfaces (e.g., polymer catheters). The change in cell wall properties makes it possible for the cells to colonize new niches, however it comes at a cost, as these cells are sensitive to osmotic pressure changes. These two projects paint a picture of the remarkable behavior of bacterial motility in anisotropic, viscous environments and connect back to the puzzle of how motile bacteria move up the urinary tract against the flow of urine to cause infections that can eventually reach the kidneys.

COLL 415

Growth, coarsening, and alignment of compositional lipid domains in supported bilayer membrane systems

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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, both single and multi-lamellar ones. The emergence of such correlated domains can be attributed to the presence of a thermodynamic coupling between the layers, 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, experiments to date have only provided 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 presented for the threshold shear stress associated with such de-registration processes, and these formulas have enabled us to extract the magnitude of the thermodynamic coupling from experimental data. I will also discuss the extension of this work to investigate the growth, coarsening, and alignment of compositional domains within bilayer membrane stacks.

COLL 416

Influence of periodic boundary conditions on lateral diffusion in membranes

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The Saffman-Delbruck hydrodynamic model for lipid-bilayer membranes is modified to account for the periodic boundary conditions (PBC) commonly imposed in molecular simulations. Model calculations indicate that diffusion coefficients for lipids and membrane proteins determined in computationally viable simulation boxes are strongly affected by PBC. Simulations using the coarse-grained MARTINI model support the theoretical predictions.

COLL 417

Evaluating the raftophilicity of rhodopsin photoreceptor in a patterned model membrane

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Lipid rafts in the cell membrane are believed to affect various membrane functions, including the signaling by G protein coupled receptors (GPCRs). However, the regulatory roles of lipid rafts on GPCRs' functions are still poorly understood, partially owing to the lack of the methods to quantitatively evaluate the affinity of membrane proteins to lipid raft (raftophilicity). We report on a new methodology to gauge the raftophilicity of a representative GPCR in vertebrate photoreceptor, i.e. rhodopsin (Rh), and its cognate G protein transducin (Gt) by using a patterned model membrane. We generated a substrate supported planar lipid bilayer that has patterned regions of liquid ordered (Lo) and liquid disordered (Ld) membrane domains. We reconstituted Rh and Gt into the patterned membrane and observed their lateral distribution and diffusion. Mobile and functional Rh molecules could be reconstituted through the rapid dilution of solubilized Rh. We determined the partition and diffusion coefficients of Rh and Gt in the Lo-rich and Ld-rich regions. Both Rh and Gt were predominantly localized in the Ld phase, suggesting their low affinity to lipid rafts. Patterned model membrane offers a robust and scalable platform for systematically and quantitatively studying the functional roles of lipid rafts in biological membranes including retinal disc membranes.

COLL 418

Short range interactions in model membranes measured by atom recombination and mass spectrometry

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We would like to measure intermolecular associations and proximity in membranes on the length scale of the molecules themselves (i.e. nm or less). FRET is commonly used; however, lipid molecules modified by dyes are very different from the lipids themselves, therefore a label-free method is desirable. We use secondary ion mass spectrometry to

probe the nanometer scale structure of supported lipid bilayers by taking advantage of the *intermolecular* recombination of atomic ions into diatomic species that occurs in dynamic SIMS. In this experiment, one can measure mean distances between molecules on a length scale far below the lateral resolution of the NanoSIMS 50L instrument, which combines high spatial resolution and high mass resolution for chemical imaging. As an example, we show that in lipid bilayers, the efficiency of atomic recombination to form secondary $^{13}\text{C}^{15}\text{N}^-$ ions depends on the distance between ^{13}C and ^{15}N atoms installed on head groups of *different* lipid molecules. Specifically, with site-specific isotopic labeling of lipid head groups, we determine the dependence of recombination efficiency on the average distance between ^{13}C - and ^{15}N -labeled phospholipids in supported monolayers and bilayers. We refer to this method of measuring nanometer-scale distances between isotopically-labeled molecules as a *chemical ruler*, similar in concept to FRET but different in physical phenomenon. High precision isotope ratio analysis with the NanoSIMS 50L makes this a potentially unique way to study proximity between membrane-associated components on the sub-5 nm length scale without the use of fluorescent dyes that perturb bilayer structure. We then apply this chemical ruler to study the structure of supported lipid bilayers of lipid compositions commonly believed to contain nanometer-scale liquid-ordered domains that often serve as models for lipid rafts.

COLL 419

Spatiotemporal control of membrane fusion through photolabile PEGylation of liposome membranes

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Membrane fusion results in the transport and mixing of (bio)molecules across otherwise impermeable barriers. As such, there has been significant interest in developing simple, synthetic systems capable of controlled membrane fusion, not least toward applications in vector-based drug delivery. In this communication, we demonstrate, for the first time, temporal control of targeted membrane fusion in model systems using light as an external and exclusive trigger. Our method relies on the steric shielding and rapid, photo-induced de-shielding of complementary fusogenic peptides tethered to opposing liposomal membranes. In an analogous approach, we also demonstrate spatiotemporal control of liposome accumulation at cellular membranes *in vitro*, paving the way towards high resolution spatiotemporal control of drug and gene delivery, direct to the cell cytoplasm, both *in vitro* and *in vivo*.

COLL 420

De novo lipid membrane synthesis using chemoselective reactions

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Living organisms carry out the *de novo* synthesis and subsequent remodeling of phospholipid membranes. The development of comparatively dynamic artificial lipid membranes will require simple methods to mimic how native phospholipid membranes are synthesized and remodeled. We have developed several strategies to generate lipid membranes from reactive precursors using chemoselective coupling reactions. Using reversible coupling reactions, we have also been able to sequentially form and remodel artificial lipid membranes. Interestingly, *in situ* remodeling of phospholipids is capable of controlling micrometer scale changes in vesicle spatial organization, composition and morphology.

COLL 421

Glycan density controls the phase behavior of lipid membranes

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Hydrated networks of glycans in the form of cell walls, periplasms, or gel-like matrices are ubiquitously present adjacent to cellular plasma membranes. Yet despite their abundance, many of the functions of glycans in the extracellular milieu are unknown. Eukaryotic cells compartmentalize their membranes to carry out biological function. These domains are important for signal transduction, virus entry and budding, and for the development of degenerative diseases such as Alzheimer's. The factors that govern the formation of these membrane domains are also incompletely understood. In this talk I will describe an experimental platform that consists of spatially patterned glycan ligands on hydrophilic surfaces. Lipid membranes that are deposited onto these surfaces appear to interact directly with these glycans. Because of this interaction, the spatial configuration of the glycans control the phase behavior of the membranes: inhomogeneous glycan networks stabilize large lipid domains at the characteristic length scale of the network, while homogeneous glycan networks suppress macroscopic lipid phase separation. Glycan-patterned phase separation is thermally reversible—indicating that the effect is thermodynamic rather than kinetic—and preferential interactions of glycan with ordered lipid phases seem to control patterning. The discovery that glycan networks can control the length scale of domains in lipid membranes necessarily has implications for biological transport processes and potentially rationalizes some puzzling observations that differentiate the behavior of native cell membranes from model membranes. The exact nature of the interactions remains to be elucidated, and may be related to other observations of lipid domain patterning due to interactions of membranes with cytoskeleton proteins.

COLL 422

From nano to micro and back: Theranostic porphyrin assemblies and their *in vivo* fate

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Porphyrins are aromatic, organic, light-absorbing molecules that occur abundantly in nature, especially in the form of molecular self-assemblies. In 2011, we first discovered 'porphysomes', the self-assembled porphyrin-lipid nanoparticles with intrinsic multimodal photonic properties. The high-density porphyrin packing in bilayers enables the absorption and conversion of light energy to heat with extremely high efficiency, making them ideal candidates for photothermal therapy and photoacoustic imaging. Upon nanostructure disruption, fluorescence and photoreactivity of free porphyrins are restored to enable low background fluorescence imaging and activatable photodynamic therapy. Metal ions can be directly incorporated into the porphyrin building blocks of the preformed porphysomes thus unlocking their potential for PET and MRI, making them a true "one-for-all" nanoplatform. We have validated porphysomes' multimodal theranostic utilities in different cancer types (prostate, ovarian, head & neck, pancreatic and brain cancer), tumor models (subcutaneous, orthotopic, chemically-induced and primary) and animal species (mice, hamsters and rabbits). By changing the way porphyrin-lipid assembles, we developed porphyrin lipoprotein nanoparticles (20nm), trimodal (ultrasound/photoacoustic/fluorescence) porphyrin shell microbubbles (~2um), microscopy-controlled porphyrin protocells (10-100um), and hybrid porphyrin-gold nanoparticles, thus expanding the purview of porphyrin nanophotonics. Most recently, we discovered that porphyrin microbubbles could be converted in situ by ultrasound into nanoparticles and visualized optically within tumor. Bursting the microbubbles with ultrasound would increase the permeability of the vasculature, while forming and delivering porphyrin nanoparticles to the tumor, then used for imaging or therapy. Therefore, there is no dependence on the enhanced permeability and retention effect to deliver the nanoparticle. By closing the nano-micro-nano loop, the simple yet intrinsic multimodal nature of porphyrin-based cancer theranostics represents a new nanomedicine frontier.

COLL 423

Building nanoparticles *in situ* for molecular imaging applications

Jianghong Rao, jrao@stanford.edu. Stanford University, Stanford, California, United States

Advances in nanotechnologies and nanomaterials offer numerous opportunities to develop powerful probes for in vivo molecular imaging. However, after systemic introduction into living subjects, nanoparticles often encounter difficulties in specific targeting and rapid renal clearance partially due to their size and surface chemistry. In this presentation I will explore a different concept of developing nanoparticle probes—in situ synthesis of nanoparticles for cancer imaging. Instead of synthesizing nanoparticles in vitro and applying them in vivo, this new approach will deliver small molecules to cells as building blocks and then synthesize nanoparticles from them inside cells.

Our strategy is based on a biocompatible chemical condensation reaction between two chemical groups -- 1,2-aminothiols and 2-cyanobenzothiazole. We have demonstrated that this condensation chemistry can lead to the formation and assembly of nanoparticles in vitro, in living cells under the control of pH, disulfide reduction and/or enzymatic cleavage. This in situ nanoparticle assembly strategy is also working in living animals and compatible with several imaging modalities. I will present examples of applying this strategy to image treatment-induced apoptosis in tumor cells in vivo with whole-body fluorescence, positron emission tomography (PET), and magnetic resonance imaging (MRI).

COLL 424

Application of optical probes in preclinical imaging and translational disease research

Kevin P. Francis, *kevin.francis@perkinelmer.com*. *Preclinical Imaging, PerkinElmer, Alameda, California, United States*

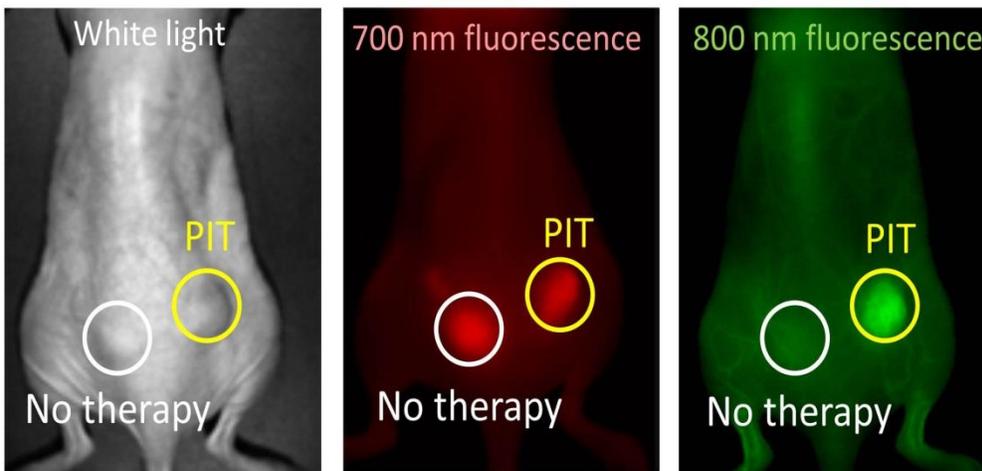
PerkinElmer is a global leader in the development of instrumentation and probes for small animal non-invasive imaging, including optical, PET and μ CT imaging. Through optical imaging, we have developed a technology which allows biological processes, including gene expression that is temporally and spatially defined, to be non-invasively monitored both longitudinally and in real-time. Genes encoding optical reporters, luciferases and fluorescent proteins, are engineered into cells (e.g., cancer cells, stem cells) and pathogens (e.g., bacteria, viruses), or directly into animals (e.g., monitoring host responses) to enable the generation of light that can be visualized through the tissues of a live animal. PerkinElmer is the only company to have optimized this technique to allow true three-dimensional optical imaging and tomographic multimodality imaging (e.g., through co-registration of optical imaging with μ CT and MRI). Furthermore, this technique is equally applicable to imaging of fluorescent dyes and particles, allowing fluorescently tagged biological events (e.g., tracking of antibodies, peptides and viral capsids) to be monitored both independently and in combination with genetically tagged events. PerkinElmer has also recognized the importance of moving optical imaging beyond monitoring small animals, allowing its fluorescent probes to be seamlessly translated from preclinical to diagnostic and surgical applications in large animals (e.g., veterinary), with the view of eventually moving this technology into routine clinical settings. An overview of optical imaging in a range of disease backgrounds will be presented, showing how this approach can be used to refine and improve fundamental biological research, as well as drug development strategies and surgical procedures.

COLL 425

Super-enhanced nano-drug delivery after photoimmunotherapy (NIR-PIT): Oncologic applications

Hisataka Kobayashi, *kobayash@mail.nih.gov*. Molecular Imaging Program, NCI/NIH, Bethesda, Maryland, United States

Target-specific drug delivery that treats cancers but leaves normal tissue unharmed, is the ultimate goal of cancer therapy. Nano-sized drugs have virtually limitless synthetic possibilities enabling a variety of payloads to be delivered to the tumor resulting in effective therapy. Tumors have relatively higher concentrations of nano-sized drugs than normal tissue due to the leaky nature of tumor vasculature, a phenomenon known as enhanced permeability and retention (EPR). The EPR effect, while permitting an increase in intratumoral nano-drug concentration, nonetheless has a limited ability to achieve concentrations that take full advantage of the capabilities of nano-sized drugs. Thus, a method for better nano-drug delivery might lead to improved cancer therapy. We have recently developed a new type of highly selective, molecularly-targeted cancer therapy, named near infrared photoimmunotherapy (NIR-PIT), that is based on conjugating a near infrared silica-phthalocyanine dye, IR700, to a monoclonal antibody (MAb) thereby targeting cancer-specific cell-surface molecules. After the administration of the conjugate and the targeted application of light, the intratumoral vascular barrier is significantly disrupted enabling a dramatic (up to 24 fold) increase in nano-drug concentration in NIR-PIT treated cancer tissue compared with non-treated control tumors. In this lecture I will discuss general pharmacokinetic characteristics of nano-sized molecules in the body, especially focusing on drug delivery in cancer tissue and routes of excretion that are important for improving the safety profile. In addition, I will discuss the basis and applications of the NIR-PIT-induced super-enhanced permeability and retention (SUPR) effect that could dramatically improve nano-drug delivery thereby enhancing the therapeutic effects of nano-sized anti-cancer agents.



PEGylated quantum dots 800 (50 nm in diameter; right panel) accumulate at 24-fold higher concentration in a PIT-treated tumor (right tumor with yellow circle) than in non-treated control tumor (left tumor with white circle) in a two A431 tumor bearing athymic mouse model.

COLL 426

Rationally designed theranostic nanoparticles for applications of precision oncology for image-guided cancer treatment

Lily Yang, *lyang02@emory.edu*. Surgery, Emory University, Atlanta, Georgia, United States

Development of cancer imaging and therapeutic nanoparticles has to address several major challenges in cancer therapy. Highly heterogeneous human cancers require integration of imaging-therapy approaches for personalized cancer treatment to maximize intratumoral drug delivery, and timely assessing delivery efficiency and tumor response. Magnetic iron oxide nanoparticles (IONPs) are promising biodegradable and MRI capable nanoparticles for the development of theranostic nanoparticles for clinical applications. We have developed NIR-dye labeled and uPAR or IGF1R targeted IONPs that are able to target cancer cells and tumor stromal fibroblasts and macrophages. Efficiency of targeted delivery, intratumoral distribution and therapeutic efficacy were examined in human pancreatic or triple negative breast cancer (TNBC) patient tissue derived xenograft (PDX) models as well as transgenic mouse tumor models. We found that this targeting strategy led to an increased retention of the nanoparticles in tumor tissues by active vessel targeting (uPAR) and passive targeting (uPAR and IGF1R). A high level of targeted nanoparticles accumulated in the peripheral tumor areas and a low level in the tumor center following repeated systemic administration. Furthermore, repeated injections of receptor-targeted theranostic nanoparticles carrying chemotherapy drugs resulted in induction of cell death in cancer cells and tumor stromal cells. Breaking stromal cellular barriers by theranostic nanoparticles led to improved intratumoral distribution and tumor cell delivery of the nanoparticles in the tumor center. In pancreatic and TNBC PDX tumor models, uPAR and IGF1R targeted delivery of theranostic nanoparticles enabled NIR optical and MR imaging of targeted drug delivery and monitoring tumor responses to therapy. Significant tumor growth inhibition and induction of tumor cell death were also found in those tumor models. Therefore, those receptor targeted theranostic nanoparticles have the potential for translation of image-guided and targeted cancer therapy of stroma rich human tumors.

COLL 427

Beyond fluorescence: Small and bright upconversion nanoparticles for biological applications

Gang Han, *gang.han@umassmed.edu*. Biochemistry and Molecular Pharmacology, University of Massachusetts-Medical school, Worcester, Massachusetts, United States

Lanthanide-doped upconversion luminescent nanoparticles (UCNPs) are promising materials for in vitro and in vivo optical imaging due to their unique optical and chemical properties. UCNPs absorb low energy near-infrared (NIR) light and emit high-energy shorter wavelength photons. Their special features allow them to overcome various problems associated with conventional imaging probes. In this talk, I will present a new type of biocompatible UCNP. They are free of autofluorescence for in vitro cell imaging,

and exhibit significantly improved signal-to-noise-ratio (i.e., 300 for Balb-c mice) and outstanding tissue penetration depth (>3cm), and minimal light scattering, all highly desired for *in vivo* whole animal imaging. I will also present a new development regarding about engineering UCNPs towards *in vivo* phototherapy.

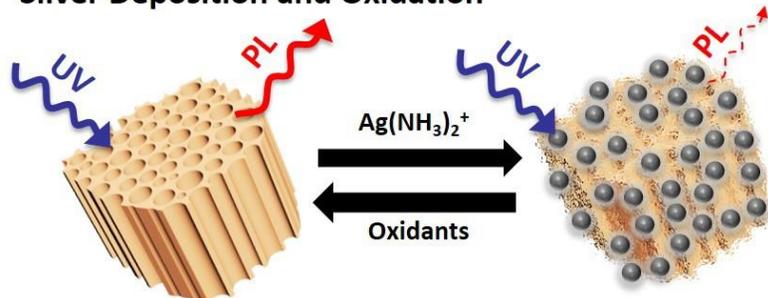
COLL 428

Silver deposited in porous silicon nanoparticles as a potent theranostic antibacterial agent

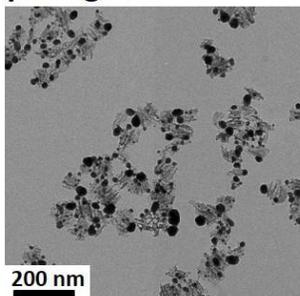
Taeho Kim, taehokim13@gmail.com, Michael J. Sailor. Chemistry and Biochemistry, University of California, San Diego, San Diego, California, United States

Metallic silver (Ag) was uniformly deposited onto porous silicon (pSi) nanoparticles by galvanic displacement reaction. The pSi-Ag nanoparticles (overall size of 90-110nm) are colloiddally stable and the silver content is readily controllable. The Ag nanoparticles embedded within the pSi nanoparticles quench the intrinsic photoluminescence (PL) from the porous silicon matrix, and the degree of quenching is dependant on the density of Ag nanoparticles. When exposed to an aqueous oxidant, the Ag nanoparticles are preferentially etched and Ag^+ is released into solution. The released Ag^+ resulted in 90% reduction of growth of Gram-negative *P. aeruginosa* and Gram-positive *S. aureus* within 3h. Etching of the Ag nanoparticles also regenerates PL from the pSi carrier.

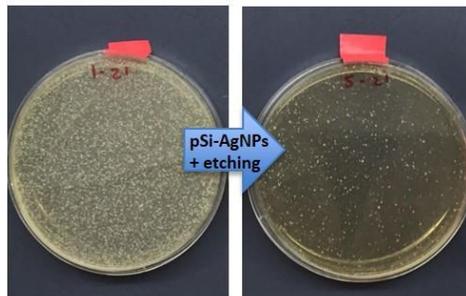
Silver Deposition and Oxidation



pSi-AgNPs



Bacteria Killing



COLL 429

Plasmonic nanoparticles: From fundamental optical properties to applications

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A surface plasmon in a metal nanoparticle is the coherent oscillation of the conduction band electrons leading to both absorption and scattering as well as strong local electromagnetic fields. These fundamental properties have been exploited in many different ways, including surface enhanced spectroscopy and sensing, photothermal cancer therapy, and color display generation. The performance of plasmonic nanoparticles for a desired application not only depends on the particle size and shape, but is tunable through nanoparticle interactions on different length scales that support near- and far-field coupling. Chemical synthesis and assembly of nanostructures are able to tailor plasmonic properties that are, however, typically broadened by ensemble averaging. Single particle spectroscopy together with correlated imaging is capable of removing heterogeneity in size, shape, and assembly geometry and furthermore allows one to separate absorption and scattering contributions. In this talk I will discuss our recent work on understanding the radiative, non-radiative, chiral, and mechanical properties of individual and coupled plasmonic nanostructures. In addition, I will present passive and active mechanisms for color generation and tuning using coupled plasmon resonances of gold and aluminum nanoparticles.

COLL 430

Dynamically responsive plasmonic nanostructures

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Nanostructures of plasmonic noble metals (e.g. gold and silver) have attracted extensive attention in research community due to their strong localized surface plasmon resonance which leads to significant scattering and absorption in the visible and infrared spectrum. The plasmon excitation of these nanostructures is strongly dependent on their size, shape, and the chemical environment. In this talk, we demonstrate that through well controlled chemical synthesis or assembly processes, it is possible to produce anisotropic plasmonic nanostructures with plasmon resonance mode strongly dependent on their orientation relative to the incident light. Such dependence provides enormous great opportunities for developing novel stimuli-responsive colorimetric devices. Here we will introduce some of our recent works in designing stimuli responsive materials by taking advantage of the orientational dependent plasmonic property of anisotropic nanostructures and the interparticle near-field plasmon coupling effect of nanoparticle assemblies.

COLL 431

Recent theory studies of vibrations at surfaces: SERS, FSRS

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This talk describes recent advances in the use of plasmon enhanced spectroscopy to describe chemical processes, taking advantage of theories that combine electrostatics with quantum mechanics. One project is concerned with a recent discovery in the Van Duyne lab of time-resolved single molecule SERS spectra which fluctuate as a function of time. We use a recently developed method for calculating resonance Raman spectra for open-shell molecules to show that the fluctuations arise from radical anions that are transiently produced. Another project is concerned with surface enhanced FSRS (femtosecond stimulated Raman spectra), which has been found to show asymmetric lineshapes in Van Duyne's measurements. We show that these lineshapes arise naturally from the plasmon enhancement process due to phase reversal effects in the nonlinear driving force that produces the FSRS coherence.

COLL 432

Bifunctional Ag@Pd-Ag nanocubes for highly sensitive monitoring of catalytic reactions by surface-enhanced Raman spectroscopy

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We present a route to the generation of Ag@Pd-Ag nanocubes by co-titrating Na_2PdCl_4 and AgNO_3 into an aqueous suspension of Ag nanocubes at room temperature in the presence of ascorbic acid and poly(vinyl pyrrolidone). By increasing the total volume of the solutions titrated, we identified that the Pd and Ag atoms were co-deposited onto the edges, corners, and side faces of Ag nanocubes in a site-by-site manner. By maneuvering the ratio of Pd to Ag, we could optimize the SERS and catalytic activities of the Ag@Pd-Ag nanocubes for *in situ* SERS monitoring of Pd-catalyzed reduction of 4-nitrothiophenol by NaBH_4 .

COLL 433

Plasmon-exciton coupling with colloidal metal nanoparticles

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Plasmon-exciton coupling occurs when a propagating surface plasmon or localized surface plasmon resonance (LSPR) mode is resonant with the exciton transition of an emitter, such as a molecular dye or a semiconductor nanocrystal. In this talk, I will present our work on two novel colloidal metal nanoparticle systems. The first involves colloidal metal nanoparticles chemically conjugated to molecular fluorophores. Strong coupling results in hybridization (a coherent superposition) of the exciton and plasmon modes due to interaction between the electric field produced by the plasmon and the

electric dipole moment of the exciton transition. We demonstrate that this coupling is distance-dependent. Rabi splitting features in the scattering signature of the colloidal nanoparticle can be used to distinguish particle-fluorophore distances in 0.5 nm increments. Second, I will present our work on investigating plasmon-exciton coupling in colloidal semimetal nanoparticles. We observe that CuS nanodisks exhibit plasmon-exciton coupling within the same nanostructure, where there is no physicochemical interface between the components to dictate strong or weak coupling interactions. The colloidal nanodisks synthesized in this work are novel solid-state materials that will be used to gain new insight into this unexplored coupling regime.

COLL 434

3D reconstruction of colloidal superstructures at atomic resolution

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A clear knowledge on the three dimensional (3D) structures of colloidal superstructures is of paramount importance as they provide some of the key interactions involved in the self-assembly. Electron microscopy (EM) tomography and single particle reconstruction (SPR) methods are emerging as powerful tools to study biological assemblies at atomic resolution. As a result, 3D reconstructions are complementary/alternative tools to X-ray crystallography.¹ We have undertaken EM tomography and sub-tomography reconstructions to study the self-assembled magnetic colloidal superstructures composed of 5 nm nanoparticles as building blocks (Fig. 1a) at subnanometer resolution.² We have explored the possibilities of using SPR methods,³ by direct picking approach of the particles from the whole-mounted spherical colloidal superstructures using EMAN2 (Fig 1a and 1b) image-processing software for electron microscopy.⁴ It was assumed that the particles picked directly from the spheres were randomly oriented. Using EMAN2 the contrast transfer function (CTF) phase flipping was performed (Fig. 1c) and wiener filter (Fig. 1d) was used to gain insights on the quality of the particles to select the initial model (Fig. 1e). Final structures were obtained using Bayesian RELION-SPR method.⁵ Using this approach, we obtained the 3D structures of nanoparticles at atomic resolution of 2.5 Å, which resembled the lattice fringes of the nanoparticles obtained using HRTEM.

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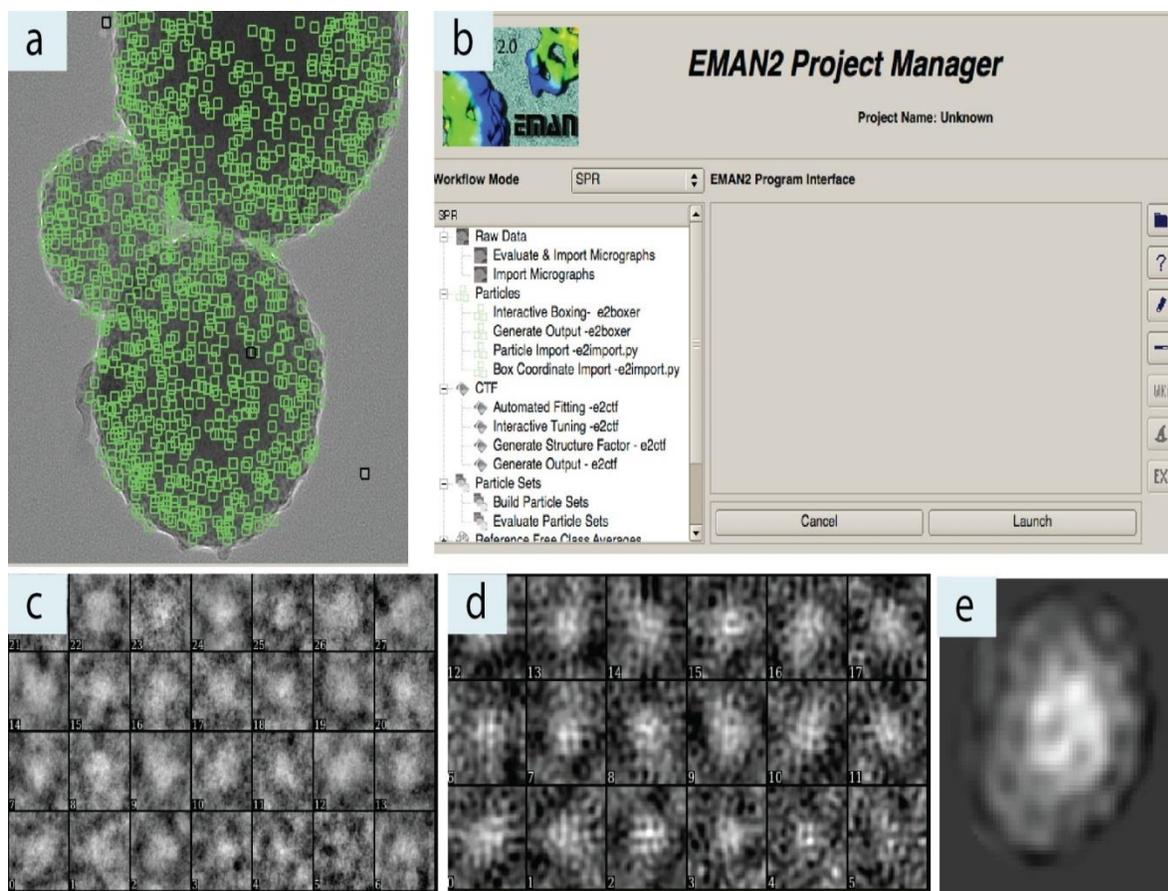


Figure 1. (a) TEM showing direct-particle-picking from the colloidal superstructure ; (b) EMAN2.1 project manager; (c) the nanoparticles after CTF correction; (d) nanoparticles with wiener filter and (e) the initial model used in this study.

COLL 435

Three-dimensional positions of individual atoms in nanometals revealed by electron tomography

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Visualizing the arrangement of atoms has played an important role in the evolution of modern science and technology. Crystallography has long been used to reveal globally averaged 3D atomic structures. Scanning probe microscopes can determine surface structures at atomic level. Electron microscopes can routinely resolve atoms in 2D projections of 3D crystalline samples. In this talk, I will present a general method for 3D determination of *local* structures at atomic resolution. By combining scanning transmission electron microscopy with a novel data acquisition and 3D image reconstruction method, known as equal slope tomography (EST), we achieved electron

tomography of a ~10 nm Au nanoparticle at 2.4 Å resolution and identified several major grains in three dimensions (1). We also observed nearly all the atoms in a Pt nanoparticle and, for the first time, imaged the 3D core structure of edge and screw dislocations in the nanoparticle at atomic resolution (2). More recently, we determined the 3D coordinates of thousands of individual atoms and a point defect in a tungsten needle sample with a precision of ~19 picometer (3), where the crystallinity of the sample is not assumed. From the coordinates of these individual atoms, we measured the atomic displacement field and the full strain tensor with a 3D resolution of 1 nm and a precision of 10^{-3} . We expect this general atomic resolution electron tomography method to find broad applications in solid state physics, chemistry, materials sciences, nanoscience and biology.

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COLL 436

Molecular electronics using carbon: A reliable device platform for rock and roll

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Molecular electronics has been envisioned as a way to increase the density, diversity, and functionality of electronic devices. There are many platforms for studying molecular electronics that enable study of various aspects of molecular devices. We have a platform for fabrication of large area molecular junctions containing molecular layers from ~1 to ~60 nm in thickness using carbon contacts and diazonium reduction of aromatic molecules. Advantages of this "all-carbon" paradigm including excellent reproducibility, stability, and the ability to scale-up fabrication for large scale manufacturing. These features have enabled a practical application for molecular electronics in the realm of electronic audio signal processing, where the non-linear curves of the molecular devices can be used to provide intentional distortion (through Fourier component generation) of a source signal, particularly (but not exclusively) electric guitars. Thus, the molecular junction is shown to be an active component in audio clipping circuits (i.e., "overdrive" pedals), with results from a fully-functional

“molecular clipping prototype” demonstrating differences in operation between conventional electronic clipping components (often pn junction diode arrays) and molecular devices, where the electronic properties attributed to the nanoscale charge transport in molecular junctions leads to measurable and audible differences in sound quality (that are often subjectively evaluated as desirable). An additional advantage of molecular junctions in this application is the ability to tune the electronic response in a way that enables better control over the resulting character of the distorted sound (i.e., by control over the thickness and structure of the molecular component). Since it is possible to manufacture “all-carbon” electronic devices with sufficient stability, a consumer product that uses molecular electronics is now a reality.

COLL 437

Molecular charge rectification

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We will present a recent work where we discuss the range of validity of coherent versus incoherent theory treatments for the understanding of some recent experimental results obtained in molecular tunnel junctions and employ them to determine some noteworthy characteristics of the junctions in view of potential applications in molecular electronics. Specifically, we will discuss single-level transport models employed to explain experiments performed in SAM-based EGaIn junctions of S(CH₂)_nFcC_{13-n} electrical rectifying molecules in where the Ferrocene (Fc) unit is placed at different positions (n) within the alkyl chain, enabling the determination of the electrostatic potential profile in the junction, which we find highly non-linear.

COLL 438

Interface engineering in future of computing technologies

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The electronics industry is facing two critical challenges; the increasing complexity to make smaller, faster high performance components and the “electronics everywhere” phenomena requiring portable, low power, niche roles of electronic components. Both of these challenges require fundamental innovations and understanding of electronic processes at interfaces. I will describe advances made in our ability to manipulate and measure organic and molecular interfaces at the nanometer scale and the impact on the resulting electronic performance. In particular, I will focus on the measurement

advances made in molecular electronics, highlighting our understanding of the interface science and characterization. This talk will contain two illustrative case studies demonstrating the impact of interface engineering on charge trapping memory devices and spin-based paradigms.

Organic molecules are advantageous for trapped charge memory devices due to their small size, discreet nature, and tunability. I will describe a series of advances in creating and characterizing molecular memory devices incorporating a novel ruthenium based redox-active molecule as the charge storage layer.(1)

Spin-based paradigms are increasingly important for future electronics and of special interest is the manipulation of spin in organic materials. I will describe a series of advances that examine the impact of organic monolayers on the ferromagnetic oxide interface and the role interface engineering can play in organic spintronics.(2)

- 1.“Non-volatile memory devices with redox-active diruthenium molecular compound” S. Pookpanratana, H. Zhu, E. G. Bittle, S. Natoli, T. Ren, D. J. Gundlach, C. A. Richter, Q. Li, and C. A. Hacker *J. Phys. Chem.: Condens. Matter*, a special issue on “Molecular functionalization of surfaces for device applications” (invited) Oct 2015 accepted
- 2.“Modifying spin injection characteristics of Co/Alq₃ system by using a molecular self-assembled monolayer”, Hyuk-Jae Jang, J.-S Lee, S. J. Pookpanratana, I. C. Tran, C. A. Hacker, and C. A. Richter, *J. Phys. Chem. C* 119, 12949 (2015)

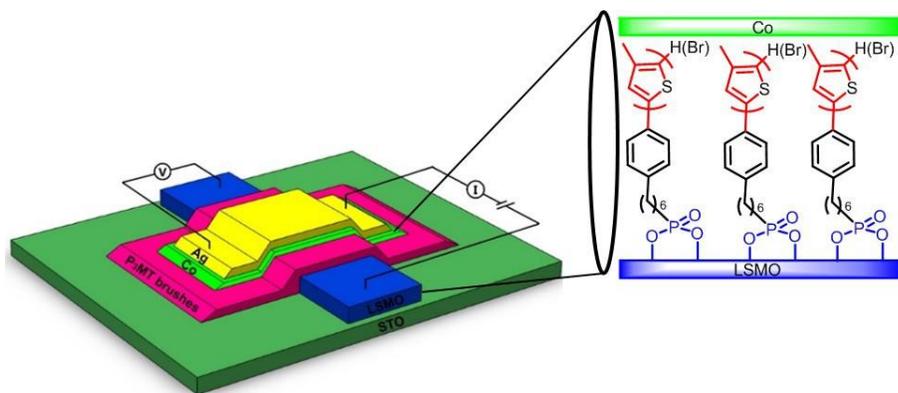
COLL 439

Engineering of spin injection and spin transport in organic spin valves (OSVs) using π -conjugated polymer brushes

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The talk will be focused on how a large magnetoresistance (MR) response is obtained in an OSV, by modifying the spinterface through covalent immobilization of conjugated polymer (poly-3-methylthiophene) brushes from electrode surface. Charge transport in amorphous organic semiconductors is governed by carrier hopping between localized states with small spin diffusion length. Furthermore, the interfacial resistance in OSVs is poorly controlled resulting in controversial reports of the magnetoresistance response. Here, we used surface initiated Kumada catalyst transfer polycondensation to covalently graft π -conjugated poly(3-methylthiophene) brushes from the La_{0.67}Sr_{0.33}MnO₃ (LSMO) bottom electrode. The covalent attachment along with the brush morphology allows control over the LSMO/brush interfacial resistance and large spacer mobility.

Remarkably, with 15 nm brush spacer layer, we observed an optimum MR effect of 70% at cryogenic temperatures and a MR of 2.7% at 280K. The temperature dependence of the MR is nearly an order of magnitude weaker than that found in control OSVs made from spin-coated poly(3-hexylthiophene). Using a variety of brush layer thicknesses, the thickness dependent MR at 20K was investigated. A spin diffusion length of 20 nm at 5 mV junction voltage rapidly increased to 55 nm at -280 mV. In conclusion, we believe this new device fabrication method provides a new dimension to the field of OSV devices.



Schematic of polymer brush-based OSV with four-probe measurement technique

COLL 440

Towards molecular electronics: Using solution-based methods to deposit nano-objects

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Nano-objects, including nanowires, nanopores, nanochannels and nanorings have many applications in electronics, sensing, energy conversion, optoelectronics and non-linear optics. One of the major challenges in the practical use of these structures is their integration into complex functional structures in a predictable and controlled way. We have recently introduced two promising new techniques by which to direct the *in situ* growth of metallic and semiconducting nano-objects. ENDOM, or Electroless Nanowire Deposition On Micropatterned substrates, employs electroless deposition (ELD) to form metallic nanostructures on substrates. SENDOM, or Semiconductor Nanowire Deposition on Micropatterned surfaces, uses chemical bath deposition (CBD) to deposit semiconductor nanowires. Using these processes we demonstrate the production of nanowires (diameters < 100 nm), mesowires (100 nm < diameter < ~3000 nm), nanorings, nanopores and nanochannels. These nanostructures can follow complex paths, such as arcs or right-angle bends, and are formed in parallel over cm² areas. Fundamental to the optimization and application of these methods is an understanding of the interaction of reactants with the terminal functional groups of organic thin films.

These interactions significantly affect transport and reaction rates, the control of which is critical in optimizing ENDOM and SENDOM and their extension to different materials. Finally, we discuss the formation of complex architectures, such as cross-bars, using these methods.

COLL 441

Investigating the assembly and binding of tetrazine to alkenes via scanning tunneling microscopy (STM) for sensing applications

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Tetrazines have been shown to bind alkenes and show a chemiresistive sensing response in carbon nanotube-tetrazine composites. The binding event resulting in a sensing response, however, has been largely unstudied. In this work, Scanning Tunneling Microscopy (STM) was used to study the reaction between tetrazine and various alkenes. These insights are relevant to better understand the association of the sensor compound and the analyte and can help investigate the key sensing mechanism by observing the changes in assembly at the molecular level.

COLL 442

Molecular rectifiers: Role of the Fermi level alignment and new design based on asymmetric anchoring moieties

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Nowadays best single molecule rectifiers[1] exhibit limited performances, with typical rectification ratios lower than one order of magnitude.[2] In previous works,[3, 4] we focused on the Fermi level alignment problem in molecular junctions, more particularly the characterization of the Fermi level pinning phenomenon,[5, 6] at the theoretical level. We showed that this effect has a deep influence on the response of the transmission spectrum to an applied bias. Indeed, the Fermi level pinning leads to a control and a splitting of the energy levels coupled to their respective electrodes. This is at the origin of a consequent orbital polarization effect.[3, 4]

Relying on our characterization of these effects, we introduce here three simple rules to design an efficient rectifying molecule, and demonstrate its functioning at the theoretical level, using the NEGF-DFT technique.[7] The design rules notably require both the introduction of asymmetric anchoring moieties and a decoupling bridge. They lead to a new rectification mechanism based on the compression and control of the HOMO/LUMO gap by the electrode Fermi levels, arising from a pinning effect.

Significant rectification ratios up to two orders of magnitude can easily be obtained and are theoretically predicted, as the mechanism opposes the resonant to the non-resonant tunneling transport mechanisms.

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COLL 443

Functional high-yield molecular electronic devices

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Molecular devices that utilize molecules as electronic device components are fascinating, however molecular monolayer devices are not practical because a typical vertically structured molecular devices has a very low devices yield. In this talk, I will explain a few methods to overcome this low yield problem; specifically (1) a method by introducing an intermediated protective layer between the molecular layer and the top electrode [1,2], and (2) a method for high-yield molecular junctions with a direct metal transfer technique [3]. I will further explain our recent demonstration of molecular electronic devices with high yield structure and with some device functionalities such as rectifying or photoswitching [4].

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COLL 444

Characterization of polymer/epoxy buried interfaces with silane adhesion promoters before and after hygrothermal aging for the elucidation of molecular level details relevant to adhesion

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Buried interfacial structures containing epoxy underfills are important in the microelectronics industry and their structures determine the interfacial adhesion properties of electronic devices and ultimately their lifetime. Weak adhesion and delamination at such interfaces lead to premature failure of microelectronic devices. In this work, sum frequency generation (SFG) vibrational spectroscopy, an intrinsically surface sensitive technique, was utilized to investigate the molecular structure of buried epoxy interfaces before and after accelerated stress testing. This technique was used in order to relate the molecular-level structural changes of the epoxy systems to the macroscopic adhesion strength and determine if silane adhesion promoters can affect a polymer/epoxy system. Two control systems were used; a hydrophilic and hydrophobic surface, interfacial water was detected after hygrothermal aging on the hydrophilic surface but was not detected on the hydrophobic surface. Lap shear analysis was performed and it was found that the hydrophilic surface had greatly reduced in adhesion strength after aging, much more reduced than the hydrophobic surface. To determine if the adhesion strength could be increased after aging, silane adhesion promoters, (3-aminopropyl)trimethoxysilane (ATMS), (3-glycidopropyl)trimethoxysilane (GPS), and octadecyltrimethoxysilane (OTMS), were introduced into the system. For the hydrophilic model surface, each silane prevented interfacial water from forming and increased adhesion strength after aging. For the hydrophobic model surface, ATMS and GPS increased the adhesion strength, while OTMS did not change the adhesion strength after aging. This research demonstrates that molecular structural studies of buried epoxy interfaces during hygrothermal aging using SFG vibrational spectroscopy can greatly contribute to the overall understanding of moisture-induced failure mechanisms of organic adhesives found in microelectronic packaging.

COLL 445

Curing behavior & surface characterization of BADGE-based epoxy resins

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For the assembly of high-voltage devices such as transformers and generators, insulating adhesives based on epoxy resins are frequently used. In this study, adhesives based on bisphenol A diglycidylether BADGE and four model amine hardeners, namely diethylenetriamine DETA, 1-(2-aminoethylamino)-2-propanol AEAP, isophorone diamine IPD, and m-xylylenediamine mXD, were investigated in order to understand the adhesion behavior between the epoxy resin and the cellulose-based transformer board (for use in high-voltage applications) as well as the curing of the resin.

BADGE/DETA and BADGE/AEAP resins, which were cured at 60 °C / 2 h, had comparatively high surface energies. After curing at 150 °C for 4 h, they had a similar surface energy like all other resins after curing, namely in the range from 44-49 mN•m⁻¹. The isoelectric points of BADGE/DETA and BADGE/AEAP after curing at 60 °C / 2 h were significantly higher than that of the other two resins, which suggested a higher content of residual amine functionality at the surface. All resins cured at 150 °C had similar isoelectric points (Figure 1).

The curing degrees of epoxy resins at a heating rate of 10 K/min (Figure 1) showed that BADGE reacted most quickly with AEAP due to the autocatalytic effect of the hydroxy group. The system BADGE/IPD cured most slowly; complete curing could only be reached at high temperatures due to steric hindrance of the cyclohexane ring. The glass-transition temperatures T_g were determined at different curing temperatures (60-160 °C / 1 h): The systems BADGE/DETA, BADGE/mXD and BADGE/IPD needed to be cured at 160 °C / 1 h to reach the maximal curing degree; BAGDE/AEAP was completely cured at 120 °C / 1 h. Completely cured BADGE/AEAP had a T_g of only 75 °C due to the lower cross-link density (hydroxy group).

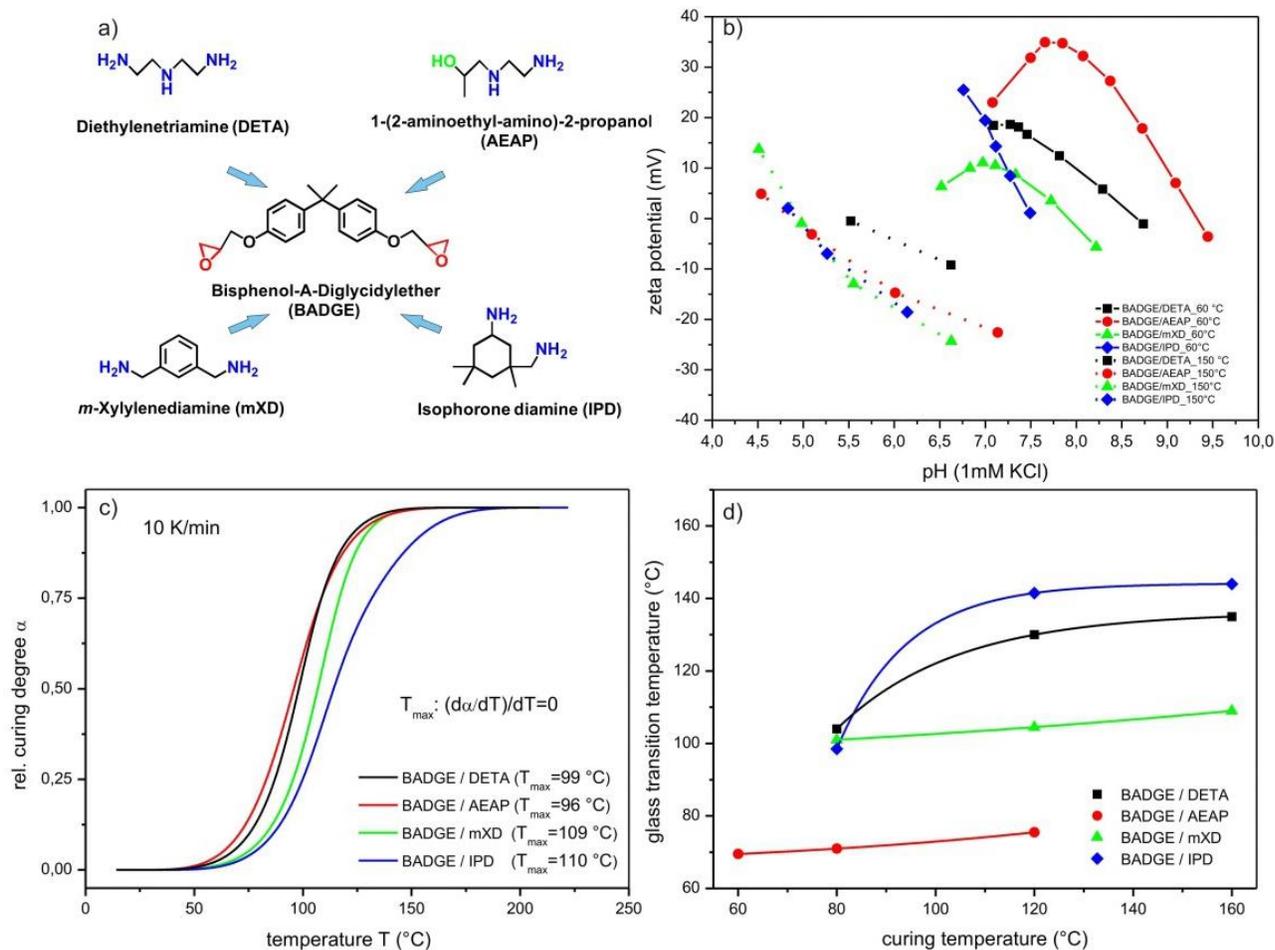


Figure 1: Selected amine hardeners for BADGE (a); zeta potential vs. pH (b); Curing degree vs. temperature (c); T_g vs. curing temperature (d).

COLL 446

Patterning of Au on PMMA using contact printing of chloroform for adhesion promotion

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The ability to create gold patterns on polymer surfaces is useful in many fields including optical and microfluidic devices. However, due to its inertness, adhering thin films of gold onto polymer surfaces is difficult. In previous studies, JMU researchers have discovered that when poly(methyl methacrylate) (PMMA) is treated with chloroform,

gold that is deposited to the surface is more adhesive compared to untreated PMMA. We report here the use of polydimethylsiloxane (PDMS) stamps soaked in chloroform as a means of selective exposure. The purpose for this project was to determine the size of the features that could be made using this method. At first large features (1-3 mm) were made by curing PDMS stamps in large molds made by a VLS 3.50 laser cutter. Later smaller features (3-14 μm) were made using a mold made from photolithography. After being deposited with gold, features less than 8 micrometers across could be observed.

COLL 447

Array-based profiling for diagnostics and high-throughput screening

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The "chemical nose/tongue" approach presents a potential alternative to specific biomarker approaches. In this strategy a sensor array is generated to provide differential interaction with analytes via *selective* receptors, generating a stimulus response pattern that can be statistically analyzed and used for the identification of individual target analytes and also for profiling of complex mixtures. In our research, we have applied this methodology to sensing of proteins and cell surfaces, focusing on areas of biomedical importance. This talk will present the use of nanoparticle-fluorophore sensing arrays for diagnostic and high content screening (Figure 1).

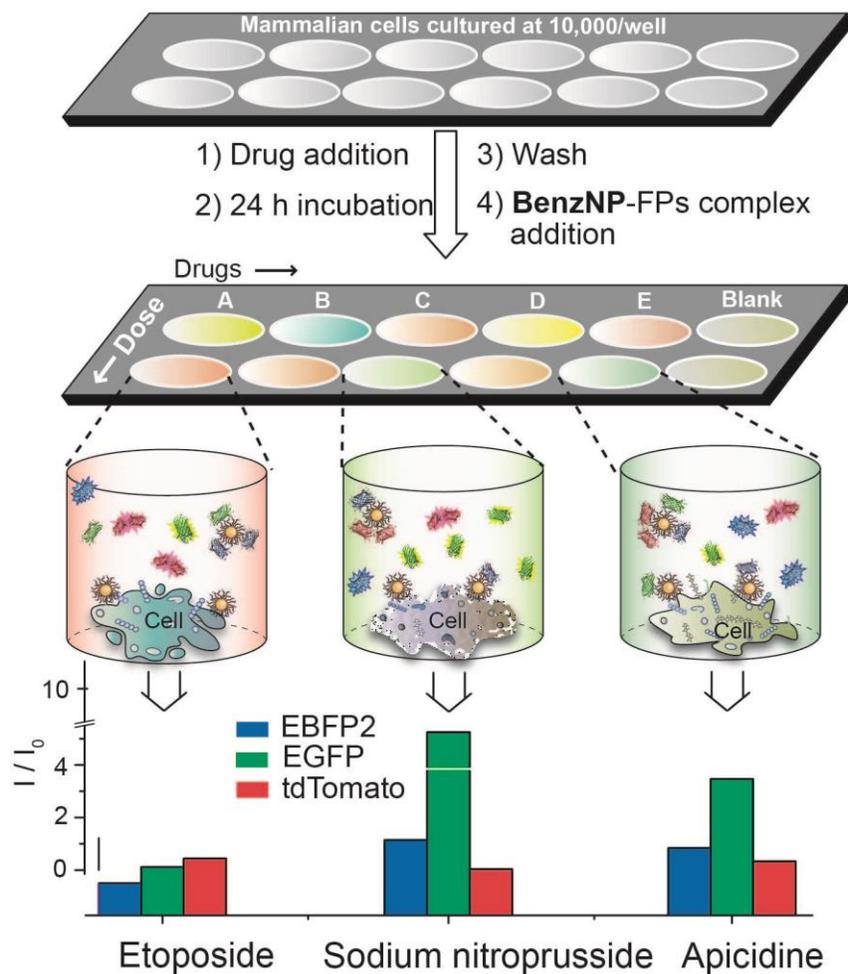


Figure 1. High-content screening of therapeutic mechanisms using a multichannel nanoparticle-fluorescent protein sensor.

COLL 448

Noble metal nanoparticles for rapid diagnostics

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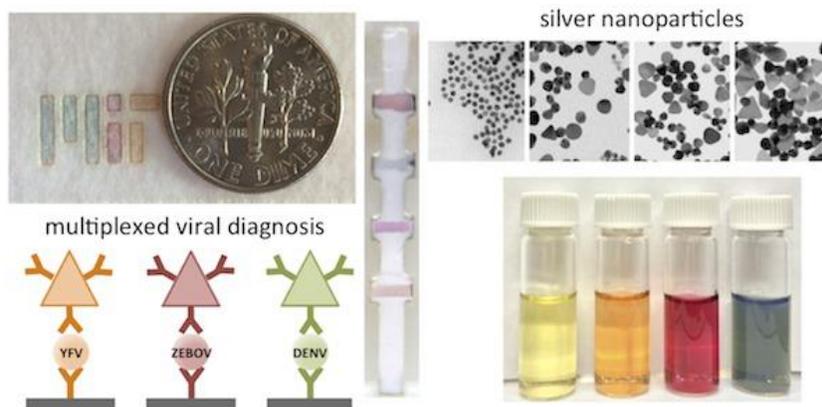
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Rapid point-of-care (POC) diagnostic devices are needed for field-forward screening of severe acute systemic febrile illnesses. Multiplexed rapid lateral flow diagnostics have the potential to distinguish among multiple pathogens, thereby facilitating diagnosis and improving patient care. The colored line that provides a visual readout for test results are due to noble metal nanoparticles conjugated to antibodies that can recognize the biomarker of interest. Because test lines can be imaged by eye or a mobile phone camera, the approach is adaptable to low-resource, widely deployable settings. This design requires no external excitation source and permits multiplexed analysis in a single channel, facilitating integration and manufacturing.

Here, we present results in which we tune the physical properties of the nanoparticle in order to impart new capabilities to the lateral flow diagnostic. The size and shape dependent optical properties of noble metal nanoparticles can be tuned to optimize diagnostic performance and impart new capabilities.

We developed a platform for multiplexed pathogen detection using multi-colored prism-shaped silver nanoparticles (AgNPs). AgNPs of different sizes were conjugated to antibodies that bind to specific biomarkers. Red AgNPs were conjugated to antibodies that could recognize the glycoprotein for Ebola virus, green AgNPs to those that could recognize nonstructural protein 1 for dengue virus, and orange AgNPs for non structural protein 1 for yellow fever virus. Presence of each of the biomarkers resulted in a different colored band on the test line in the lateral flow test. Thus, we were able to use NP color to distinguish among three pathogens that cause a febrile illness.

We will also discuss the synthesis and characterization of Au nanoparticles of different shapes, such as Au nanostars, and their use in lateral flow tests. Finally, because lateral flow assays are complex environments and can result in many complex interface issues, manipulation of the bio-nano interface is critical. We will discuss studies of how NP surface chemistry modifications and antibody conjugation strategies impact the lateral flow test performance.



COLL 449

Quantitative multiplexed nanoparticle platform for the identification and imaging of mammalian cells by surface-enhanced Raman spectroscopy based on surface receptor overexpression

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The reliable and fast identification of different types of cells is of utmost importance in several biomedical applications. The detection of cancer cells in bio-fluids such as urine and blood could be crucial to detect patient response to therapy, to monitor drug resistance effects, as well as for early identification of disease recurrence, and ultimately for a personalized medicine approach. Fast detection of bacteria in the blood is a fundamental requisite for higher chances of survival during septic events. We developed bright, spectrally rich, multiplexing SERS Biotags (SBTs), composed of a silver nanoparticle dimer core, and an affinity tag coating to bind to surface receptors on cells. The SERS spectrum of an individual SBT acts as a unique barcode that is easily differentiable in a composite SERS spectrum originating from many tags. The SERS intensities achieved are comparable to fluorescence and can all be excited with one laser. We have now developed a platform that employs SBTs for the identification of individual cells based on the ratio between surface receptors. We synthesized a cocktail of two to four SBTs, each one targeting a different surface receptor on the cell's membrane, with one SBT being a universal control. Point-by-point 2D Raman maps depicting the ratio of each receptor to the universal control were constructed with subcellular resolution from cells simultaneously incubated with the SBTs while in suspension, thus simulating the cells' capture from blood. We demonstrate the identification of individual cells by spectral unmixing of the Raman signature through a quantitative model based on classical least squares signal deconvolution that our lab developed. In summary, we demonstrate the multiplexed identification of cancer cells by SERS subcellular imaging and quantitative ratiometric analysis of surface receptor expression using up to four SBTs simultaneously.

COLL 450

Engineering lanthanide-doped multifunctional nanoparticles for biomedical diagnostic and therapeutic applications

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Multifunctional nanoparticles, including polymeric, metallic and oxide nanoparticles, have attracted great research interest as they can be integrated with various functions for different applications. Lanthanide-doped materials have shown great prospects for fabricating multifunctional nanostructures with unique properties that are especially attractive for biomedical applications. To date, the widely explored upconversion nanostructures in this class of materials have focused on ytterbium/erbium or ytterbium/thulium co-doped systems that can be excited with 980 nm near-infrared (NIR) light. Recent works have shown the limitations with biological setting for this wavelength (980 nm) due to the strong water absorption. Efforts to shift the excitation wavelength to bio-benign NIR wavelength (800 nm) have attracted lot of attention recently. Towards this goal, we have developed an upconversion platform excitable at 800 nm that allows enhanced photodynamic therapy (PDT) within the first biological window. Moreover, the developed platform allows for simultaneous multi-modal imaging using X-ray computed tomography (CT), and magnetic resonance imaging (MRI). The versatility of this system makes it highly promising research tool for multifunctional theranostic applications.

COLL 451

SPIONs and the protein corona: Importance for cellular binding and T₂ relaxation

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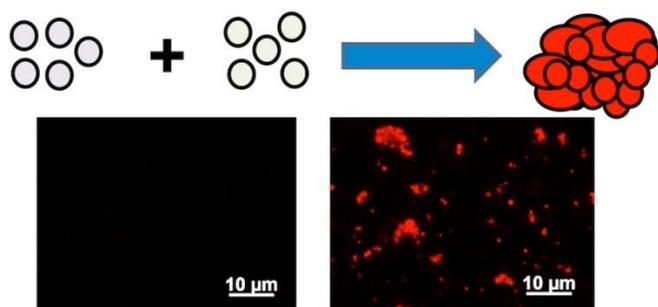
Nanoparticles are increasingly important for medical imaging. To take full advantage of their benefits, while minimizing potential hazards, we need a mechanistic understanding of how nanoparticles interact with proteins and cells. Using a model system of polystyrene nanoparticles, we have used a combination of microscopy and spectroscopy to characterize the cellular interaction of nanoparticles following the adsorption of a “corona” of serum proteins onto the nanoparticle surface. Adsorption of protein onto a nanoparticle surface results in structural changes to the protein that lead to off-target binding of the protein-nanoparticle complex. Subsequent studies have examined superparamagnetic iron oxide nanoparticles (SPIONs) used as MRI contrast agents. Using a combination of fluorescence microscopy and flow cytometry, we find that the cellular binding of carboxymethyl dextran-modified SPIONs to macrophages and epithelial cells is significantly inhibited by serum proteins. We find a comparable decrease in cellular binding for carboxymethyl dextran–polystyrene nanoparticles, suggesting that the surface modification is the key factor in SPION–cell interactions. Importantly for medical imaging, NMR measurements show that T_2 relaxation times are not affected by corona formation.

COLL 452

In-solution biosensing via aggregation of nanodroplets containing mutually reactive, fluorogenic hydrocyanine/quinone reporter molecules

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Mutually-reactive, fluorogenic molecules have been explored as a simple and novel technique for in-solution biosensing. The hypothesis behind this work was that aggregating colloidal nanoemulsions into close proximity would cause rapid mixing of their contents. To take advantage of this effect, a novel pair of fluorogenic redox molecules were designed to remain in lipid-stabilized oil nanodroplets but mix once aggregated. First, the hydrophobic cyanine dye Dil was reduced with sodium borohydride to form a non-fluorescent hydrocyanine analog (HDil). Hydrophobic quinone derivatives were then screened as oxidizing agents, and it was found that p-fluoranil oxidized non-fluorescent HDil back to fluorescent Dil. Next, HDil and p-fluoranil were loaded into non-toxic NEOBEE oil nanodroplets of average diameter ~600 nm that were stabilized by a monolayer of phospholipids and polymer-lipids, namely, DPPC, DSPE-PEG, and DSPE-PEG-biotin. For proof-of-concept studies, streptavidin was added leading to aggregation of droplets and content mixing, causing the appearance of red fluorescent aggregates within 30 min. Absence of streptavidin provided little or no aggregation or fluorescence. Next, utilizing a sensitive Nanoparticle Tracking Analysis method (NanoSight, Malvern), the fluorescence of the droplets and their aggregates were recorded. By integrating the fluorescence emission of the tracked droplets, streptavidin could be detected down to a concentration of 100 fM. Subsequently, to apply this technique to a biologically relevant analyte, the droplets were reformulated to sense for Vascular Endothelial Growth Factor (VEGF), a biomarker for tumor metastasis. Using modified anti-VEGF aptamers attached to DSPE-PEG incorporated into the nanodroplet monolayer, VEGF could also be similarly detected down to 100 fM. This is a bulk sensing mechanism with only one complementary antibody/aptamer required, and with no washing steps involved, in contrast to most currently available sandwich assays. In future studies, the work described here will be expanded for biosensing of more complex analytes via antibody interactions.



Sensing membrane potential by inorganic semiconductor nanorods

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Unraveling emergent brain activities requires simultaneous recording of action potentials from a large number of neurons. Electrical recording methods such as patch clamp and optical recording by voltage sensing dyes and proteins have been developed for years and are widely utilized. However, such techniques have insufficient spatial and/or temporal resolutions and/or suffer from poor photostability, posing a need for probes that circumvent these limitations. Improved probes, with high sensitivity and photostability, could afford the study of large neural networks (in a large field-of-view) and/or at very high spatial resolution. Using bandgap-engineering and colloidal synthesis methods, we have synthesized seeded semiconductor (SC) nanorods (NRs) with Type-II heterojunctions that exhibit a large Quantum Confined Stark Effect (QCSE) at room temperature¹. For using these NRs as voltage sensors, however, one needs to impart them with membrane-protein like properties so that they can be stably inserted into the membrane. We report here spontaneous insertion of SC NRs into liposomes and cell membranes by functionalizing them with specially designed peptides. We provide evidences for insertion from cryo transmission electron microscopy (TEM) and polarized light microscopy. We also report on first attempts to sense membrane potential with these particles with single-particle sensitivity. With further improvements, SC NRs could potentially be used to study signals from whole neural networks in a large field-of-view. Moreover, successful implementation of SC NRs would allow for the analysis of voltage signals at the nano- (single synapse-) scale.

*Equal contributions.

¹: Park, K.; Deutsch, Z.; Li, J. J.; Oron, D.; Weiss, S., Single Molecule Quantum-Confined Stark Effect Measurements of Semiconductor Nanoparticles at Room Temperature. *ACS Nano* **2012**,6 (11), 10013-10023.

COLL 454

Self-assembled split-FP/metal nanoclusters as Raman enhancers for molecular and cellular detection

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The use of bio-inspired scaffolds to assemble nanomaterials into photonic nanostructures is a highly promising approach to design new nanoscale biosensors for biomedical applications. Here, we describe novel hybrid colloidal Raman nanoprobe based on the self-assembly of metal nanoparticles functionalized with split-fluorescent protein fragments (split-FPs). In our system, split-FPs serve as both unique Raman fingerprint reporters and molecular glue to assemble metal (Au, Ag) nanoparticles into photonic active surface enhanced Raman scattering (SERS) nanoclusters. For oriented grafting at the surface of metal nanoparticles, we engineered recombinant split-FPs (sGFP, sYFPs, sCFPs) and their complementary peptide fragments with metal binding domains. Various sizes of metal nanoparticles (5-50 nm in diameter) were coated with these split-FPs fragments and characterized by electrophoresis, HPLC, DLS, TEM, and immunoblotting. *In vitro*, the self-assembly of complementary metal nanoparticles and the formation of nanoclusters were confirmed by electrophoresis and TEM measurements. Furthermore, collected SERS signals from these assembled nanoclusters display the unique Raman signature of FP chromophores confirming that the assembly process is driven by biomolecular interactions of the split-FP fragments and result in large electromagnetic field enhancements at stable plasmonic hotspots. We additionally performed 3D-FDTD simulations of these FP/metal nanoparticle hybrid nanoclusters to confirm the plasmonic coupling effects, to characterize the enhanced electromagnetic field and to optimize the spatial organization of nanoparticles within nanoclusters for maximal SERS responses. Finally, we show that these novel SERS nanoprobe can self-assemble at the plasma membrane of live cells as confirmed by scanning electron microscopy and by *in vivo* Raman microscopy imaging. These results denote that split-FP/metal nanoparticle hybrid nanoprobe hold great potential for highly selective and sensitive SERS detection of targeted cells.

COLL 455

Fluorescent silica nanoparticles for selective detection of small ovarian tumors during surgery

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Background

Ovarian cancer is a deadly disease that afflicts approximately 22,000 women per year in the US. Once it has reached stage III and metastasized to the abdominal cavity, there is a 5-year survival rate of only 34%. Surgery is the frontline therapy for this disease and has two purposes. The first is to stage the cancer – to see how far the cancer has spread from the ovary. The second is to remove as much of the disease as possible – this is called debulking. Surgery is critical to patient outcomes with survival linked to the degree of tumor removed from the abdomen. The current clinical standard is to remove all tumors larger than 1 cm in diameter, as this is roughly the limit of detection by eye. Despite achieving no gross visible disease at the end of surgery, 50-70% of patients will relapse. Therefore, there is a need for better detection techniques during surgery, to enable surgeons to detect smaller tumors and remove them. In the present study we **hypothesize** that NIR-fluorescently-labeled silica nanoparticles can be used to selectively and sensitively detect small ovarian tumors in the abdominal cavity and by that improving surgery outcome.

Results

We have shown that when the fluorescently-labeled silica nanoparticles are administered IP, they can selectively and sensitively detect ovarian tumor metastases, while not targeting other healthy tissues, hence showing selective tumor targeting. For these studies, the nanoparticles were injected IP and after 4 days, the animals were euthanized, the organs in the IP cavity were removed and a fluorescent whole-body imaging system was used to demonstrate that nanoparticles were selectively localized at tumor sites. Tumors and adjacent healthy tissue were then removed and prepared for confocal imaging which confirmed that nanoparticles only bound to cancer tissue.

Conclusions

Our study demonstrates that when fluorescently labeled silica nanoparticles are injected intraperitoneally (IP) they selectively bind to ovarian tumors, with no observed signal from any healthy tissue. Use of such particles during surgery to detect tumors not visible to the naked eye could enhance the surgeon's ability to remove cancerous tissue and enable more accurate staging of the disease.

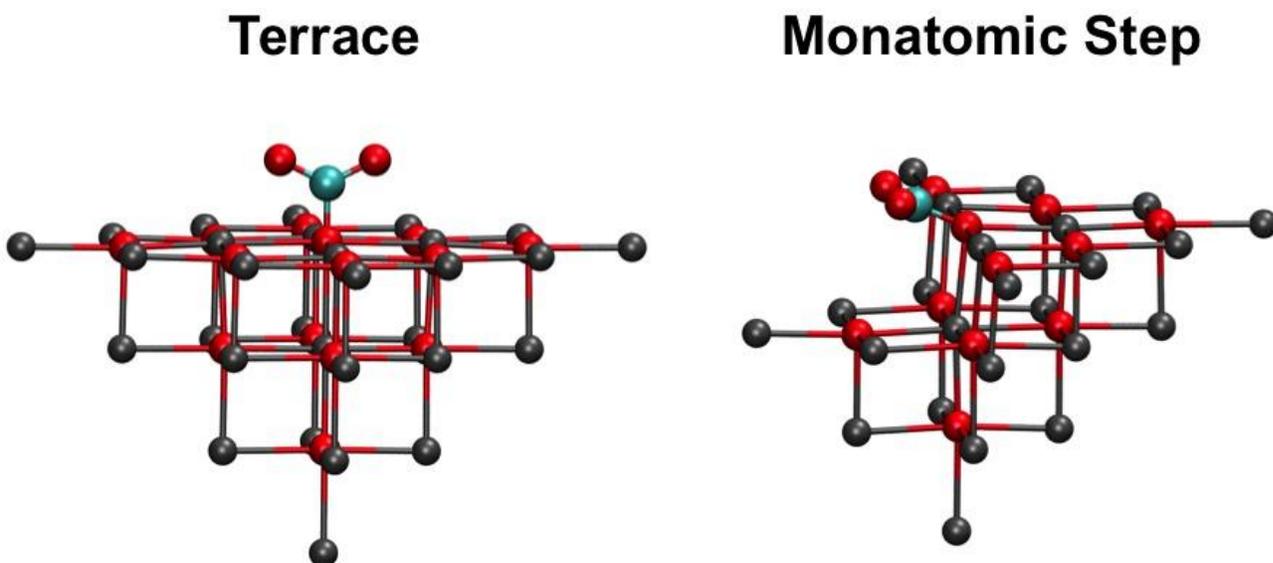
COLL 456

Adsorption of CO₂ on clean CaO(001) surfaces: A joint computational-experimental investigation

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Metal oxide surfaces are increasingly studied as catalysts for alkane conversion, such as methane reforming. Additionally, MgO and CaO surfaces impart CO₂ adsorption, which can affect the rate and mechanism of catalysis. CaO is particularly adept at CO₂ adsorption, and is therefore a viable candidate for carbon-capture technologies. Previous experimental and theoretical studies of CO₂ adsorption on CaO powders

suggest the presence of surface carbonates due to partial agreement with the infrared (IR) absorption spectra. Well-ordered CaO(001) thin films are grown on Mo(001) and Ru(0001) substrates to explore surface morphology of CO₂ adsorption via scanning tunneling microscopy (STM) and IR spectroscopy. CO₂ adsorption onto CaO(001) is studied via density functional theory (DFT) with an extended-surface model as well as with the periodic electrostatic embedded cluster method (PEECM). The possibility of CaO hydroxylation from adventitious water is explored, along with molybdenum migration to the surface from the substrate. Calculated infrared peak positions and intensities, in addition to predicted peak shifts upon isotopic labeling, are compared to experiment. New insights into CO₂ adsorption onto CaO single crystals have implications for surface catalysis of hydrogen production from hydrocarbons as well as advances in carbon sequestration



Cluster models for the adsorption of CO₂ onto CaO(001): terrace (left) and monatomic step (right).

COLL 457

DFT study of the Mars – van Krevelen mechanism for ammonia synthesis on Co₃Mo₃N (111)-surfaces

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Cobalt Molybdenum nitride ($\text{Co}_3\text{Mo}_3\text{N}$) is one of the most active catalysts for ammonia synthesis, however, the atomistic details of the mechanism for ammonia synthesis are currently not known. We find that there are six different surface compositions for $\text{Co}_3\text{Mo}_3\text{N}$ of which only one can adsorb and activate N_2 . We have used this surface to model the Mars – van Krevelen (MvK) mechanism for ammonia synthesis in which 3-fold hollow nitrogen vacancies are the active sites for the activation and dissociation of N_2 . Through a semi-empirical formalism that takes into account the entropy of N_2 and configurational entropy we have calculated the concentration of active sites at temperature and pressure conditions relevant to ammonia synthesis (380-550 °C, 100 atm) which were found to range from 1.6×10^{16} to $3.7 \times 10^{16} \text{ cm}^{-2}$. We find that the catalytically active surface is one where 3f-hollow-nitrogens are bound to the molybdenum framework with a hexagonal array of embedded Co_8 cobalt nanoclusters and that the vacancy formation energy (VFE) can be used as a descriptor for the screening of other materials that activate multiple bound molecules.

COLL 458

Box effects in nonliving and living polymerization of slow or non-diffusing monomers confined to a 2D surface

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The molecular weight distribution for living polymerization confined to a surface with little or no monomer diffusion is very different from that in solution. At low $[\text{initiator}]/[\text{monomer}]$ (I/M), the average number of monomers consumed per initiator (X_n) reaches a limiting value of 72 with polydispersity index = 1.50, because the active chain end is *boxed-in intramolecularly* by its own growing chain. Large amounts of monomers remain unreacted. At higher I/M , X_n decreases further because the active chain end is *boxed-out intermolecularly* (from pools of monomers) by other propagating chains. In particular, $1/X_n = 0.0133 + 0.9 I/M$, and monomer conversion is $X_n = 75 - 2/3 \times$ percent conversion. For nonliving polymerization, X_n is limited to $8 < X_n < 72$, for the entire I/M range, regardless of the kinetic parameters.

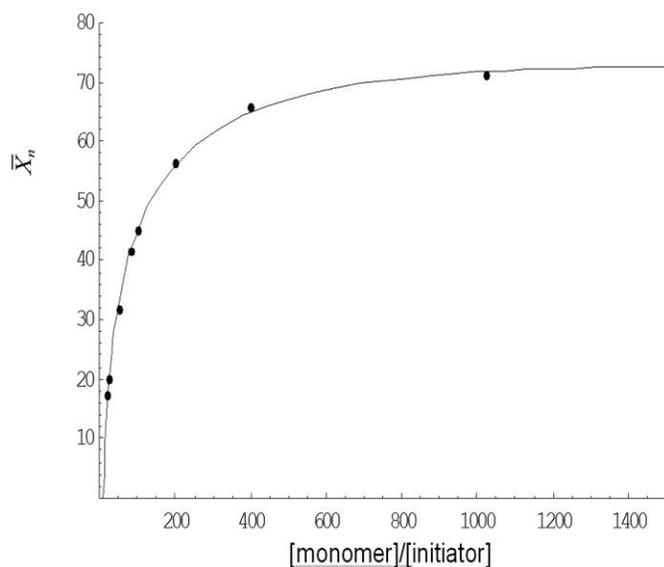


Fig. 1: The number-average degree of polymerization X_n as a function of [monomer]/[initiator] for living polymerization of slow or non-diffusing monomers confined to a surface

I/M^a	$\bar{X}_n(\text{surface})^b$	% conversion ^c	$\bar{X}_n(\text{solution})^d$
0.01 %	71.6 ± 1.0	0.72	10,000
0.1 %	71.3 ± 1.1	6.96	1000
0.25 %	65.9 ± 0.75	16.5	400
0.50 %	56.2 ± 0.65	28.1	200
1.0 %	44.9 ± 0.23	44.9	100
1.2 %	41 ± 0.8	50	83
2.0%	31.7 ± 0.21	63.4	50
4.0%	20.2 ± 0.08	80.6	25
5.0%	17.2 ± 0.06	86.1	20

^a [initiator]/[monomer] in the system

^b the number-average degree of polymerization for living polymerization in a surface at 95% confidence interval

^c refers to percent conversion of monomer to polymer; also known as extent of reaction

^d the expected number-average degree of polymerization for living polymerization in solution

Table 1: Cellular automata results for number-average degree of polymerization for living polymerization of slow or non-diffusing monomers confined to a 2D surface (X_n , surface)

COLL 459

Effects of surface geometry and surface-interaction potential on water freezing temperature

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Heterogeneous ice nucleation is a common process in nature. Although the freezing efficiency of several materials have been studied, it remains challenging to predict the ice nucleation ability of a specific surface, thereby inhibiting the design of new surfaces with increased efficacy. We use molecular dynamics simulations to characterize ice nucleation on surfaces with two different geometries – a surface with graphite geometry and a surface with geometry of the basal face of ice Ih. For the surface with graphite geometry, varying the surface-water interaction potential creates surfaces with different degrees of ice nucleating capability and even allows the surface to become ice prohibiting. In contrast, for the surfaces with ice Ih geometry, the freezing temperature is insensitive to the surface-water interaction potential.

COLL 460

Charge dynamics at the silica-electrolyte interface

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The aqueous biomolecule-silica interface is a technically important component present in many biosensors. For example, Biologically-sensitive Field Effect Transistors (BioFETs) are a class of biosensors designed to sense extremely small changes in the electric field at this interface. Understanding the physical and chemical nature of this surface region is crucially important to improving design of these devices.

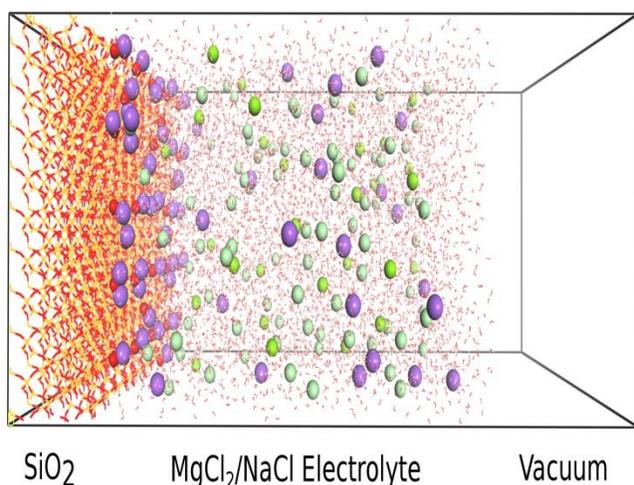
There are two influences on the electric field at this interface: surface charge from charging of silanol groups; and the structure/dynamics of mixed valency electrolytes near the charged silanolate surface.

Density Functional Theory methods were used to explore the proton transfer rate to/from the surface, revealing a new reaction mechanism and demonstrating that it is limited by the rate of reorientation of nearby water molecules. Dynamic silica-surface charging can be therefore be modelled as an activationless, diffusion-limited process. [1]

Classical Molecular Dynamics simulations were used to investigate electrolyte structure and dynamics under physiological conditions. The model showed that water polarisation plays an important role in determining the electric field near the interface, particularly for mixed valency magnesium/sodium electrolytes.

This atomistic simulation work highlights the complexity of the silica-water interface, and provides detail which cannot be adequately described using conventional mean-field models such as the Poisson-Boltzmann description of the electric double layer.

[1] Lowe, B. M., Skylaris, C.-K. & Green, N. G. *Journal of Colloid and Interface Science* 451, 231–244 (2015). doi: 10.1016/j.jcis.2015.01.094



COLL 461

Ono-kondo lattice modeling of CO₂ adsorption on various solid adsorbents

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The sequestration of CO₂ from combustion gas effluent or removal of CO₂ from air is receiving significant attention in recent times. There is a worldwide concern regarding emission of CO₂ gas as a byproduct of fossil fuel combustion. CO₂ adsorption is equally important in gas processing industry, aerospace industry, hydrogen production, purification process etc. As such, understanding the adsorption behavior of CO₂ on various matrices is important. A number of theoretical frameworks can be used to model the CO₂ adsorption phenomenon. Among these, the Ono-Kondo (OK) lattice model offers some advantages over its alternatives, including its ability to describe monolayer

and multilayer adsorption and the facility to generalize the model parameters in terms of adsorbent and adsorbate characteristics.

In this study, we evaluated the OK model representations of CO₂ gas adsorption on Al₂O₃, TiO₂, and Mg₂ (dobdc) as well as activated carbon and Pennsylvanian coal at various temperatures. The results indicate that a monolayer OK model can represent precisely the adsorption behavior of the different adsorbents. Specifically, the following absolute average percent deviations (%AAD) were obtained for the different matrices: Al₂O₃ (AAD=0.5% to 4.5%), TiO₂ (AAD =3.1%), Mg₂ (dobdc) (AAD=1.7%), activated carbon (AAD=1.0% to 3.5%), and Pennsylvanian coal (AAD=1.1% to 3.6%). Further, the model parameters appear amenable to generalization in terms of adsorbent characteristics and temperature.

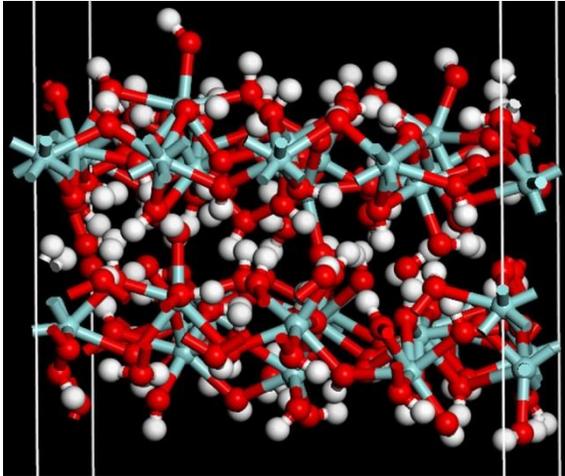
In a follow up study, we will address the efficacy of multilayer adsorption using a database involving a wider variety of adsorbents.

COLL 462

DFT modeling of zirconium hydroxide

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A number of experimental studies have shown that Zirconium hydroxide (Zr(OH)₄) holds great promise for filtration and decontamination of various chemical warfare agents (CWA). However, despite the wealth of experimental data (IR, TEM, TGA, etc.), so far there has not been sufficient theoretical ab initio calculations that could fully explain the basic structure and reaction chemistry of Zr(OH)₄. In this work, we use plane wave DFT calculations in order to gain a better understanding of the structure and reactivity of Zr(OH)₄. Molecular dynamics calculations at temperatures in the 300K - 1000K range determine several properties that match well against the experimental results published in the literature, such as the Zr/O and bridging/terminal OH ratios, as well as the interplanar distance. Having confirmed the model against experiment, we then look at the interactions of Zr(OH)₄ with CWA such as GB and VX, and environmental contaminants like SO₂. Ultimately, we expect that this model can be used to determine the reaction chemistry of CWA with Zr(OH)₄.



Optimized $\text{Zr}(\text{OH})_4$ double layer

COLL 463

Effect of surface polarity on physisorption of biomolecules: Molecular modeling

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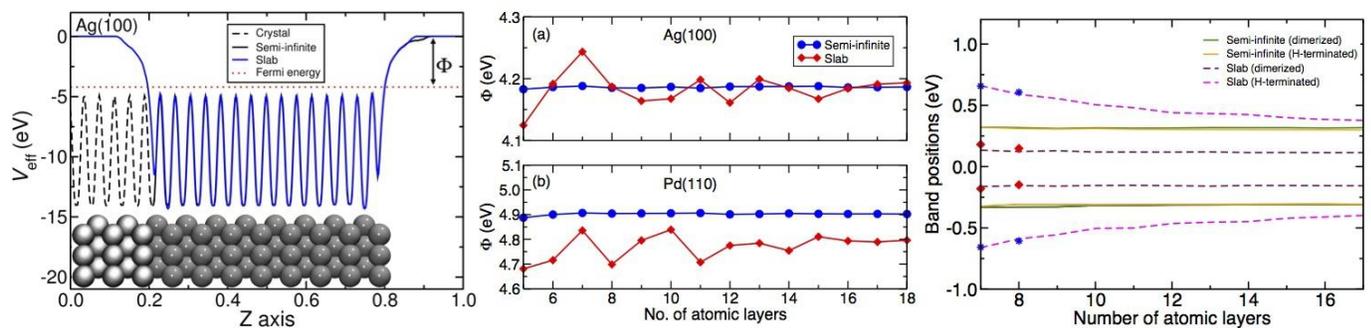
Physisorption of biomolecules to surfaces plays a role in many applications including sensors, bio-adhesion, drug delivery, composites, and coatings. For example, it is known that structural changes of interfacial biomolecules are crucial for properties of sensing surfaces and thus device performance. However, the desired surface properties for optimal change in bio-molecular structure are difficult to predict. Computer simulations can provide detailed information on the interfacial dynamics and aggregation behavior between biomolecules and various surfaces. Using all-atoms MD simulations we investigated the interactions between DNA and silk and various surfaces with different polarity (graphene, graphene oxide 5 % to 60 % oxygen content and SiO_2 surfaces). For DNA, our simulation results showed that graphene denatures DNA, whereas polar surfaces can retain base pairs and overall structure of DNA. We found that pi-pi stacking is the key interactions for unfolding DNA on graphene but functional groups on polar surface could prevent DNA from forming these interactions. For silk, its secondary structure was lost on both polar and non-polar surfaces but it was observed that graphene oxide with 20 % oxygen content can retain and recover ordered secondary structure better than more polar structure such as SiO_2 surface. Our results also found that combinations of electrostatic interactions, water bridging interactions and hydrogen bonds between silk and surface play a pivotal role in conformational changes and recovery motions of secondary structure of silk on surfaces. Overall, graphene has strong binding with biomolecules due to its propensity to form strong van der Waals interactions such as pi-pi stacking, while polar surface is better for secondary structure retention due to strong electrostatic interactions with biomolecules.

Semi-infinite solid model for DFT calculations of surface properties, rather than slab

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A method for carrying out DFT calculations of surface properties using a semi-infinite solid model and a fixed chemical potential of electrons is presented along with applications to metal and semiconductor surfaces. A Green function approach [1] is used to simulate a system consisting of two regions: (A) the bulk solid represented by a minimal unit cell and subject to periodic boundary conditions in three dimensions, and (B) a surface region represented by a few atomic layers subject to periodic boundary conditions in two dimensions with a free surface on one side but matched to region (A) on the other side. Not only is this a more accurate description of a solid surface but the computational effort is also an order of magnitude smaller than with the commonly used slab model. The semi-infinite solid approach has been implemented in the ATK software using atomic basis sets. Results of calculations demonstrate fast and systematic convergence of, for example, work function and band gap with the number of layers in region (B), while results of slab calculations show erratic convergence or even lack of convergence with the number of layers in a slab (see figures below).

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Left: Comparison of semi-infinite and slab calculations of Ag(100). Effective potential for an electron and work function estimate. Atoms in region (B) and slab shown by dark spheres, while atoms in region (A) are shown by light spheres. Middle: Convergence of work function for Ag(100) and Pd(110) from semi-infinite calculation using ATK (blue) and slab calculation using VASP (red). Right: Band gap at a Si(100) surface, either dimerized or H-terminated, calculated using semi-infinite and slab models with the ATK software (curves, see legend), and VASP (diamonds and stars).

COLL 465

***Ab initio* thermodynamics of surface properties of ruthenium and rhenium nanoparticles**

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The Fischer-Tropsch synthesis is a widely known catalytic reaction that converts carbon monoxide and hydrogen into liquid hydrocarbons: $(2n+1) \text{H}_2 + n \text{CO} \rightarrow \text{C}_n\text{H}_{2n+2} + n \text{H}_2\text{O}$. Usually achieved within heterogeneous catalysis,¹ nanocatalysts have proven to be of interest as their special structural and electronic properties enhance their activity for Fischer-Tropsch synthesis as well as for a large range of reactions.² From the theoretical point of view, the study of such reactions implies the understanding of the nanocatalyst surface steric and electronic effects in order to be able to design relevant models usable as starting point for reactivity studies. One important point to take into account is the catalyst coverage, according to the experimental pressure and temperature conditions. *Ab initio* thermodynamics³ applied to nanoparticles covered with H, CO or H and CO co-adsorbed leads to (T,p) diagrams, exhibiting stability domains for a wide range of experimental conditions. On hydrogenated ruthenium surfaces, the maximum coverage is of $1\text{H}/\text{Ru}_{\text{surface}}$.⁴ The same methodology applied to hydrogenated ruthenium nanoparticles evidence a larger saturation coverage, in agreement with experimental observations⁵. Calculations on nanoparticles with co-adsorbed CO and H give insight on the H/CO coverage under experimental conditions and therefore allows to perform reactivity studies on realistic models of nanocatalysts. This computational strategy exemplified in the case of ruthenium nanoparticles for the Fischer-Tropsch reaction can be applied to any metallic nanoparticle. Therefore, theoretical results on small rhenium nanoparticles⁶, for which fewer experimental data regarding the surface coverage are available, are also shown. Reverse Monte Carlo⁷ generated RDF profiles are used to shed light on the ReNPs surface properties regarding H and CO adsorption.

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COLL 466

Thin film oxide systems for electron transfer control

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We have studied thin oxide films supported on metal single crystals in order to model fundamental phenomena in heterogeneous catalysis. These films are prone to electron transfer through the film by tunneling. Depending on the electron affinity of the adsorbate on the film surface and the response of the oxide film itself, electrons may be trapped on the adsorbate. We have demonstrated this, both for metals such as Au as well as molecules such as O₂ (Angew. Chem. Int. Ed., **52** 11385 (2013); Angew. Chem. Int. Ed., **50** 11525 (2011)). This concept has recently been extended to the activation of CO₂. While CO₂ is a thermodynamically very stable molecule, the presence of electrons leads to a considerable destabilization to a point where the transfer of electrons is energetically favorable. Electron rich metal nanoparticles, which accumulated charge via electron tunneling from the metal substrate underneath the film, are therefore potential sites for CO₂ activation. We have utilized this knowledge to study the transformation of CO₂ into oxalate C₂O₄²⁻ species at Au nanoparticles as a function of the nanoparticles shape.

COLL 467

Kinetic and surface analysis of active sites in the hydrogenation of phenol using palladium nanoparticles

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The hydrogenation of phenol is an important industrial reaction in that it produces cyclohexanone, a key intermediate in the manufacture of nylon polymers. In our work phenol was hydrogenated in water at moderate temperatures and hydrogen pressures in a bench top reactor using polyvinylpyrrolidone (PVP) capped palladium nanoparticles. These nanoparticles were prepared using solution based colloidal methods in order to generate catalysts of a specific size. A gas chromatograph/mass spectrometer (GC/MS) was used to monitor the reaction and for comparison additional reactions were performed with a commercial 5% palladium on silica catalyst and PVP-capped palladium nanoparticles. For each catalyst the turnover frequency was determined and was used to compare catalytic activities, as well as reaction selectivity for cyclohexanone. Surface binding sites on the palladium nanoparticle surfaces are being analyzed through attenuated total reflectance infrared (ATR-IR) spectroscopy by the adsorption of carbon monoxide on the nanoparticle surface. The number of surface binding sites will be used to calculate the dispersion factor, or ratio of active surface sites to total palladium atoms, in order to “correct” the turnover frequencies. This information will allow us to determine the catalyst particle size most efficient for the formation of cyclohexanone. Through varying reaction conditions of temperature and

reactant concentrations, as well as nanocatalyst particle size and PVP capping agent molar mass, we aim to elucidate the factors that influence the atomic scale design of greener and more efficient catalytic materials.

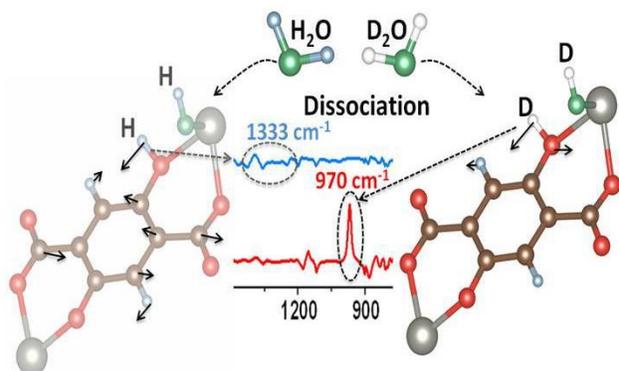
COLL 468

Chemistry in confined environments: Water reaction in MOF-74

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Water dissociation represents one of the most important reactions in catalysis, essential to the surface and nano sciences. However, the dissociation mechanism on most oxide surfaces is not well understood due to the experimental challenges of preparing surface structures and characterizing reaction pathways. We have used the metal organic framework MOF-74 as an ideal model system to study water reactions. Its crystalline structure is well characterized with a metal oxide node that mimics surfaces with exposed cations. Combining *in situ* IR spectroscopy and first-principles calculations, we find that, while adsorption is reversible below the water condensation pressure (~19.7 Torr) at room temperature, a reaction takes place at ~150 °C even at low water vapor pressures. First-principles calculations derive a pathway and kinetic barrier for the reaction and the final configuration, namely the H atom is transferred to the oxygen of the linker phenolate group and the OH binds to the open metal sites. Furthermore, they show that water confinement leads to water networks that reduce the activation barrier. The formation of these networks can be effectively hindered by introducing noble gases, thus making it possible to control the degree of water dissociation.

These findings and detailed understanding of the reaction mechanism lay the groundwork for the design of water stable MOF-74 and add to the understanding of molecular water interaction with cation-exposed surfaces.



Schematic of water reaction in MOF-74 with reaction products and spectroscopic signatures. Only D₂O products can be detected.

COLL 469

Conversion of small alcohols on ceria surfaces: A DFT study

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The key question we investigate is how surface structure of ceria catalysts affects chemical reactivity and selectivity. The use of nanostructured ceria exposing different surfaces depending on morphology opens new opportunities for catalyst tuning where acid/base and redox catalytic sites cooperatively promote reaction. Using density functional theory (DFT), we study the conversion of small alcohols as probe reactions on the (111), (100), and (110) ceria surfaces, which are exposed by octahedral, cube, and rod shaped ceria, respectively. We compute the selectivity towards dehydration and dehydrogenation of ethanol for idealized reaction steps and the C-H activation in methanol as a function of the surface structure. Challenging the commonly applied approach of single molecule reaction on surfaces, we are also creating a comprehensive kinetic model of methanol conversion considering adsorbate interactions and diffusion events explicitly. The DFT data is used as input for kinetic Monte Carlo simulations of temperature programmed desorption experiments.

This research was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division. Parts of this work were conducted at the Center for Nanophase Materials Sciences under a user proposal. The Center is sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy. This research was in part supported by an allocation of advanced computing resources provided by the National Science Foundation and performed on Kraken and Darter at the National Institute for Computational Sciences (<http://www.nics.tennessee.edu/>). This research also used resources of the National Energy Research Scientific Computing Center, a DOE Office of Science User Facility supported by the Office of Science of the U.S. Department of Energy under Contract No. DEAC02-05CH11231.

COLL 470

Improved supported metal oxides for the oxidative dehydrogenation of propane

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The abundance of shale gas has initiated a renaissance in the chemical industry. One of the effects is a shift from naphtha to ethane cracking at the heart of the chemical value chain. As a consequence, the United States is now one of the low cost producers

of ethylene. However, this feedstock shift also brings about challenges for the production of other olefins, in particular propylene. Indeed, the demand for propylene is growing far more rapidly than can be satisfied by steam cracking. The oxidative dehydrogenation of propane (ODHP) is a highly attractive and energy-efficient alternative to endothermic DeHydrogenation for the on-purpose production of propylene. Unfortunately, rapid consecutive over-oxidation of the desired olefin limits the selectivity and hampers the industrial feasibility. Supported metal oxides, and in particular dispersed vanadium containing materials, have shown promising results. Yet one has to improve both the selectivity and activity (space-time-yield) to make this reaction attractive. During the presentation I will show how we were able to increase the dispersion of group V metal oxides on silica, and how we used this to prepare a ternary metal oxide catalyst based on vanadium and tantalum that shows superior selectivity and productivity.

COLL 471

Degree of rate control: A tool for analyzing microkinetic models and high-throughput computational screening of catalyst materials

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Applications of the degree of rate control (DRC) in catalysis research will be reviewed. It was initially designed as a tool for sensitivity analysis of microkinetic models to determine which elementary step(s) are the kinetic bottlenecks, i.e., the most rate controlling. It was later generalized such that it quantifies, in a thermodynamically consistent way, the sensitivities of the net reaction rate to a small change in the energy of each species in the reaction mechanism. Thus, the DRC for any elementary step's transition state or for any adsorbed intermediate is defined as the fractional increase in the net rate that results from a tiny decrease in the energy of that species, keeping all other energies and entropies constant. It is scaled such that, when there is a single rate-determining step, the DRC for its transition state is unity. It has proven to be a powerful tool for analyzing catalytic reaction mechanisms to determine which species are most critical in effecting the desired rate or selectivity. Recently it has been applied as the central basis of a new method for computational catalyst screening, which uses the energies of the few species with the highest DRCs for a reference catalyst as descriptors to estimate the rates on related materials, and to predict which are most active or selective (C. A. Wolcott, A. J. Medford, F. Studt, and C. T. Campbell, *J. Catalysis*, 330 (2015) 197). Comparison of the predictions of this method regarding the relative rates of twelve late transition metals for methane steam reforming, with the predictions of the most commonly-used approach for computation catalyst screening, the Nørskov-Bligaard (NB) method (based on linear scaling relationships) shows that it has advantages and disadvantages, and suggests a simple way to improve the accuracy of the NB method. It is estimated to be computationally faster than the NB method when screening a moderate number of materials (<100), thus adding a valuable complement to the NB approach. It can be implemented without a microkinetic model if

the degrees of rate control are already known from experiments.

Support for this work by the DOE-OBES Chemical Sciences Division under grant #DE-FG02-96ER14630 and #DE-SC0012702 (the EFRC Inorganometallic Catalyst Design Center PI Laura Gagliardi at the University of Minnesota) is gratefully acknowledged.

COLL 472

Continuous flow catalytic reactors: Opportunities for *in situ* time-resolved mechanistic investigations

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Innovative *in situ* characterization tools are essential for understanding the catalytic reaction mechanisms. Though techniques, such as *in situ* transmission X-ray microscopy, fast single-particle spectroscopy, small-angle X-ray scattering, etc., are currently being developed, these tools are complex, not easily accessible, and do not necessarily provide the temporal resolution required to follow the catalytic reactions in real time. In this presentation the concept of utilizing continuous flow catalytic reactors for time resolved mechanistic studies would be introduced. In comparison with traditional batch reactors, through examples, it will be shown how continuous flow devices offer simplified solutions for carrying out kinetic studies and have the potential to revolutionize a broad range of fields from chemistry, catalysis, and nanotechnology. Particularly, in combination with spectroscopy tools such as synchrotron radiation-based XAS, SAXS and other spectroscopy probes like UV-Vis spectroscopy, Raman spectroscopy, FT-IR, these tool can be utilized to obtain time resolved information in investigating the mechanistic aspects of a vast number of catalytic reactions.

Specifically, more recent results in utilizing the technique to follow in a time-resolved fashion not only the nanostructured gold catalyst coating process but also for mapping the sequential transformation of catalytic reactions (using conversion of HMF to FDCA catalyzed by nanostructured gold as an example) at various spatial intervals leading to a better understanding of the time-resolved kinetics of the catalytic reaction. While our most recent investigations shared here are focused on *in situ* gold catalyzed reactions, the technique can be applied to analyze the time-resolved mechanisms of a broad range of catalytic reactions.

COLL 473

Confined liquid crystals: Harnessing director fields to direct colloid assembly

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We have been exploring elastic energies stored in director fields by confining nematics in vessels with well-defined anchoring conditions to guide colloids to assemble in reconfigurable structures. Colloids seed defects into the liquid crystal, which interact

with distorted director fields and defects to form ordered structures. Corners are rich sites for imposing highly distorted director fields and defects, allowing us to generate a number of interesting associated assemblies. Gently curved wells are also interesting sites for localizing particles and guiding structure formation. In this talk, I describe a series of studies for colloids immersed in nematics and trapped at their interfaces, and the properties of the structures that form.

COLL 474

Stimuli responsive LC/polymer material combinations

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LC/Polymer material systems which respond to various stimuli including heat, light, and e-fields are explored. As the amount of polymer content is increased, differing effects on the response behavior of the LC system are observed.

COLL 475

Spontaneous emergence of chirality in lyotropic chromonic liquid crystals in cylindrical confinement

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The ground state of a nematic fluid confined in a cylinder with planar anchoring is presumed to correspond to that of an axial configuration, wherein the director, free of deformations, is along the long axis of the cylinder. However, upon confinement of lyotropic chromonic liquid crystals in cylindrical geometries, we uncover a surprising ground state corresponding to a doubly twisted director configuration. The stability of this ground state, which involves significant director deformations, is rationalized by the saddle-splay contribution to the free energy. We show that sufficient elastic anisotropy in the elastic constants drives the transition from a deformation-free ground state to a doubly twisted structure, and results in spontaneous reflection symmetry breaking with equal propensity for either handedness. Enabled by the twist angle measurements of the spontaneous twist, we determine the saddle-splay elastic constant for chromonic liquid crystals.

COLL 476

Combining theory and experiment for designing liquid crystal-based chemical sensors

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Surface-anchored nematic liquid crystals can undergo orientational changes in response to select chemical stimuli, presenting opportunities for the design of highly sensitive chemical sensors. We present an approach to materials design that combines theoretical predictions, synthesis, and experimental characterization and evaluation for the accelerated discovery of new sensor materials. Our previous work has shown that the surface-induced ordering of the liquid crystal 4-cyano-4'-pentylbiphenyl (5CB) depends strongly on the chemical functionality of the surface, and that an orientational change can be triggered by the presence of small molecules such as dimethyl methylphosphonate (DMMP).¹⁻³ We developed a computational model for this process, based on quantum mechanics, showing that orientational changes can be predicted on the basis of the relative binding energies of the 5CB and DMMP to the metal cation-functionalized surfaces.

In this presentation, we will describe the use of our computational model to design of new classes of liquid crystal-based sensor materials for detection of a wide range of small molecules, by varying the chemical functionalities of liquid crystals as well as the metal cations used in the metal surfaces. We present a number of promising candidate sensors for specific small molecules on the basis of their relative binding energies to metal cations.

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COLL 477

Award Address (ACS Award in Colloid and Surface Chemistry sponsored by the Colgate-Palmolive Company). Colloidal and interfacial phenomena with liquid crystalline solvents

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Molecular self-assembly, colloidal interactions, and interfacial solvation are examples of physicochemical phenomena that have been widely studied in structured isotropic solvents such as water. Changes in the ordering of solvent molecules – and entropic contributions to free energies – play a key role in determining the organization and properties of these systems. This presentation will go beyond these past studies by addressing systems containing liquid crystalline solvents, where the long range ordering

of solvent molecules gives rise to fundamentally new colloidal and interfacial phenomena based, in part, on the presence of elastic strain and topological defects. In one approach, we are exploring the ordering of liquid crystals at bio/chemically complex interfaces, to understand how changes in the structure of interfaces on the molecular-scale are amplified into the ordering of liquid crystals on micrometer-scales. In a second approach, we are investigating the use of elastic strain within liquid crystalline droplets to create dynamic templates that can be used to synthesize chemically patchy and non-spherical particles. In a third approach, we have used the nanoscopic physical environments created by topological defects to direct the self-assembly of biological amphiphiles in ways that have strong analogies to polymer-templated self-assembly processes in aqueous systems. Such systems form the basis of new materials that permit ordering to propagate from the nanoscale to the optical scale with remarkable sensitivity. Finally, we are using the anisotropic mechanical properties of biocompatible liquid crystals to design materials that can be used to regulate the organization and function of living bacterial systems. These various lines of investigation, which encompass a broad range of colloidal and interfacial phenomena involving liquid crystals, will be discussed. Fundamental challenges and technological opportunities will be described.

COLL 478

Binding and partitioning behavioral study of novel sulfonamide-derived compound interacting with conventional cationic surfactants

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Micellization of a novel sulfonamide derivative, Sodium{3-methyl-2-[(phenylsulfonyl)amino]butanoate}trihydrate (SBS) was demonstrated with conventional cationic surfactants. SBS proved to exhibit strong bindings with cationic surfactant moieties. The characteristics of partition and binding interactions of SBS with cetyltrimethyleammonium bromide (CTAB) and ethylehexadecyldimethyleammonium bromide (EHDAB) were quantitatively elucidated using simple UV-visible spectroscopy, differential UV-visible spectroscopy and steady state fluorescence spectroscopic techniques. The enhanced solubilization of SBS in the SBS-CTAB and SBS-EHDAB systems was confirmed through binding capacity and Stern-Volmer quenching constant (K_{sv}) values. These findings extend the proficiency of additive molecule as a reporter for sensing electrostatic environment in lipidic membranes and related organized assemblies.

COLL 479

Diclofenac sodium-induced micelle-to-vesicle transition in ionic liquid based surfactant systems: Relevance to drug delivery

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The effect of anti-inflammatory drug, diclofenac sodium (DS) on the transformation of various surfactant aggregates from spherical micelles to vesicles via branched worm-like micelles of two ionic liquid based surfactants (ILBs), 1-(1-hexadecyl)-3-vinyl imidazolium bromide, [C₁₆Vim][Br], 1-(1-hexadecyl)-3-methyl imidazolium bromide [C₁₆Mim][Br] and cetyltrimethyl ammonium bromide, CTAB were evaluated in aqueous solution at 298.15 K. Turbidity, viscosity, dynamic light scattering (DLS) and transmission electron microscopy (TEM) measurements were used to study the DS-induced formation of unilamellar vesicles of different sizes. From the viscosity data we found that transition of spherical micelles to wormlike micelles occurred at low concentration of DS for [C₁₆Vim][Br] as compare to [C₁₆Mim][Br] and CTAB. This shows a stronger interaction between cations of ILs and Anions of the drug. Hydrodynamics diameter obtained from DLS and TEM analysis revealed that DS/[C₁₆Vim][Br] mixtures in aqueous solution lead to the formation of large unilamellar vesicles compare to DS/[C₁₆Mim][Br] and DS/CTAB. These systems have potential application in drug delivery.

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COLL 480

Shape persistence micelles having the same aggregation numbers with the platonic solids

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A series of calix[4]arene-based lipids with alkyl chains of varying length were newly synthesized and found that some of them form spherical micelles with a defined aggregation number. These aggregation numbers are 6, 8, 12, and 20, interestingly coinciding the numbers of the Platonic solids. Synchrotron small-angle X-ray scattering (SAXS) patterns exhibited a sharp intensity minimum, indicating high symmetry and shape monodispersity. The size monodispersity of the micelles was confirmed with analytical ultracentrifugation and asymmetric field flow fractionation. The present results indicate that a suitable combination of tail length, head volume, and rigidity of the building block is necessary to attain the shape persistency. With a shape determination program of Dummy and molecular dynamics calculation, the micellar architecture was determined and an atomic scale model to reproduce SAXS profile was constructed. We have a hypothesis that can rationalize why the aggregation numbers are taking such a discreet manner and chosen from the numbers of the Platonic solids; the aggregation number is determined by the J. J. Thomson's theorem to determine the minimum electrostatic potential energy configuration of N electrons on the sphere

surface that repel each other. We suppose this can be extended to the other spherical micelles when the aggregation numbers are small enough.

COLL 481

Enhanced solubility and self-assembly of nonionic surfactants in electrolyte solution

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Nonionic surfactants are widely used in many industrial applications ranging from emulsion polymerization to crude oil production. The solubility of a nonionic surfactant in water, however, decreases with increasing temperature, until the surfactant becomes insoluble when reaching the cloud point temperature. Moreover, the presence of electrolyte in aqueous solutions suppresses the cloud point of a nonionic surfactant. The decrease in aqueous solubility with increasing temperature and electrolyte concentration makes it particularly challenging for application of nonionic surfactants in this type of environment. In order to enhance the solubility of nonionic surfactants in electrolyte solutions and at elevated temperatures, additives such as hydrotropes, solvents, and co-surfactants are used in surfactant formulations. In this presentation, we will describe an approach to enhance the solubility of polyethoxylated nonionic surfactants in electrolyte solution by addition of di-sulfonated anionic surfactants. Although it is generally accepted that the solubility of polyethoxylated nonionic surfactants in water increases linearly with increasing the level of ethylene oxide units in the molecule, our studies show that in the presence of a di-sulfonated anionic hydrotrope in solutions containing high levels of electrolyte, the dependence of cloud point on the ethylene oxide chain length departs from this linear trend. Our results suggest that optimal solution stability can be achieved by tailoring the number of ethylene oxide units in the nonionic surfactant molecule to an optimal length, by decreasing the length of the hydrocarbon tail of the di-sulfonated anionic surfactant, and by varying the concentration of the anionic surfactant in solution. Finally, we will present diffusion NMR studies performed to obtain fundamental insights into the self-assembly of these surfactant systems, which suggest that anionic surfactants with different molecular structures lead to enhanced solubility of polyethoxylated nonionic surfactants in electrolyte solution by different mechanisms.

COLL 482

Interfacial structure of small molecule surfactant, polymeric surfactant and particle stabilised air-in-water foams

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Small-angle neutron scattering has been used to probe the interfacial structure of nitrogen-in-water foams created using a series of small molecule surfactants, triblock polymeric surfactants of the poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide)(EOx-POy-EOx) range, their blends and partially hydrophobic particles. Universally, the data follow a pronounced Q^{-4} decay, along with a number of inflexions and weak but well defined peaks. For the surfactants, these characteristics were well described by a model embodying paracrystalline stacks of adsorbed surfactant layers, whose formation is induced by the presence of the air-water interface, adsorbed at the flat air-water (film lamellae) interface. Typically, a minimum of five paracrystalline surfactant layers of thickness of the order 85-160 Å, interspersed with somewhat thicker (400 Å) films of continuous aqueous phase were found to best fit the data. For the triblock copolymer data, the thickness of the layer (L) was shown to follow a simple empirical relationship with the EO and the PO block sizes. Similar features were observed in the particle foams data, but it is less obvious how to interpret these data. A selection of data will be discussed and set into the wider context of how surface active species assemble at air/water interfaces.

COLL 483

Thermodynamic study of the self-assembly behaviors of the giant amphiphiles (dihydroxy groups functionalized polyhedral oligometric silsesquioxane-polystyrene) in solution

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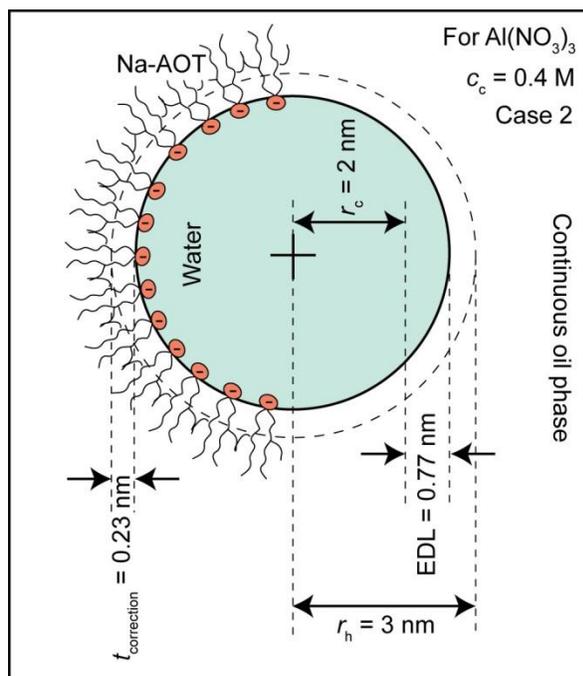
With the advancement of technology, regular amphiphiles (regular surfactants and amphiphilic diblock copolymers) could not meet the higher requirements of the materialists. Recently, one unique amphiphiles are designed and successfully synthesized-giant surfactants. Such giant surfactants choose molecular nanoscale particle (MNP) as polar heads and polymer as tails, bridging the gap between the two traditional self-assembling materials and possesses advantages of both at an intermediate length scale of ~10 nm. In order to build materials with hierarchical complex structure using such giant amphiphiles as building blocks, one question arise we need to answer: will the self-assembly process be thermodynamic control, like small surfactants, or kinetic control like block polymers? It is well-known that the self-assembly processes of the small surfactants are thermodynamic control due to the fast mobility of the molecules in solution; on the other hand, for the linear amphiphilic diblock copolymers, the kinetic control are often involved during the self-assembly process because of high molecule weights. Although in early work, based on the TEM images, it has been pointed that the PS tails in micellar core, similar to small surfactants, are highly stretched, exhibiting fast relaxation and self-assembly dynamics. There are still controversies about the nature of the self-assembly process. In this work, the question will be solved.

COLL 484

Structure and stability of reverse micelles with salt additions: Experimental and modeling insights

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In this work, we present the effect of NH_4OH , $\text{Al}(\text{NO}_3)_3$, and ZrOCl_2 on the structure of reverse micelles for the system AOT/water/isooctane. An analytical approach, coupled with experimental results from dynamic light scattering, have been used to gain insight on the reverse micelle structure under different electrostatic environments (*i.e.*, ionic systems of varying charge and concentration). A change in slope in the average reverse micelle size with respect to salt concentration is observed at low values of salt concentration and this is used to estimate the Stern layer ion occupancy at the surfactant interface. In addition, the hydrodynamic radii obtained have been corrected with surface charge density estimates. Furthermore, the water core sizes and Stern layer ionic occupancy have been used to determine the electrical double layer thickness and the core zone. The calculations support the formation of an onion-type reverse micelle structure that contains a core, an electrical double layer zone with two overlapping electrical potentials, a Stern layer, and an outer surfactant layer. In all systems, as salt concentration is increased up to the critical concentration, the reverse micelle core zone approaches a value close to 2 nm, as illustrated in the figure. Preliminary results on a AOT/ethanol/heptane system will also be presented and correlated to the model developed for the AOT/water/isooctane system.



Impact of rock wettability on surfactant-enhanced aquifer remediation

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Surfactant-enhanced aquifer remediation (SEAR) is a potentially viable technology for the removal of non-aqueous phase liquids (NAPLs) from rocks. The surfactant selection and displacement mechanism depend on an intricate interplay between fluid-fluid and fluid-rock interactions. For example, mobilization is desirable in aquifers contaminated by LNAPLs. On the other hand, the adsorption of DNAPLs can significantly alter the wettability of rocks, as shown in Figure 1. The degree of wettability alteration varies in heterogeneous rock surfaces. Therefore, effective remediation strategies can be achieved through fundamental understanding of displacement mechanisms of contaminants in rocks, which depends on surfactant structure and rock mineralogy. The majority of SEAR studies were performed in homogeneous rocks and as a result, the mechanism of NAPL desorption from heterogeneous rocks using surfactants is still unclear.

The objective of this study is to investigate the wettability alteration of heterogeneous aquifer rocks caused by NAPL adsorption and the impact of various surfactants on NAPL desorption. Aquifer rock samples were obtained from the Fountain formation located in eastern Colorado and Wyoming. This is a heterogeneous Pennsylvanian sedimentary rock consisting primarily of carbonate, sandstone, and arkose. The ability of surfactants to alter the wettability of contaminated minerals to its original water-wet state is assessed through an extensive set of interfacial tension and contact angle measurements. The surfactants used in this study are environmentally friendly and are chosen based on their tendency to create a separable and stable micro-emulsion phase between NAPL and water, which is evaluated from phase behavior tests and high-resolution transmission electron microscopy. Spontaneous imbibition tests in NAPL-saturated rock samples with surfactant-in-water solutions also helped understand the remediation mechanism with each surfactant.

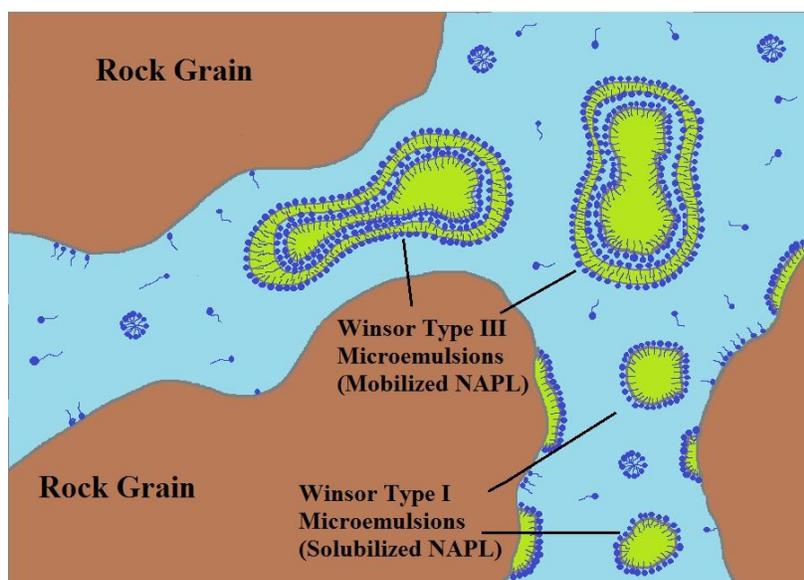


Figure 1. Mobilization and solubilization of NAPLs by surfactants in porous aquifers

COLL 486

Expanding applications and structures of modified sophorolipid derivatives

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Surfactants are ubiquitous molecules throughout many industries. However, the most common surfactants are made from nonrenewable feedstocks and may be toxic or bioaccumulative. Sophorolipids are biosurfactants produced from the fermentation of *Candida Bombicola* using natural, renewable feedstocks. They have attracted significant interest due to their biodegradability, but surface activity and solubility limits have limited their widespread adoption. Previous work has shown that modified sophorolipids, made with simple, green chemistry, can greatly improve the surface activity and solubility of natural sophorolipids when used in interfacial applications while remaining non-bioaccumulative.

Hydrophobic phases and modifications studied in previous work has been limited to lemon oil, almond oil, and paraffin oil with a series of de-acetylated n-alkyl ester sophorolipids. This paper reports new simple modifications of the sophorolipid head and tail that cause drastic changes in surface activity beyond what would have been previously expected with respect to surface and interfacial tension. Modified sophorolipids with improved solubility while having desirable interfacial characteristics will be discussed. This work has also resulted in knowledge that has widened the scope of applications for which modified sophorolipids are effective.

COLL 487

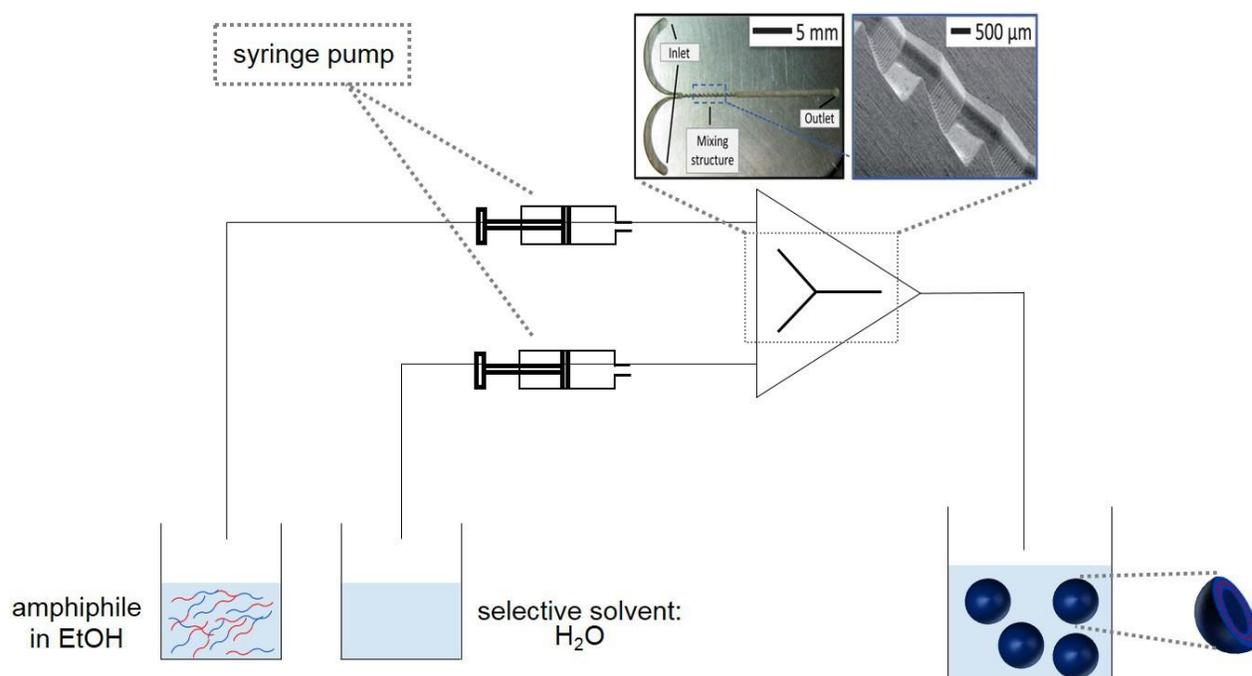
Controlled self-assembly of dendritic amphiphiles in micromixers

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The controlled synthesis of supramolecular aggregates formed by the self-assembly of dendritic amphiphiles is a challenging task. Conventional batch-based techniques such as the solvent injection method or the film hydration method typically go along with a lack of control over mixing and thus over size, morphology and size distribution.

The micromixer technology is a promising method for the controlled preparation of supramolecular assemblies as it allows control of mixing at microscale level. In addition, such microfluidic systems benefit from a high mixing efficiency, a low mixing time as well as from a reproducible and continuous synthesis.

Herein, we report on the microfluidic-controlled self-assembly of several dendritic amphiphiles and the impact of the mixing parameters on the self-assembly process.



Schematic illustration of the continuous microfluidic-controlled self-assembly of dendritic amphiphiles.

COLL 488

Surfactants and polymers in rinse-off cosmetics: Challenges and innovations

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Complex colloids containing mixed surfactants and multi-functional polymers have been used for decades as rinse-off cosmetic ingredients to provide general hygiene and beauty benefits. The current challenges focus primarily on minimizing the effect of surfactants and polymers on the permeability barrier of skin without negatively impacting the sensorial and hygiene aspects experienced during the personal cleansing and care process. In recent years significant progress has been made to design rinse-off cosmetics that minimize the damage potential to skin or hair and instead provide significant beauty platforms that address concepts such as all day moisturization, anti-acne, anti-aging, and sun protection. This paper focuses on reviewing current techniques, rationales and progressive innovations in this field based on the usage of novel surface-active and polymeric ingredients that have been incorporated in products to simultaneously deliver the mildness without sacrificing the functionality, aesthetics, and cosmetic benefits that today's consumers demand.

COLL 489

Development of neutron reflectometry as a probe of biomembrane structure

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Neutron reflectometry (NR) has become a well-established and valuable probe of biomembrane structure. By proper analysis of specular reflectivity data measured as a function of wavevector transfer Q normal to the surface of a biomembrane, an unambiguous scattering length density profile as a function of depth into the film along that normal can be obtained, in certain cases with a spatial resolution of a fraction of a nanometer, limited only by the statistical accuracy of the data and the maximum attainable value of Q . Relatively low concentrations of proteins embedded in or extending out from lipid bilayers can be accurately studied by this method and remarkable results have been obtained, as reported, for example, in other talks presented in this symposium. This presentation critically examines what makes NR such a powerful method for studying biomembrane systems and addresses specific aspects regarding uncertainty, spatial resolution, inversion of scattering data, the phase problem for strongly scattering potentials, the uniqueness of the structural results obtained, and the role of neutron coherence. Recent developments in instrumentation that promise to significantly advance the capabilities for NR measurements of biomembranes are also considered.

COLL 490

Evolution of membrane systems for neutron scattering: From lipid vesicles to living cells

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The existence and role of lateral lipid organization in biological membranes has been studied and contested for more than 30 years. Lipid domains, or rafts, are hypothesized as scalable compartments in biological membranes, providing appropriate physical environments to their resident membrane proteins. This implies that lateral lipid organization is associated with a range of biological functions, such as protein co-localization, membrane trafficking, and cell signaling, to name just a few. Neutron scattering techniques have provided an excellent tool with which to investigate these structural features in model lipids, and more recently, in living cells. I will discuss our recent work using neutrons to probe the structure and mechanical properties of model lipid systems [1] and our current efforts in using neutrons to probe the structure and organization of the bilayer in a living cell. Our efforts in living cells have used genetic and biochemical strategies to create a fatty acid obligate organism used to generate a large neutron scattering contrast, making the membrane 'visible'. I will present our preliminary results showing the *in vivo* bilayer structure and discuss the outlook for this approach.

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Neutron scattering and contrast matching techniques reveals bilayer structure on the nanometer length scale.

COLL 491

Investigating the mechanism of electromechanical coupling in voltage-gated ion channels by time-resolved x-ray & neutron interferometry

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Although x-ray crystal structures exist for several voltage-gated ion channel (VGIC) proteins, the mechanism of coupling voltage dependent conformational changes in the voltage sensor domains to opening and closing the pore domain remains controversial. This situation persists because the usual physical techniques for protein structure determination cannot access the dependence of their structures on a transmembrane voltage. As a result, less direct experimental approaches and sophisticated computational techniques have been utilized to develop consensus models of the voltage-dependent conformations responsible for electromechanical coupling in VGIC proteins. Alternatively, we have developed two methods for vectorially-orienting VGIC proteins within single phospholipid bilayer membranes at the solid-liquid interface within electrochemical cells designed for the investigation of the scattering-length density (SLD) profile structures of these membranes by x-ray and neutron reflectivity. The spatial resolution, or sensitivity to detail within the profile structure, can be dramatically enhanced using interferometric techniques. We have employed time-resolved “pump-probe” techniques to investigate changes in both the x-ray and neutron SLD profile structures of the isolated voltage-sensor domain of a voltage-gated potassium channel as a function of the applied transmembrane voltage. The changes in each of these two independent SLD profile structures were found to be consistent with molecular dynamics simulations of the voltage sensor domain within a fully-hydrated phospholipid bilayer investigated as a function of the transmembrane voltage. This agreement allowed us to relate the voltage-dependent changes in the SLD profile structure to the conformational changes in the 3-D atomic level structure of the voltage sensor. These approaches are now being applied to the complete homotetrameric VGIC proteins wherein each subunit contains a voltage sensor and $\frac{1}{4}$ of the pore domain. This is more complicated because unlike their isolated voltage sensor domains, the complete VGIC proteins typically exhibit inactivation upon prolonged exposure to depolarizing voltages, with respect to the resting transmembrane voltage, which requires the cyclic application of polarizing and depolarizing voltages of much shorter duration on the order of milliseconds. Our goal is to understand how anesthetics interfere with electromechanical coupling.

COLL 492

Using neutron scattering in biology: The case for membrane proteins and lipoprotein particles

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Neutron Scattering in solution and at interfaces offers many unique opportunities in soft matter. Selective deuteration adds the possibility to elegantly match out specific components in a mixture. The ability to match out a component is of particular importance for protein-lipid systems such as membrane bound and transmembrane proteins incorporated in a lipid membrane as well as the lipoprotein particles in the blood. Some of the outputs for neutron scattering based techniques include the overall low-resolution structure of the system studied in biological like environment. This can give detailed effects of the environment (lipid component/solution composition/temperature) on for example the equilibrium conformation of membrane bound protein and the dynamics involved in these systems. In this talk I will present the efforts done in my group to study lipid-protein systems of various types including our most recent results on the use of nanodisc films for the study of the structure of membrane bound proteins. We will also present a newly developed fitting procedure that increases the structural information obtained from neutron reflectivity by using results from molecular dynamics simulations as molecular constrains.

COLL 493

Structure determination of peripheral membrane proteins adopting multiple configuration

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The structural characterization of peripherally associated membrane proteins saw significant technical advances over the last decade using neutron reflectometry.¹ Due to experimental and computational improvements, it is now possible to reliably resolve one-dimensional protein profiles along the bilayer normal with high spatial and volume resolution while protein surface coverage can be as low as 5 vol%. The penetration depth of a protein into the lipid membrane can be resolved in special cases to within only a few Ångstrom. The achievement of those technical specifications finally made neutron reflectometry a useful tool for biomedical research. The improved resolution also makes the technique much more sensitive to the existence of multiple configurations of a protein at the membrane. Neutron reflectometry averages over protein configurations at the membrane, and in most cases, the coexistence of multiple configurations complicates data analysis or prevents individual structure determination altogether. Here, I lay out strategies and scientific developments to tackle this problem and to obtain structural information on multiple conformations. I will discuss an improved thermodynamic characterization of protein binding to lipid membranes taking place before the scattering experiment, and computational tools employed during data analysis. I will demonstrate those methods using examples from biomedical projects concerning HIV, T-Cell signaling, and cancer.

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COLL 494

New tools for probing the spatial organization of biomimetic membranes

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The three-dimensional spatial organization of lipids and proteins in biological membranes has functional consequences for the living cell. Within the plane of the outer leaflet, lipids are thought to self-organize into distinct microdomains enriched in high-melting lipids and cholesterol, with diverse evidence supporting participation of these “raft” domains in membrane processes including protein sorting and signaling. Furthermore, cells actively maintain an asymmetric distribution of different lipid types between the inner and outer leaflets of the plasma membrane, resulting in monolayers with different fluidity and charge density. Despite intense interest, the fundamental mechanisms controlling raft size and morphology, as well as coupling between leaflets of different composition, remain elusive. The precise determination of phase-separated and asymmetric bilayer structure therefore represents a crucial step toward a deeper understanding of these mechanisms. Among biophysical tools, small-angle neutron scattering (SANS) is a particularly powerful tool for probing lateral and transverse bilayer structure, especially when combined with the selective use of deuterium-labeled lipids. I will describe approaches for obtaining structural information from SANS of biomimetic membranes, with an emphasis on new analytical models.

COLL 495

Frontiers in membrane biophysics

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One of the major challenges of modern physics is to contribute to biology and life-sciences. Neutron and X-ray beams are prime tools to study molecular structure and dynamics in membranes in-situ, under physiological conditions [1].

The experiments give access to nanoscale diffusion processes within and across the membranes, effects of macromolecules on membrane properties, such as ethanol and cholesterol, the interaction with common drugs, such as aspirin, ibuprofen and

cortisone, and their side effects, detection and characterization of membrane raft structures and protein-protein interactions in Alzheimer's disease. The quantitative measurements lend themselves for comparison with computer simulations. I will talk about current topics in membrane biophysics, the associated experimental challenges and present exciting recent results and potential biomedical applications.

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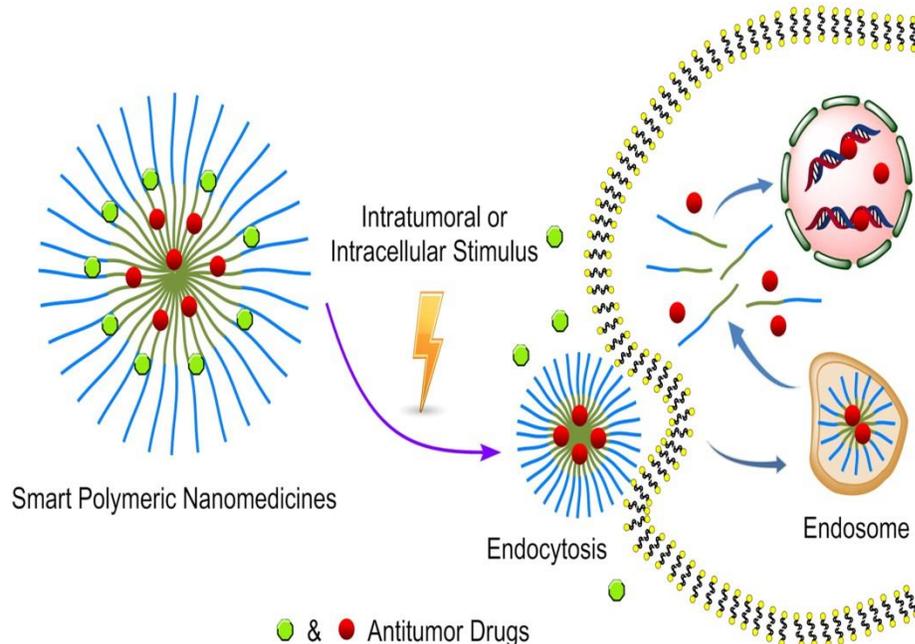
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COLL 496

Smart polymeric nanomedicines at work in rational antitumor drug delivery

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Recently, the development of smart polymeric nanomedicines enables the personalized and on-demand treatments to be highly possible. The intelligence not only endows the polymeric nanocarriers with the capabilities of identifying diseased tissue or cells and triggering the positive response of cells, but also can serve as a switch to achieve the directional drug delivery in the lesion sites. Based on the above background, our group has designed and prepared various stimuli-responsive nanoscale polymeric nanomedicines, including loading micelles, nanogels, prodrugs, and so on. The platforms can selectively accumulate in tumor tissue through the enhanced penetration and retention (EPR) effect and/or active targeting, enter cells through endocytosis, and release payload triggered by the specific intratumoral or intracellular microenvironment (Scheme 1). In addition, we are improving their properties through the following two aspects of researches: (1) codelivering various antitumor drugs with different mechanisms to enhance tumor inhibition through synergistic effect; (2) exploiting the light-, voltage-, and radiation-responsive smart nanocarriers and combining with photodynamic therapy, electrotherapy, and radiotherapy, respectively, to further accelerate the drug release and improve the efficacy. After long-term exploration, it is possible to obtain the smart polymeric nanocarriers with desired properties for clinical malignancy therapy.



Scheme 1. Schematic illustration of Intratumoral or intracellular stimulus-triggered antitumor drug release from smart polymeric nanomedicine

COLL 497

Tools for mapping and understanding complex biological systems in normal and disease states

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Complex biological systems like the brain present a challenge: their molecular building blocks are organized with nanoscale precision, but support physiological processes and computations that occur over macroscopic length scales. Similarly, complex diseases like cancer exhibit pathological changes that are observable from the tissue level down to the molecular level. In the first part of the talk, I will introduce the Boyden lab's technology suite for imaging large 3-D specimens with nanoscale precision. We embed a specimen in a swellable polymer, which upon exposure to water expands isotropically in size, enabling conventional diffraction-limited microscopes to do large-volume nanoscopy. We called this process expansion microscopy (ExM). We are developing strategies for multiplexed readout of anchored DNA barcodes, in order to identify and localize thousands of different kinds of biomolecule, with nanoscale precision, in cells throughout intact tissues -- a key step towards understanding the configuration of

complex biological systems in normal and disease states. In the second part of the talk, I will focus on a newly developed ExM-based technology, expansion pathology (ExPath). ExPath allows examination of a broad range of clinical samples with unprecedented detail, using only conventional optical microscopes. ExPath opens up new opportunities for morphological and molecular cancer diagnosis. In addition, ExPath can serve as a powerful research tool to investigate the pathology of complex diseases such as cancers in nanoscale level.

COLL 498

Using elasticity to control biological transport of polymer nanogels

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The impact of hydrogel matrix elasticity is known to significantly impact the differentiation and growth of biological cells and tissues. Much less studied, however, is the impact elasticity of nanoparticles has on the circulation and organ or cellular targeting, such that the potential benefits of tuning nanoparticle elasticity are not clear. Here, we describe a method to synthesize a series polyethylene glycol (PEG)-based hydrogel nanoparticles of uniform size and surface charge density with elastic moduli ranging from very soft (~0.2 kPa) to very hard (3 MPa). These particles possess well-characterized microstructure and exhibit low toxicity compared to other nanoparticle vehicles, and are thus well-suited to investigating the role of particle elasticity on key biological transport processes including blood circulation, biodistribution, antibody-mediated targeting, endocytosis and phagocytosis. Our results demonstrate that softer nanoparticles offer enhanced circulation and subsequently enhanced targeting compared to harder nanoparticles *in vivo*. Furthermore, *in vitro* experiments show that softer nanoparticles exhibit significantly reduced cellular uptake in immune cells (J774 macrophages), endothelial cells (bEnd.3) and cancer cells (4T1). Tuning nanoparticle elasticity potentially offers a method to improve biological fate of nanoparticles by offering enhanced circulation, reduced immune system uptake and improved targeting.

COLL 499

Hemorrhage control using biocompatible polyphosphate bound silica nanoparticles

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On the battlefield, uncontrolled bleeding remains the leading cause of death predominantly due to penetrating combat injuries, while in the civilian sector, it is the second highest cause of mortality. Hence, stemming blood loss is crucial for initial survival and essential for recovery. Current hemostatic agents available for field use are designed for compressible hemorrhage, while none are available for incompressible hemorrhage. We propose to address this problem by developing a silica functionalized polyphosphate nanoparticle system that can be intravenously or topically delivered, effective at controlling hemorrhage at any injury site, and safe. Our proposed system consists of silica nanoparticles as the carrier with polyphosphate as the targeting component that controls internal hemorrhage by accelerating the blood clotting process without undesired side effects. Silica was selected as the carrier platform material due to its surface chemistry versatility, procoagulant property, biocompatibility, and use in biomedical applications. Silica is found in human connective tissue and bone, and is known to be absorbable and biodegradable. Polyphosphate was incorporated into the nanoparticle system for its ubiquitous presence in biological systems and its role in the blood clotting process. Of particular interest is the existence of polyphosphate in human platelet and the ability of polyphosphate to modulate the blood clotting cascade depending on its chain length. Leveraging components that are native to human physiology is advantageous for safety and biocompatibility considerations. Upon thorough chemical characterization, we conducted efficacy and biodistribution studies of our silica-polyphosphate nanoparticle system. Results indicated that the polyphosphate bound silica nanoparticle system is a viable solution for hemorrhage control applications.

COLL 500

Anticancer platelet-mimicking nanovehicles

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Introduction: Recently, the recognition and interaction between platelets and circulating tumor cells in blood have aroused considerable attention because of its crucial contribution to tumor metastasis[1,2]. Thus, functionalizing synthetic nanoparticle with platelet membrane holds great potential for cancer therapy and diagnostics.

Materials and Methods: We have developed a platelet-mimicking nanovehicle of an anticancer protein and a chemotherapeutic agent for combination cancer treatment (**Figure 1**). The designed nanovehicle is generated through coating the purified platelet membrane on the surface of synthetic nanovehicles, which is composed of a nanogel based inner core part and the platelet membranes based outer shell. Dox is loaded into the nanogel and TRAIL is conjugated to the platelet membrane.

Results and Discussion: The MDA-MB-231 cells were applied as a cell model to investigate the site-specific delivery of TRAIL and Dox. IC₅₀ of TRAIL-Dox-PM-NV was determined to be 19.3 ng/mL (TRAIL concentration) and 193 ng/mL (Dox concentration), which increased cytotoxicities of TRAIL-Dox-NV, Dox-PM-NV and TRAIL-PM-NV to 2.2-, 2.6- and 7.8-fold, respectively. Furthermore, TRAIL-Dox-PM-NV showed the strongest tumor growth inhibition *in vivo*. Additionally, TRAIL-Dox-PM-NV could effectively eliminate the circulating tumor cells (CTCs) *in vivo* and inhibit development of tumor metastasis.

Conclusions: In summary, we have developed a platelet-mimicking nanovehicle platform that could selectively target to the tumor site and sequentially deliver TRAIL and Dox, led to significant enhancement of the antitumor efficacy and effective inhibition of the tumor metastasis.

Acknowledgements: This work was supported by the grant from NC TraCS, NIH's Clinical and Translational Science Awards (CTSA, NIH grant 1UL1TR001111) at UNC-CH.

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Figure 1. Schematic design of anticancer platelet-mimicking nanovehicles for sequentially delivering TRAIL and Dox.

COLL 501

Therapeutic enzyme-responsive nanoparticles for targeted delivery and accumulation in tumors

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Controlling the pharmacokinetics and targeting of small molecule drugs is at the core of medicinal chemistry and pharmaceutical science. This work utilizes enzyme-responsive, drug-conjugated, peptide-polymer amphiphiles that assemble into micellar nanoparticles with a surface comprised of enzyme-susceptible peptides and a hydrophobic paclitaxel core. Notably, the drug is polymerized directly (*i.e.*, in a graft-through fashion) and is covalently bound via a degradable linkage. Paclitaxel (PTX) is the therapeutic moiety in this motif, as it is a potent microtubule-stabilizing agent and standard component of chemotherapy regimes for many malignant and metastatic cancers. The hydrophilic peptide shell contains a substrate for matrix metalloproteinases (MMPs), which are overexpressed in an array of cancer types and present as catalytic, extracellular or membrane-bound tumor markers. Upon exposure to the enzyme, these materials undergo a nano- to micro-scale change in size, coupled with a change in morphology (from spherical micelles to aggregates). In this way, the tumor guides the accumulation process through MMP expression patterns resulting in active accumulation through catalytic amplification.

This work represents a proof-of-concept study demonstrating the utility of enzyme-responsive nanoscale drug carriers capable of targeted accumulation and retention in tumor tissue in response to overexpressed endogenous enzymes. Critically, we observed low systemic toxicity in healthy mice following intravenous (IV) administration, with the maximum tolerated dose (MTD) exceeding 240 mg/kg with respect to paclitaxel (16 times the MTD of the free drug). Furthermore, we observed efficacy against tumorigenesis paralleling that of paclitaxel at equivalent intravenous dosing, and near complete tumor growth suppression when administered intratumorally. This work represents a significant departure from traditional targeted drug delivery systems and presents a new avenue of exploration for nanomedicine.

COLL 502

Gold nanorod-assisted selective photothermolysis of adipose tissue

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Gold nanorods represent one of the leading candidate nanomaterials for the photothermal treatment of cancer. In this work we apply them in a different setting: to photothermally disrupt adipose tissue to facilitate fat removal through liposuction. Although liposuction is the leading cosmetic procedure performed in the United States, it has one of the lowest success rates due to the difficulty of the procedure. By pretreating adipose tissue with a photothermal technique which induces structural changes in the adipose tissue to liberate adipocytes and entrapped fatty acid, the liposuction procedure is improved in efficacy. We present proof of concept demonstration in a pig model. Furthermore, biodistribution of colloidal nanoparticles large animals was investigated, the results of which may offer insights into the clinical translation potential of noble metal nanomaterials.

COLL 503

Targeted photodynamic therapy with size-controlled nanoscale MOFs

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The metal-organic frameworks (MOFs) field has rapidly evolved as tremendous research has been conducted to discover new structures and study their structure-property relationships. However, studying MOFs as nanomaterials has not been much explored yet. Tunability of conventional nanomaterials can provide useful tools for unraveling the complex biological interactions as physical parameters of nanomaterials have shown to be strong determinants to cellular processes. Here we show targeted photodynamic therapy with size-controllable MOF-based nanoparticles. Size-controlled synthesis of porphyrinic Zr-MOFs were studied showing well-controlled size of nanoparticles with pure phase. Having confirmed, the size-dependent cell uptakes and ensuing photodynamic therapy (PDT) efficacy were then studied with MOF nanoparticles. Furthermore, an active targeting modality via surface modification on MOF showed enhanced PDT efficacy. The findings provide implications in the future design of a theranostic platform with MOF-based nanoparticles as well as exemplify that size-controlled MOF nanoparticles can serve as a useful tool for deciphering challenging biological interaction.

COLL 504

Bioresponsive nanoparticles to prevent systemic inflammatory response syndrome

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Systemic inflammatory response syndrome (SIRS) remains a major clinical challenge, affecting >30% of all hospitalized patients, and >80% of surgical ICU patients. A sustained inflammatory process may lead to multiple organ dysfunction and ultimately organ failure. Early prevention and treatment of SIRS remains challenging due to unreliable prediction criteria for determining timing and therapeutic dose of drugs. A controlled drug delivery system using prophylactically administered nanoparticles would ensure timely drug-delivery to the organs that would otherwise fail.

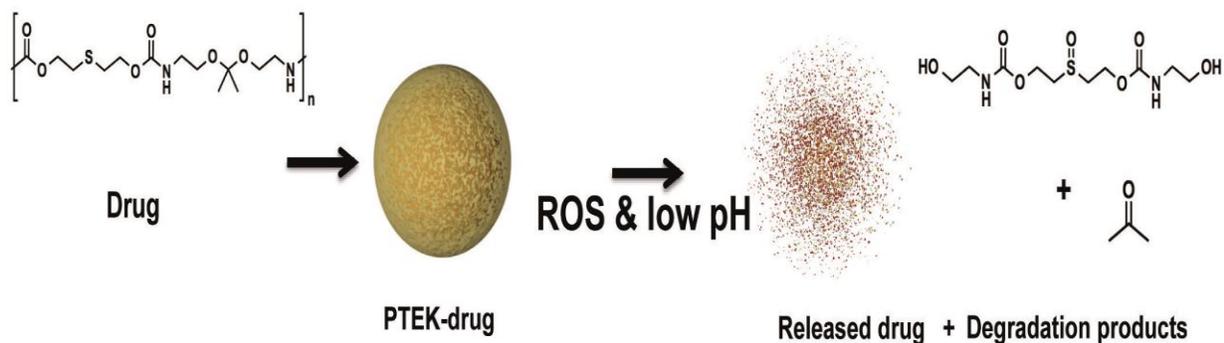
To address this issue, we developed an inflammation-sensitive system for delivering dexamethasone and the novel anti-inflammatory specialized pro-resolving mediators. The dual-responsive logic gate nanoparticles are comprised of a polymer that degrades in response to the hallmarks of SIRS thus targeting the microenvironment in inflammation: increased levels of reactive oxygen species and local acidosis. The particles undergo two chemical transformations; oxidation of thioether groups along the

polymer backbone allows for a transformation switch from hydrophobic to hydrophilic, which in mildly acidic environments causes rapid acid-catalyzed degradation of ketal groups also along the polymer backbone.

Prophylactic administration of these drug-loaded bioresponsive nanoparticles greatly reduced SIRS lethality by reducing the plasma content of pro-inflammatory cytokines as compared to both free drugs and drugs loaded in non-bioresponsive-nanoparticles.

These studies demonstrate enhanced efficacy of anti-inflammatory drugs when administered 12 h prior to SIRS onset and inflammatory insult, and suggests the use of these nanoparticles as a prophylactic to prevent acute systemic inflammatory conditions.

In conclusion, these studies use bioresponsive polymeric nanoparticles to offer and expand drug delivery opportunities to prevent the systemic inflammation in SIRS.



Schematic representation of ROS/pH responsive PTEK nanoparticles and their degradation

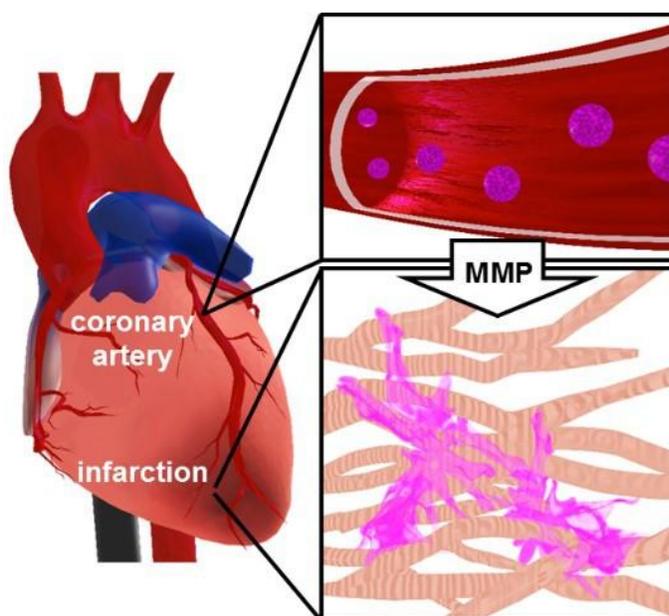
COLL 505

Enzyme-responsive nanoparticles for targeted accumulation and prolonged retention in heart tissue after myocardial infarction

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Injectable biomaterials have gained attention for use as inhibitors of negative left ventricular (LV) remodeling post-myocardial infarction (MI). However, current strategies such as preformed scaffolds and nanoparticles, are not feasible for clinical application as they utilize invasive delivery methods or suffer rapid tissue clearance, respectively. A method for targeting to and retaining intravenously injected nanoparticles at the site of acute myocardial infarction in a rat model is described. Enzyme-responsive peptide-polymer amphiphiles are assembled as spherical micellar nanoparticles, and undergo a

morphological transition from spherical-shaped, discrete materials to network-like assemblies when acted upon by matrix metalloproteinases (MMP-2 and MMP-9), which are up-regulated in heart tissue post-myocardial infarction. We show by fluorescence that the resulting micro-scale assemblies accumulate specifically at areas of infarct, bypassing healthy heart tissue, and remain up to 28 days. Furthermore, histopathology of satellite organs at various time points post-injection (1, 7, 14, and 28 days) revealed healthy tissue, providing evidence of non-toxicity. These initial studies set the stage for the development of targeting systems for therapeutic delivery to an acute MI. Critically, with this development, injection of materials is possible via the non-invasive IV route, resulting in targeted accumulation and long term retention at the site of MI.



Nanoparticles delivered via systemic injection circulate freely in the blood system until acted upon by inflammatory enzymes at the site of damaged heart tissue.

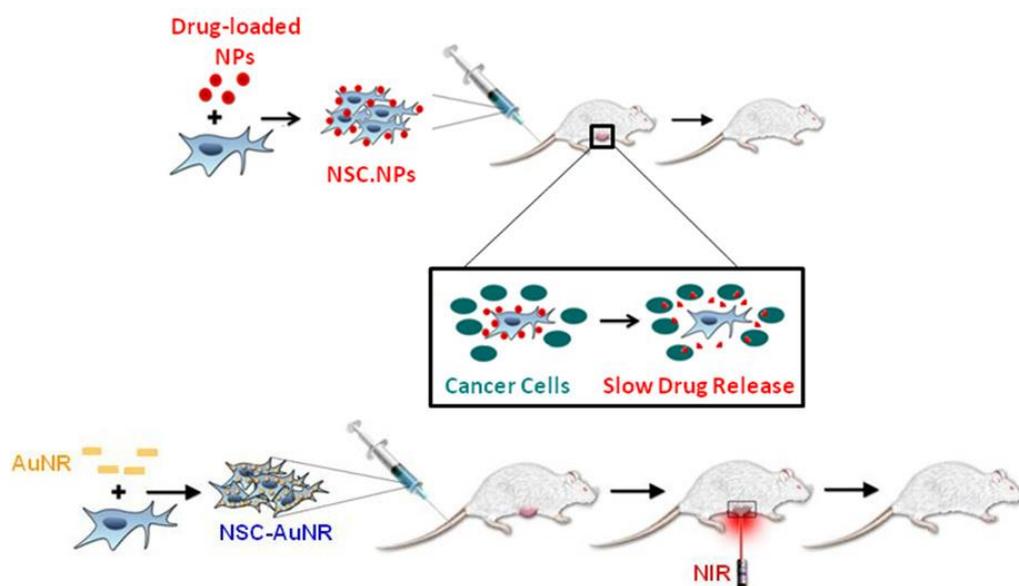
COLL 506

Neural stem cell/nanoparticle hybrids for targeted cancer therapy and imaging

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Targeted drug delivery is a long-standing goal for cancer therapy. Nanoparticles have shown promise as platforms for targeted drug delivery, but major challenges remain for controlling the distribution of nanoparticles within tumors. Neural Stem Cells (NSCs) are appealing candidates for use as carriers for nanoparticles in order to overcome these biodistribution challenges. NSCs have demonstrated inherent tumor tropic properties in invasive and metastatic tumor models, migrating selectively to invasive tumor foci, penetrating hypoxic tumor regions, and even traversing through the blood-brain barrier to access intracranial tumor foci following intravenous administration. NSCs do not

intrinsically have any anti-tumor efficacy; they must be modified in some way to exploit their tumor targeting abilities. My collaborator, Dr. Karen Aboody, is a pioneer in genetically altering NSCs to express an enzyme that will convert a prodrug into the active compound. This approach was recently evaluated in a first-in-human safety/feasibility clinical trial using modified NSCs to treat recurrent gliomas. As NSC-based therapy moves into the clinic, there is an opportunity to develop complementary techniques to enable NSCs to destroy tumors. The combination of NSCs and nanoparticles offers the potential of a general drug targeting system. We have demonstrated that NSCs can either be modified to bear nanoparticles on their surface or can internalize them. The nanoparticles can release drugs or used for photothermal ablation. In all cases, the NSCs remained viable and targeted the delivery of the nanoparticles to tumors *in vivo*, enhancing the therapeutic efficacy of the nanoparticles.



Neural stem cells target the delivery of conjugated or internalized nanoparticles. This enhances chemotherapy or thermal ablation.

COLL 507

Synthetic tailoring of Pt-based nanowires for enhanced catalysis

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Benefiting from the structural anisotropy and preferential exposure of low energy facets, 1-dimensional (1-D) nanowires (NWs) have emerged as a promising class of materials in the field of catalysis. We have been working on the synthetic control of Pt-based

NWs. Through the rational tailoring of these NWs, they can be used as active catalysts for oxygen reduction reaction (ORR) and for CO oxidation. We successfully constructed catalytic active hierarchical interfaces in these 1-D materials, exemplified by the synthesis of TiO₂-supported PtFe–FeO_x nanowires (NWs). The hierarchical interface, constituting atomic level interactions between PtFe and FeO_x within each NW and the interactions between NWs and support (TiO₂), enables CO oxidation with 100% conversion at room temperature. The role of the two interfaces were investigated by probing the CO oxidation reaction with isotopic labeling experiments. The special structure also offers an attractive catalyst model to study electronic and strain effects for tuning catalysis of nanostructure.

COLL 508

Hybrid Fe₂O₃-Au nanostructures: Synthesis, properties, and applications

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The objective of this talk is to discuss our recent wet chemical synthesis procedures used to create hybrid nanoparticles of different size, shape, and composition. The characterization techniques used to elucidate nanoparticle's properties and their corresponding photothermal, magnetic and catalytic applications will be described in detail. The focus will be on a new class of cheaper, highly efficient, non-toxic, magnetically reusable nanomaterials, Fe₂O₃-Au, where the supporting Fe₂O₃ nanoparticles are of different shapes: spheres, rings, and tubes. These new hybrid nanostructures can transduce light to heat through plasmonic absorbance, and this phenomenon is exploited to demonstrate the photothermal catalytic reduction of 4-nitrophenol. The hybrid Fe₂O₃-Au nanoparticles are able to photothermally heat aqueous solutions as efficiently as pure Au nanoparticles, even with a significantly smaller concentration of Au (20 times smaller). We also found that the Fe₂O₃-Au nanoparticles are more efficient catalysts than the metallic NPs, even with significantly smaller amount loading of gold. Importantly, the hybrid structures retain the properties of both materials, creating a multifunctional structure with excellent magnetic and plasmonic properties. Our innovative multifunctional nanoparticles offer a platform to further investigate them for photothermal catalytic processes, sensing, hyperthermia practices, environmental implications, medical imaging applications (e.g. magnetic resonance imaging), among others.

COLL 509

Tuning the size and shape of magnetic-plasmonic core-shell nanoparticles

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There has been a great interest in the development of nanoparticles that combine multiple functions from individual materials. These nanostructured materials often possess unique electrical, chemical, structural, and magnetic properties allowing for use in a variety of novel applications including information storage, biosensing applications, and biomedical engineering. A number of such nanoparticles have been designed, but the ability to make anisotropic NPs with controllable size and shape remains limited. The goal of our research is to develop novel magnetic and plasmonic hybrid nanoparticles for cancer detection and treatment. We have made substantial progress in developing a facile approach to prepare iron oxide-gold core-shell nanostructures in different sizes and different shapes including stars, popcorns and spheres with integrated optical and magnetic properties. This was done by anisotropic growth of gold-seeded iron oxide nanoparticles in a growth solution containing chlorauric acid, cetyltrimethylammonium bromide, silver nitrate and ascorbic acid. While the size of the resulting nanoparticles was controlled by changing the amount of gold-seeded iron oxide nanoparticles, the shape was controlled by tuning the concentrations of silver nitrate and ascorbic acid. The core-shell structures were confirmed using energy dispersive X-ray spectroscopy and magnetic separation. The shape modification has shown a large red shift of the localized surface plasmon resonance wavelength, with spheres at 570 nm to popcorns at 650 nm and stars at 760 nm with similar size. Our studies made a great step further in manipulating and understanding magnetic-plasmonic core-shell NPs, and would make an important impact on material science and biomedicine.

COLL 510

Spectroelectrochemistry of halide anion adsorption and dissolution of single gold nanorods

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Changes in the localized surface plasmon resonance (LSPR) of gold nanorods (AuNRs) due to halide anion adsorption were probed by dark-field scattering through a spectroelectrochemical flow cell. The LSPR of the same AuNR on an indium tin oxide electrode was measured in NaF, NaCl, and NaBr to directly compare the effect of halide ion adsorption, which was tracked by changes in plasmon resonance energy, linewidth, and peak intensity extracted from a Lorentzian fit to single AuNR scattering spectra. We demonstrate that at weak electrode potentials, the change in LSPR is anion independent, indicating charge density tuning and physisorption of anions. At intermediate and strong potentials, the magnitude of the change in the LSPR follows anion reactivity due to local refractive index changes and chemical interface damping caused by anion chemisorption. The peak scattering intensity of the AuNRs decreases with each potential cycle at strong potentials and high electrolyte concentration. The decrease in intensity indicates AuNR dissolution, and particle reshaping due to the

dissolution is tracked by irreversible changes in the plasmon resonance energy and linewidth with each cycle.

COLL 511

Understanding interparticle interactions and properties for SPR and SERS

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Effective harnessing of the plasmonic coupling of nanoparticles is essential for the exploitation of the unique optical and electrical properties of metallic nanoparticles (MNPs) in molecular and biomolecular detection, which is especially important for real-time detection of the interparticle interactions. This report describes both theoretical and experimental analyses of the plasmonic coupling of MNPs in the presence of molecular and biomolecular interactions. Examples include pi-pi interactions of cyanine dyes and complimentary binding of DNA strands. Subtle changes in the surface plasmon resonance (SPR) of gold or silver MNPs leading to significant changes in surface enhanced Raman scattering (SERS), which provide detection signals for the molecular or biomolecular activities. The experimentally-observed SPR and SERS signals have been supported by theoretically-simulated spectroscopic enhancements of the plasmonic resonance and the E-field intensity for the functionalized nanoparticle dimers or trimers. The results are important for establishing the correlation between theory and experimentation to allow for better design and control of the interparticle structures and interactions with optimized plasmonic coupling and spectroscopic enhancements for molecular and biomolecular recognition.

COLL 512

Nanoporous metal films and powders formed with soft templates

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Nanoporous metals have the highest practical metal surface area per unit volume. They are of potential value for surface-catalyzed chemical reactions, supercapacitors, and chemical separations based on electrical potential-dependent adsorption, such as capacitive deionization. Methods to grow nanoporous metals using soft templates have been published by many groups over the past two decades, but the growth mechanisms, optimal procedures, and properties of the materials are not yet fully clarified. We will present our efforts to make progress on these problems, with emphasis

on palladium. The ability of palladium to reversibly store hydrogen is of value for small-scale metal hydride batteries, as well as hydrogen gas or pH sensors. These properties also lead to unique synthetic opportunities and challenges.

We have used liquid-cell transmission electron microscopy to study the mechanisms of metal growth by chemical reduction in the presence of surfactants. Our results suggest that Pd nanoparticles form and sinter around micelles present in the aqueous phase. Changing the size of the surfactant molecules affects the size of these micelles, and ultimately determines the pore dimensions. The stability of nanopores in metals is a strong function of temperature and the chemical state of the surface. Attention to these conditions is necessary when formulating a new material or synthetic method. Reactions that transport hydrogen between nanoporous palladium and the gas or aqueous phase are significantly faster than those involving lower-surface area materials.

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COLL 513

Nanospace-confined solid-state conversion chemistry for morphology-controlled syntheses of metal/metal-oxide hybrid nanocrystals

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Synthesis of heterostructured hybrid nanocrystals (HNCs), in which two or more inorganic domains of chemically dissimilar materials are fused together through a nanoscale interfacial area, is an important and challenging subject in current nanochemistry. To date, most HNCs have been synthesized through wet chemical processes that include the heterogeneous nucleation of a secondary domain on the seed particle or the coupling of preformed nanocrystals. In this context, we would like to present our attempts at developing a sophisticated solid-state conversion-based strategy for synthesizing diverse HNCs by exploiting the unique transformation behavior of multicomponent nanocrystals in an in-situ generated hollow silica nanosphere. During investigating the high temperature reactions of silica encapsulated Fe₃O₄ and Au nanocrystals and Pd²⁺ complexes, we observed that they could be transformed into a FeAuPd nanocrystal while maintaining nanometer size in a thermally stable silica medium. More interestingly, the *in-situ* reduced metal alloy nanocrystal was found to move outward thereby leaving a space at the core, generating a unique hollow structure, which traps the migrating metallic nanocrystal in the silica nanoshell.

Moreover, the subsequent oxidative process could convert the alloy nanocrystal back to phase-segregated HNCs with diverse morphologies, while guided by the *in situ* developed hollow silica mould. Therefore, the morphological parameters of the resultant HNCs, including the number and shape of component domains, were defined by the degree of migration of the alloy nanocrystal in the hollow silica nanoshell (Figure1). We will discuss successful syntheses of a range of Fe₃O₄/metal HNCs by using the explored solid-state protocol, which entails a series of nanocrystal conversion processes, including alloying, migration, and phase segregation, all within the confines of a silica nanosphere.

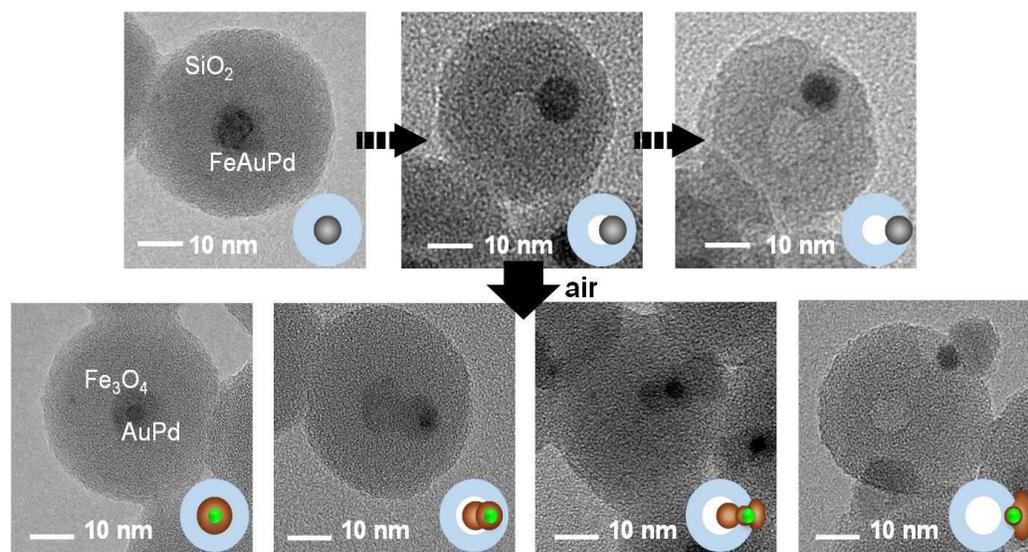


Figure 1. Hollow silica-cast transformation of metal nanocrystal into HNC

COLL 514

Withdrawn.

COLL 515

Nanometal synthesis, morphogenesis, and colloidal stabilization enabled by amphiphilic polymers

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Nano-size metals exhibit novel optical and catalytic properties, and attract considerable interest in a range of applications, e.g., photonics, diagnostics. The morphology (size and shape) of the nanoparticles and their surface/colloidal properties are very important in the various applications. A patented methodology [1] for the synthesis in aqueous media of metal nanoparticles with controlled size and shape and exceptional colloidal stability is reviewed [2]. This methodology is based on designer polymers that can

exhibit multiple functions on the basis of the polymer intramolecular and supramolecular organization. In addition to being water based, this methodology requires no external energy input and employs commercially available polymers, e.g., poly(ethylene oxide)-containing Pluronics or Poloxamers, resulting in low cost and potential environmental benefits. Recent results are presented on the use of PEO-based polymers with different end-functionality for gold [3] and silver [4] nanoparticle synthesis and stabilization.

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COLL 516

Synthesis of Au nanocages from Pd templates

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The galvanic replacement reaction currently used in nanoparticle research is a simple and versatile method to synthesize hollow nanostructures. Ag-Au bimetallic hollow nanostructures represent an appealing system because of their relative ease of synthesis and their near-IR surface plasmon resonance (SPR) band. However, the toxicity of any residual silver, and the possible fragmentation of such alloyed nanostructures, limits the medicinal applications of this system. Herein, we report a new synthetic pathway for Au nanocages from a palladium template. Starting with Pd nanocubes, we used an optimized set of reaction conditions (e.g., ionic species and pH environment) to facilitate the galvanic replacement reaction of Pd with Au³⁺ to produce Pd@Au nanoboxes. This reaction was then followed by the conversion of the Pd@Au nanoboxes to Au nanocages via the selective removal of the Pd core through an etching process. We believe the present work provides a promising method for synthesizing stable, nontoxic hollow plasmonic nanostructures for medicinal applications.

Keywords: Galvanic Replacement Reaction, Hollow Nanostructures, Nanocubes, Nanoboxes, Nanocages.

COLL 517

Voltage control of magnetization in FePd nanocrystals for the next generation of magnetoelectric memory

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There is significant interest in creating new types of memory and logic devices that have higher information storage densities than current devices and operate with significantly reduced energy consumption, while maintaining a high level of performance. Magnetoelectric memory offers a potential route towards achieving these goals by using stable magnetic moments to store data, and electric fields to write data. In this work, we specifically focus on a phenomenon called voltage-controlled magnetocrystalline anisotropy (VCMA), which utilizes voltage, rather than current, to write information which is significantly more energy efficient. Previous work has shown that ultrathin films of FePd have a large dependence of magnetocrystalline anisotropy on voltage. Here, we extend these ideas by examining the VMCA effect in FePd nanocrystals which have the potential to reach >10 nm bit sizes. We synthesized FePd nanocrystals via a wet chemical route in the A1 (fcc) phase and then deposited them as a monolayer before thermally converting them into the more magnetic L1₀ (fct) phase. We find significant changes in magnetic anisotropy as a function of voltage in these samples. These results suggest that FePd nanocrystal-based devices are a promising candidate for the next generation of VCMA devices

COLL 518

Withdrawn.

COLL 519

Simultaneous reduction of metal ions by multiple reducing agents initiate the asymmetric growth of metallic nanocrystals

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Thermodynamically unfavorable metallic nanocrystals can be prepared only by the growth of the nanocrystals under kinetically controlled experimental conditions. The common technique to drive the growth of metallic nanocrystals under kinetic control is to adjust the rate of the generation of metal atoms to be slower than the rate of deposition of such atoms onto the surface of nanocrystal nuclei, which form in the first step of the nanoparticles synthesis. The kinetically controlled growth leads to the formation of seeds with crystal defects, which are needed for the growth of anisotropic nanocrystals

such as silver nanodisks (AgNDs). The simultaneous multiple asymmetric reduction technique (SMART) is introduced here to successfully prepare AgNDs of controllable sizes and in large scale within a few seconds. SMART is simply based on the simultaneous reduction of silver ions with a strong reducing agent such as borohydride (redox potential of 1.24 V) and a weak reducing agent such as L-ascorbic acid (redox potential of 0.35 V) in the presence of a polyvinyl pyrrolidone capping agent. The random formation and deposition of silver atoms by the two different reducing agents generated stacking faults in the growing nanocrystal. The hexagonal close-packed {111} layers of silver atoms were then deposited on the surface of the growing nanocrystal containing stacked faults along the [111] plane. This initiated asymmetric growth necessary for the formation of plate-like seeds with planar twin defects, which is required for the formation of anisotropic AgNDs.

COLL 520

Strong coupling between periodic arrays of gold nanostructures and excitonic states in light-harvesting complexes

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Using interferometric lithography (IL), macroscopically extended (ca. 1 cm²) arrays of gold nanostructures have been formed using a double exposure process in combination with an alkylthiolate self-assembled monolayer resist formed on polycrystalline gold on Cr-primed silica. Rotation of the sample between exposures enables the fabrication of a wide range of morphologies, from dots to needles with controllable periods and geometric organisation. Annealing of these structures yields arrays that are highly crystalline and exhibit strong plasmon bands. The samples are robust and may be re-used after cleaning in cold piranha solution. According to the previous literature, the adsorption of proteins onto plasmonic structures yields a small red shift of the plasmon band but no other significant changes in extinction spectra. However, when wild-type light harvesting complex 2 (LH2) from the purple bacterium *Rhodobacter sphaeroides* was attached to our arrays of gold nanostructures, dramatic changes were observed in the extinction spectrum. New peaks were observed at ca. 430 nm, between 500 and 600 nm and at ca. 850 nm. Spectra of mutant proteins in which the carotenoid had been changed from sphaeroidene to lycopene yielded significant changes between 500 and 600 nm, indicating remarkable sensitivity to variation in protein structure. Similar strong new features were observed in extinction spectra acquired for light harvesting complex 1 (LH1) from *R. sphaeroides* and from light harvesting complex II (LHCII) from chloroplasts. Changing the array geometry from square to hexagonal also caused significant spectral changes. These features were absent in spectra of films of adsorbed bacteriochlorophyll (BChl) and in spectra of chlorosomes from green sulphur bacteria. We conclude that observation of these unexpected spectral features requires the presence of both a periodic array of gold nanostructures and also the presence of BChl

in a specific spatial presentation – as found in LH1, LH2 and LHCII. We believe that they are signatures for strong coupling between lattice plasmons and the excitonic states found in LH1, LH2 and LHCII, and measurements on such systems could prove to be a valuable aid to the investigation of mechanisms of photosynthetic light harvesting

COLL 521

Impedance spectroscopy as useful tool to study molecule-electrode interfaces and the dielectric response of molecular tunnel junctions

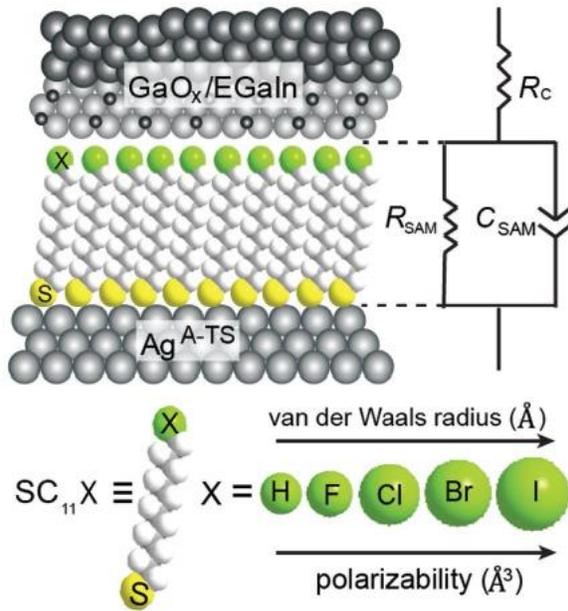
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monolayer) are appealing because of their potential of inducing, and controlling, electronic function at the nanometer length scales. Understanding the nature of the molecule-electrode contacts in these two-terminal junctions is crucial but the interfaces are difficult to characterize.[1] Recently we showed that impedance spectroscopy makes it possible to isolate the contribution of each component of the junctions to the total impedance of EGaIn based junctions (Figure 1).[2,3] Here I will present that temperature dependent and potentiodynamic impedance spectroscopy make it possible to elucidate the bias and temperature dependency of each circuit component (contact resistance, SAM resistance, and the capacitance of the SAM) of two-terminal SAM-based junctions, unlike DC measurements, independently from each other. We found that the metal–electrode contact resistance is ohmic in nature and has 4 orders of magnitude smaller resistance than the thinnest SAM measured.

I will also discuss how by changing the polarizability of a single atom the dielectric constant of the SAM can be increased by a factor of four.[4] We believe that impedance spectroscopy is a useful and complementary tool to DC measurements to elucidate how each component of two-terminal SAM-based junctions impedes charge transfer and it opens the door to investigate dielectric response in 2-terminal junctions at the molecular scale.

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COLL 522

Replacing a solid with a liquid needle for measuring static and advancing contact angles

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The optical determination of static and advancing contact angle is made on drops applied or extended, respectively, onto a substrate through the use of thin solid needles. Although this method has been used extensively, this method of dosing can be time consuming, cumbersome and if not meticulously performed can lead to erroneous contact angle results. Herein, we present an alternative way of applying drops onto substrates using a small liquid jet, which is produced by a liquid pressure dosing system acting as a "liquid needle." A comparative static contact angle study on 14 different surfaces with two different liquids (water and diiodomethane) were performed utilizing two different ways of dosing: the conventional solid and a novel liquid needle based technique. We found, for all but one sample, that the obtained results were highly comparable. Observed differences can be explained by the characteristics of either way of dosing. We show that the contact angles of μL size drops measured with both methods are highly comparable. In addition, we used the liquid pressure based dosing system for optical advancing contact angle measurement on two different samples. The liquid needle based method facilitates the expansion of a drop from 0.1 to 22 μL within less than 1.2 seconds, which provided constant contact angle versus drop base diameter curves. The obtained results were compared with data from tensiometric dynamic Wilhelmy contact angle measurements. These data, in conjunction with

sequences of live images of the dosing process of the liquid pressure dosing system, illustrate how this system can replace the solid needle by a liquid needle.

COLL 523

Scanning Kelvin probe microscopy for understanding the causes of electrical disorder in organic semiconductor

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This talk will describe the use of scanning Kelvin probe microscopy (SKPM) to measure and map potentials on the surfaces of organic semiconductor thin films and single crystals. We have found using SKPM (also known as KFM, or Kelvin probe force microscopy) that the work function (ionization potential) of organic semiconductors is sensitive to epitaxial growth modes, substrate types, strain, and defect densities. Likewise, all of these factors can be sources of electrical disorder in organic films. The talk will focus in particular on recent experiments in which the work function of the benchmark organic semiconductor rubrene was measured as a function of tensile and compressive strain. Strains as small as 0.1% can yield work function shifts on the order of 100 meV. Collectively, these results provide the first concrete link between mechanical strain and the WF of an organic semiconductor and have important implications for understanding the connection between structural and electronic disorder (charge traps) in soft organic electronic materials.

COLL 524

Surface modification of gallium liquid metal alloy interfaces

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Gallium liquid metal alloys (GaLMAs) are room temperature fluidic conductors that have recently been used to create a variety of paradigm shifting concepts in stretchable and reconfigurable electronics^[1-3]. They serve as an alternative to mercury based systems because of the non-toxic nature of GaLMAs. Like many other metals, a thin native oxide skin forms spontaneously on the surface. Unlike most other metals at room temperature though, the underlying metal remains fluid with the skin serving as a viscoelastic solid which allows remarkably unprecedented fluidic structures to be constructed^[4]. This oxide also has detrimental effects to fluidic behavior in microchannels because it tends to adhere to the channel walls. Traditional solutions to mitigate this adhesion behavior have been to utilize strongly acidic or basic co-fluids to continuously react with the oxide^[5]. This approach results in the need to replenish the chemical reactants as well as remove byproducts from the surface, not to mention limiting application of these fluids as electronic materials. Our work takes two approaches to mitigate these effects. The

first approach is to utilize an ion exchange polymer to serve as the interface to the GaLMA fluid to both deliver minute concentrations of reactant to the surface and remove undesired byproducts^[6]. The second approach utilizes surface modification of the gallium oxide surface with phosphonic acids to allow molecular control of the surface chemistry and control the interfacial chemistry at a molecular level. To date, phosphonic acid treatment has only been used on solid oxide thin films such as ITO and ZnO to modify the work function for thin film electronics^[7]. We leverage these surface chemistries to control the GaLMA work function and the fluidic properties simultaneously. Detailed surface spectroscopy verifies the presence of the phosphonic acid linkers on the liquid surface and AFM is used to characterize mono and multilayer film growth.

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COLL 525

Chemical self-assembly strategies for conductive metal-organic surface structure

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A self-assembly process, in which extended, oligomeric structures grow parallel to a surface is described based on isocyanide-containing molecules, in particular, with 1,4-phenylene diisocyanide (PDI), which forms long, one-dimensional chains when adsorbed on the Au(111) surface. It is found that the isocyanide functionality binds strongly enough to gold to extract gold atoms from low-coordination sites on a Au(111) surface to form one-dimensional Au-PDI structures that incorporate gold adatoms such that the π -conjugation is maintained throughout the oligomeric species. The self-assembly pathway is explored using density functional theory calculations. It is also found that the oligomers are capable of bridging between gold nanoparticles on a mica substrate thereby providing a conductive linkage between them. Analogous chemistry occurs with thiol-functionalized analogs of PDI, for example, 1,4-benzenedithiol, which forms zig-zag rather than linear chains.

COLL 526

Insights on molecular junctions through applied density-functional theory: Examining the changes in molecule and substrate properties upon junction formation

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A clear understanding of the detailed interactions between single molecules and surfaces is required in order to develop novel and functional molecular devices. Despite the fact that simulations have been performed in this connection, the understanding of the electronic interactions at play remains elusive.

Normally, the magnitude of the systems investigate in this connection require that density-functional theory (DFT) based approaches be employed, as these methods are capable of simulating electronic structure at a computational cost that is lower than wavefunction-based methods. Nevertheless, there are numerous challenges associated with modeling surface-molecule interfaces using DFT. These include:

- 1) “Molecular” modeling techniques require the use of truncated (i.e. non-periodic) representation of bulk systems, which will not have a band structure, valence band or conduction band levels that correspond to those in bulk materials.
- 2) Many DFT methods are not capable of accurately predicting the energy levels associated with molecular orbitals.
- 3) The details of the molecular and surface structures are absolute requirements for obtaining representative electronic structure details.

Periodic DFT computational approaches provide band structures and energy levels for bulk systems, but many DFT methods implemented in period DFT programs do not predict the energy level to be correct in an absolute or a relative sense. On the other hand, DFT-based methods implemented in “molecular” codes are capable of predicting molecular energy levels that are more consistent with experimental results, but these are subject to the limitations laid-out in point 1 above. Finally, many surfaces, including the conducting carbon substrates in which we have interest, have ill-defined structures making the prediction of representative electronic structure a “best guess”.

We will present the results of a systematic investigation of molecules bound on conductive carbon substrates, modeled as regular graphene, using both periodic planewave DFT methods and molecular methods. The technical challenges associated with the application of DFT to problems of this type will be discussed.

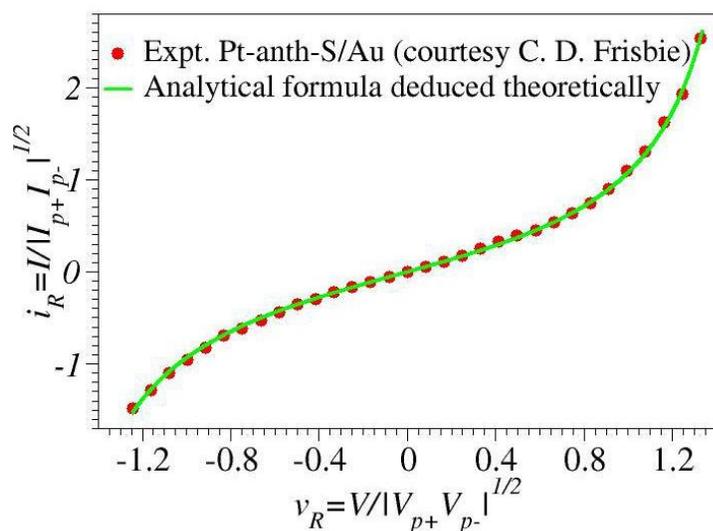
COLL 527

Law of corresponding states, scaling properties and other related issues for the charge transport in molecular junctions

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Peak voltage (V_p) spectroscopy (PVS)^{1,2} is an alias for transition voltage (V_t) spectroscopy (TVS) introduced to eliminate confusions in the molecular electronics community, emphasizing that, rather than marking a mechanistic transition between direct and Fowler-Nordheim tunneling (as initially claimed³), $V_p \equiv V_t$ is a reproducible property of molecular junctions. In cases where the charge transport is dominated by a single molecular orbital (MO), V_p is simply related to the MO energy offset relative to the Fermi energy (e.g. ref. 4). The profound role played by V_p in the charge transport via tunneling was exemplarily demonstrated in a recent joint theoretical and experimental study¹ demonstrating that, after appropriate voltage (V) and current (I) rescaling, an appealingly simple law of corresponding states $i_R \equiv I/I_p$ vs. $v_R \equiv V/V_p$ holds for benchmark junctions with symmetric I - V curves, which is free of *any* empirical parameters. As a further step in this direction, I demonstrate here that, in cases of asymmetric I - V curves, by using polarity dependent peak voltages $V_{p+} \neq -V_{p-}$ ⁵ (and corresponding currents $I_{p+} \neq -I_{p-}$) for rescaling, current-voltage curves in dimensionless variables $i_R = f(v_R; V_{p-}/V_{p+})$ can be expressed in a simple analytical form containing a single dimensionless parameter, namely the ratio V_{p-}/V_{p+} of the peak voltages. For illustration (see the attached figure), I present theoretical and experimental results for a representative CP-AFM junction consisting of anthracene monothiol molecules linked to Pt substrate and Ag tip. Related issues to be discussed include limitations of approaches based on low order expansions I vs. V and surprisingly large inaccuracies and artifacts that they might generate.

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Current-voltage curve rescaled using PVS-based quantities.

COLL 528

Characterizing surface chemistry of high-N-content mesoporous carbon oxygen reduction electrocatalysts

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Transition metal- and nitrogen-containing carbon materials have been the subject of intense recent research interest, due to their desirable properties, including high oxidation stability, high conductivity, and high electrocatalytic activity. One promising application of such materials has been as replacements for platinum-based oxygen reduction catalysts in fuel cells. Based on the importance of nitrogen inclusion, there have been efforts to enhance nitrogen contents, though increasing nitrogen contents beyond ~4 wt% usually results in decreased electrical conductivity and correspondingly reduced suitability for use as electrode materials. To obtain insights regarding the properties of N-containing carbon oxygen reduction electrocatalysts, we have examined the surfaces of materials prepared from a novel eutectic mixture of precursors that results in order-of-magnitude higher nitrogen contents, while still exhibiting high electrical conductivities (2.0 S/cm). When synthesized with mesoporosity, high surface areas (>800 m²/g), and the inclusion of Fe-containing salts, these materials have been found to exhibit high oxygen reduction activities. Electrocatalytic activities are observed to vary significantly for different templating materials, synthesis conditions, and/or the presence of transition metals. X-ray photoelectron spectroscopy (XPS) and solid-state ¹⁵N NMR analyses reveal that surface interactions between the organic precursors and templating materials, as well as variations in quantity of Fe, strongly influence the concentration and types of surface nitrogen-containing moieties in the products. Correlation of surface compositions with the electrocatalytic activities of the materials indicate optimal surface transition metal:N ratios, with both components contributing to the observed catalytic properties. Understanding the molecular compositions and structures of these functionalized mesoporous carbon materials aids the optimization of synthesis conditions that are expected to lead to improved performances of fuel cells and related electrochemical devices.

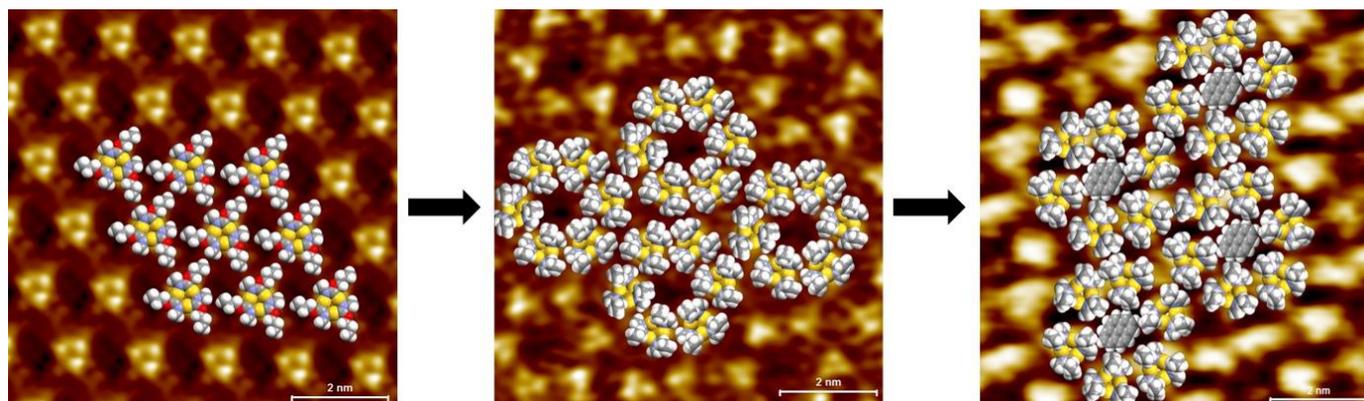
COLL 529

Epitaxial self-assembly of polymorphic, porous, and host-guest nanostructures on surfaces using monolayer-substrate interactions

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Molecular self-assembly of the gold(I) cyclic trinuclear complexes (CTCs) on the 1-phenyloctane/highly ordered pyrolytic graphite (HOPG) (0001) solution-solid interface is studied with scanning tunneling microscopy (STM). The gold(I) cyclotrimers form epitaxial nanostructures on the HOPG surface. At a concentration of $\sim 1 \times 10^{-4}$ M, Au(I) carbeniate (Au_3Cb_3) complexes exhibit a polymorphology. Two polymorphs, one non-porous and the other porous, are observed at 22.0 ± 2.0 °C. A non-porous, low-surface-density (0.82 molecules/ nm^2) Au_3Cb_3 nanostructure forms first then transforms into a high-density (1.43 molecules/ nm^2) porous nanostructure. This is the first time any porous surface nanostructure is reported for an organometallic system. The porous structure is thought to be stabilized by a combination of hydrogen bonding and monolayer-substrate interactions. These pores are utilized to incorporate pyrene into the film, rendering this the first organometallic host-guest system imaged at the solid-solution interface. Molecular and periodic density functional theory (DFT) calculations shed light on the two-dimensional topography and polymorphic self-assembly revealed by STM; these calculations suggest significant electronic hybridization of the Au_3 trimer orbitals and HOPG. The multiple-technique approach used herein provides insights concerning molecule-substrate and molecule-molecule interactions which can be used toward rational functionalization of graphene based electronic devices.

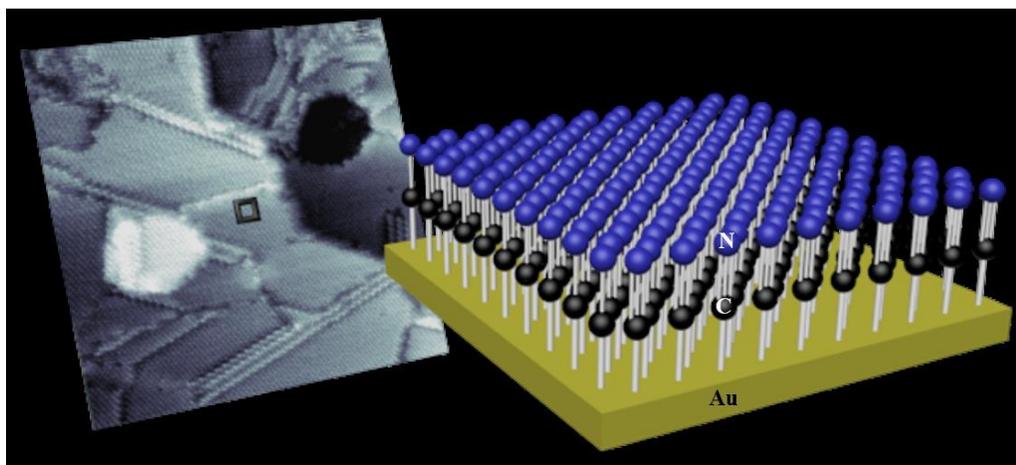


COLL 530

Precious poison: The self-assembly of cyanide on Au{111}

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A vibronic resonance between Au{111} surface states and adsorbed CN vibrations has been predicted, which we target for study. We have formed stable monolayers of cyanide on Au{111} and observe a hexagonal close-packed lattice with a nearest neighbor distance of 3.8 ± 0.5 Å. Cyanide orients normal to the surface attached via a Au-C bond. We show that the substrate-molecule coupling is particularly strong, leading to fast electron transfer from the cyanide molecules to the Au{111} substrate as measured by resonant Auger spectroscopy using the core hole clock method. The CN/Au{111} system is a simple example of a strongly interacting adsorbate-substrate system and will be the subject of a number of further studies to be discussed.



COLL 531

X-ray spectroscopic characterization of organic semiconductor nanowires

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One-dimensional organic nanowires provide a valuable platform for understanding emergent electronic phenomena in organic semiconductor materials. We have prepared a new class of organic nanowires consisting of stacked pi-conjugated building blocks covalently attached to a solubilizing backbone. We have formed self-assembled monolayers from nanowires of various lengths and sequence contexts on gold substrates and characterized their properties with a range of spectroscopic techniques, including x-ray photoelectron spectroscopy (XPS), near-edge x-ray absorption fine structure spectroscopy (NEXAFS), and resonant photoemission spectroscopy (RPES). These studies have elucidated the nanowires' electronic structure, geometric orientation at solid substrates, and interaction with the surrounding environment. Our experiments

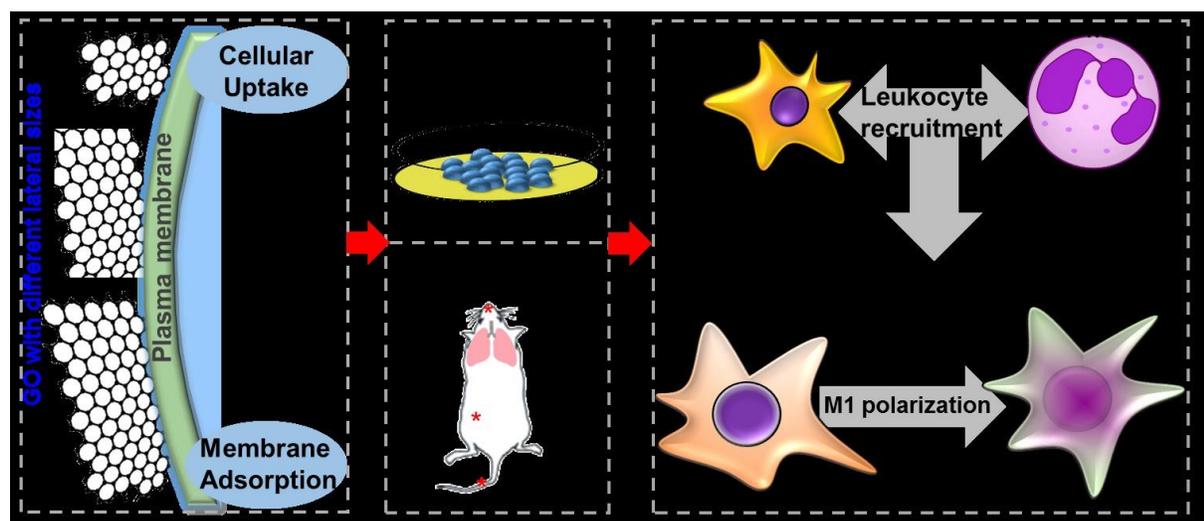
may offer improved insight into the design of pi-conjugated materials for organic electronic applications.

COLL 532

Crucial role of lateral size for graphene oxide in activating macrophages and stimulating pro-inflammatory responses in cells and animals

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Graphene oxide (GO) is increasingly used in biomedical applications because it possesses not only the unique properties of graphene including large surface area and flexibility but also hydrophilicity and dispersibility in aqueous solutions. However, there are conflicting results on its biocompatibility and biosafety partially due to large variations in physicochemical properties of GO, and the role of these properties including lateral size in the biological or toxicological effects of GO is still unclear. In this study, we focused on the role of lateral size by preparing a panel of GO samples with differential lateral sizes using the same starting material. We found that in comparison to its smaller counterpart, larger GO showed a stronger adsorption onto the plasma membrane with less phagocytosis, which elicited more robust interaction with toll-like receptors and more potent activation of NF- κ B pathways. By contrast, smaller GO sheets were more likely taken up by cells. As a result, larger GO promoted greater M1 polarization, associated with enhanced production of inflammatory cytokines and recruitment of immune cells. The *in vitro* results correlated well with local and systemic inflammatory responses after GO administration into abdominal cavity, lung or blood stream through tail vein. Together, our study delineated the size-dependent M1 induction of macrophages and pro-inflammatory responses of GO *in vitro* and *in vivo*. Our data also unearthed the detailed mechanism underlying these effects: a size-dependent interaction between GO and the plasma membrane.



The lateral size-dependent pro-inflammatory effects of GO *in vitro* and *in vivo*

COLL 533

Self-assembling peptide nanotubes. Modulation of internal and external properties

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Peptide Nanotube are a tubular-shaped supramolecular structure made of cyclic peptides that stack on top of each other. The side-chains of the amino acids are pointing outwards allowing the tuning of their surface properties. In the last few years we have been working with peptides in which alpha-amino acids are alternated with cyclic gamma-amino acids. The incorporation of these non-natural residues facilitates the stacking of the peptide to form the nanotube. In addition, these peptides also allow the modification of the internal properties of the nanotube. In this communication we will present our latest results in this respect, showing the interaction with metal ion and cluster that provide new properties to the nanotube.

COLL 534

Fluorine labels for ¹⁹F-magnetic resonance imaging

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Fluorine 19 (¹⁹F) based MRI is a field with promising features which complement proton-based traditional MRI. The most interesting advantage of ¹⁹F over ¹H is the negligible endogenous ¹⁹F-MRI signal, for which any detectable signal can only come from an exogenous probe. However, in order to achieve a quality of image similar to that obtained with conventional MRI, a high load of fluorine atoms with the same resonance frequency is required. One of the main challenges in this field at the moment is the improvement of existing contrast agents in order to increase the SNR and circumvent the intrinsic hydrophobicity of fluorinated probes. Nanotechnology has widely contributed to the field of contrast-enhanced imaging, and nowadays nanoparticles (NPs) as imaging probes are ubiquitous in preclinical MRI studies. Taking this into account, the use of NPs bearing a high number of identical fluorinated ligands could be an appealing strategy to increase the local concentration of chemically equivalent fluorine atoms. In this context, novel fluorine labels for nanoparticles have been designed, synthesised and tested as potential imaging probes.

COLL 535

Anisotropic nanoparticles for multimodal imaging and therapy

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One of the areas of nanotechnology that has captured great interest by scientific community worldwide is the development of nanoengineered multifunctional systems, which may be potentially used in a clinical strategy that simultaneously combine a (multi)diagnostic test and single or combined therapies based on the test results, the so-called nanotheranostic devices [1]. In this work, we present different hybrid nanoplatforms either with an inorganic or an organic core with anisotropic shape recently developed by our research group which are able to combine different elements in their structure to provide several simultaneous imaging (magnetic resonance (MR), fluorescence imaging, etc) and therapeutic (photothermal (PTT), photodynamic (PDT), chemo- and/or silencing therapies) capabilities in a single nanodevice. These nanodevices can be passively accumulated or targeted to specific receptors by suitable functionalization and are observed to be extensively accumulated in cancerous cell and tumors, exerting an enhanced imaging contrast and/or cytotoxic functions as observed in biological models.

COLL 536

Functionalization of metal, metal oxide and semiconductor nanocrystals using a multi-coordinating polymer

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Nanocrystals made semiconductors, metals and metal oxides possess unique physical and spectroscopic properties. Additionally, because their sizes are comparable to those of biomolecules, nanocrystals are very attractive for use as in vivo and in vitro probes in a variety of biomedical applications. We introduce a new set of metal-coordinating polymers as ligands adapted to functionalize QDs, iron oxide nanoparticles and anisotropic gold nanocrystals. The ligand design relies on the introduction of multiple anchoring groups, hydrophilic moieties and reactive functionalities into a single polymer chain, via one-step nucleophilic addition reaction. This surface-functionalization yields nanocrystals that exhibit long-term colloidal stability over a broad range of biological conditions. Furthermore, when zwitterion groups are used as the hydrophilic motif, this provides nanocrystals that are compact in size, allowing conjugation with His-tagged proteins. We have also shown that the resulting hydrophilic platforms can be used to develop specific biosensors and for imaging of live cells.

COLL 537

Effect of morphology and surface chemistry of gold nanoparticles on cellular uptake and cytotoxicity

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Use of gold nanoparticles (AuNPs) as surface-enhanced Raman spectroscopy (SERS)-tags for early cancer detection and targeted therapy has significantly increased over the past few decades. SERS-based imaging offers ultra sensitivity up to single molecule detection, multiplexing capability, increased photo stability, and has been shown to outperform fluorescence. However, in order to use SERS tags for early cancer detection, it is important to understand their interaction with cells and cytotoxicity. In this study, we carried out a multi-parametric *in vitro* study to look at the cytotoxicity and cellular uptake of gold nanoparticles on human glioblastoma and human dermal fibroblast cell lines. Cytotoxicity was evaluated by incubating cells with three different morphologies of AuNPs: nanospheres, nanorods, and nanostars, each having three different surface chemistries (cetyltrimethyl ammonium bromide (CTAB), poly (ethylene glycol) (PEG), and human serum albumin (HSA)). Our results showed that the morphology of the nanoparticles had no effect on cell viability. CTAB coated particles were found to be the most toxic to cells while PEGylated nanostars were least toxic. Caspase-3 assay and LDH assay revealed that the mechanism of cell death was different for both cell lines. This study provides valuable information on morphology and surface chemistry-induced cytotoxicity of gold nanoparticles that is necessary for the development of gold nanoparticle based cancer detection systems.

COLL 538

In-vitro imaging with biodegradable hybrid organic-inorganic bridged silsesquioxane nanoparticles

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Bridged silsesquioxane (BS) nanomaterials with chemical structures $O_{1.5}Si-R-SiO_{1.5}$ where R organic groups are emerging as the next generation of organosilica nanocomposites. Physical and chemical properties of BS materials can be governed by the nature of homogeneously distributed organic fragments within the siloxane network.¹ Nonetheless, due to the synthetic challenge to control the kinetic in sol-gel processes, most non-porous BS materials that have been extensively studied in the past two decades were macroscaled.² For biomedical purposes BS NPs should be non-aggregated sub-200 nm nanomaterials to benefit the enhanced permeation and retention effect and have long circulation time, thus, accumulate in cancerous tissues and organs.

Nature-inspired oxamide bridged silsesquioxane was used as a key component to endow nanoparticles with degradable feature. The designed nanomaterials were non-aggregated with biologically relevant sizes (sub-200 nm) for preferential accumulation in tumors. The unique constitution of the materials with a very high organic content (~50%) was found to be homogeneously distributed within individual particle and confirmed by various techniques: FTIR, solid state NMR and STEM-EELS elemental mapping. The biodegradation of NPs was demonstrated in the presence of the trypsin enzymes in simulated biological media. Moreover, for in-vitro imaging nonporous fluorescent BS NPs were obtained via incorporation of fluorescein isothiocyanate moieties (Fig. 1). We described the first example of enzymatically degradable BS NPs based on oxamide bridges. These novel hybrid organosilica NPs can find significant interest as future biomedical applications of inorganic silica NPs require higher biodegradability. Currently the work with mesoporous BS nanomaterials based on the same precursor is conducting.

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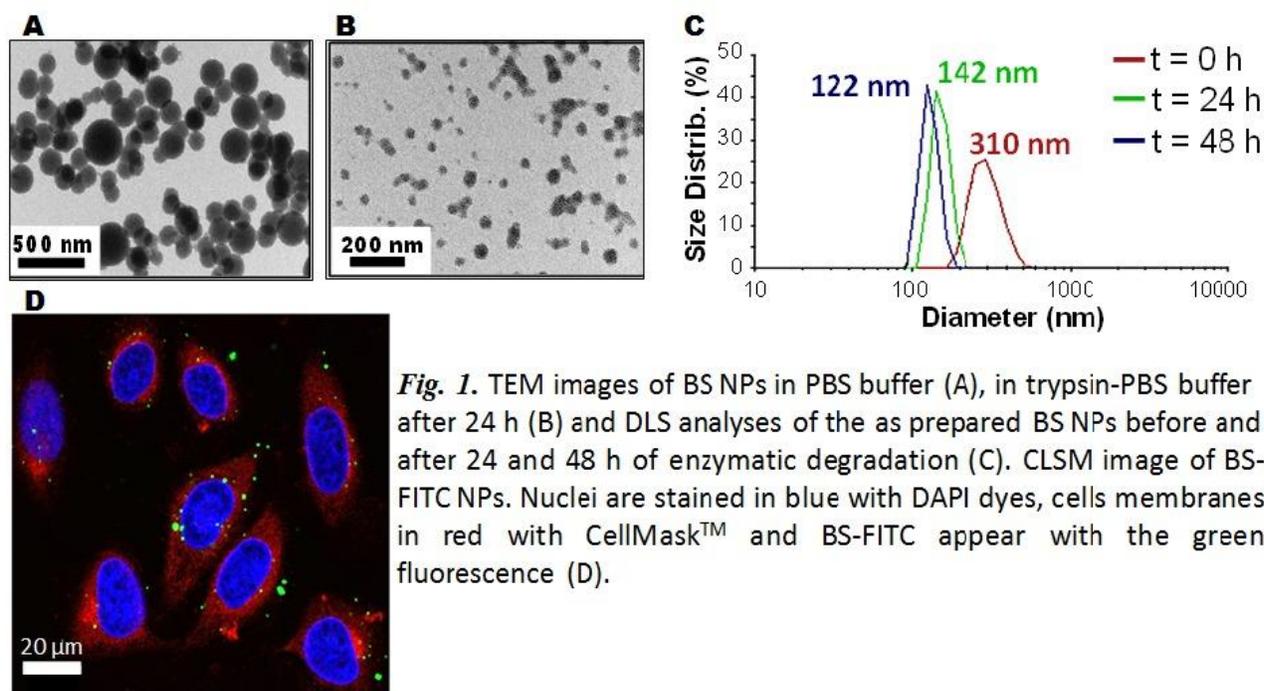


Fig. 1. TEM images of BS NPs in PBS buffer (A), in trypsin-PBS buffer after 24 h (B) and DLS analyses of the as prepared BS NPs before and after 24 and 48 h of enzymatic degradation (C). CLSM image of BS-FITC NPs. Nuclei are stained in blue with DAPI dyes, cells membranes in red with CellMask™ and BS-FITC appear with the green fluorescence (D).

Crossing blood–brain–barrier and bio-imaging using carbon dots: A zebrafish model study

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Drug delivery to the central nervous system (CNS) is currently a major medical challenge due to the presence of the blood–brain–barrier (BBB) which blocks the transport of a drug. Carbon dots (C-Dots) have recently been studied for drug delivery with potential to treat CNS disease. However, there is no study on whether C-Dots or C-Dots conjugates can cross the BBB to enter the CNS. Here we use a zebrafish model to explore the possibility of using C-Dots or C-Dots conjugates to ferry compounds across the BBB. The experimental observations suggest that the transferrin-C-Dots can enter the CNS possibly through the receptor mediated endocytosis while C-Dots alone cannot. The results from this study provide a strategy to deliver C-Dots to cross the BBB. Our most recent experiment also demonstrates that the “dark” C-Dots can be applied for bioimaging bones with high specificity *in vivo* with strong fluorescence.

COLL 540

Exchange-coupled core-shell ferrite nanoparticles for maximal hysteretic loss

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The maximal heat release from magnetic nanoparticles to the environment depends on intrinsic properties of magnetic nanoparticles (e.g. size, magnetization, and magnetic anisotropy), and extrinsic properties of the applied fields (e.g. frequency, field strength). Often, the biomedical hyperthermia application limits flexibility in setting of many parameters (e.g. nanoparticle size and mobility, field strength and frequency). We show that core-shell nanoparticles combining a soft (Mn ferrite) and a hard (Co ferrite) magnetic material form a system in which the effective magnetic anisotropy can be easily tuned independently of the nanoparticle size. A theoretical framework to include the crystal anisotropy contribution of the Co ferrite phase to the nanoparticles total anisotropy is developed. The experimental results confirm that this framework predicts the hysteretic heating loss correctly when including non-linear effects in an effective susceptibility. Hence, we provide a guide on how to characterize the magnetic anisotropy of core-shell magnetic nanoparticles, model the expected heat loss and therefore, synthesize tuned nanoparticles for a particular biomedical application.

COLL 541

Hydration repulsion between carbohydrate surfaces mediated by temperature and specific ions

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Hydration repulsion is the universal force that acts between well-solvated surfaces in water and balances other surface attractions such as the van der Waals forces in the nanometer range which ultimately prevents the aggregation and precipitation of suspensions. Although this phenomenon is observed through a multitude of experimental methods in various systems, an atomistic-level understanding of the mechanism remains elusive. Furthermore, it is well known that temperature and specific ions can drastically change the hydration repulsion. Using atomistic molecular dynamics simulations to calculate accurate pressures and thermodynamic energetics for approaching carbohydrate surfaces in DI water or in salt solutions at different temperatures, we show here that hydration repulsion decreases at high temperatures due to lowering of the dehydration energy for the first hydration layer. In salt solutions, the carbohydrate-complexing Ca^{2+} ions increase hydration repulsion due to extended water structures. Experimental studies investigating the colloidal stability and swelling behavior of polysaccharide-coated nanoparticles confirm the optimal hydration repulsion for the polysaccharide coatings in CaCl_2 solution; when subjected to high temperatures in DI water the polysaccharide coating de-swells, and at the same elevated temperatures in MgCl_2 solution the nanoparticles lose their colloidal stability and aggregate. Both instances of de-swelling and aggregation indicate less hydration repulsion. Our results provide mechanistic evidence relating temperature and specific ion effects on the hydration repulsion, which has great implications for regulating colloidal stability of suspensions in all aqueous systems.

COLL 542

Insight on growth mechanism of gold nanorods from molecular dynamics simulations

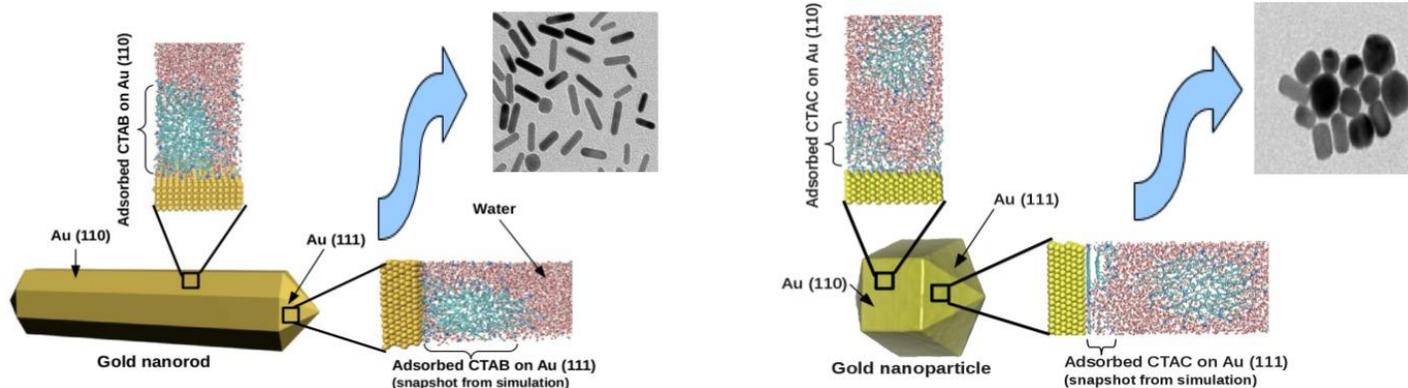
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Gold nanoparticles are widely used in many areas such as photothermal cancer therapy, biochemical sensing and medical imaging due to their size and shape-dependent optical properties. Directly manipulating and controlling the size and shape of metal nanoparticles is, therefore, a key step for their tailored applications. Gold nanoparticles are normally prepared using seed-mediated growth technique, which

require gold seeds, ascorbic acid, reactant HAuCl_4 and aqueous cetyltrimethylammonium bromide (CTAB) or cetyltrimethylammonium chloride (CTAC) surfactant. However, the microscopic origin of the anisotropic growth is still missing. Microscopic mechanism for the role of halides in regulating the anisotropic growth of gold nanoparticles has been investigated through molecular dynamic simulations and experiments. Our simulations revealed that CTAB form a layer of micelles on the gold surface immersed in the growing electrolyte solution where channels among micelles provide direct access of gold ions to the surface of gold nanorod. The Au(111) surface exhibits the lower CTAB packing density and the higher electrostatic potential with respect to Au(110) and Au(100) surfaces. Both elements would favour the growth of the nanorods in the direction of Au(111) facet [1]. On the other hand, CTAC micelles prefer to be in the solution, leaving the gold surfaces unprotected. Only a few CTAC molecules adsorbed on the gold surfaces which would favour a faster isotropic growth. Predictions from our simulations have been confirmed by two sets of experiments where nanoparticle's growth in different CTAB/CTAC surfactant mixtures show a more isotropic and faster growth as the amount of Cl^- increases. Also, the surfactant layer thickness measured on nanorods exposed to CTAB and CTAC quantitatively agrees with the simulation results [2].

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COLL 543

Emergence of a stern layer from the incorporation of hydration interactions into the Gouy–Chapman model of the electrical double layer

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In one of the most commonly used phenomenological descriptions of the electrical double layer, a charged solid surface and a diffuse region of mobile ions are separated from each other by a thin charge-depleted Stern layer. The Stern layer acts as a capacitor that improves the classical Gouy–Chapman model by increasing the magnitude of the surface potential and limiting the maximal counterion concentration. We show that very similar Stern-like properties of the diffuse double layer emerge naturally from adding a nonelectrostatic hydration repulsion to the electrostatic Coulomb potential. The interplay of electrostatic attraction and hydration repulsion of the counterions and the surface leads to the formation of a diffuse counterion layer that remains well separated from the surface. In addition, hydration repulsions between the ions limit and control the maximal ion concentration and widen the width of the diffuse double layer. This mean-field model, which we express in terms of electrostatic and hydration potentials, is physically consistent and conceptually similar to the classical Gouy–Chapman model. We make a direct comparison to the Gouy–Chapman–Stern model and conclude that the two models predict effectively the same surface potential only when the charge at the Stern plane is assumed zero. This new model allows the incorporation of ion specificity, accounts for hydration properties of charged surfaces, and predicts Stern layer properties, which we analyze in terms of the effective size of the hydrated counterions.

COLL 544

Molecular dynamics simulations for emerging computational immunology

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Nanoparticles (NP) are promising candidates for numerous biomedical applications such as imaging, diagnostics and drug delivery. The surface functionalization of NP dictates interfacial properties and regulate interactions with biosystems. These interactions play a predominant role in determining the efficacy and toxicity of NP in biological and environmental systems. Recent experimental studies have shown that nanomaterials with specific size and properties may increase immune response by inducing cytokine gene expression. One of the main factors that affect immune response is the hydrophobicity of nanoparticle coating. Computational (*in silico*) immunology is emerging field. Therefore, the development of rapid computational protocols is of great importance. Such atomistic simulations can provide useful insight into the process of nanoparticle uptake by the living cell. In the

present work series of molecular dynamics simulations have been carried out in order to study interaction of functionalized fullerene with lipid bilayer. Functional groups were chosen based on previous experimental work.

COLL 545

Sensing power of two nanoparticles at near sub-nanometer, in different orientations

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Using DDA calculations, the plasmonic spectra, the electromagnetic field distributions and the polarization vector plots are calculated for a pair of Ag nanoparticle dimers oriented in two orientations. We have found that as the separation distance of the nanoparticle dimer is decreased the orientation of the dimer drastically affects the near-field coupling behavior. The expected dipole-dipole coupling behavior between the oscillating electrons on the surfaces of the two nanoparticles is found to depend on the orientation and the separation distance of the nanoparticles.

COLL 546

Reaxff reactive force field study of oriented attachment of TiO₂ nanocrystals in non-aqueous solvents

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Solvent selection critically influences the aggregation and crystal growth of suspended metal oxide nanoparticles. We use ReaxFF molecular dynamics simulations to study the aggregation of various titanium dioxide (anatase) nanocrystals suspended in the following non-aqueous solvents; methanol, ethanol, propanol, iso-propanol and ethylene glycol. The nanocrystals are in the 2-6 nm size range and they generally possess shapes dictated by the Wulff construction. Wulff-shaped nanocrystals are terminated by {101} and {001} facets. To mimic the effects of HCl in the hydrothermal synthesis of anatase¹, we also create {112} facets on the surfaces of some of the particles. We find that methanol and ethylene glycol can facilitate aggregation by oriented attachment (OA) giving rise to single crystals. We observe that alignment of nanocrystals along a specific crystallographic direction is a necessary precursor to aggregation by OA. Alignment is accomplished by the creation of a hydrogen-bonding network by the adsorbed solvent species at the particle-particle interface. Organic solvents with shorter hydrocarbon chains or with higher concentration of hydrogen bonding species like ethylene glycol are conducive to the formation of this hydrogen-

bonding network and thus can facilitate OA. Organic solvents with longer hydrocarbon chains like ethanol, propanol and iso-propanol inhibit the formation of this hydrogen-bonding network and gives rise to the formation of polycrystalline material. This indicates the important role that solvent plays in nanocrystal aggregation and how solvent can be a powerful tool for directing and controlling nanocrystal growth to fabricate nanostructures with desired shapes and sizes.

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COLL 547

Beyond DLVO: Solvation structure and effective interactions of nanocolloids in solutions from 3D-RISM-KH molecular theory of solvation

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The phase behavior of nanocolloids in solution is determined by an interplay of their van der Waals and electrostatic interactions on one side and mean solvation forces on the other side. Colloids charges are screened by a solvent dielectric constant and Debye screening by counterions in solution. This picture is captured in the Deryagin-Landau-Verwey-Overbeek (DLVO) effective potential empirically constructed as a van der Waals attractive well and a Yukawa screened repulsive potential of the electric double layer. DLVO has been widely used to explain dispersion and flocculation of colloids in aqueous solution. However, the picture gets complicated for non-aqueous solvents and solvent mixtures with such additives as polymers to control flocculation. Understanding and design of these systems requires solvation theory beyond DLVO empirical level. A molecular description is provided by the three-dimensional reference interaction site model with the Kovalenko-Hirata closure relation (3D-RISM-KH molecular theory of solvation)¹⁻³ which properly accounts in a single formalism for both electrostatic and non-polar effects and readily reproduces structural and phase transitions in molecular liquids and solutions. The method produces 3D maps of solvation structure and free energy, and potentials of mean force (PMFs) in solution orders of magnitude faster than molecular simulations.³ In particular, 3D-RISM-KH describes effective forces between cellulose nanocrystals (CNC) forming suspensions in aqueous NaCl at concentration 0.0–0.25 mol/kg.^{4,5} The CNC electric interfacial layer thickness dependence on electrolyte concentration plays an important role in the mechanisms of phase transitions and chiral ordering in CNC suspensions.^{4,5} As another example, 3D-RISM-KH yields potentials of mean force of kaolinite nanoplatelets in non-aqueous solvents,^{6,7} as well as in aqueous electrolyte solution with polymer flocculants. This opens up a possibility of high throughput screening of polymer additives as flocculants and dispersants. Furthermore, it provides means to derive coarse-grained force fields for suspensions of

mineral and organic nanoparticles.⁸

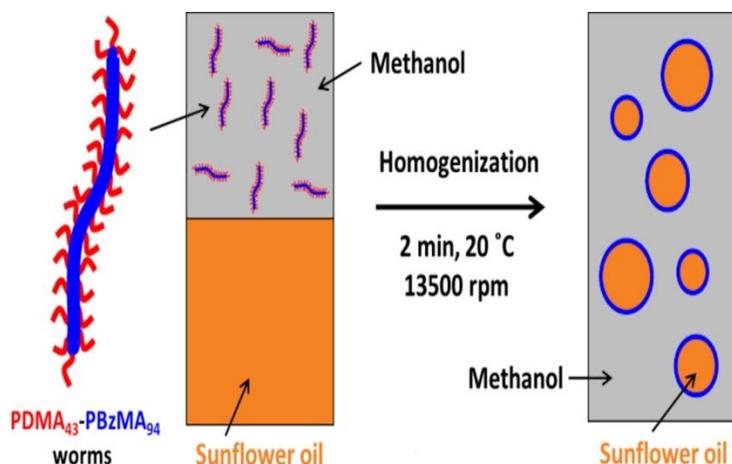
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COLL 548

Preparation of non-aqueous pickering emulsions using anisotropic block copolymer nanoparticles

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In this work we show that amphiphilic diblock copolymer worms prepared via alcoholic RAFT dispersion polymerization can be used to stabilize non-aqueous Pickering emulsions. A previously reported synthesis protocol based on polymerization-induced self-assembly (PISA) was modified to enable the preparation of poly(2-(dimethylamino) ethyl methacrylate)-poly(benzyl methacrylate) (PDMA-PBzMA) worm-like particles directly in methanol at relatively high solids. A dilute dispersion of these highly anisotropic nanoparticles was then homogenized with sunflower oil to produce sunflower oil-in-methanol emulsions. The mean droplet diameter ranged from 9 to 104 μm , depending on the nanoparticle concentration and the stirring rate used for homogenization. The sunflower oil content was increased systematically, with stable emulsions being obtained up to a volume fraction of 0.60. In all cases, the sunflower oil droplets gradually increase in size on ageing for up to four days. However, stable emulsions were obtained after this time period, with no further change in the mean droplet diameter for at least two months on standing at ambient temperature. Turbidimetry studies of the continuous phase after sedimentation of the relatively dense emulsion droplets indicated that the initial adsorption efficiency of the PDMA-PBzMA worms is very high, but this is reduced significantly as the droplet diameter gradually increases during ageing. There is a concomitant increase in fractional surface coverage over the same time period, suggesting that the increase in droplet diameter is the result of limited coalescence, rather than an Ostwald ripening mechanism.



COLL 549

Highly stable titanate nanowire dispersions as potential nanocarriers

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We aimed to investigate the effect of PAMAM dendrimers of different generations on the dispersion stability of titanate nanowires (TiONWs) to develop potentially biocompatible delivery systems. Electrophoretic mobility measurements revealed that PAMAMs strongly adsorbed on the oppositely charged particles and charge neutralization as well as reversal occurred (Figure 1a). These phenomena were independent from the molecular weight of the macromolecules. The results of time-resolved dynamic light scattering experiments showed that the dispersions were stable at low and high dendrimer doses at low ionic strength where the particles possessed sufficiently high negative or positive charge, respectively (Figure 1b). Rapid aggregation and unstable systems were obtained near the dose of the charge reversal point. The orientation of the nanowires in the aggregates resulted in the formation of bundles or “spaghetti-like” structures regardless of the generation of the dendrimers as clarified by transmission electron microscopy images. The ionic strength dependence of the aggregation rates pointed out an enormous stabilization effect of the PAMAM macromolecules of higher generations since the coated TiONW dispersions were stable even at salt levels where the bare particles undergo rapid aggregation. In conclusion, TiONWs to be used in biomedical applications can be stabilized by PAMAM macromolecules of higher generations and on the basis of our results, appropriate doses can be calculated to obtain highly stable dispersions to be further investigated as biocompatible delivery systems. Accordingly, TiONWs coated with higher generation dendrimers are potential candidates in delivery processes as carriers where unwanted aggregation is prevented by the PAMAM layer even under extremely high ionic strengths.

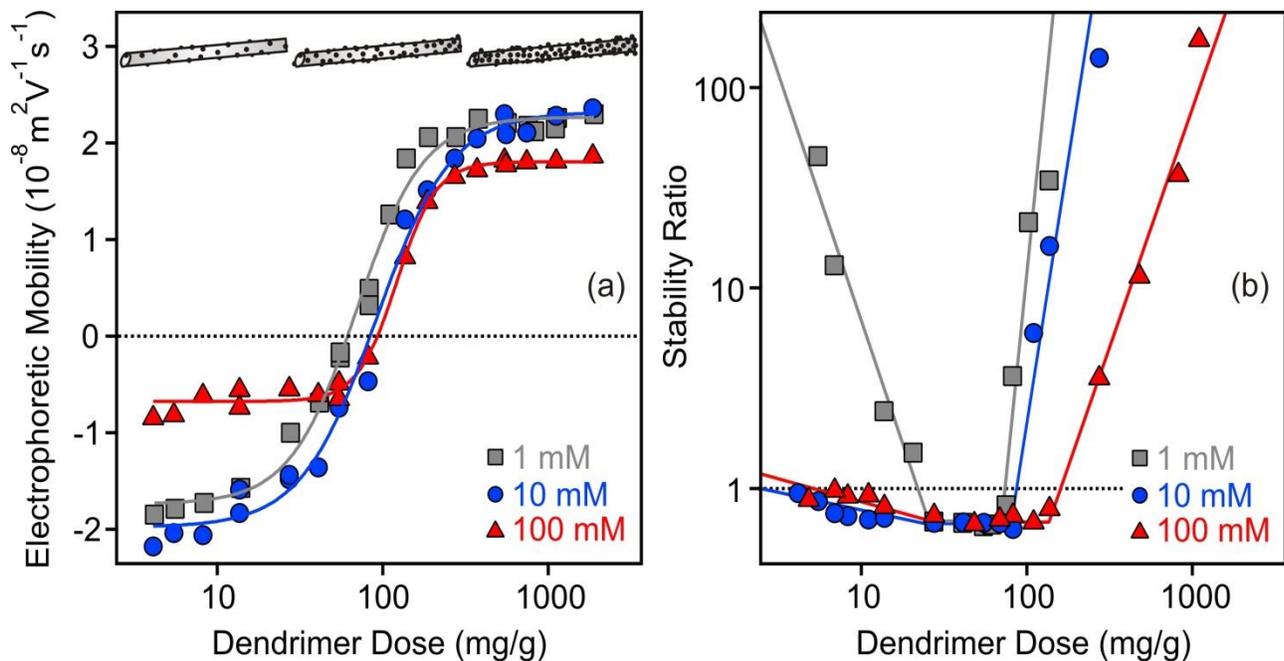


Figure 1. Electrophoretic mobility (a) and stability ratio (b) values as a function of the dendrimer dose measured in dispersions containing TiONW and G6 PAMAM dendrimer at different ionic strengths. Stability ratio close to unity indicates rapid aggregation.

COLL 550

Destabilization of nonionic surfactant stabilized oil-in-water emulsions: Effect of particle wettability

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De-emulsification of emulsions by different additives or external forces is very important in a variety of industrial applications. The de-emulsification process involves flocculation, coalescence of emulsion droplets, and separation of two immiscible liquids. Emulsion stability is largely affected by the nature of the adsorbed layer, interfacial and rheological properties of molecules at the oil-water interface, and interactions between the emulsion droplets. Currently, different methods are being used to achieve de-emulsification, including the use of chemical additives, application of electric fields, and increasing emulsion temperature. Most of these methods are energy intensive, and it is often hard to separate the additives after the de-emulsification process. Here, we studied the use of colloidal particles as de-emulsifiers. Particles are relatively easy to separate, and it is often possible to tune the interactions between surfactant molecules and colloidal particles for specific needs. In particular, we investigated the effect of

particle wettability on the stability of nonionic-surfactant stabilized oil-in-water emulsions. Rapid coalescence of the emulsion droplets is observed when partially-wettable particles are added to the continuous phase. A combination of visual and microscopic observations were used to determine the emulsion stability, and the adsorption isotherms were used to determine the interactions between the surfactant molecules and the particles, including their subsequent effects on emulsion stability.

COLL 551

Holographic characterization of individual colloids in complex mixtures

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Holographic video microscopy characterizes individual colloidal microspheres with great accuracy and precision even in multi-component colloidal suspensions. The sample is illuminated by a laser as it flows through a microfluidic channel creating a hologram of each passing particle. These holograms are analyzed using Lorenz-Mie theory to determine the size, index of refraction, and 3D position of particles in the difficult to measure size range of 200nm to 20 μ m. Here we report measurements of colloidal mixtures made from combinations of various colloidal particles (silica, polymethyl methacrylate (PMMA), polystyrene (PS)) varying in size from 400nm to 7 μ m. Every particle is characterized multiple times as it flows through the microscope. The results of these characterizations are tracked and statistically analyzed to provide high precision analysis of each particle population. Using the resulting data, we were able to identify each particle population even in samples with particles of the same size but different refractive index. We demonstrate this capability in samples with 7 distinct particle populations coexisting in the same sample.

COLL 552

Colloidal dimerization of hard annular sector particles

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We design annular sector particles (ASPs), which have a 270-degree opening angle (*i.e.* idealized C-shapes), as monomer building blocks and mass-produce millions of them using photolithography. We make an aqueous dispersion of microscale ASPs and a nanoscale depletion agent, load this dispersion into a rectangular cuvette, and slightly tilt this cuvette to form a two-dimensional (2D) gravitational column. These Brownian ASPs, which experience hard interactions and roughness-controlled depletion attractions, are osmotically compressed to high densities slowly. After three months, near the top of column, the ASPs predominantly appear as individual monomers and

form a low-density fluid-like region. However, below this surface region, at a higher applied 2D gravitational osmotic pressure (Π_{2D}), ASPs at higher densities begin to form a large population of interpenetrating, lock-and-key dimers, which co-exist with monomers in a reaction zone. Below this reaction zone, ASPs in the bottom of column form a disordered, jammed racemic mixture of chiral (+) and (-) dimers in which a few isolated monomers are seen. We measure the particle area fractions of monomers and dimers as a function of depth from microscope images and calculate the ASPs system's 2D osmotic equation of state. From these area fractions in the reaction zone, we determine the equilibrium constant K of the dimerization reaction using the law of mass action. Overall, K grows exponentially with Π_{2D} , leading to a high degree of dimerization in the bottom of the column.

COLL 553

Mechano-switchable, luminescent gels derived from salts of a long-chained, fatty acid gelator

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Due to the reversible nature of their noncovalent interactions, stimuli-responsive supramolecular gels have attracted considerable attention for their numerous potential and realized applications as nanostructured materials. Here, we report a novel system based on metal salts of the luminescent gelator, 9,10-dioxooctadecanoic acid (DODA). In it, the mechano-responsivity and the luminescent properties can be modulated dramatically by the nature of the metal ion within fibrillar assemblies of the gel networks. DODA has an α -diketo group and is derived from the naturally occurring molecule, oleic acid. Whereas the DODA zinc(II) and calcium(II) salts are inefficient gelators, < 5 wt% of the nickel(II), copper(II), terbium(III) and europium(III) salts can gelate various aromatic liquids, alkanes, and long-chained alcohols. Powder X-ray diffractograms indicate that the inefficient gelators pack in a non-interdigitated bimolecular organization; the efficient gelators do not pack in dimeric units within their crystalline lattices. As a result of their enhanced aggregation, DODA gels exhibit emission spectra that are blue-shifted by ~25 nm with respect to those of their sol phases. Unlike the DODA gels, no difference is observed in the positions of the emission spectra of the sols and gels with metal salts of DODA. We hypothesize that molecular packing arrangements are an important factor in controlling the different gelation behaviors and luminescent properties. In addition, unlike the DODA gels and those of the other salts of DODA, the ones based on the nickel(II) salt are fully and rapidly mechano-switchable over multiple cycles. From analyses of gelator packing in the solid and gel states, and the morphology differences between the gels made from the nickel(II) salt and the other gelators, we hypothesize that the degree of recovery of the viscoelastic properties after the cessation of destructive strain depends acutely on the ability of spherulitic objects and junction zones between the fibers to reestablish strong contacts. Overall, the results provide a facile

approach to the design of mechano-responsive, luminescent materials by modifying the molecular packing arrangements within the fiber assemblies. Additional results to support the model outlined here will be presented.

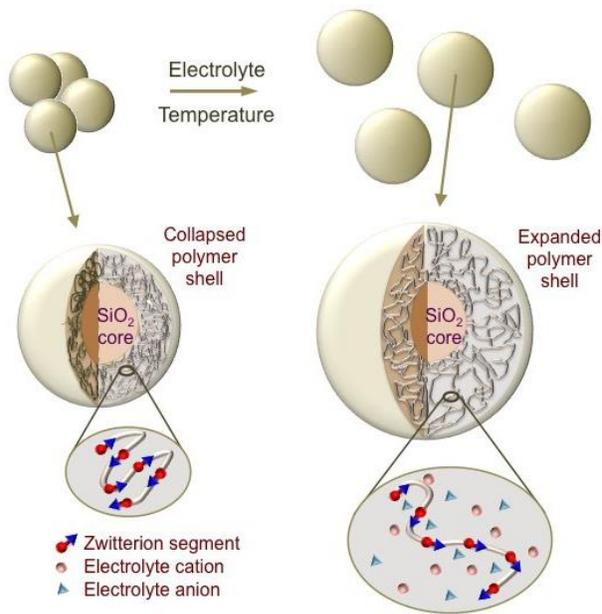
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COLL 554

Responsive stabilization of nanoparticles for extreme salinity and high-temperature reservoir applications

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Colloidal stabilization of nanoparticles under extreme salinity and high temperature conditions is a key challenge in the development of next generation technologies for subsurface reservoir characterization and oil recovery. Polyelectrolytes have been investigated as nanoparticle stabilizers, but typically fail at high ionic strengths and elevated temperatures due to excessive charge screening and dehydration. We report an approach to nanoparticle stabilization that overcomes these limitations, and exploits the antipolyelectrolyte phenomenon, in which screening of intrachain electrostatic interactions causes a polyelectrolyte chain to undergo a structural transition from a collapsed globule to a more open coil-like regime with increases in ionic strength and temperature. Small-angle neutron scattering on a model zwitterionic polymer in solution indicated an increase in both radius of gyration and excluded volume parameter of the polymer with increases in ionic strength and temperature. The model zwitterion was subsequently incorporated within a polymeric stabilizer for nanoparticles under harsh reservoir conditions, and used to functionalize hydrophilic (silica) as well as hydrophobic (polystyrene) nanoparticles. Long-term colloidal stability was achieved at salt concentrations up to 120,000 mg/dm³ at 90°C, approximately twice the stability limit previously reported in the literature. The approach can be broadly generalized to a large class of synthetic polyelectrolytes, and can be adapted to a wide variety of other colloidal systems in which demands placed by extreme salinity and temperature conditions must be met.



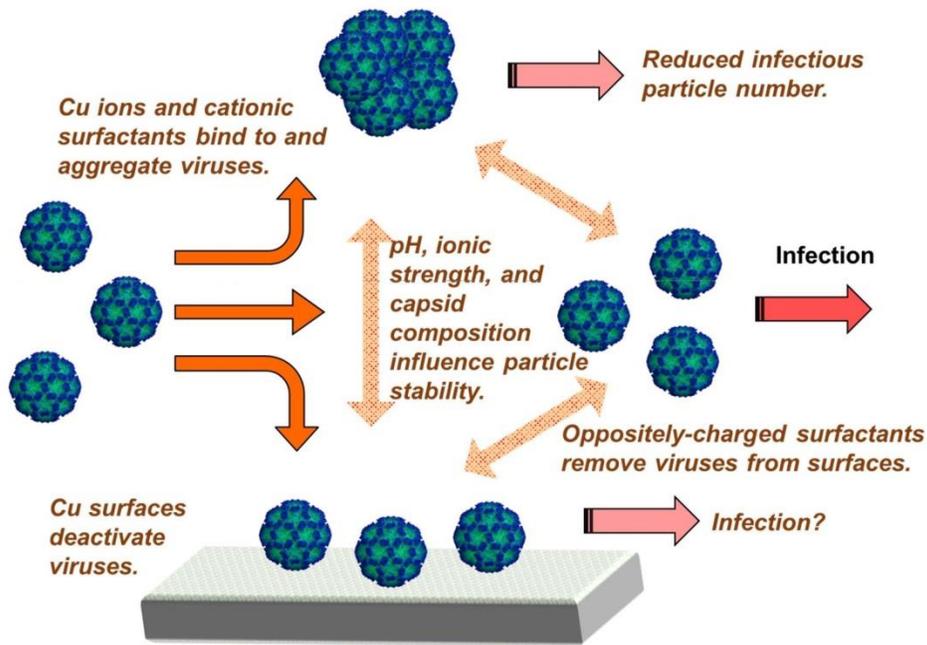
COLL 555

Characterization of Norovirus colloidal interactions as means of controlling virus stability and infectivity

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We characterize the colloidal interactions of Norovirus virus-like particles (VLPs) in aqueous solution and seek means to control and modify them by using various classes of surfactants. The fundamental understanding of these interactions could aid in virus inactivation and removal from contaminated surfaces. The effects of solution pH and surfactant type and concentration on virus particle aggregation, dispersion, and disassembly were characterized using dynamic light scattering and electrophoretic light scattering (Mertens and Velev, *Soft Matter*, 2015). The results indicate that a strong ionic surfactant above its critical micelle concentration (CMC) causes capsid disassembly and breakdown of aggregates. Below CMC, surfactant adsorption onto the virus capsid follows simple adsorption models, depending on the charge of the surfactant and the net charge of the capsid. Ionic surfactant adsorption leads to modified apparent surface charge and subsequent aggregation or dispersion, depending on the surfactant charge. We also characterize the effects of copper ions on virus colloidal interactions to explain empirical data indicating virus inactivation by copper alloy surfaces. Above the isoelectric point of Norovirus VLPs, very low concentrations of divalent copper ions ($\approx 1 \mu\text{M}$) rapidly bind and aggregate the particles. Below the isoelectric point of the VLPs, copper ions do not induce VLP aggregation. Copper ion binding to the capsid surface and subsequent virus aggregation depends on

the amino acid composition of the major capsid protein and varies depending on the Norovirus strain. These colloidal interaction data will assist in the formulation of novel mixtures for efficient virus cleanup and deactivation.



COLL 556

Nanofiber composites containing fumed silica fillers: From controlled wettability to physical characteristics

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Fumed silica (FS) particles with hydrophobic (R805) or hydrophilic (A150) surface functionalities are incorporated in polyacrylonitrile (PAN) fibers by electrospinning to produce mats with controlled wettability. Rheological measurements are conducted to elucidate the particle-polymer interactions and characterize the system while microscopic and analytic tools are used to examine FS location within both fibers and films to aid in the fundamental understanding of wetting behavior. Unlike traditional polymers, we find these systems to be gel-like, yet electrospinnable; the fumed silica networks break down into smaller aggregates during the electrospinning process and disperse both within and on the surface of the fibers. Composite nanofiber mats containing R805 FS exhibit an apparent contact angle over 130° and remain hydrophobic over 30 minutes, while similar mats with A150 display rapid surface-

wetting. Wicking experiments reveal that the water absorption properties can be further manipulated, with R805 FS-impregnated mats taking up only 8% water relative to mat weight in 15 minutes. In contrast, PAN fibers containing A150 FS absorb 425% of water in the same period, even more than the pure PAN fiber (371%). The vastly different responses to water demonstrate the versatility of FS in surface modification, especially for sub-micron fibrous mats. As a model platform for fumed silica containing composites, we have expanded our research to explore characteristics beyond that of solely wetting behavior.

COLL 557

Anomalous dispersion of 'hedgehog' particles

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Dispersion of hydrophobic colloids in water or hydrophilic colloids in hydrophobic solvent is unstable and readily undergoes irreversible aggregation. A stable dispersion of colloids in 'phobic' environment are known to require interfacial chemical camouflages that imparts particle-solvent affinity through polarity matching with the environment. Such provides steric and electrostatic effects that renders increase in the inter-particle repulsive potential. Generating additional repulsive effects by a physical canopy would overcome the limitations imposed by the traditional chemical modification and also would preserve the pristine colloidal properties and functionalities. In this research, we show that the 'hedgehog' particles with arrays of high aspect ratio ZnO nanowires coated on a surface of microsphere exhibit stable dispersion in both 'philic' and 'phobic' media. Verifying the experimental findings through EDLVO based calculations, high surface corrugation leads to limited contact area and increased minimum interaction distance that drastically reduces the attractive potential. Furthermore, solvent-ionization at the air-water interfaces of trapped air-pockets in the nano-topography provides extra repulsive potential in the case of aqueous dispersion of hydrophobic HPs. Low ionic strength provides longer-range repulsive potential in the case of hydrophilic HPs in non-polar organic media. The findings could lead to reduction in the use of the volatile organic compound in a wide spectrum of industries ranging from pharmaceutical to paint, enable new strategies for exotic colloidal behavior and self-assembly, and exhibit unexplored or enhanced physicochemical properties ranging from photophysics to catalysis.

COLL 558

Inorganic chiral nanomaterials: Design strategies and origin of homochirality

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The importance of chirality was discovered in 1963, when the critical birth defects were caused by the presence of wrong handed thalidomide in a drug that was supposed to cure morning sickness. Considering that chiral molecular drugs shared one-third of all drug sales worldwide in 2000, chiral selective synthesis and separation of enantiomers are critical for disease diagnosis and therapy in the pharmaceutical industry. Recently, chirality of inorganic nanomaterials has been considered of much importance because they are of prime fundamental and practical interest due to the favorable power-law scaling of near-field enhancements.

A further motivation to study chirality of inorganic nanostructures is to discover the origin of homochirality in natural compounds. The prevalence of only L-type amino acids and D-type sugars in nature is well-known example of homochirality. This dominant existence of only one of the two enantiomers among natural products has kept scientific attentions for decades. Several chemical routes are being debated, including chiral amplification and influence of circularly polarized light (CPL) from the cosmos.

Chemical reactions affected by spin angular momenta of circularly polarized photons are rare and display low enantiomeric excess. Because of high optical and chemical activity, nanoparticles (NPs) signifies the possibility of converting spin angular momenta of absorbed photons into structural changes of nanoscale materials by self-assembling. However, such processes are currently unknown. Here, we demonstrate that CPL strongly affects the nature of self-assembly of racemic CdTe NPs. In particular, illumination of NP dispersions with right- and left-handed CPL induces the formation of right- and left-handed twisted nanoribbons, respectively. Enantiomeric excess of such reactions exceeds 30% which is ~10 times higher than other CPL-induced reactions. This observation of imprinting the polarization information of incident photons by NPs opens new pathways for the synthesis of chiral photonic materials and allows for better understanding of the origins of biomolecular homochirality.

COLL 559

Enhancing oil recovery using nanoemulsions

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The objective of this study is to investigate the effect of surfactant-based nanoemulsions (NEs) on oil recovery from various formations. NEs consist of a blend of demulsifying surfactant, biodegradable solvent, co-solvent, and water. When these components exist in unique balanced ratios, they can create a three-phase fluid phase that is kinetically stable with droplet size below 200 nm, as shown in Figure 1. At low concentrations in water, nanoemulsions have extremely high contact areas and can efficiently diffuse through the small throats of porous media to recover residual oil trapped in pores. Nanoemulsions can also reduce the interfacial tension by 3-4 orders of magnitude and alter the wettability of reservoirs according to their physicochemical properties. Although NEs often outperform surfactants alone, their ability to enhance oil recovery depends on test conditions and the proper selection of their components. Thus, a systematic study is required to achieve the best outcomes.

In this study, several environmentally friendly surfactants were used to create stable NEs using low-energy emulsification techniques. These surfactants have been screened based on their phase behavior in oil/water systems, high-resolution transmission electron microscope (HRTEM) imaging, and spontaneous imbibition tests at ambient conditions. The ability of nanoemulsions to reduce oil/water interfacial tension and alter the wettability of aged quartz and calcite were also assessed to investigate the mechanisms of interaction. Preliminary results on sandstones and carbonates indicate that the rock wettability plays an important role in the mechanism of oil recovery with NEs. The effects of several parameters such as surfactant type, rock surface, and water chemistry have been investigated in a systematic manner.

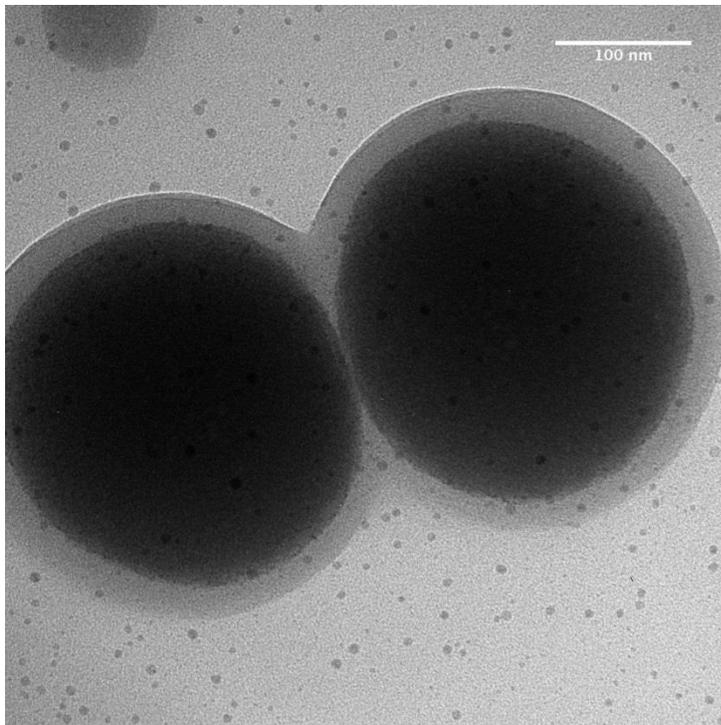


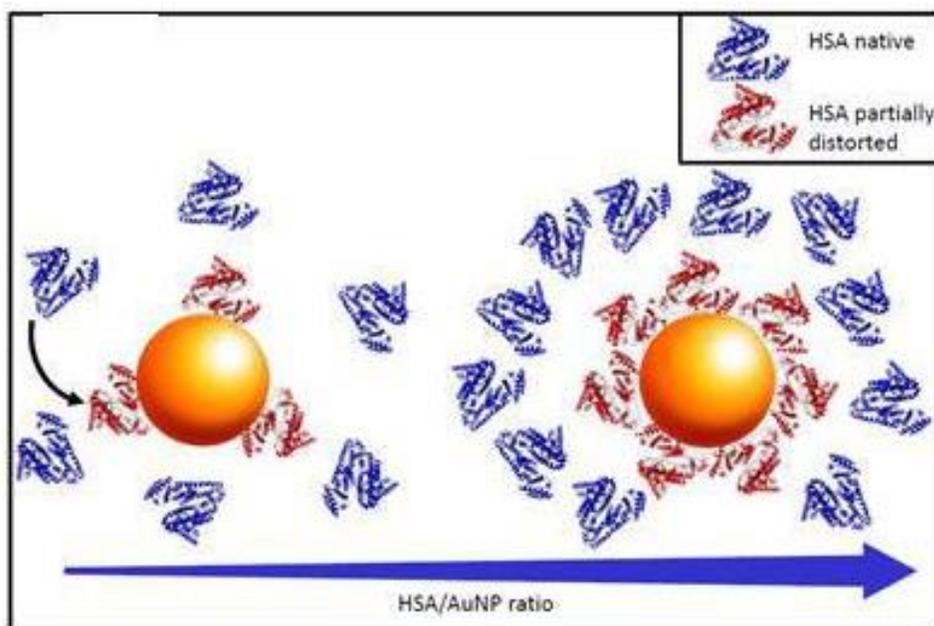
Figure 1. HRTEM micrograph of nanoemulsions

COLL 560

Determination of structure and morphology of gold nanoparticle-HSA protein complexes

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We propose a simple method to determine the structure and morphology of nanoparticle protein complexes. By combining a separation method with online size measurements, density measurements and circular dichroism, we could identify the number of proteins bound to each nano particle and their secondary structure changes in the complex. This method provides much-needed experimental information on the interaction of proteins with nanoparticles and on the behavior of nanoparticles in biological systems.



COLL 561

Importance of lipopolysaccharide aggregate disruption for the anti-endotoxic effects of host defense peptides

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Lipid membrane and lipopolysaccharide (LPS) interactions were investigated for a series of amphiphilic and cationic peptides derived from human heparin cofactor II, using dual polarization interferometry, ellipsometry, circular dichroism (CD), cryoTEM,

and z-potential measurements. Antimicrobial effects of these peptides were compared to their ability to disorder bacterial lipid membranes, while their capacity to block endotoxic effects of LPS was correlated to the binding of these peptides to LPS and its lipid A moiety, and to charge, secondary structure, and morphology of peptide/LPS complexes. In particular, fragmentation and densification of LPS aggregates correlate to the anti-endotoxic effect of these peptides, thus identifying peptide-induced packing transitions in LPS aggregates as key for anti-endotoxic functionality. PEGylation of these peptides reduces peptide binding to lipid membranes, an effect accentuated at increasing PEG length but less sensitive to conjugation site. The reduced binding causes suppressed liposome leakage induction, as well as bacterial lysis. As a result of this, the antimicrobial effects of KYE28 is partially lost with increasing PEG length, but hemolysis also strongly suppressed and selectivity improved. Through this, conditions can be found, at which the PEGylated peptide displays simultaneously efficient antimicrobial effects and low hemolysis in blood. Importantly, PEGylation does not markedly affect the anti-inflammatory effects of these peptides. The combination of reduced toxicity, increased selectivity, and retained anti-inflammatory effect after PEGylation, thus shows that PEG conjugation may offer opportunities in the development of effective and selective anti-inflammatory peptides.

COLL 562

Observing the dynamics of stimuli-responsive nanomaterials at high resolution by liquid cell transmission electron microscopy (LCTEM)

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Liquid Cell Transmission Electron Microscopy (LCTEM) is a unique analytical method for observing the dynamics of nanomaterials in real time at high magnification. In particular, the ability to image dynamic biological events in real time with nanometer resolution in environmentally relevant conditions is essential to our understanding of how these systems work, and, consequently, to advancement in fields such as nanoparticle drug delivery and synthesis. We are interested in enzyme-responsive soft nanomaterials, stimuli-induced phase transitions, and polymerization-induced assemblies, which have otherwise not yet been investigated by LCTEM. Here we demonstrate the dynamics of several model systems, including DNA- and peptide-networked nanoparticles which undergo drastic morphology changes upon interaction with a stimulus. Our findings demonstrate how LCTEM can be used to study stimuli-responsive nanomaterials and prove for the first time that biological events can occur during an LCTEM experiment.

COLL 563

Chitosan-coated BSA nanoparticles for oral delivery

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Despite years of research, chronic pathologies, like cancer and chronic inflammatory diseases, are still in need of therapeutic approaches that allow easy administration, high compliance of the patient to the treatment and few or minor side effects. Engineered medicines, like surface-decorated nanoformulations, have the potential to accomplish all these important goals. However, oral administration of these formulations is a challenge due to the need to overcome the gastric harsh environment and be absorbed in the intestinal tract, reaching the blood flow as a whole functionalized particle.

We developed BSA nanospheres coated with chitosan and/or poloxamer 407 as mucoadhesive and mucopenetrant polymers. The formulations showed to be non-toxic to Caco-2 cells in the tested concentrations. Stability assays in simulated digestive fluids showed differential profiles in terms of the size of the spheres coated with only one or with the two polymers and also in the amount of BSA that is released to the fluids, as measurement of spheres degradation. Preliminary results of *ex vivo* experiments with pig intestine showed the permeation of some material, however further improvements are being implemented in the analytic protocols.

The overall results point to need of using both chitosan and poloxamer 407 as coating for BSA nanospheres to be orally administered and reach the target tissues.

COLL 564

Single-particle tracking of lipoproteins and lipid vesicles

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Small particles are prolific in many different areas of science and present technical challenges to characterize in solution. In particular, lipid particles such as lipoproteins, synaptic vesicles, and exosomes are of fundamental importance, both for biological function and their potential as biomarkers for disease. For example, lipoproteins vary in size, shape, lipid composition, and protein content and these heterogeneous properties cannot be distinguished by traditional bulk measurements which may average out crucial features. We have developed an experimental method to track individual lipid particles and measure their properties by confining them in an easily constructed confinement chamber (~100 nm thickness). The diffusion of the particles is used to determine their relative sizes and total bound protein content is quantified by fluorescence intensity. We have applied this technique to studies of lipoproteins and lipid vesicles. Using lipoproteins, which have well-defined size regimes, we have demonstrated that a lipid particle down to a radius of 5 nm can be tracked. Further, we have extended this method to study α -synuclein, a neuronal protein involved in Parkinson disease, and its membrane interactions at the single-vesicle level to understand the biophysical basis for curvature sensing by α -synuclein. We envisage this

method will have broad applicability for the study of heterogeneous particles including colloids and nanomaterials.

COLL 565

Facile synthesis of archaea-inspired lipids for the assembly of archaeosomes

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Liposomes composed of natural or synthetic phospholipids are self-assembled colloidal vesicles that have shown great promise as therapeutic agents for the delivery of both hydrophobic and hydrophilic drugs. Despite their unique applications as drug delivery systems, liposomes suffer immensely from membrane permeability of encapsulated materials such as small molecules, ions, and drugs. As a biomedical application, this causes great concern for the passive leakage and accumulation of toxic drugs in undesired tissues. To address the problem of membrane stability, given their desirable and highly stable membrane properties, we focused our efforts on the synthesis and development of archaea-inspired lipids as stable lipid materials. To this end, we proposed a reasonable and facile synthetic route towards the synthesis of archaeal-type lipid analogues via click to generate a diverse library of lipids. In this presentation, we report the tunable and modular synthesis of archaeal-type lipids for the preparation of archaeosomes as new materials for potentially stable systems.

COLL 566

Protein adsorption to charged nanospheres

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Nanoparticles (NP) are rapidly becoming more common in the medical field. Applications like imaging, drug delivery, and therapeutics require careful design of the surface chemistry of the particle to reach their target. When NPs are introduced into a biological system the particles encounter a milieu of proteins that alter the surface chemistry by forming a "protein corona". Increasing evidence suggests that the biological fate and targeting efficiency of NPs are heavily influenced by the protein corona necessitating fundamental research into adsorption of proteins onto NP surfaces. The aim of this work is to employ the facile and complimentary methods of plasmon shift and hydrodynamic diameter shift to probe the adsorption of proteins to negatively and positively charged gold nanoparticle (AuNP) surfaces. Bovine serum albumin (BSA), β -lactoglobulin (BLG), and α -amylase (A-Amy) were chosen for this

study because these proteins denature via different pathways under acidic conditions suggesting that they might adsorb differently to highly charged NP surfaces. Citrate AuNPs were used as negatively charged surface while poly(allylamine hydrochloride) (PAH) was used as the positive surface. Binding constants were measured for all three proteins on the citrate surface, and both measurement methods were in good agreement. A binding constant was measured for A-Amy on PAH AuNPs, but could not be determined for BSA and BLG. Rather large protein/particle agglomerates formed that increase in size with increasing protein concentration. These results confirm that the underlying surface chemistry plays an important role in adsorption, and that the identity of the protein influences adsorption behaviors.

COLL 567

Picosecond energy relaxation dynamics of amyloid beta peptide at nanoscale interface

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The conformation of amyloid beta peptide 1-40 (Ab₁₋₄₀) as they were adsorbed over nanogold colloid was investigated through two different approaches of fluorophore. An internal energy relaxation process of Ab₁₋₄₀ was monitored by the fluorescence of fluorescein attached Ab₁₋₄₀: FAb. The energy relaxation of Ab₁₋₄₀ aggregation was observed through fluorescence of Thioflavin –T (ThT) dye inserted to Ab₁₋₄₀ adsorbed nanogold colloid. The fluorescence intensity and picosecond fluorescence decay time were investigated over various gold colloidal sizes ranging from 10 nm to 100 nm between pH 2 and pH 12. As a general trend, the fluorescence intensity was increased as the size of nanogold increased. For a fixed size of nanogold, the slowest life time was observed around pH 7 and a drastic quenchings were observed at pH 2 or pH 12. The enhancement of fluorescence can be simply originated to an increase of the number of fluorophores available on the surface. The larger the size of nano gold, the more spacing between monomers were expected resulting in less interactions. The folded and unfolded conformations of monomers can be prepared at basic and acidic conditions, respectively. An interactions between monomers must be more enhanced at pH 2 due to networking between unfolded monomers. On the other hand, more interaction between folded monomers and nanogold surface was speculated at pH 12. The energy relaxation was accelerated as the residual temperature was increased from 20 °C to 65°C, indicating that nonradiative channels through gold colloidal surface must enhance the quenching.

COLL 568

Inhibition of amyloid fibrillation of β -lactoglobulin by hydrolyzed hydrophobic alkoxi- and fluoro- silanes

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Proteins often self-assemble and form insoluble amyloid type fibrils, which are responsible for diseases like Parkinson's, Huntington's, Cataracts, Spongiform Encephalopathy, and Alzheimer's. Amyloid fibrils comprised of highly ordered β -sheets are stabilized by an extensive network of intermolecular hydrogen bonds, hydrophobic surfaces and favorable packing of side chains. Due to these highly organized structures, amyloid fibrils become resistant to degradation and depolymerization. Our recent work demonstrates hydrophobic silanes such as n-propyltrimethoxy silane (nPM) and 3,3,3-trifluoropropyl methoxy silane (3F) are strong inducers of protein secondary structure in both sol and gel states. In our current study hydrolyzed nPM and 3F are employed to control the fibrillation of a small globular protein β -lactoglobulin (BLG), which forms amyloid-like fibrils at low pH and high temperature. nPM (0.4M) and 3F (0.4M) were hydrolyzed in aqueous solution at pH 1.7 and 23°C and pre-incubated with BLG (1 mg/ml) for 10 min, followed by increasing the temperature to 90°C to induce fibrillation. The effect of the hydrolyzed silanes on BLG fibril formation was assessed using AFM. AFM analysis revealed that hydrolyzed nPM and 3F both inhibited BLG fibrillation. The activities of nPM and 3F against pre-formed fibrils were also tested, and AFM data showed both acted as strong fibril degrading agents. AFM data also revealed formation of nanosized polymeric particles from hydrolyzed nPM and 3F during fibril degradation. This study demonstrates the unique activity of hydrolyzed hydrophobic silanes as potential therapeutic agents against amyloid diseases.

COLL 569

Membrane domain formation on nanostructured scaffolds

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The spatial organization of lipids and proteins in biological membranes seems to have a functional role in the life of a cell. Separation of the lipids into distinct domains of greater order and anchoring to the cytoskeleton are two main mechanisms for organizing the membrane in cells. We propose a novel model membrane consisting of a lipid bilayer suspended over a nanostructured scaffold consisting of arrays of fabricated nanopillars. Unlike traditional model membranes, our model will have well-defined lateral structure and distributed substrate attachments that will emulate the connections of cellular membranes to the underlying cytoskeleton. Membranes will be characterized using neutron reflectometry, atomic force microscopy and fluorescence to verify a suspended, planar geometry with restricted diffusion at suspension points, and free diffusion in between. This architecture will allow the controlled study of lipid domain reorganization, viral infection and signal transduction that depend on the lateral structure of the membrane.

COLL 570

Structure analysis of membrane fusion by X-ray diffraction: From model membranes to organelles

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Understanding the physical mechanisms underlying membrane fusion requires a multi winged approach, involving model systems as well as biological membranes. We study fusion intermediates occurring in form of ordered passages or stalks connecting neighbouring bilayers in multilamellar model membrane stacks. The stalks exhibit long range crystalline order with rhombohedral symmetry in a fluid 'host' membrane stack, which is studied by high resolution x-ray diffraction under grazing incidence angles. Information on membrane curvature, and hydration interaction can be revealed by analyzing the quantitative electron density maps, collected for controlled environmental parameters and membrane composition [1]. Phase diagrams can be analyzed in view of stabilizing or destabilizing agents for stalk formation.

While in these equilibrium phase, dehydration forces bring bilayers together favoring at some point the formation of stalks, it is specific membrane proteins and their interaction which set the local boundary conditions for membrane apposition in biological membrane fusion. In view of studying fusion in the presence of SNARE proteins, we have started a x-ray structural characterization of synaptic vesicles (SV) by small-angle x-ray scattering, and currently extend this work towards studies of SV docked to and interaction with model bilayers [2], and work towards reconstituting SNARE complexes into the stalk phase for structural analysis.

[1] S. Aeffner et al., Proc.Natl.Ac.Sc.. doi: 10.1073/pnas.1119442109 (2010)

[2] S. Ghosh et al., Biophys.J. 2012 Biophysical Journal (102), 1394–1402, (2012).

COLL 571

Stress-free asymmetric lipid vesicles for the study of transverse lipid motion

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Chemically well-defined liposomes have long served as model systems for the controlled study of lipid bilayer properties, and the behavior of membrane-associated proteins. Despite the chemical control over these model systems the ability to measure fundamental physical behaviors has proven exceedingly difficult if not at all. Recently, we have made significant progress on the preparation and characterization of asymmetric liposomes.

Our new methodology for the construction of free floating asymmetric vesicles was optimized for the construction of stable, and stress-free 100 nm isotopically asymmetric vesicles. More importantly, we have developed new analytical procedures allowing for precise measurement of the composition of each leaflet of the asymmetric bilayer. Together, these improvements in preparation and characterization methods constitute a significant step toward the realization of a longstanding goal of membrane biophysics, and should facilitate the rapid advancement of model membrane studies.

Among these advancements is the new ability to examine lipid transverse diffusion, commonly known as flip/flop. Lipid flip/flop rates, which have historically been challenging to obtain, can now be accurately determined using our novel high-yield method for generating isotopically asymmetric vesicles, and the methodology for the robust quantification of their structure and asymmetry. Here we begin to investigate long-standing questions regarding the influence of bilayer structure and composition on flip/flop rates in stress-free vesicle systems.

COLL 572

Computational and experimental study on the 2D self-assembly of the carboxysome's shell proteins

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Bacterial micro-compartments, BMCs, are small organelles that exist in cyanobacteria and enteric bacteria. BMCs have a proteinaceous icosahedron-like shell that encapsulates enzymes that perform reactions necessary for the lifecycle of the bacteria. Three types of BMCs have been studied in detail, i.e. the carboxysome (CB), the propanediol- (Pdu) and the ethanolamine-utilization (Eut). The CB has been studied most extensively and it is considered the prototype BMC. However, despite considerable efforts put into understanding its structure and functioning, many questions still remain unanswered.

One of these questions has to do with the structure and composition of the CB's proteinaceous shell. Various component proteins have been identified and models exist

that propose that the facets of the icosahedral shell are composed of hexagonal units that self-assemble into a 2D layer. Here, for the first time, we use computational techniques to probe the mechanism of 2D self-assembly of one of CB's shell proteins, i.e. CcmK2. By comparing the coarse grained (CG) potential of mean force (PMF) with the standard all-atom PMF, the best CG model that aptly represents the CcmK2 protein building block has been identified. Using this CG model we performed a Metropolis Monte Carlo (MC) simulation to identify the mechanism of self-assembly. We found that the assembly of CcmK2 follows the nucleation growth kinetics. The nuclei size of CcmK2 is four units and a critical nucleation concentration of 0.007 units/nm². These calculations are being coupled with experimental results that investigate the self-assembly of hexagonal units into 2D layers.

COLL 573

Observation of nanoscale structure in the liquid ordered phase by molecular simulation and small angle neutron scattering

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Recently published molecular simulations reveal the liquid ordered phase to be inhomogeneous, with areas of hexagonally packed saturated chains separated by cholesterol rich interstitial regions.^{1,2} In this talk I will report on our efforts to detect the signature of these hexagonal regions through a combination of analysis of simulation data, small angle neutron scattering, and a series of different deuteration schemes. The analysis of the simulation data is complicated by the need to distinguish lateral and transverse variations in scattering length density; several different approaches to this end will be discussed.

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2. Sodt, A.; Pastor, R. Lyman, E. Hexagonal Substructure and Hydrogen Bonding in Liquid-Ordered Phases Containing Sphingomyelin, *Biophys J.* **109**, 948 (2015)

COLL 574

Lateral organization and inter-leaflet coupling of biological membranes

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Understanding of cell membrane organization has evolved significantly from the classic fluid mosaic model. It is now recognized that biological membranes are highly organized structures, with differences in lipid compositions between inner and outer leaflets and in

lateral structures within the bilayer plane, known as lipid rafts. These organizing principles are important for protein localization and function as well as cellular signaling. However, the mechanisms and biophysical basis of lipid raft formation, structure, dynamics and function are not clearly understood. In this talk, I will discuss our work towards addressing how lateral organization and leaflet asymmetry are coupled using HPC capabilities at Oak Ridge National Laboratory.

COLL 575

Hydrophobic mismatch tunes lipid bilayer dynamics

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Lipid membranes are highly complex systems with a hierarchy of structure and dynamics that span several decades in length and time scales and that in turn significantly influence membrane functions. While a large body of research has been dedicated to multiscale structural investigations in these systems, nanoscale dynamical characterization has lagged far behind. The experimental challenge here is the need to simultaneously access the desired length and time scales for the motions of interest. Over the past decade, neutron spin echo spectroscopy has proven to be a unique tool for capturing nanoscale collective lipid membrane dynamics. For instance, lipid membrane bending moduli can be estimated from the relaxation time of single membrane fluctuations in unilamellar vesicles. More recently, lipid membrane thickness fluctuations have also been measured with relaxation times on the order of 100 ns and with amplitudes of a few tenths of nanometers in fluid lipid bilayers. We show that hydrophobic mismatch between lipids with different acyl chain lengths tunes the thickness fluctuation amplitude and relaxation times in a way not achievable in single component systems. Using deformation free energy calculations, we contextualize these results in terms of bilayer elastic parameters, the total compressibility modulus and the fluctuation wavelength. In the mixed lipid bilayers, the increase in total compressibility compared to the pure component membranes enhances the fluctuation amplitude, while changes in the lateral arrangement of the membrane structure are expected to modify the fluctuation time scale. The fluctuation wavelength is also influenced by lipid composition and is on the order of 20 nm in single component bilayers and increases with temperature in mixed lipid bilayers. It is noted that these fluctuation wavelengths are on the same size scale as laterally inhomogeneous bilayer structures such as the ripple phase and raft domains, which may suggest possible interplay between collective membrane dynamics and intra-bilayer structural arrangements.

COLL 576

Controlled synthesis of Au-CuS heterodimers with tunable light absorption for photothermal therapy in the second NIR window

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Optical transmission through tissue is optimal in the second near-infrared (NIR) window, which also allows higher maximum permissible exposure to laser irradiation relative to the commonly studied first near-infrared window. This highly promising yet under-explored optical window for photothermal therapy calls for high efficiency photothermal agents. As hybrid nanoparticles which contain two or more domains each having a unique feature can possess properties more than the sum of their individual parts, herein, we describe controlled synthesis of metal sulfide and metal-metal sulfide semiconductor hybrid nanoparticles, in particular dual plasmonic Au-CuS heterodimer nanoparticles for high efficiency photothermal therapy in the second NIR window. The localized surface plasmon resonance (LSPR) of CuS nanoparticles is centered around 1100 nm, with an absorption cross section comparable to Au nanoparticles. Moreover, the photothermal transduction efficiency of CuS is measured to be 37%. In addition, the absorption of CuS is enhanced up to 50% in the presence of Au. This observation is confirmed by simulation results showing the enhanced local field as well as the optical power absorption on CuS surface due to the neighboring Au nanoparticle. The enhanced optical absorption cross section, high photothermal transduction efficiency, excellent X-ray attenuation ability, and low cytotoxicity of Au-CuS hybrids making them a robust photothermal agent in the second near-infrared window with X-ray CT imaging capability. Efficient photothermal ablation is demonstrated in vitro and in vivo with low nanomaterial dose under low laser flux.

COLL 577

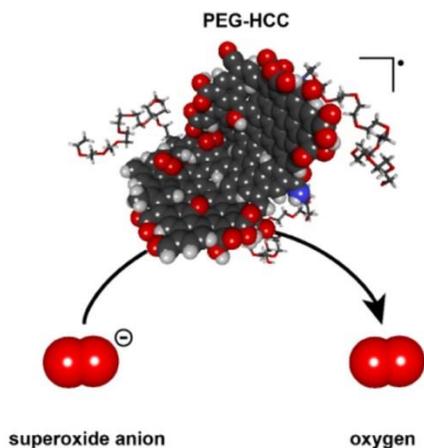
Carbon nanoparticles as a platform therapeutic for oxidative stress

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Oxidative stress is a challenge inherent to biological systems adapted to an oxygenated environment. Under normal cellular conditions, oxidative stress is balanced by a complex system of antioxidant vitamins and enzymes. However, in instances of acute injury, ischemia/reperfusion, inflammation,¹ premature birth,² and certain diseases, oxidative stress is a major pathophysiological factor. While the antioxidant system can be bolstered *before* acute injury by supplementation with additional vitamins or enzymes, no clinical trial has shown antioxidant therapy to be effective *after* injury, ostensibly because the complex, interdependent antioxidant system becomes saturated and ineffective due to the cascade of radical formation during extreme oxidative stress.

Encouragingly, we have developed a new class of antioxidants that does not form any down-stream radical cascade, thereby acting in a manner that neither a small molecule nor an enzyme has demonstrated. These antioxidants, based on small graphitic domains, are termed polyethylene glycol-functionalized hydrophilic carbon clusters (PEG-HCCs). These possess the highly favourable characteristic of being superoxide-to-oxygen generators, generating one O₂ and one H₂O₂ from two superoxide molecules, the same two products made by superoxide dismutase (SOD). Hence these are SOD mimetics with kinetics faster than most single-site-enzyme catalysts showing rates of 87,000 s⁻¹.³ These new antioxidant nanoparticles have shown exceptional performance in a number of different animal models of disease (multiple sclerosis and rheumatoid arthritis⁴) and acute injury (traumatic brain injury⁵ and stroke⁶)

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Model of the antioxidant nanoparticle

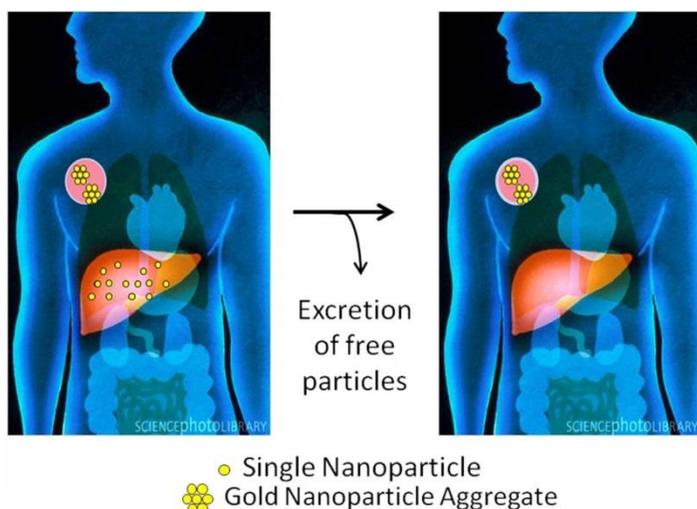
COLL 578

Controlled assembly of biocompatible metallic nanoaggregates using a small molecule crosslinker

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Metallic nanoparticles are promising drug delivery vehicles that can increase the amount of drug at a tumor relative to free drug. However, when we deliver nanoparticles that sufficiently accumulate in the tumor there is also accumulation in the healthy liver.

The metallic nanoparticles that accumulate in the liver persist for long periods of time; these particles could interfere with future tests, limit repeat dosing of a therapy and hinder the translation of these materials into the clinic. In order to overcome this accumulation, aggregates could be used which upon accumulation in the liver, are broken down into their small and renally-clearable components. As a first step to achieve this, metallic nanoparticle aggregates have been assembled using a small molecule crosslinker. Aggregates can be assembled from particles of varied size and composition and the size of the aggregates can be systematically adjusted. By capping the 60 nm nanoparticle aggregates with PEG the aggregates are non-toxic to macrophage cells up to 55 mM Au.



COLL 579

Tumor targeted ferritin nanocages for efficient photodynamic therapy

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Photodynamic therapy (PDT) is an emerging treatment modality that is under intensive preclinical and clinical investigations for treatments of many diseases including cancer. For the purposes, it is paramount to develop a reliable drug delivery vehicle that can deliver photosensitizers (PSs) to tumors in a site-specific manner. Previous efforts have been focused on polymer- and liposome-based nanocarriers, which are usually associated with a suboptimal PS loading rate and a large particle size. Recently, we found that ferritin (FRT) nanocages can be conjugated with targeting motifs, such as RGD4C and folic acid, and serve as a safe and efficient PS carrier. In particular, we found that zinc hexadecafluorophthalocyanine (ZnF₁₆Pc), a potent PS with a high ¹O₂ quantum yield (0.85 in THF) but poor water solubility, can be encapsulated into FRTs at a high loading rate (up to ~60 wt %) without comprising the colloidal stability of the nanoparticles (hydrodynamic size of the conjugates is ~8.6 ± 2.6 nm). When tested in

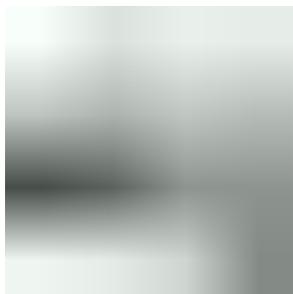
murine U87MG subcutaneous tumor models, ZnF₁₆Pc-loaded and RGD4C-modified FRTs (P-RFRTs) showed high tumor selectivity (tumor-to-normal-tissue ratio of 26.82 ± 4.07 at 24 h), excellent tumor control under photoirradiation (tumor growth inhibition, or TGI, rate of 83.64% on day 12), and low toxicity to the skin as well as major organs. When tested in 4T1 tumor bearing BALB/c mice, ZnF₁₆Pc-loaded and folic acid conjugated FRTs (P-FA-FRTs) efficiently suppressed not only primary tumor growth (TGI rate of 82.65% on day 14) but also tumor metastasis to the lung, which is attributable to a PDT-stimulated anti-tumor immune response. The technology can be extended to deliver other PSs or chemotherapeutics to tumors and holds great potential in clinical translation.

COLL 580

Plasma membrane-derived vesicles with engineered transmembrane protein ligands: A new system for cellular targeting

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Nanoparticle-based drug delivery systems have the potential to target diseased cells on the basis of their receptor expression profiles. Toward this goal, synthetic materials conjugated with antibodies against specific cellular receptors have been shown to concentrate in solid tumors. However, chemical conjugation reactions are difficult to control and frequently compromise the affinity of receptor binding. Further, the difficulty of implementing multiple distinct attachment chemistries effectively limits the number and complexity of targeting ligands that can be used. To overcome these limitations, here we demonstrate that plasma membrane vesicles (PMVs) derived from donor cells can be engineered to express transmembrane protein ligands that precisely target cells on the basis of the expression level of a specific cellular receptor. In particular, PMVs expressing ligands for EGFR bound with high specificity to breast cancer cells expressing distinct levels of this receptor. Furthermore, PMVs can express various other natural and engineered transmembrane proteins to selectively target cell surface proteins. As an example of the generality of this approach we created PMVs expressing a single domain antibody against GFP and showed specific binding to GFP-tagged receptors. Our results demonstrate the versatility of PMVs as targeted drug delivery systems. Further, PMVs provide an approach to insert intact and functional transmembrane proteins into liposomal materials. Moving forward, these capabilities will enable the development of multi-functional bio-material systems that control the fate of cells and tissues by participating in cellular communication and signal transduction.



A. Cellular blebbing B. PMVs selectively bind EGFR overexpressing cells C. Binding correlates with receptor expression

COLL 581

Characterizing polymeric micelles employed for DDS combining SAXS and FFF

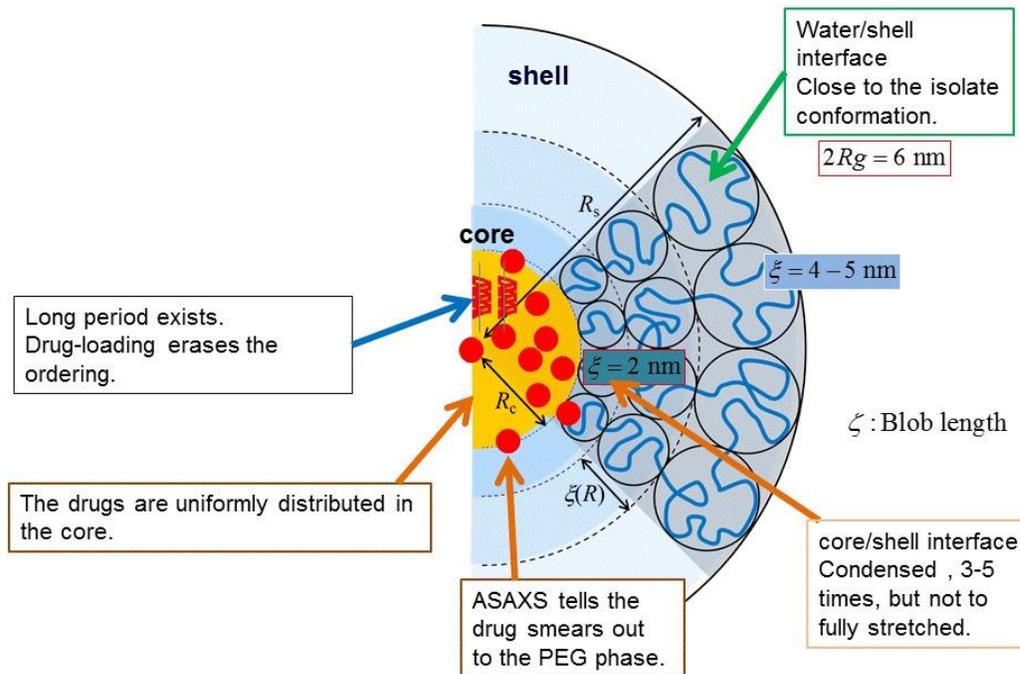
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Polymeric micelles have been extensively studied as nano-scale drug carriers. The studies of the micellar inner-structures that encapsulate hydrophobic drugs is important to design effective carrier. Poly(ethylene glycol)-block-poly(partially benzyl-esterified aspartic acid) is one of the most studied systems from both synthesis and biological aspects. However, little know about fundamental physical properties. We synthesized various samples with different compositions and characterized them with field flow fractionation (FFF) and synchrotron small-angle X-ray scattering (SAXS).

We found that the major factor to determine the micellar structures and the aggregation number is the benzylation rate of the core block: hydrophobicity of the core. By knowing the aggregation number and the core size, we can determined how the tethered PEG chains are overcrowding. We are first to quantitatively correlate the PEG-chain crowdedness and biological activity of the micelles.

We also used as hydrophobic compound tetrabromocathecol (TBC) as a drug-equivalent model molecule. The bromine atoms in TBC act as probes in anomalous small-angle X-ray scattering (ASAXS) allowing for its localization in the polymeric micelles. We found that the radius of the spherical region populated with bromine atoms was larger than the one of the sphere corresponding to the hydrophobic core of the micelle. This result suggests that the TBC molecules infiltrate the PEG hydrophilic domain in the vicinity of the core/shell interface.

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COLL 582

Filomicelles self-assembled from degradable di-block copolymers delay clearance *in vivo*, and deliver retinoids & chemotherapeutics in irreversible control of carcinoma cell fate

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Conventional injection of semi-soluble drugs hit both healthy and tumor cells, causing side effects that limit dose. This approach might be broadened with better delivery, and herein, flexible ‘filomicelles’ demonstrate effective delivery of two very different hydrophobic compounds. Retinoic acid (RA) and other retinoids regulate RA receptor transcription factors that induce differentiation and arrest proliferation of many cell types, including cancer cells. Lamin-A is transcriptionally regulated by RA receptors, and as a structural protein surrounding chromatin, lamin-A can affect differentiation and karyokinesis as well as nuclear viscosity. Paclitaxel, on the other hand, stabilizes microtubules and induces aneuploidy by blocking mitosis at the metaphase-anaphase

transition, which greatly increases cell death. When cancer cells are treated with either of the drugs alone over several periods of the normal cell cycle, cancer cell populations revert back to the original proliferative state, consistent with relapse commonly seen after conventional chemotherapy. On the other hand, combining RA with select chemotherapeutics has for several decades produced durable cures of select cancers, notably pro-myeloblastic leukemia (PML) where RA differentiates cells while chemotherapeutic kills the cancer stem cell. With carcinoma lines, we find dual treatment with RA plus Paclitaxel increases lamin-A levels, aneuploidy, and cell death beyond those achieved by either drug single-handedly, with effects appearing irreversible. Trends with the key cell cycle factor Cyclin-D1 and proliferation marker Ki-67 help clarify the basis for drug synergy. These effects are greatly enhanced by loading the drugs into the abovementioned filomicelles. Self-assembled from degradable di-block copolymers of Polyethylene glycol-Polybenzyl caprolactone (PEG-PBCL), the aromatic polymer improves performance over other conventional aliphatic ones due to better loading of chemotherapeutics in its aromatic core. Flexible 'filomicelles' delay clearance by phagocytes, allowing them to circulate longer and accumulate in the tumors, thus increasing the efficacy of delivery over other nano-carriers. Preliminary tests in vivo demonstrate sustained delivery for days as well as efficacy in shrinking tumors. These results highlight the irreversible synergy of killing cancerous cells while driving differentiation.

COLL 583

Immunomodulatory activity of colloidal supramolecular particles made from guanosine derivatives

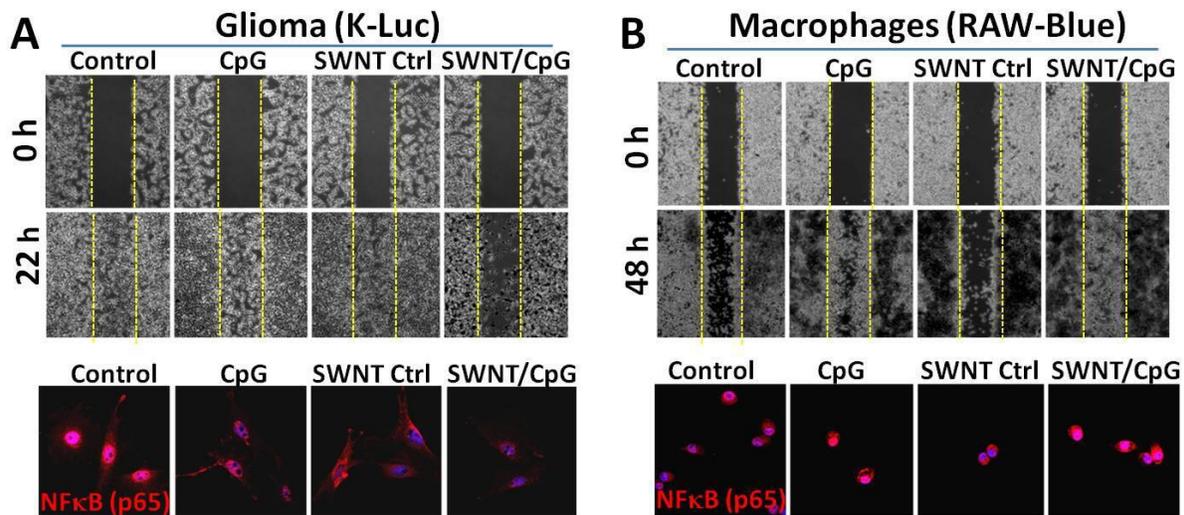
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Despite the many reports of using novel colloidal particles in to modulate the immune system to treat or prevent diseases, there is still a large gap in their translation to the clinic. Some of the main reasons for this is the difficulty for many said systems to be manufactured reliably and in large enough scale. We will present our results on the development of a new family of colloidal particles we term supramolecular hacky sacks (SHS) that are readily made from the self-assembly of guanosine derivatives (8ArGs). We will present the synthesis and characterization of a small library of these SHS particles and will show that they are suitable for the encapsulation and cellular delivery of a number of biologically active molecules including anti-cancer drugs, polysaccharides, DNA and proteins. Furthermore, we will show results that indicate that the SHS have very promising in vitro and in vivo activity as immunomodulators, as well as vaccine adjuvants and delivery agents. We will discuss how some of these SHS particles could overcome the translational gap because of the following features: (a) small-molecule based technology; (b) easily customizable and suitable for structural activity relationships (SAR) studies; (c) the most promising 8ArGs could be readily scaled up to perform further development aimed a clinical applications.

Carbon nanotube-based immunotherapeutic both enhances immune stimulation and inhibits tumor migration

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CpG oligodeoxynucleotides are a well-known group of immunostimulatory DNA sequences that have been studied in both cancer immunotherapy and vaccines. Previously, we have shown that the immunotherapeutic efficacy of CpG treatment in a mouse glioma model was enhanced by conjugation of the CpG sequence to single-walled carbon nanotubes. While investigating this treatment in a more aggressive orthotopic brain tumor model (K-Luc), we made a serendipitous discovery: the CpG-carbon nanotube conjugate also appeared to inhibit tumor invasion *in vivo*. To study this phenomenon more closely, an *in vitro* wound healing assay was utilized. A library of variants was synthesized and screened in order to probe the structure-activity relationship of the CpG-carbon nanotube conjugate. From this screening study, we determined that the original conjugation chemistry was unnecessary and that single-walled carbon nanotubes simply dispersed in CpG (SWNT/CpG) was the minimal necessary construct. Interestingly, the effects of SWNT/CpG are cell type specific. In K-Luc glioma cells, SWNT/CpG treatment caused inhibition of cell migration. However when an identical SWNT/CpG treatment was given to a macrophage cell line, it caused enhancement of cell migration. Preliminary mechanistic investigations indicate that SWNT/CpG may exert its effects through modulation of both NFκB activity and intracellular levels of reactive oxygen species.



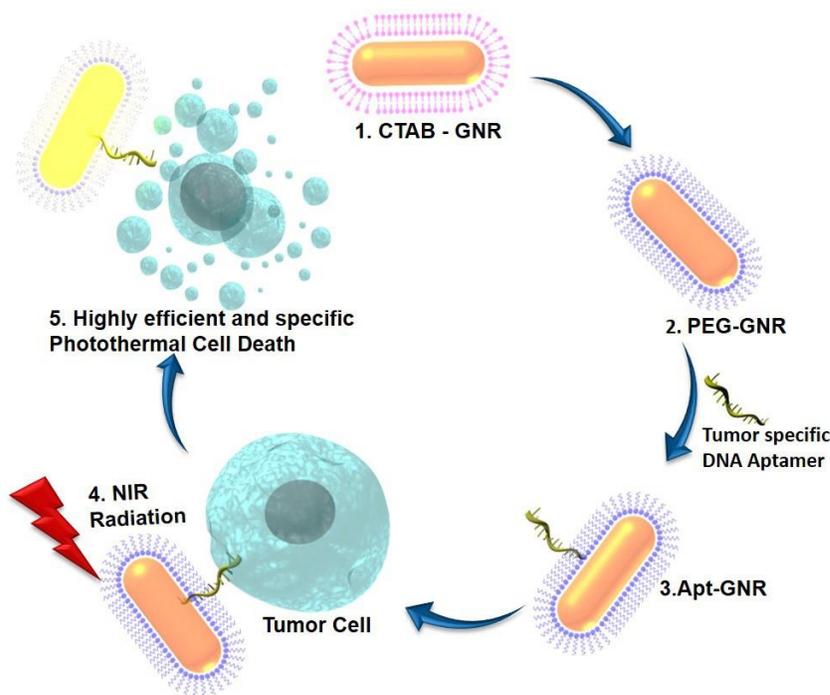
Dual antitumor activity of SWNT/CpG. **A**, SWNT/CpG (but not free CpG or SWNT Ctrl) inhibited the migration (upper panel, scratch assay) and NF κ B activity (lower panel, immunofluorescent stains) in K-Luc gliomas. **B**, In contrast to gliomas, macrophage migration and NF κ B activity was enhanced by SWNT/CpG.

COLL 585

Selective photothermal killing of tumor cells by SELEX-derived DNA aptamer-targeted gold nanorods

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Highly specific recognition towards tumor cells is necessary to establish a treatment that does not affect the surrounding healthy cells which have a similar genotype in the tissue cell population. The available cytotoxic chemotherapeutic agents remain elusive in this fact. Recent developments in terms of plasmonic nanoparticles capable of photothermal killing have some promise when targeted to tumor cells. Targeting moieties like antibodies, folic acid, peptides are not truly tumor specific as their epitopes or receptors are usually expressed in normal cells, but to a lesser extent. In this work, we have demonstrated the use of novel, tumor specific DNA aptamer- tethered gold nanorods (GNRs) for targeted plasmonic photothermal therapy (PPTT). For the first time we have used isogenic tumor and normal cells for direct comparison to ensure high tumor specificity of our aptamer. The aptamer KW16-13 selected through a modified Cell-SELEX process, showed high specific uptake by MCF10CA1h human breast ductal carcinoma cell line but not by their isogenic normal counterpart MCF10A. When attached to gold nanorods, the KW16-13-GNRs showed strong internalization by the tumor cells with minimal uptake by the normal cells. This Apt-GNRs upon near infrared (NIR) light irradiation photothermally destroyed >96% of the tumor cells compared to only < 1% of the normal cells. Our KW16-13 aptamer-targeted GNRs thus showed >71-fold tumor cell death than GNRs-targeted with a previously described aptamer. The cell viability after irradiation monitored by flow cytometry showed that KW16-13-GNRs caused >71% tumor cell death endorsing its specificity and photothermal efficiency. This demonstrates the significant potential of our Aptamer functionalized-GNRs as selective and effective theranostic agent for both molecular imaging and photothermal cancer therapy.



COLL 586

Development of capecitabine microspheres for colorectal cancer

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Capecitabine, a prodrug of 5-fluorouracil, is widely employed drug for the treatment of early and advanced colorectal cancer. The conventional Capecitabine tablets (Xeloda®) are administered twice daily at a recommended dose of 2500 mg/m². Hence, the aim of the present work was to formulate sustained release multiparticulate systems for once daily dosing. The microspheres were prepared by emulsion solvent evaporation method using ethylcellulose and HPMC as sustained release polymers. A 3² full factorial design was employed to study the effect of independent variables, ratio of ethyl cellulose and HPMC (X₁) and concentration of Span 80 (X₂) on dependent variables, namely- mean particle size (Y₁) and % Entrapment efficiency(Y₂). The microspheres were evaluated in terms of particle size, flow properties, drug content, *in vitro* drug release, % entrapment efficiency and surface morphology. The experimental results of optimized batch exhibited particle size of 319.23 μm. %EE was found to be 79.86 % and drug release was found to be 100.94 % in 24 hours. Scanning electron microscopy images suggested that the microspheres are small, spherical and discrete. Accelerated stability studies showed no significant change in the mean particle size, % entrapment efficiency and drug release after storage at 40°C/75% RH for the period of three months. The

developed formulation has reduced frequency of administration with improved patient compliance and may lead to reduction in dose and dose related side effects.

COLL 587

Deliberate design of optical properties in DNA-programmed nanoparticle superlattices

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The manipulation of matter on the nanoscale provides a means to achieving material properties that are difficult or impossible to achieve in the bulk state. Progress toward nanoscale architectures with tangible utility requires (1) the development of methods to controllably and precisely locate nanoscale objects in multiple dimensions and (2) the formation of rigorous structure-function relationships across multiple size regimes. We use DNA as a programmable ligand to arrange metallic nanoparticles into two- and three-dimensional crystalline superlattices with predictable optical properties. By controlling the spacing between gold nanoparticle building blocks, the superlattices can be transitioned from exhibiting the properties of the constituent plasmonic nanoparticles to adopting the photonic properties dictated by the mesoscale crystal habit. Multiple theoretical frameworks, including effective material approximations that assume material homogeneity and explicit electrodynamics simulations, illustrate that the properties of DNA-programmed nanoparticle superlattices can be predicted *a priori* and deliberately designed to have a myriad of functions, including tunable color, photonic scattering, and precisely controlled reflectivity. Together, this work provides a path toward the rational and deliberate design of new materials with exciting optical properties, including those that cannot be found in nature.

COLL 588

Directed movement of magnetic nanoparticle-loaded immune cells using a compact 3D printed chamber

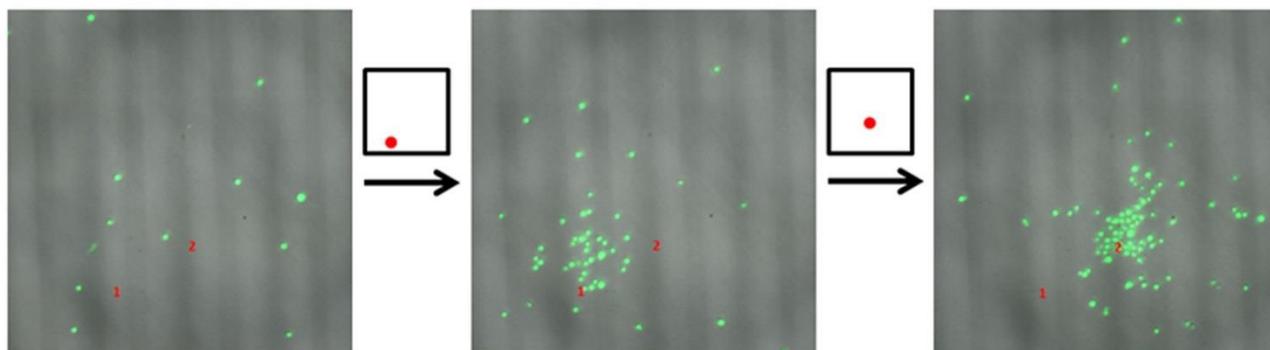
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Brain cancer treatment is one of medicine's biggest challenges. Median survival is only 1-2 years even after surgery, radiation and chemotherapy. The immunotherapy approach has been studied as a treatment due to its high degree of selectivity and long-

lasting memory of the immune system which will prevent local tumor recurrence. City of Hope is currently carrying out a first-in-humans study that investigates chimeric antigen receptor (CAR)-T cells in injection form, administered directly to brain tumors. Despite the great potential offered by immunotherapy for brain cancer, the retention and homing of CAR T cells at tumor sites remains a major hurdle.

Our ultimate goal is to direct magnetically-labeled CAR T cells to brain tumors under a programmable magnetic field.

Here, we propose a method for loading magnetic nanoparticles (NPs) to cells *in vitro* and testing their directed movements using a device that generates dynamically programmable magnetic fields (DPMF). First, we synthesized and characterized two types of colloidally-stable magnetic iron oxide NPs that were used to load THP-1, neural stem cells, and CAR T cells. We then demonstrated the construction of a 3D printed cell chamber that allows culturing, manipulating and imaging NPs as well as cells loaded with magnetic NPs. The system can dynamically actuate over a wide variety of magnetic field profiles and can toggle between them. Moreover, this system provides a research tool for the magnetic manipulation NPs and cells in a bulk media solution. We were able to load all three cell lines with magnetic NPs, perform live imaging experiments under the DPMF in the cell chamber, and demonstrate movements in response to the magnetic field. This proof-of-principle work verified that the DPMF can be used to move immune cells in a controlled fashion *in vitro*. Current work focuses on the development of a 3D helmet that will be used to move magnetically-labeled cells *in vivo*.



COLL 589

***In vivo* renewable persistent luminescence nanoparticles**

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Persistent luminescence, also called afterglow/long-lasting phosphorescence.

Persistent phosphors usually possess super-long lifetimes over hours or even days, while the lifetimes of common fluorescent dyes are within microseconds. A most famous example of this phosphor is legendary luminous pearls, the gemstones that glow in the

dark. Prior to our work, they must endure high-temperature solid-state annealing reactions and subsequent complicated physical post-treatments. We now report on simple direct aqueous-phase chemical synthesis route to NIR PLNPs and present their enhanced in vivo renewable NIR PL. Our method leads to monodisperse PLNPs as small as ca. 8 nm. Such nanoparticles emit photons in the optical bio-imaging window (~650-1000 nm) and provide vivid images after a brief LED excitation through deep tissue of live mouse. This signal gradually decreases in 30 minutes after excitation without influencing the next imaging cycle, and it then can be reactivated repeatedly at any desired time point.

Compared to other existing in vivo optical imaging probes, such nanoparticles possess an outstanding signal-to-noise-ratio with no need for the excitation resource (light) during the imaging and can be directly adapted to the commercially available imaging systems. We believe that their superior performance and unique luminescence renewability provides numerous unprecedented opportunities in medical imaging, diagnosis and that of therapy.

COLL 590

Mechanistic investigation into the effect of DNA in shape control of metal nanoparticles

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Controlling the shape and size of metal nanoparticles such as Ag, Au, Pt, and Pd enables the fine tuning of their inherent physical and chemical properties. This translates to more effective use of these materials for various applications such as imaging and catalysis. The ligand employed during the synthesis of metal nanoparticles plays an important role by influencing the rates of precursor reduction and providing facet stabilization. Our lab has been exploring the use of DNA as a ligand in nanomaterial synthesis by extending the function of DNA beyond its traditional role as a genetic material.¹ Given DNA's excellent sequence programmability with the four nucleotides cytosine (C), guanine (G), adenine (A) and thymine (T) and its ease of chemical modification, DNA can serve as an ideal candidate for nanoparticle shape control. Recently we have also demonstrated successfully that DNA can be used as a ligand for shape control of gold² and silver³ nanoparticles. In the case of the overgrowth of gold nanorods (AuNRs) in the presence of DNA it has been shown that by programming the combination DNA sequence used, the corresponding LSPR peak of the final nanoparticle can be tuned.⁴ We have also expanded the scope of DNA-mediated shape control into bimetallic nanoparticle systems.

The use of DNA oligomers on the growth of gold nanoprisms results in interesting shapes such as rough round, six-pointed star, hexagon and smooth round shapes respectively, for A, T, G and C pristine oligomers. Despite the interesting finding, the mechanism of DNA mediated growth remains unclear. We have focused on elucidating the role of DNA using spectroscopic and microscopic characterization of particle growth

kinetics.⁵ The extent of growth was found to be correlated to the trend of binding affinity of the bases to gold surfaces (A>C>G>T). The role of DNA binding to the nanoprism seed and the gold precursor in guiding the nanoparticle growth is comprehensively explained.

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COLL 591

Bimetallic nanostructures as artificial peroxidases for sensitive colorimetric detection of cancer biomarkers

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Introduction: Artificial peroxidase (peroxidase mimics) with dimensions at the nanoscale have received great interest as emerging artificial enzymes for biomedicine and environmental protection. While a variety of peroxidase mimics have been actively developed since 2007, limited progress has been made toward improving their catalytic efficiency.

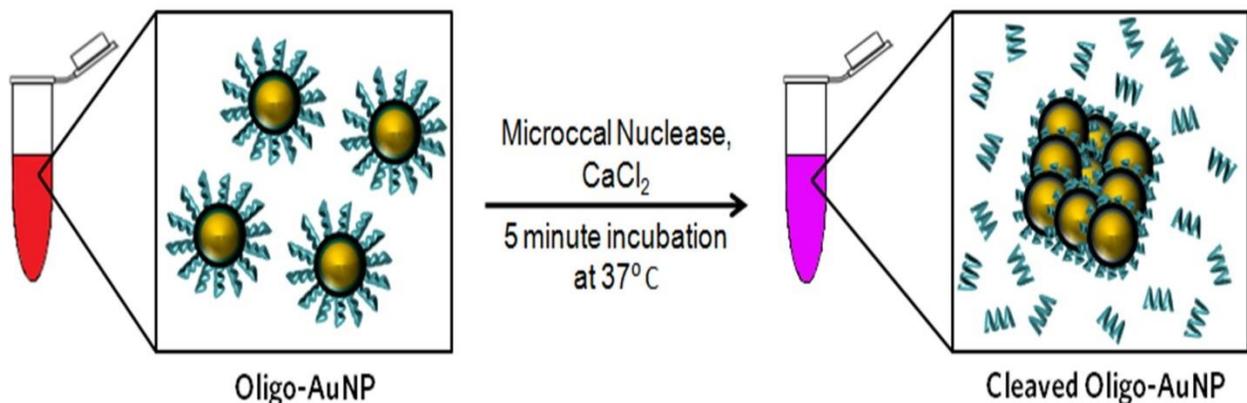
Methods and Results: In our recent work (*ACS Nano*, 2015, DOI: 10.1021/acs.nano.5b03525), we reported a novel type of peroxidase mimic with record high efficiency. Our peroxidase mimic was engineered by depositing Ir atoms as ultrathin skins (a few atomic layers) on Pd nanocubes (i.e., Pd-Ir cubes) using seed-mediated growth method. The Pd-Ir cubes exhibited significantly enhanced efficiency that is over 20- and 400-fold higher than those of the initial Pd cubes and horseradish peroxidase (HRP), respectively. As a proof-of-concept demonstration, the Pd-Ir cubes were applied to the colorimetric enzyme-linked immunosorbent assay (ELISA) of human prostate surface antigen with a detection limit of 0.67 pg/mL, which is ca. 100-fold lower than that of the conventional HRP-based ELISA using the same set of antibodies and the same procedure.

Discussion: The Pd-Ir cubes presented in this study show the highest peroxidase-like efficiency among all the reported peroxidase mimics with comparable sizes. To understand the observed enhancement in catalytic efficiency, related experiments and density functional theory (DFT)-based theoretical calculations were conducted. The results indicated that the deposition of an ultrathin skin of Ir on Pd cubes could increase both the efficiency in decomposing H₂O₂ to hydroxyl radicals and the binding affinities of key chemical species in the reaction, which were believed to be responsible for the enhanced peroxidase-like efficiency.

Selective colorimetric detection of *Staphylococcus aureus* using oligonucleotide-functionalized gold nanoparticles

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Staphylococcus aureus (*S. aureus*) affects more than 500,000 people each year in the U.S. It can cause potentially life-threatening infections if not detected and treated promptly. Current clinical methods for diagnosing *S. aureus* require culturing the bacteria and take days to complete. This is a significant limitation in the setting of treating patients with life-threatening infections as well as evaluating food and water sources that may be contaminated. Novel methods for rapid and selective detection of *S. aureus* have been reported, including our work using a short DNA oligonucleotide as a fluorescent probe for micrococcal nuclease (MN), which is specifically expressed by *S. aureus*. However, this probe and alternative strategies for rapid and selective detection, such as PCR or liquid chromatography-tandem mass spectrometry, all require sophisticated instrumentation. There is a pressing need for a portable, simple point-of-care diagnostic for detecting *S. aureus*. Here, we demonstrate that oligonucleotide-functionalized gold nanoparticles (Oligo-AuNPs) can be used to rapidly and selectively detect *S. aureus* through a change in color. The particles can be stored as a lyophilized powder and reconstituted at time of use. This approach requires no extraneous instrumentation or prior sample preparation and has a rapid diagnostic read-out that could be used in clinical settings for testing patient samples or in field tests to monitor food and water sources.



Micrococcal nuclease cleaves the oligonucleotides functionalized on the Oligo-AuNPs causing aggregation to occur and the solution to change from red to purple.

Novel method based on photothermal cleavage of thermolabile molecules on Au nanoparticles for controlled release

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New methods for the controlled delivery of chemical and/or biochemical species using low-energy visible light present major facilities in photo-dynamic therapy[1], photothermal therapy[2] and photolithography[3]. Gold (Au) nanostructures absorb light of particular frequencies and then convert into heat due to photothermal characteristics[4]. This property has been effectively used to trigger cancer cell death[5] within the surroundings of the nanoparticles.

We recently develop a novel drug release method based on the photothermal effect of Au nanoparticles (AuNPs). We demonstrated the precisely controlled delivery of a molecule (i.e. cancer drug) from AuNPs via cleaving the thermolabile chemical bonds by controlling the power density and irradiation time of the light source. The gold nanospheres were synthesized by using Turkevich method using sodium citrate[6]. The thermolabile molecules are composed of thermolabile covalent bonds and a thiol/disulfide group for gold conjugation. Newly synthesized thermolabile dye molecule was used for the preliminary release study because of easy detection of the released cargo by using UV-Vis spectrophotometer. The release profiles of the organic dye and cancer drug from thermolabile molecules on the AuNPs were successfully demonstrated using different power density of a laser at constant duration or constant power density at different time intervals. When the laser is turned off, heating or cleavage of thermolabile molecules will immediately cease. Thus, we can control the release dosage by manipulating the power density and/or irradiation time of laser.

ACKNOWLEDGEMENTS

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COLL 594

Plasmonic modulation of fluorescence in gold nanostar-NaYF₄: Yb/Er for multimodal imaging, photothermal, and photodynamic therapy

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Developing methods to effectively integrate rare earth doped upconverting nanoparticles (UCNPs) with gold nanostructures are currently being sought for nanoscale theranostics due to their ability to convert near infrared (NIR) photons into visible light and heat. Because the large NIR absorption cross-section of the gold nanoparticles can significantly hampers the photoluminescence of UCNPs, methods to optimize the ratio of gold nanostructures to UCNPs must be developed and studied. Herein, we demonstrate nucleic acid assembly methods to conjugate spherical gold nanoparticles (AuNPs) and gold nanostars (AuNSs) to silica-coated UCNPs and investigate their effect on upconversion photoluminescence. In these studies, the number and type of Au nanostructure were found to play significant roles in modulating the optical output from the UCNPs. The results showed that while UCNPs fluorescence enhancement was observed from the AuNP-UCNPs clusters, to a large extent fluorescence quenching was observed for the AuNS-UCNP assemblies. However, by tailoring the ratio of AuNS to UCNPs, we found that little photoluminescence quenching was observed. More importantly, at these AuNSs concentrations, we were still able to observe a large temperature increase induced by the AuNSs upon 980nm irradiation. The optical measurements were also confirmed by simulation studies which demonstrated that the orientation and distance of the UCNPs with respect to the core and arms of the gold nanostructures played significant roles in photoluminescence. Finally, more recently we have loaded photosensitizers into the silica shells on the UCNPs whose absorption spectra matched well with emission of UCNPs to generate measureable quantities of singlet oxygen for photodynamic therapy. The combined photodynamic and photothermal effects the AuNS-UCNP clusters can potentially enable their eventual use as highly effective photodynamic and photothermal therapy imaging agents for nanomedicine.

COLL 595

Layer-by-layer assembled gold nanoring-photosensitizer complex for enhanced photodynamic therapy in the near infrared

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A gold nanoring (Au NR)-photosensitizer (PS) complex was developed for near-infrared (NIR) photodynamic therapy (PDT). A layer-by-layer (LbL) assembly strategy was used to incorporate high concentrations of Al(III) phthalocyanine chloride tetrasulfonic acid (AIPcS₄) PS onto plasmonic Au NRs for increasing the cellular uptake of AIPcS₄ and subsequently enhancing the efficacy of PDT of human breast cancer cells (MDA-MB-231) in the NIR range. We showed that Au NRs with two layers of AIPcS₄ (Au NR/(AIPcS₄)₂) markedly increased the cellular internalization of AIPcS₄ and elevated the generation of reactive oxygen species (ROS). Quenching the photosensitivity of AIPcS₄ on the Au NR surface during the uptake and then significant ROS formation only upon PS release inside the cellular compartment made it possible to achieve a high PDT specificity and efficacy. PDT of breast cancer cells following 4 h of incubation with various formula revealed the following cell destruction rate: ~10% with free AIPcS₄, ~23% with singly layered Au NR/(AIPcS₄)₁ complex, and ~50% with doubly layered Au NR/(AIPcS₄)₂. Incubation with Au NR/(AIPcS₄)₂ for an additional 2 h resulted in ~85% cell killing, more than 8-fold increase compared to AIPcS₄ alone. Together, synergistic integration of LbL of PS with Au NRs holds a significant promise for PDT therapeutic treatment in various cancers.

COLL 596

Biogenic silver metal nanoparticle enhanced bioassays

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A wide range of biological analyses employ nanoparticles (NPs) to enhance detection. In particular, metal NPs have become useful for labeling and enhanced spectroscopy due to their size dependent optical properties. Surface plasmon excitation of NPs principally underpins optical detection methods. We and others have shown that chemically modified spherical gold NPs can be used as extrinsic labels for surface enhanced Raman scattering (SERS) detection of surface based assays. Thus far, all assays have used chemically synthesized NPs and routes to modify these NPs are well established. In this presentation, we will describe our efforts to incorporate biogenic spherical silver metal NPs as plasmonic labels for enhanced spectroscopy applications. Biogenic silver NPs are stabilized with a surface corona that is unique relative to their chemically prepared counterparts. We will present our results that characterize this layer as a mixture of protein and carbohydrate. Chemical properties of the corona presents interesting opportunities for surface modification of biogenic silver NPs. Potential advantages of a native biomolecular layer include simpler or milder modification strategies compared to chemically prepared NPs. Our efforts to modify the surface layer and demonstrate the use of antibody-conjugated nanoparticles in

sandwich immunoassays will be presented. Also, choice of substrate is being explored to enhance plasmonic coupling with the NP label. Finally, our preliminary results in developing a companion diagnostic assay for prostate cancer treatment will be presented.

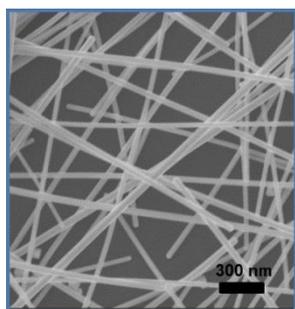
COLL 597

Transparent flexible electrodes based on copper and silver nanowires integration into devices and stability study

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This report deals with on the synthesis, purification and use of silver or copper nanowires to fabricate flexible transparent electrodes.¹⁻³ The performances of these electrodes are excellent, typically less than 20 ohm/sq at 90 % transparency. These electrodes have been integrated in various optoelectronic devices. We will show that it affords a large area, low-cost deposition method, with good performances in devices such as organic photovoltaic cells and flexible touch sensors . We will also present results dealing with the use of such electrodes to realize transparent film heaters (TFH), with very good performances.⁴ This solution-processable technique appears as a really promising alternative to ITO (indium tin oxide), and stability issue has now to be tackled. We will present results about the stability of these electrodes in particular with regard to environmental stresses.⁵

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COLL 598

Understanding the properties of electroactive poly (amic) acid membranes, their interaction with nanoparticles and applications

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Our laboratory at SUNY-Binghamton has discovered a new class of nanostructured, π -conjugated, poly (amic) acid - PAA. The uniqueness of PAA lies in its excellent chromatic, electronic, biodegradable and mechanical properties. PAA membranes showed remarkable potential as sensors for engineered nanoparticles. However its conductivity, conjugation and electroactivity have been hampered by the structure of one of the monomers. This talk specifically focuses on understanding the properties of different forms of poly (amic) acid, their interaction with nanoparticles (Gold and silver) and the applications of both PAA polymer and PAA-nanoparticle composites.

COLL 599

Organic surface functionalization technique for colloidal silver nanoparticles designed to inhibit precipitation caused by hydrogen sulfide gas

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Studies of metal toxicity to sulfate reducing bacteria (SRB) have proved challenging due to rapid formation of metallic sulfide precipitates fueled by the bacterial production of hydrogen sulfide gas. This effect limits the bioavailability of the metal to the SRB and severely hampers the accuracy of toxicity assays. Growth mediums designed to eliminate abiotic metallic precipitation have been developed for these studies, though they are poor analogs to *in situ* SRB growth. A new method of preventing metal sulfide formation was developed that utilizes standard growth media for SRB. Silver (Ag) nanoparticles were surface modified using organic functionalization by sodium acrylate molecules. The functionalized particles have been qualitatively shown to inhibit precipitation with >99% efficacy when introduced to standard ATCC 2755 and 1249 Baar's growth media for SRB; NMR precipitation studies are underway to provide more quantitative data. In addition, the surface modification of the particles does not degrade the toxic effect to SRB; 50% inhibition in maximum specific growth rate is seen at metal concentrations of approximately 15 μ M.

COLL 600

Surface engineering of two-dimensional 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 [1], black phosphorus [2], and transition metal dichalcogenides [3].

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COLL 601

Directed assembly of 1D nanostructures on lithographically patterned surfaces

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The essence of nanotechnology is to fabricate and manipulate well-defined structures on the nanometer scale with high accuracy.¹ The integration of nanotechnology with material science, bioengineering and traditional lithography fabrication is a powerful route to create advanced, low-cost nanodevices for both optoelectronic and biotechnological applications.

Biological molecules, such as DNA, have shown great potential to precisely control functional materials at the scale of individual molecules.^{2,3} Advancements in this field of

study are of interest for the fundamental understanding of the interaction between materials, as well as for the fabrication of more complex electronic circuits. We have successfully assembled 1D DNA nanostructures with high precision via DNA hybridization in situ on properly lithographically patterned and selectively functionalized surfaces.⁴ Now we get a step forward towards the controlled and ordered assembly of 1D carbon nanotube from solutions to surfaces.⁵ Specifically, we explore the binding of single walled carbon nanotube (SWCNT) to lithographically defined nanoscale metal dots anchors,⁶ which can be selectively functionalized by single stranded DNA (ssDNA) or amine-ended polymers. Fixed-length, DNA wrapped and end-functionalized SWCNT with carboxyl group were indeed attached to nanodot anchors using covalent and noncovalent binding chemistries. Both monovalent and bivalent binding of SWCNT to nanodot pattern are explored. This represents a new approach that could pave the way toward complex SWCNT devices and circuits.

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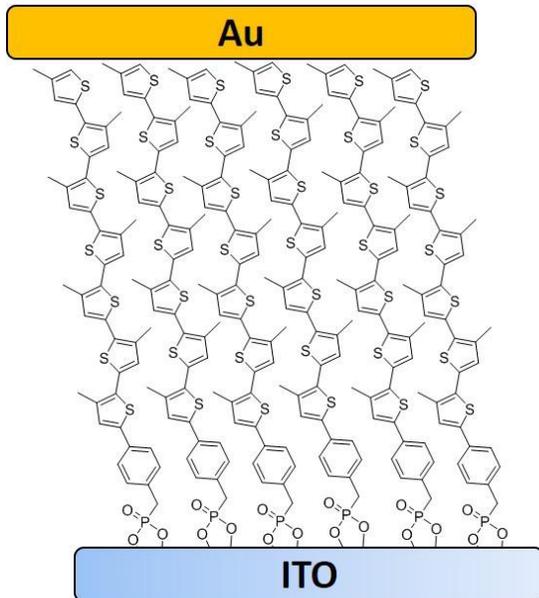
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COLL 602

Constructing molecular electronic devices incorporating organic molecules: From simple alkanes to conjugated polymers

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This talk intends to summarize our ongoing efforts in applying transfer printing techniques (including nano transfer printing and kinetic transfer printing) to construct electrode-molecule-electrode (EME) junctions, which serve as a versatile platform to investigate the electron/spin transport behaviors of organic molecules. With this platform, we have studied alkanes, oligophenylenes, oligo-metalporphyrins, and more recently, poly(3-methylthiophenes) (Figure 1). We will explain in detail how we construct the devices, the quality of as-constructed thin films, and the transport results on individual materials. Our results indicate that the nature of molecules indeed plays a crucial role in manipulating the electrical behavior of these EME junctions.



COLL 603

Lead sulfide quantum dot/lead halide perovskite heterostructures from a single colloidal suspension

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Surface passivation of semiconductor quantum dots is essential to preserve their efficient and robust light emitting properties. While molecular ligands in colloidal systems can retain efficient emission, core/shell structures are usually required to approach photoluminescence quantum yields near 100% in solution. Most electronic applications, however, require high performance in the solid state, where quantum yields are generally lower than in colloidal suspensions. By using a lattice matched (mismatch = 0.5%) lead halide perovskite matrix, we achieve shell-like passivation of lead sulfide QDs in crystalline films, leading to high solid state infrared quantum yields. These structures are made from a simple one-step spin coating process of an electrostatically stabilized colloidal suspension. Photoluminescence and transient absorption spectroscopy indicate rapid energy transfer between the perovskite matrix and the QDs, suggesting an interface with few trap states. In addition to housing the efficient infrared QD emitters, lead halide perovskites themselves have good carrier mobilities and low trap densities, making these solution-processable heterostructures an attractive option for electrically pumped light emitting devices.

COLL 604

Colloidal precursors to ultra-thin-film photovoltaics

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Our work in chalcogenide nanostructured colloids for printable photovoltaics has demonstrated that such solution-based nanomaterials are feasible for fabricating absorber materials that require specific stoichiometry, which could be priority embedded in the nanostructure composition. The depression of melting point owned to size confinement and high surface reactivity enables annealing at temperature below glass melting point and leads to polycrystalline layers with high surface uniformity and controlled thickness. The presentation will highlight our recent work in identifying the best nanoprecursor morphologies in forming ultra-thin film absorbers with thickness below 100 nm, an endeavor related to materials that have very large extinction coefficient such as Fe₂GeS₄, Fe₂SiS₄, lead perovskite-based materials, etc. Solution-based Nanoprecursors to Fe₂GeS₄, GeS₂, FeS₂, and perovskite-based materials are just a few examples that will be discussed, from their synthesis and dispersion in stable inks to films fabrication as well as to stability of as-made films during further processing steps.

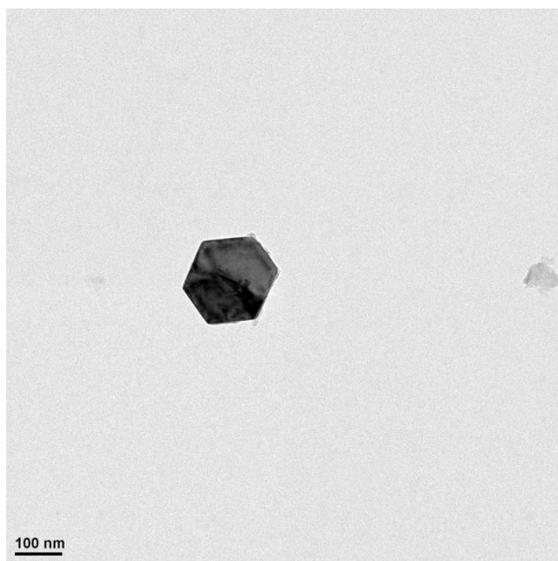


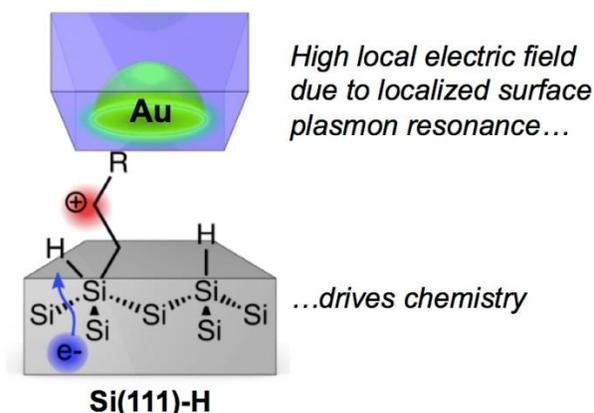
Figure 1. Fe₂GeS₄ Hexagonally Shaped Nanoplatelet

COLL 605

Making connections between molecules and silicon

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Interfacing molecules with silicon is of enormous interest for applications in molecular electronics, for passivation of the surface, for integration of silicon devices with tissues, and further miniaturization of feature sizes of transistors on silicon into the sub-10 nm regime. The formation of silicon-carbon bonds is a practical and commonly used approach to chemically functionalize the surface of silicon due to the stability of the Si-C bond, and the surprisingly diverse number of distinct mechanisms, and hence reaction conditions, that can be harnessed to enable this chemistry. For instance, illumination of a hydrogen-terminated silicon surface in the presence of an alkyne or alkene was, at least initially, expected to proceed via a radical mechanism, in much the same manner as silicon-based molecules (silanes, R_3Si-H for instance). Research over the past decade has shown, however, that the mechanisms in operation are far more diverse, and the chemistry much richer, than ever thought. The underlying electronics of the silicon play an important role in enabling the chemistry of the surface, and under many circumstances, can dominate. In this talk, we will discuss the latest developments in the surface chemistry of silicon that provide practical avenues for exquisitely precise integration of molecules with silicon surfaces. From the use of surface plasmons, to nanopatterning, to bonding via exotic elements (such as Si-S and Si-Se bonds), silicon continues to surprise.



COLL 606

Hydrogenated graphene for surface engineering and transfer

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Chemical functionalization dramatically alters the chemical and physical properties of graphene. For instance, extensive hydrogenation of graphene using a dissolving metal

reduction essentially eliminates the material's electronic conductivity, but graphene can be recovered cleanly through either thermal annealing or mild chemical oxidation.¹ Partially hydrogenated graphene exhibits room temperature ferromagnetism by introducing unpaired spin centers onto the lattice.² Hydrogenating graphene also weakens the van der Waals force between graphene and substrate; as a result, hydrogenated graphene delaminates cleanly from a substrate, and we have used this feature to transfer chemical and physical properties of the functionalized graphene surface intact from one substrate to another. By combining this delamination with the reversibility of hydrogenation, we have developed a transfer protocol for chemical-vapor deposited (CVD) graphene that avoids polymers and chemical etchants, resulting in an ultraclean graphene surface, as corroborated by spectroscopy and optical and electron microscopy.³

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COLL 607

Organometallic molecular compound integrated into a memory device by “click” chemistry

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With the explosive demand for personal electronic devices such as phones and tablets, the growth in Flash-based memory has also increased dramatically. However, the dimensional scaling of memory devices faces many critical material limitations. An essential component to the memory device is the floating gate or charge trapping layer. One approach to achieve nanometer-scale charge trapping is to use organic molecules.^{1, 2, 3} Reduction-oxidation (redox) active and organic molecules hold potential for memory devices due to their sub-nanoscale dimensions, discrete nature, and tailor-made electronic properties.

Here, we have incorporated a novel diruthenium-based redox molecule into a Flash-

based memory device architecture. The diruthenium(II,III)tetrakis(2-anilinopyridinate) (Ru_2) was attached to the SiO_2 tunneling layer by using a “click” reaction⁴ which allows for a modular approach to building molecular interfaces, and does not strictly rely on self-assembly. X-ray photoelectron spectroscopy confirmed the Ru_2 attachment and molecular density at the surface. Ultraviolet photoelectron spectroscopy identified the occupied electronic levels of the molecular interface before and after “click” reaction. To complete the memory capacitor device, an Al_2O_3 layer is deposited over the molecular layer and then a metal gate. The final memory capacitor device consists of a Pd/ Al_2O_3 /molecule/ SiO_2 /Si structure.

These Ru_2 -based molecular memory devices display a large memory window and an unsaturated charge storage window in high frequency capacitance-voltage measurements. The programming and erasing speeds are suitable, but can likely be improved by changing the molecular structure or shortening the distance between the Ru_2 and the Si layer. Successful demonstration of a Ru_2 memory device is attributed to the Ru_2 molecule, the high-quality Al_2O_3 dielectric layer, and the energy alignment between the Ru_2 and Al_2O_3 which resulted in the favorable charge trapping at the molecular interface. Our findings demonstrate the strengths and challenges with integrating molecular layers within solid-state devices, and will impact the future design considerations of molecular memory devices.

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COLL 608

Processing colloidally-synthesized 2D tin chalcogenide semiconductors for application in electronic devices

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Solution routes afford an economical and scalable means of making nanomaterials. In particular, the solution synthesis of 0D nanoscale semiconductors has proven effective in producing size-, shape-, and composition-controlled particles. Recently, solution routes to monodisperse 2D semiconductor structures have been developed; however, their incorporation into nanoscale electronic devices has been hampered by a lack of understanding of the necessary processing steps for semiconductors that are synthesized colloidally. Specifically, the means to forming an ideal interface between the semiconductor surface and metal contacts are not well understood relative to 2D materials synthesized by mechanical exfoliation and gas phase deposition techniques. Here we present an investigation on the interaction at the semiconductor-metal interface

in devices based on colloiddally-synthesized micron-scale tin chalcogenide compounds. Several post-synthetic processing routes are examined, and their effect on the resulting device performance is reported. Further, we interrogate the electronic and optoelectronic properties of these 2D semiconductors, as determined using spectroscopic and transport measurements, and relate these to the method by which they are processed.

COLL 609

Conversion of surface silanol to silicon hydride on solid silicon oxide surfaces

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Modern integrated chips (ICs) use multilayered arrangement of copper interconnects, which plays important role in electric signal and power distribution to various active components on ICs. Each copper wire is isolated from other by insulating material. Carbon doped silicon oxide (CDO) is a promising low dielectric constant (k) hybrid insulating material used in modern ultra-large scale integration (ULSI) devices^[1]. CDO is a nano porous and hybrid material composed of extensive cross linking of Si, C, and O elements. In IC fabrication oxygen plasma treatments are inevitable and causes irreversible modification of functional groups attached to silicon to hydrophilic Si-OH groups^[2]. Surface exposed hydrophilic Si-OH groups becomes active moisture absorbing sites and cause undesired increase in k value (water $k = \sim 80$) and leakage currents thereby compromising the quality of dielectric material. Several approaches have been investigated to minimize the CDO damage, such as H₂, He, NH₃ plasma pretreatments, dissolving the damaged CDO layer by hydrofluoric acid (HF) and functionalizing the hydrophilic Si-OH functional groups to short alkyl chain siloxy functional groups. However, many of the discussed methods have their own limitations like causing undesired film thickness loss, damaging the chemical structure of CDO and not effective in preventing further moisture attack. Here we present a strategy for selective functionalization of surface exposed hydrophilic Si-OH functional groups to hydrogen terminated silicon (Si-H) without affecting the rest of chemical structure of CDO. Hydrogen terminated silicon readily reverts to Si-OH termination in air, so it is further derivatized to highly hydrophobic Si-R (R= Octadecyl) groups. Long alkyl chain derivatized surface becomes highly hydrophobic and effectively prevents moisture attack thereby helps in maintaining the low- k value. FTIR, X-ray Photoelectron Spectroscopy (XPS) and water contact angle measurement techniques are employed for studying the reaction progress on CDO wafer.

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COLL 610

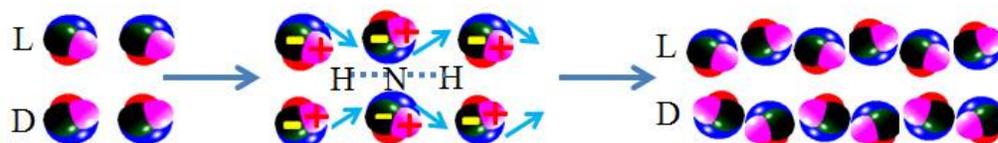
Biomimic self-assembly of chiral inorganic nanoparticles

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Natural species are created through self-assembly of heterogeneous nanoscale units to stabilize target motifs. Electrostatic, van der Waals, hydrophobic interactions and hydrogen bonds and are prevalent in naturally assembled species. In the laboratory, highly ordered assemblies have been made in controlling the nanocomponents into multi - dimensional functional materials with applications in fields ranging from biology, energy and optics. Ordered nanostructures from inorganic nanoparticles (NPs) could be assembled using DNA strands and peptides as template. Given the similarities in structures and assembly characteristics between inorganic nanocrystals and biomacromolecule, we are interested in investigation of the self-assembly of small biomolecule stabilized nanoparticles into nanoparticle supernanostructures via the coordination of overall fine balanced interparticle forces separately. Specifically, we studied the assembly mechanism of the chiral assemblies based on chiral amino acid stabilized colloidal nanoparticles, as well as corresponding optical properties, coordination between molecules and inorganic “assemblies”. In combination with the experimental data from cysteine stabilized CdTe and PbSTe nanoparticles, the assembly mechanisms were confirmed by Monte Carlo simulations respectively. This work could potentially provide new method for studying biomimic inorganic assemblies and corresponding applications.

[1] Y. L. Zhou et al. Enantioselectivity of Biomimetic Rod-Like Supraparticles: Self-Assembled from Chiral Nanoparticles. Unpublished

[2] Y. L. Zhou et al. Enantioselective self-assembly of chiral cysteine stabilized nanoparticles to chiral helical nanobelts. Unpublished.



COLL 611

Shape control of supraparticles on the three-dimensional slippery surfaces

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Supraparticles have been received numerous attention for applying their various functionalities. Till now most supraparticles assembled with smaller size particles have been synthesized spherically and difficult to control shape. Even though supraparticles have great functionalities and potentials, this limited shape has been one of the serious weak-point of supraparticle researches. Recently we have developed a strategy to synthesize spherical supraparticles on the superamphiphobic surface with various sizes and components^[1]. Thanks to the strong liquid repelling property of superamphiphobic surface^[2], spherical supraparticles could be formed by drying of nanoparticle dispersion with constant contact angle ($> 160^\circ$). In addition, during the process, no energy consumption and wasting chemicals were applied. However even with those great advantages of supraparticle synthesis on the superamphiphobic surface, shapes of supraparticles were still spherical and could not be varied. In this study, we introduce a method to control shapes of supraparticles using the three dimensional slippery surfaces. Slippery surface which contains lubricant on the surface is one of the representative liquid repelling surface with low sliding angle ($< 5^\circ$) of water. Therefore slippery surface also could be applied to synthesize supraparticles with drying nanoparticle dispersion method. In addition, by controlling thickness of lubricant and geometry of surfaces with two dimensional flat, three dimensional micro-prism, and micro-inverted pyramid patterns, shapes of synthesized particles were easily controlled. Using this shape controlling synthesis strategy with three dimensional slippery surfaces, various shapes of TiO₂ supraparticles with spherical, hemi-spherical, disk-like, rectangular, and square could be demonstrated, and it is expected that various shape of synthesized supraparticles can open a new door for widening application of supraparticles in many research areas.

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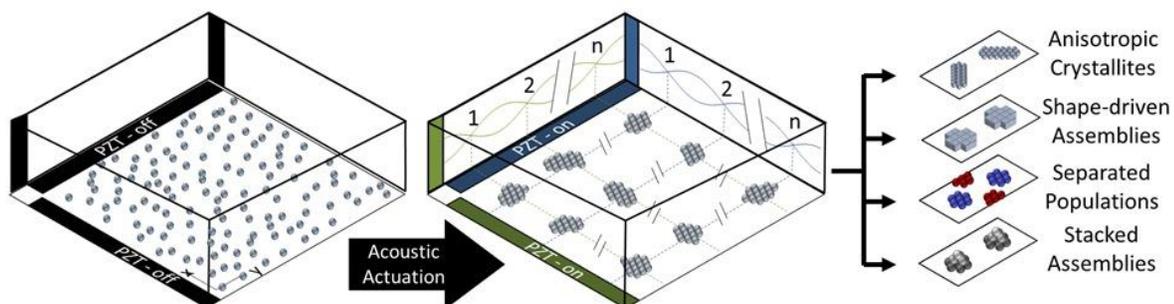
COLL 612

Acoustic radiation forces for the rapid and programmable assembly of microparticles and nanoparticles

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An enormous amount of effort has been dedicated to creating well-ordered structures from colloidal particles using magnetic fields, electric fields, capillary forces, and ionic interactions, for example. However, the potential of creating well-ordered structures from acoustic standing waves remains largely unexplored. Acoustic forces may offer numerous advantages compared to these techniques, including scalability, programmability, rapidity, and the ability to manipulate particles of various compositions (e.g., without a reliance on narrowly defined electromagnetic or surface properties). While a few studies have shown the ability to acoustically concentrate particles, the limitations to assemble particles of various sizes with precision and the morphology of these structures remains poorly understood. Here, we explore the flexibility and limitations of acoustophoresis for the rapid arrangement of micro- and nanoparticles into organized and programmable structures. We employ multi-dimensional bulk acoustic standing waves to propel particles toward the pressure nodes or antinodes, depending on their acoustic contrast factor, and can thus simultaneously create thousands of size-limited, assemblies within minutes. We pair these experiments with Brownian dynamics simulations to model the migration kinetics and assembly patterns of different particles. We also use simple analytical models to predict the limitations of this approach to manipulate particles of diminishing size, and we follow these predictions by concentrating gold nanoparticles into loosely packed clusters (unlike microparticles, which can arrange into tightly packed structures). Finally, to catalyze the assembly of these exceedingly small particles into tightly packed structures, we incorporated a simple light-based crosslinking approach that stabilizes the assemblies, which may provide utility in plasmonic and photonic applications.



COLL 613

Electrostatic assembly of functional nanoparticles for biomedical applications

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We demonstrate an electrostatic assembly approach to perform a controlled synthesis of (1) the silica microsphere (m-SiO₂) with the surface-decorated functional gold nanoparticle (AuNPs), and (2) the silver nanoparticle (AgNP)-graphene oxide (GO) hybrid nanomaterial. For the fabrication of m-SiO₂-AuNP, the surface of m-SiO₂ is modified by aminosilanes to generate a positive electric field, by which the unconjugated and partially-PEGylated AuNPs with the net negative charges are able to be attracted to the surface of m-SiO₂. For the synthesis of AgNP-GO, the cysteamine-functionalized and bovine serum albumin-functionalized AgNPs with positive surface charge are used to combine with negatively-charged GO. Material properties of individual nanoparticles, such as physical size distribution, number concentration, colloidal stability, and surface charge, can be characterized using a combination of electrospray-differential mobility analysis, transmission electron microscopy, x-ray photoelectron spectroscopy, and zeta potential analysis. The uniformity and the corresponding loading of the assembled constructs were characterized using the electron microscopy and inductively-coupled plasma mass spectrometry, respectively. The work provides the fundamental understanding useful in the synthesis of m-SiO₂-AuNP and AgNP-GO constructs for the emerging applications (e.g., chemo-radioactive therapeutics, anti-bacteria products).

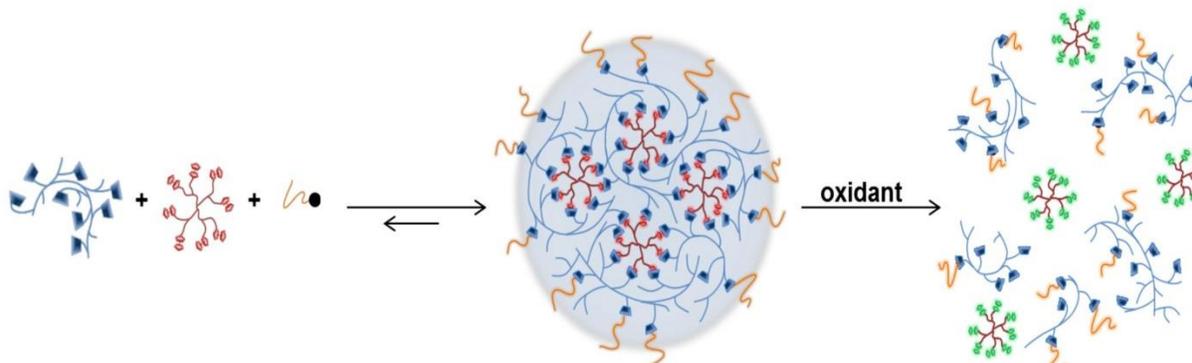
COLL 614

Size-controlled and redox-responsive supramolecular nanoparticles

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Control over the assembly and disassembly of nanoparticles is pivotal for their use as drug delivery vehicles. Here, we aim to form supramolecular nanoparticles (SNPs) by combining advantages of the reversible assembly properties of SNPs using host-guest interactions and of a stimulus-responsive moiety. The SNPs are composed of a core of positively charged poly(ethylene imine) grafted with β -cyclodextrin (CD) and a positively charged ferrocene (Fc)-terminated poly(amidoamine) dendrimer, with a monovalent stabilizer at the surface. Fc was chosen for its loss of CD-binding properties when oxidizing it to the ferrocenium cation. The ionic strength was shown to play an important role in controlling the aggregate growth. The attractive supramolecular and repulsive electrostatic interactions constitute a balance of forces in this system at low ionic strengths. At higher ionic strengths, the increased charge screening led to a loss of electrostatic repulsion and therefore to faster aggregate growth. A Job plot showed that a 1:1 stoichiometry of host and guest moieties gave the most efficient aggregate growth. Different stabilizers were used to find the optimal stopper to limit the growth. A weaker guest moiety was shown to be less efficient in stabilizing the SNPs. Also steric repulsion

is important for achieving SNP stability. SNPs of controlled particle size and good stability (up to seven days) were prepared by fine-tuning the ratio of multivalent and monovalent interactions. Finally, reversibility of the SNPs was confirmed by oxidizing the Fc guest moieties in the core of the SNPs.

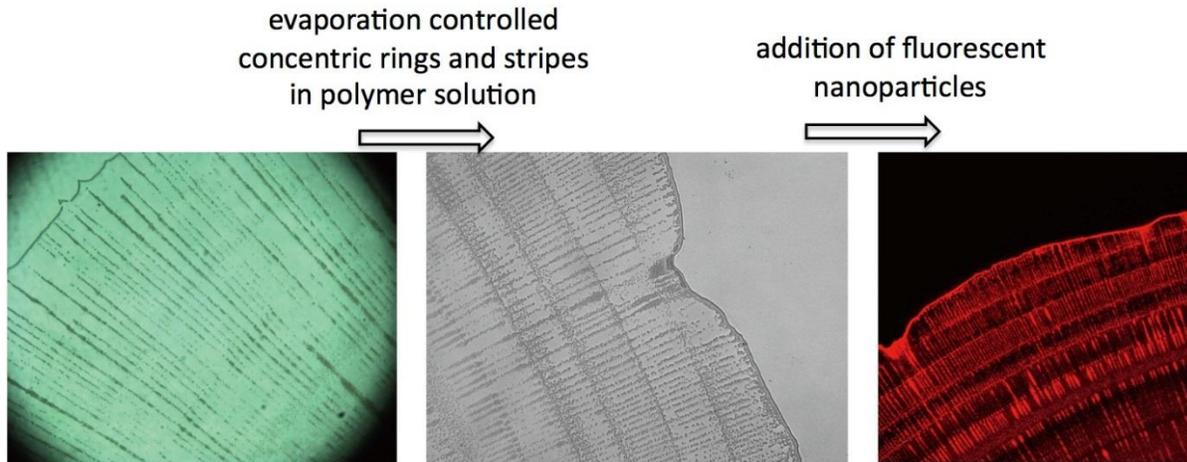


COLL 615

Evaporation controlled pattern formation in a polymer droplet

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Evaporation behavior of a water droplet containing hydrophilic polymer and colloidal particles, which are bimodal in size, was experimentally studied. We have previously shown that colloidal particles deposit into radial stripes due to phase separation between polymer and particles in addition to the Marangoni flows. This work now focuses on contact line movement to understand and control the deposition of particles into concentric rings as they also form stripes. We show that the motion of contact line is determined by two factors, the outward fluid velocity parallel to substrate, which is constant during most of evaporation time, and the inward velocity caused by the volume loss due to evaporation. By varying the evaporation rate hence contact line velocity, colloidal particles are observed to deposit into concentric rings and stripes. With the inclusion of nanospheres to the polymer-particle colloidal mixture, it is observed that nanoparticles deposit along the microspheres. The evaporation controlled ordering of bimodal sized particles into ordered patterns is governed by the dynamics of microspheres acting as dynamic templates for nanoparticles. Additionally, we will discuss our results with the pH responsive PAA-grafted 50 nm silica nanoparticles to reveal the effect of depletion forces on particle aggregation.



Polymer bridging between particles leads to the spontaneous demixing of polymer-rich and colloidal-rich phases. Concentric rings and stripes can be obtained by controlling the evaporation rate of a polymer drop.

COLL 616

Kinetics of nanocrystal superlattice self-assembly revealed by real-time *in situ* x-ray scattering

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Upon solvent evaporation, monodisperse colloids undergo a phase change in which the isolated, disordered, noninteracting colloidal particles self-assemble into a highly ordered, close-packed superlattice. While the initial and final states can be readily characterized, little is known about the pathway and dynamics *between* these two disparate states. Using *in situ* grazing-incidence X-ray scattering, we tracked the self-assembly of lead sulfide nanocrystals in real-time as they progressed from colloid to superlattice. Following the first appearance of an ordered arrangement, the superlattice underwent uniaxial contraction and collective rotation as it approached its final body-centered cubic (BCC) formation. Importantly, the nanocrystals became crystallographically aligned early in the overall self-assembly process, showing that nanocrystal ordering occurs first and on a faster timescale than superlattice densification. These experiments demonstrate that this synchrotron technique is a viable method for imaging self-assembly in its native environment, with ample time resolution to extract kinetic rates and observe previously unknown intermediate configurations. Such a technique could be used for real-time control of directed self-assembly processes, and reveals new insight into the forces governing self-organization of soft materials.

COLL 617

Dendrimer induced organization and self-assembly of colloidal nanoparticles

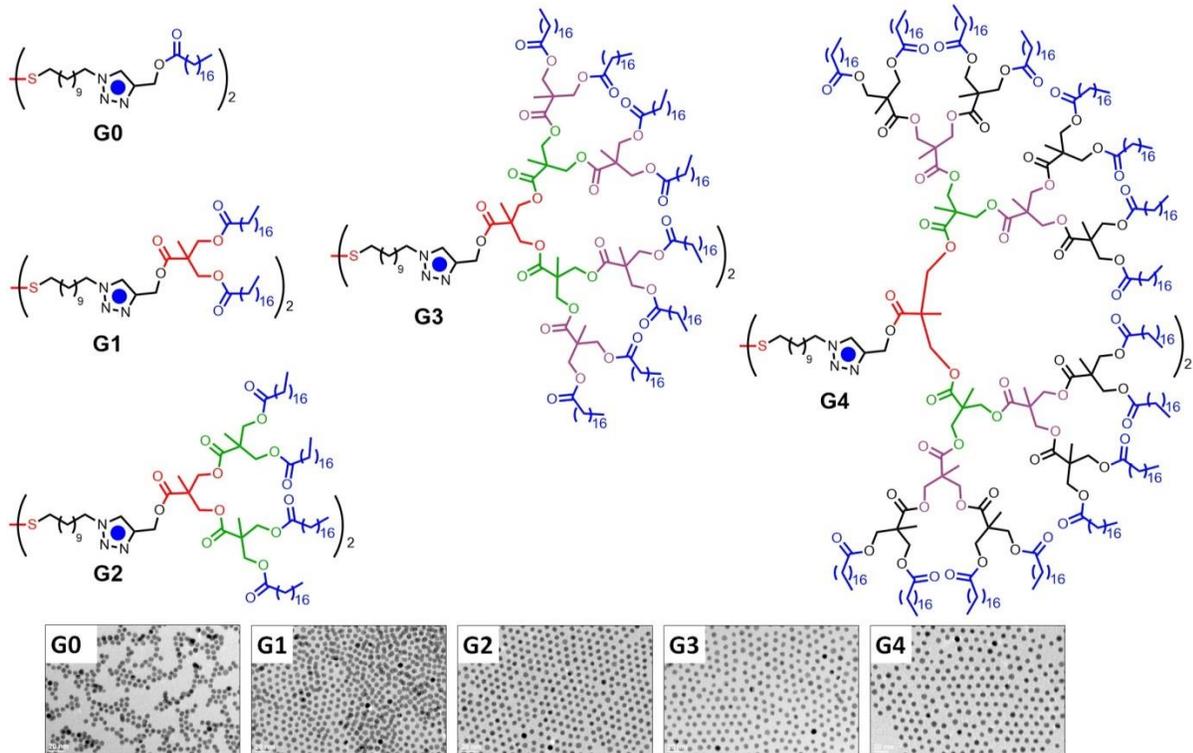
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Since the collective physical properties of nanoparticle assemblies in films depend greatly on proximity of neighboring particles, we have designed dendritic ligands to achieve fine control of inter-particle spacing.

A variety of lipophilic, highly flexible, dendritic ligands was designed to bind colloidal nanocrystals through ligand exchange. After ligand exchange, dendron-capped nanoparticle hybrids were found to self-organize into hexagonal close-packed (*hcp*) superlattices where the interparticular spacings were affected by dendrimer generation and were progressively varied from 2.2 to 6.3 nm. This is a range that is intermediate between commercial ligands and DNA-based ligands and is not easily accessed.

Dual mixtures of dendronized hybrids resulted in unprecedented binary superlattices (where both components have the same inorganic core, but different dendritic covering) which are isostructural with NaZn₁₃ and CaCu₅ crystals.

The synthetic and organization details as well as latest results will be discussed.



COLL 618

Active colloidal polymer

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In order to better understand active polymeric matter, colloidal polymers are imaged, in situ in real time, obtaining not only temporal and spatial information about each "monomer" in these living polymers but also about the time-dependent and orientation-dependent correlations between them. Our reversible colloidal polymer system is assembled from self-propelled monomeric Janus particles with dynamic "plug and play" self-assembly and programmed direction-specific interactions between the particles. Enabling this, AC voltage induces dipoles on the monomeric Janus particles that link them into chains while also generating active phoretic motility. Unique features of this system relative to conventional Brownian polymers are emphasized. Turbulence emerges from dense active solutions.

COLL 619

Understanding local and long-range 3-dimensional arrangements of components in colloidal nanocrystal frameworks using STEM tomography

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The ability to arrange colloidal nanocrystals into precise 3-dimensional architectures is increasingly important as researchers attempt to gain access to active layers in energy converting devices with tunable properties. Amphiphilic block copolymers offer a means to do so using solution and thermal processing. When the collection of interactions between micellar and nanocrystalline colloids is properly balanced, this strategy yields periodically-ordered mesoporous frameworks with tunable metrics for film thickness, pore size, pore periodicity, and wall thickness. Though we have recently assessed the physical characteristics of these colloidal nanocrystal frameworks by techniques such as SEM, GISAXS, and ellipsometric porosimetry, a 3-dimensional representation has been elusive. Nonetheless, this information is critical to the interpretation of the aforementioned indirect techniques. Here we introduce High-Angle Annular Dark Field (HAADF) STEM tomography as a powerful technique to apply to the 3-D visualization of individual components assembled into colloidal nanocrystal frameworks. This information is related throughout the entire thickness of the film and across large sample areas. Images (i.e., slices) are collected every degree over a tilt range of $\pm 70^\circ$, then reconstructed into a 3-D rendering of matter vs. empty space using IMOD tomography suite. A Fiji/ImageJ plug in allows for mathematic analysis of the segmentation of the phases, revealing pore variation and a statistical evaluation of image texture. Our results provide critical new information guiding next-generation materials and processing strategies for improving both in-plane and out-of-plane arrangements of nanocrystals within the framework.

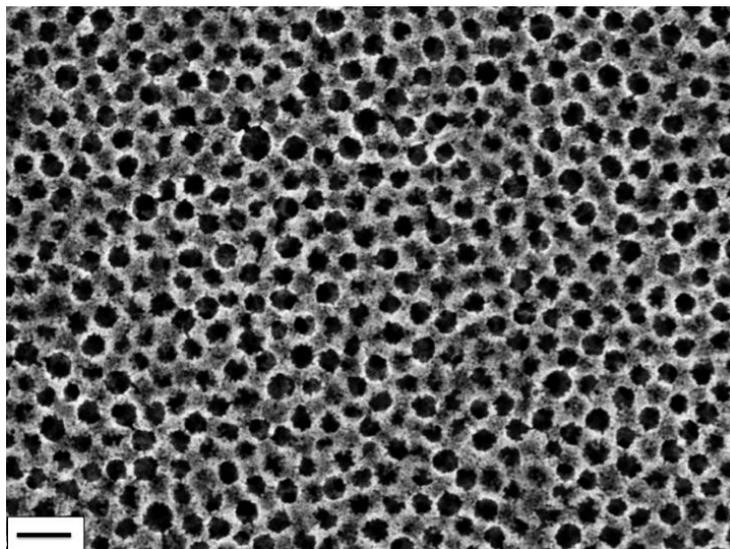


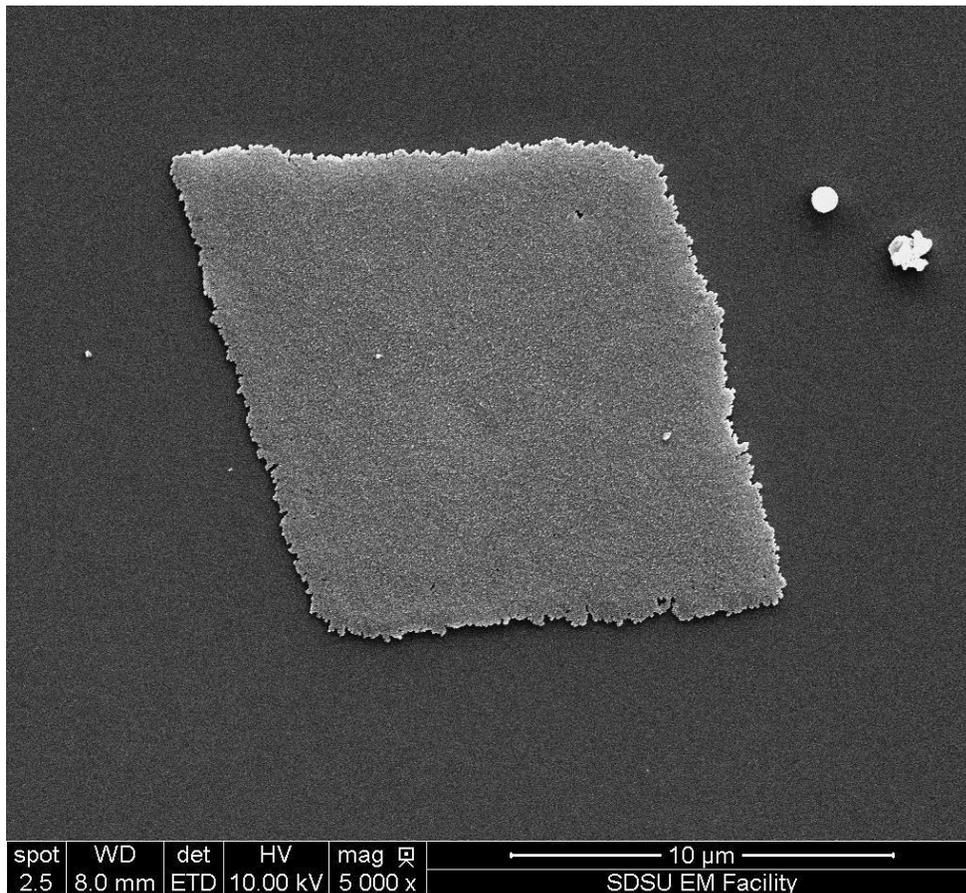
Figure 1. Top-down SEM image of mesoporous colloidal nanocrystal framework composed of ~ 5.5 nm tin-doped indium oxide nanocrystals. Scale bar represents 100 nm.

COLL 620

Formation of semifaceted, oriented thin calcite films by aggregation of nanoparticles

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It is increasingly recognized that many non-classical crystallization processes involve aggregation of sub-micron sized particles. The growth of thin (~0.5 μm) CaCO_3 films from solutions containing polyelectrolytes has been known since the end of the last century, but early proposals for the mechanism of this growth did not focus on particle aggregation. Variations on, and refinements to, the crystallization system have revealed details that were not previously analyzed, and which suggest that mechanisms for the production of these films must take particle aggregation into account. We have determined the conditions necessary to maximize the yield of angular films that appear monocrystalline by polarized light microscopy. Geometrical analysis of these films, combined with scanning electron micrographs of these films, suggest a hypothesis for morphogenesis which require both kinetic and thermodynamic consideration in modeling and analysis.



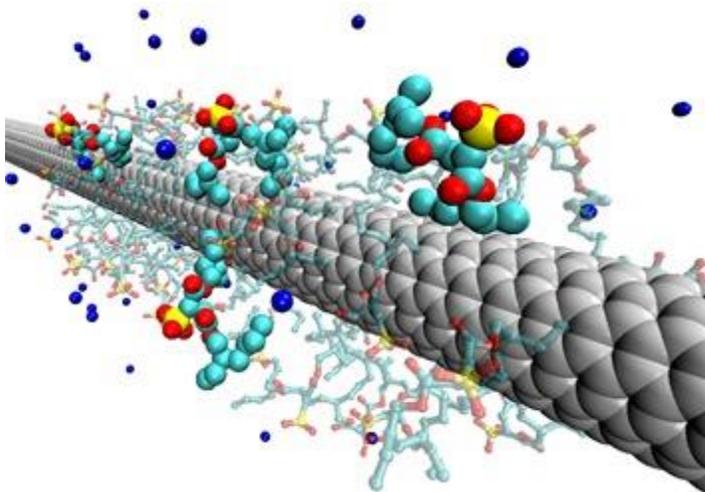
SEM micrograph of "semifaceted" calcite thin film.

COLL 621

Double-tailed surfactants simulated on single-walled carbon nanotubes: A molecular dynamics simulation study

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Preparation of uniform dispersion of single-walled carbon nanotubes (SWNTs) is a challenging task with wide ranging applications. In the last 10 years, great advances have been made in surfactant-stabilized SWNTs. However, there is still a lack of fundamental understanding regarding the behaviour of aqueous surfactant systems adsorbed on SWNTs. Using equilibrium all-atom molecular dynamics (MD) simulations, we study the adsorption and self-assembly of aqueous surfactants on SWNTs. The surfactant considered is the double-tailed sodium bis(2-ethylhexyl) sulfosuccinate (AOT), which has been found experimentally to efficiently stabilize aqueous SWNT dispersions. The simulations were conducted at ambient conditions for different surface coverages on (6,6), (12,12), and (20,20) SWNTs. The aggregate structure of adsorbed AOT was compared with that obtained from our previous results for sodium dodecyl sulfate (SDS) and sodium dodecyl benzenesulfonate (SDBS) surfactants. Moreover, the potential of mean force between (6,6) SWNTs in the presence of aqueous AOT was computed as a function of intertube separation. Our results could provide physical guidelines for selecting and/or designing surfactant formulations to improve the quality of the SWNTs dispersions.



COLL 622

Interactions between peptide-mimetic nanoparticles and synthetic cells

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Our objective is to design bio-inspired vesicles composed of different molecular species and investigate their interactions with nanoparticles of various functionalization. Multi-component vesicles are designed to be composed of different representative amphiphilic molecular species present in biological cell membranes [1]. We use a Molecular Dynamics-based mesoscopic simulation technique called Dissipative Particle Dynamics to simultaneously resolve the structural and dynamical properties of stable multi-component vesicles. The model has been used to simulate a particular system regarding peptide-bilayer interactions. We introduce nanoparticles with pin-like geometry which captures the architecture of the α -family of Antimicrobial Peptides (AMPs) which functions as antibacterial agents through membrane perturbation process [2]. These individual molecular species can differ from each other due to the dissimilar chemical properties and molecular geometry of their hydrophilic and hydrophobic groups. We investigate the factors that control the self-organization of the nanoparticles in extracellular aqueous environment and illustrate the dynamics of spontaneous insertion of AMP mimics into bilayer. By tuning the portion of hydrophilic part of the nanoparticle, we are able to model AMPs with different amphilities and hence to investigate how the length of hydrophilic part regulate the orientation of AMPs in the bilayer. In addition, we explore the effect of the relative concentrations of the molecular species on the stability and properties of the bilayers as well as on the distribution of peptide orientation in the bilayer. The results of our investigations can be used to design artificial peptide and effective cell targeting vehicles with functionalized surfaces for applications in drug delivery, sensing and imaging.

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COLL 623

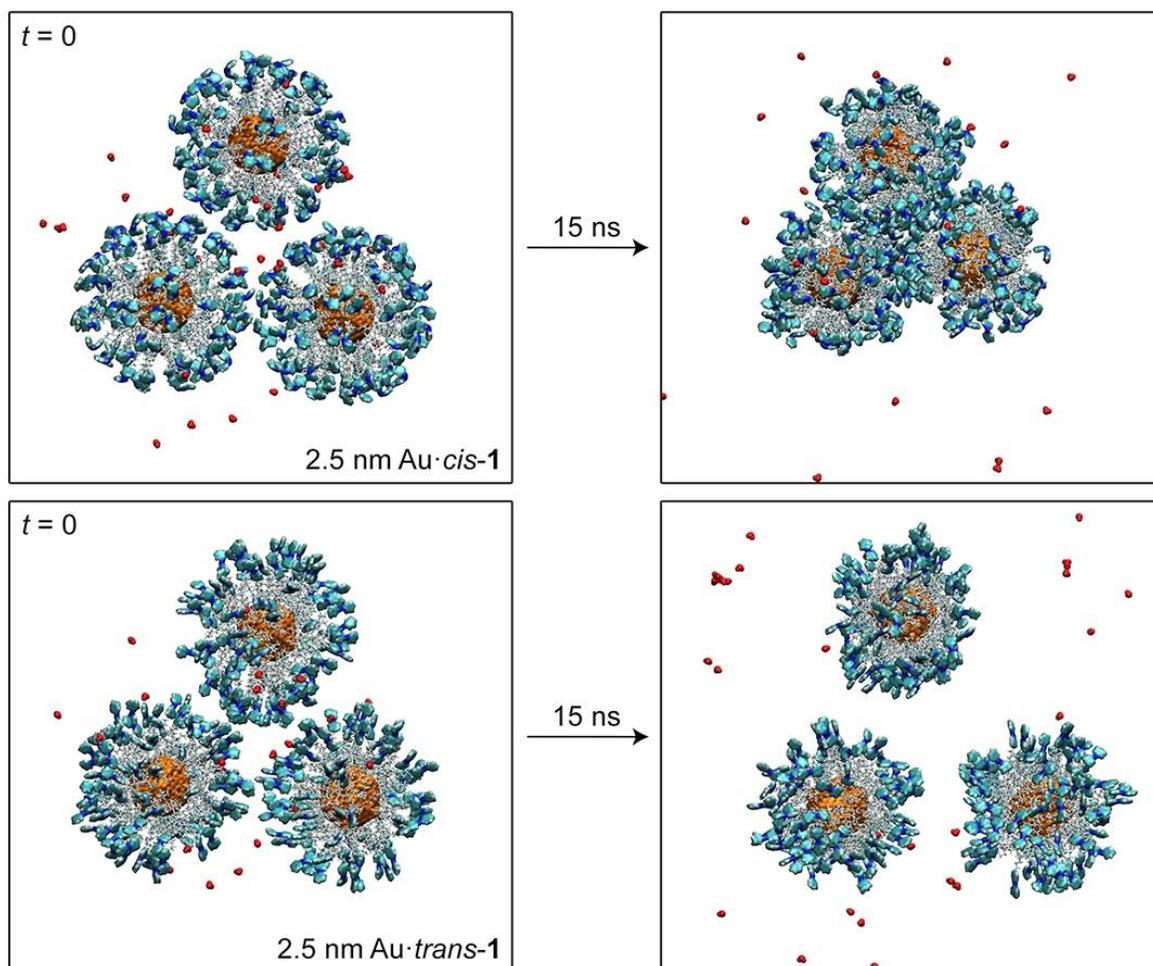
Multiscale modeling of self-assembled colloidal nanoparticles

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We present our multiscale modeling of colloidal nanoparticles self-assembled into many different lattices and superstructures, as observed in recent experiments. First, we discuss how superparamagnetic magnetite nanocubes self-assemble into chiral and other unique superstructures in the presence of magnetic fields [1]. To this goal, we have developed mean-field Monte Carlo codes where forces acting between nanoparticles are parametrized by known laws, molecular dynamics simulations, and

estimates of coupling strengths present under dynamical conditions during the self-assembly. We also use atomistic molecular dynamics simulations to describe the self-assembly of chiral CdS (truncated tetrahedra) nanoparticles in the presence of circularly polarized light and the formation of hollow nanoparticle-based capsules and other superstructures in dependence on the used pH [2]. Then, we discuss our precise atomistic modeling of the light-controlled self-assembly of nanoparticles with cis/trans-azobenzene ligands and show how these systems can be used to store molecules [3]. Finally, we model the solvation and self-assembly of different nanoparticles in bulk solvents and at electrified interfaces of ionic solutions [4]. We provide a detail analysis of the parameters that control the self-assembly processes of these nanomaterial systems.

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- [2] J. Yeom et al., Nat. Mat. 14, 66 (2015) & submitted.
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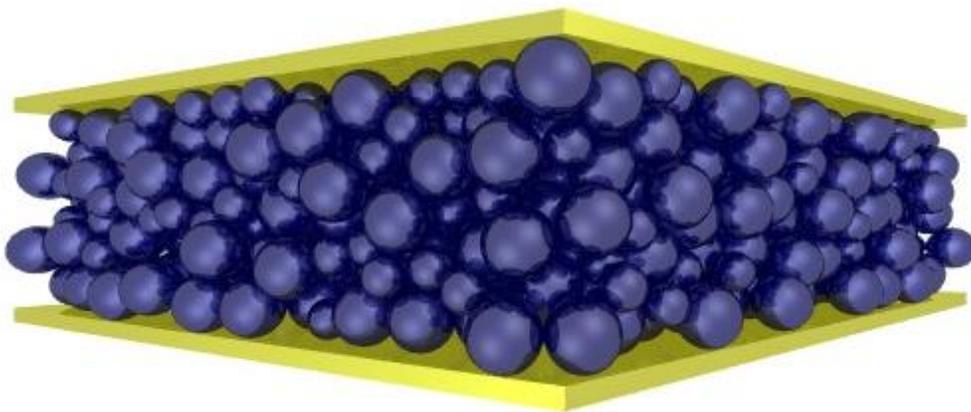
Self-assembly of cis- and trans-azobenzene covered nanoparticles in toluene [3].

COLL 624

Confined disordered jammed sphere packings in three dimensions

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Frictionless hard-sphere packings in three-dimensional Euclidean space has a venerable history because this idealized model captures the salient structural features of many complex systems such as liquids, crystals, glasses, colloids, granular media, heterogeneous materials, and powders. Disordered jammed packings under confinement have received considerably less attention than their bulk counterparts and yet arise in a variety of practical situations. To fill this gap, we study jammed binary sphere packings with maximal disorder that are confined between two parallel hard planes, which enable one to understand how packing properties transition between two and three dimensions. Specifically, we generalize the Torquato-Jiao sequential linear programming algorithm to obtain putative maximally random jammed (MRJ) packings that are exactly isostatic with high fidelity over a large range of plane separation distance H , sphere size ratios, and compositions. We find that packing characteristics can be substantially different from their bulk analogs. Our findings shed light on many important open questions and are relevant to confined packings that arise in biology (e.g., structural color in birds and insects) and may have implications for the creation of high-density powders and improved battery designs.



Representative MRJ binary packing of hard spheres confined between two parallel hard planes. Boundaries modify local and large-scale packing arrangements, for example inducing layered structures in their vicinity and leading to packing inefficiency.

COLL 625

Integrating molecular-dynamics simulations with molecular-thermodynamics to predict the interfacial tensions of non-ionic surfactants

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The reduction in interfacial tension by surfactants underlies several natural phenomena in multi-phase systems, including emulsions and foams. This effect is also responsible for many industrial processes such as spray painting, emulsion polymerization, distillation in packed bed columns, and froth flotation. The mechanisms underlying these phenomena have been described by several mathematical models in the colloid science literature. Since the interfacial tension is an essential input for the implementation of all these models, their accuracy depends on the accuracy of the estimate (s) of the interfacial tension (s) used. Here, we propose a method to evaluate the surface tensions of non-ionic surfactants using a combination of molecular dynamics (MD) simulations and molecular-thermodynamic (MT) theory.

We have developed an automated, computational workflow to carry out a series of simulations of surfactant molecules at fluid-fluid interfaces. One set of simulations studies the interactions between surfactant molecules, and attempts to characterize the intermolecular interactions in a surfactant monolayer in terms of two molecular parameters – a hard-disk radius (representative of strong intermolecular repulsions) and a second-virial coefficient (representative of weak, intermolecular, van der Waals attractions). These parameters are obtained by first calculating the potential of mean force between the two surfactant molecules at the interface, and then analyzing this potential using principles of statistical mechanics. A second set of simulations studies the change in the free energy of a surfactant molecule as it is brought from bulk solution to an interface. This free energy of adsorption is a measure of the affinity of the surfactant of interest for the interface of a given system, and provides a metric capable of ranking families of surfactants. Together with the intermolecular interaction parameters, the free energy of adsorption enables prediction of the interfacial tension as a function of the surfactant bulk concentration through the use of a suitable equation of state for the interface.

In this talk, we will present the details of our proposed computational methodology, including the results obtained for its application to a series of nonionic alkyl poly (ethylene oxide) (CiEj) surfactants at fluid-fluid interfaces.

COLL 626

Molecular dynamics simulations of NAPL removal from contaminated rocks using surfactants

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Remediation of petroleum contaminants from aquifers is an ongoing and environmentally relevant challenge. Non-aqueous phase liquids (NAPLs) can infiltrate groundwater reservoirs and pollute the water source leading to health and public safety concerns [1]. NAPLs such as asphaltenes, resins, and naphthenic acids possess high adsorptive potential making removal difficult with conventional pump-and-treat techniques [2]. As a result, surfactants have been posited as a means of mobilizing and solubilizing these contaminants for safe, effective removal. Experiments have shown that non-ionic surfactants are effective at removing aquifer contaminants, although the exact molecular-level mechanism is not clear [3]. The objective of this work was to study the mechanisms of NAPL desorption from model quartz and calcite surfaces in the presence of different environmentally friendly non-ionic surfactants. To this aim, molecular dynamics simulations were carried out using Gromacs Software with the Charmm36 force field. Simulations with water and surfactant-in-water solutions were compared to determine the effect of surfactants on contaminant removal from mineral surfaces [Figure 1]. Results showed that accessibility of water to the mineral surface is critical in inducing desorption. In addition, surfactant micelles were observed to dissociate at the water-contaminant interface. This molecular-level investigation revealed for the first time some of the driving factors in surfactant-enhanced contaminant remediation.

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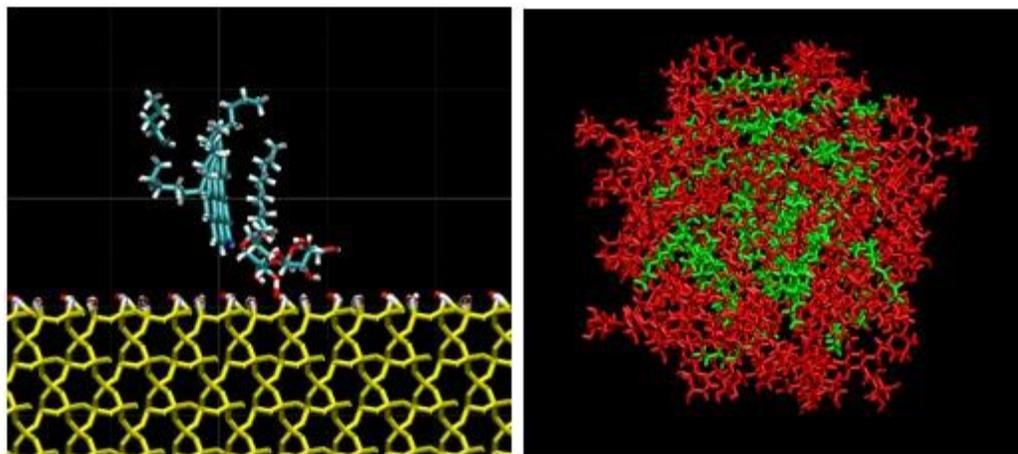


Figure 1. Surfactant interacts with an asphaltene molecule at quartz surface. Oil is solubilized into a surfactant micelle in aqueous solution

COLL 627

Molecular dynamics simulations of micelle and micelle-nanoparticle solutions: Structure, dynamics, and rheology

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We present a systematic coarse grained molecular dynamics (MD) study of the structure, dynamics and rheology of cationic micellar solutions in the presence of explicit solvent and highly binding organic salt. The simulations are capable of accurately predicting shape transitions, binary interactions, shear-induced configurational dynamics and anomalous viscosity variations as a function of salt concentration observed experimentally in such systems [1-4]. We simulate systems that contain up to a million beads, and access microsecond timescales, while still preserving the underlying physical chemistry. For the first time, estimates of micelle size distribution, persistence length, end-cap energy and recombination time are obtained directly from MD simulations. Effect of counterions on the dynamics and energetics of wormlike micelles under uniaxial extensional flow will be presented. Specifically, two mechanisms will be discussed: (i) counter ion-induced stiffening of rodlike micelles, and (ii) energy redistribution along the micelle contour caused by flow-induced advection of counter ions leading to mid-plane scission of the micelle. The addition of nanoparticles (NPs) to wormlike micellar fluids is shown to result in the formation of electrostatically stabilized junctions. Effect of NP volume fraction on the equilibrium structure and shear rheology of such solutions will be discussed. Non-equilibrium MD simulations of such mixtures exhibiting complex rheological behavior including shear thinning, shear thickening and shear-induced isotropic to nematic transition will also be presented. Acknowledgements: The authors gratefully acknowledge NSF grants No. CBET-1049454 and No. CBET-1049489 for partial support of this research. This work used the computational resources provided by Extreme Science and Engineering Discovery Environment (XSEDE), which is supported by NSF grant number OCI-1053575. [1] A. V. Sangwai and R. Sureshkumar, *Langmuir* 27, 6628 (2011). [2] A. V. Sangwai and R. Sureshkumar, *Langmuir* 28, 1127 (2012). [3] A. Sambasivam, A. V. Sangwai, and R. Sureshkumar, *Phys. Rev. Lett.* 114, 158302 (2015). [4] S. Dhakal and R. Sureshkumar, *J. Chem. Phys.* 143, 11, 024905 (2015).

COLL 628

Modeling of dynamically self-assembling nanoflasks

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In collaboration with experimentalists, we model optically controlled self-assembly and disassembly of azobenzene-covered gold nanoparticles (NPs) of a diameter of 2.6 nm. The azobenzene ligands can be switched between cis and trans forms using light of specific wavelength (UV light for trans to cis and visible blue light for cis to trans). Experiments show that NPs with polar cis azobenzene ligands can self-assemble in a hydrophobic solvent (toluene), whereas trans NPs cannot. During the cis NPs self-assembly, polar molecules present in the medium, become adsorbed on the NPs surfaces and eventually trapped in cavities formed between the NPs, where they can serve as reactants. We model this behavior by precise atomistic molecular dynamics simulations and show that water molecules are captured by cis NPs clusters. When the cis ligands are converted to the trans form in vacuum, the clusters explosively disassemble and water molecules are fast released.

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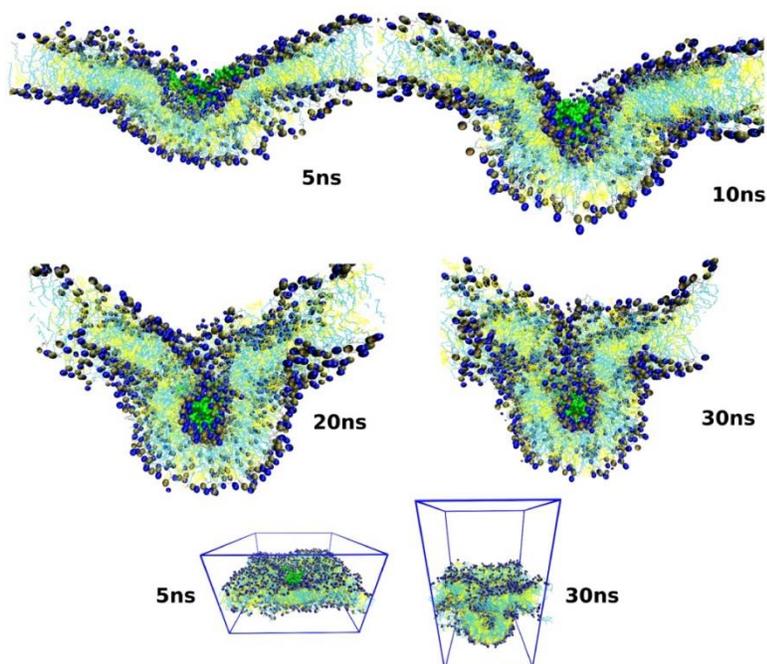
COLL 629

Molecular dynamics simulations together with experimental studies reveal strong membrane activity of a small peptide

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Cell-penetrating peptides (CPPs) and antimicrobial peptides (AMPs) are generally defined as small cationic peptides with the ability to interact with lipidic membranes, in a process driven by electrostatic and hydrophobic processes. The interaction with CPPs is known to lead to its translocation across the membrane, while with AMPs lead to membrane damage.

Here we present one synthetic anionic peptide, which strongly interacts with model membranes, showing properties of the two peptide classes, namely the translocation through lipidic membranes on a mechanism usually described for cationic CPPs and membrane destabilization like AMPs promote. These properties were shown through molecular dynamic studies, experimental studies with liposomes and mammalian cells in vitro. Based on the peptide properties here demonstrated, small modifications in its structure could make it a very promising tool for drug delivery.



COLL 630

Photoinduced electron transfer as a means to modulate the plasmon resonance of Cu_{2-x}S quantum dots

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Copper sulfide (Cu_{2-x}S) nanocrystals with nonstoichiometric composition exhibits plasmon resonance in the near infrared region. Compositional changes and varying electron density markedly affects the position and intensity of the plasmon resonance. We report a simple photochemical phenomenon of transferring electrons to Cu_{2-x}S and modulating the plasmon resonance in a controlled way. As photogenerated methyl viologen radicals transfer electrons to Cu_{2-x}S in inert solutions, we observe a decrease in localized surface plasmon resonance (LSPR) absorbance at 1158 nm. Upon exposure to air the plasmon resonance band recovers as stored electrons are scavenged away by oxygen. This cycle of charge and discharge of Cu_{2-x}S nanocrystals is reversible and can be repeated through photoirradiation in N_2 saturated solution and then exposing to air. The spectroscopic study that provides mechanistic insights into the reversible charging and discharging of plasmonic Cu_{2-x}S will be discussed.

COLL 631

Vibrational spectroscopy of single quantum dots

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Semiconductor nanocrystals (SNCs) have been extensively studied due to their unique properties, arising from quantum size effects. Their size-tunable fluorescence, high fluorescence quantum yield, stability against photobleaching, and broad excitation range have made SNCs attractive for a wide range of applications. Among many analytical techniques, vibrational spectroscopy has been proven to be a powerful tool to explore the phonon modes and the structure of the core, shell, surface, core-shell interface, and core-ligand interface in SNC systems. The present work studies the vibrational spectra of single thioglycolic acid (TGA)-capped CdTe quantum dots (Qdots) by Surface-enhanced Raman Scattering (SERS). One challenge in Raman spectroscopy of Qdots is the intense fluorescence background which masks the Raman signal. Our nanoAg-on-Ge SERS substrates enable us to overcome this problem by quenching the fluorescence by resonance energy transfer (RET). Furthermore, by studying single Qdots, we eliminate the heterogenous broadening. This feature is particularly advantageous in studying Qdots, since their optical properties are highly sensitive to variations in the size, core-shell structure and surface chemistry. In the present study, time series SERS spectra of single CdTe Qdots are captured at 40 ms intervals in the form of sudden spectral jumps sustaining less than a second. These spectral jumps are characteristic of the surface thiols, thiol-core interface, as well as the CdTe core. We have captured three distinct types of spectral jumps, which we attribute to different chemisorption of the thiols at facets of different crystal directions. Currently, we are investigating these binding configurations and the interface formed between CdTe and the thiol molecules at different facets.

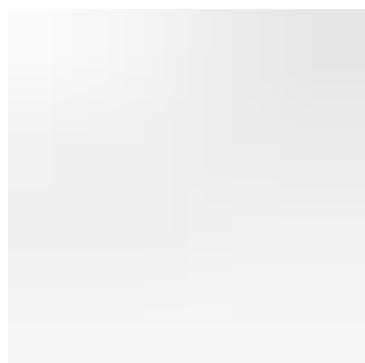


Figure 1. Time series SERS spectra in 40 ms intervals capturing a single TGA-capped CdTe quantum dot.

COLL 632

Size- and surface ligand- dependent photocatalytic performance of CuInSe₂ nanocrystals in water

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Because of low cytotoxicity effects and capable of absorbing near infrared light in the solar spectrum, copper-based ternary semiconductor nanocrystals have shown promises in the fabrication of photovoltaic devices. However, their photocatalytic application is its infancy. Here we demonstrate first sustainable photocatalytic properties of CuInSe₂ nanocrystals for visible light-driven organic dye degradation in water. We have found that the size of the nanocrystals, which are varied from 1.5 to 5 nm, and charge transport properties of their surface passivating ligands control the photocatalytic properties. Most importantly, through solution-phase electrochemical characterization, we also show that thermodynamic driving force for oxygen reduction is the dominant contributor to photocatalysis over columbic interaction energy of electron-hole pairs.

COLL 633

Non-spectroscopically dependent study of neutral amine ligand binding interactions with CdSe quantum dots

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Elucidation and optimization of the exciton relaxation processes that result from the electronic structure of CdSe quantum dots (QDs) and their electronically coupled ligands are critically important for nanomaterial application in bioimaging, photocatalysis and light harvesting. Amine ligand interactions with CdSe QDs have been frequently examined since these neutral ligands bind relatively strongly, exhibit a dynamic adsorption/desorption stabilization and greatly influence photoluminescence. While there seems to be concurring evidence that increased amine coverage on the QD surface tends to yield improved optoelectronic properties, consistent thermodynamic profiles with suitably determined equilibrium constants are lacking. The most commonly recognized limitation in previous reports is the inability to directly analyze thermodynamic information for the QD–ligand interactions. We have developed a novel gel permeation chromatography purification technique that is used to provide reproducible, well-defined QD starting materials for the investigations of amine ligand interactions using isothermal titration calorimetry (ITC). ITC allows extremely sensitive characterization of the dynamics within the QD–ligand system without relying on a spectroscopic signature which may be indistinguishable or suppressed in such a complex equilibrium environment. This presentation will describe how ITC and common spectroscopic techniques can be used concomitantly to continue building a more mechanistic understanding of neutral ligand interactions with CdSe QDs.

COLL 634

Mechanism of energy transfer between molecules and PbS nanocrystals during upconversion

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Upconversion, the ability to convert low frequency light to high frequency light, has attracted enormous attention due to its wide range of applications in solar cells, biological imaging, and data storage. Here, we focus on a newly introduced hybrid molecular-nanocrystal upconversion system. We use PbS nanocrystals capable of upconverting NIR light as the sensitizer and rubrene molecules as the annihilator. Light can be absorbed by the PbS nanocrystal, and then the energy can be transferred from the triplet state of the nanocrystal to the triplet state of the rubrene through a process called triplet-triplet energy transfer (TTET). Finally, the two excited rubrene molecules annihilate to upconvert the light during triplet-triplet annihilation. Here we study the mechanism of TTET and the effect of the nanocrystal ligand length on TTET quantum yield (QY) in the PbS/rubrene upconversion system. We synthesized PbS NPs with oleylamine ligands, and replaced the original ligands with carboxylic acid molecules that have 6 different alkane chain lengths ($C_nH_{2n+1}COOH$, $n = 3, 7, 9, 11, 13, 15$). We observed that the upconversion QY increases exponentially with decreasing ligand length, indicative of Dexter energy transfer mechanism.

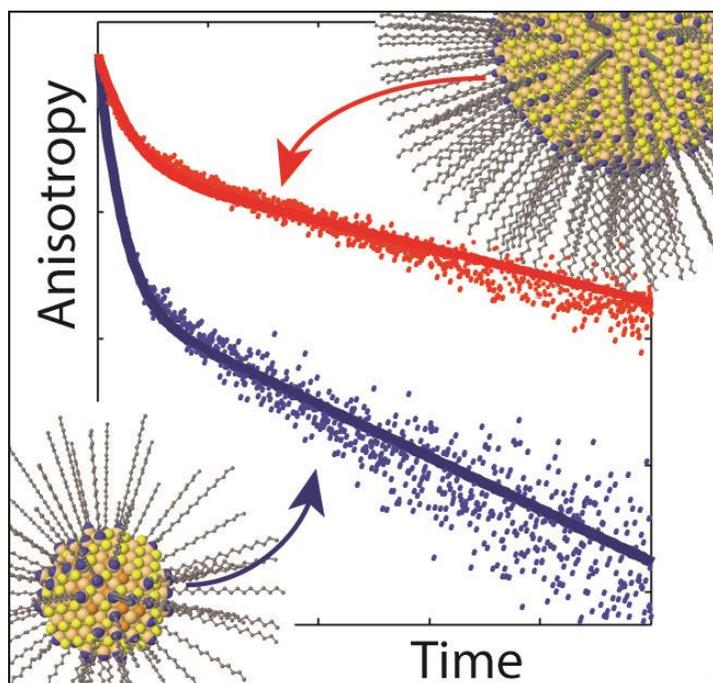
COLL 635

Size dependent ligand layer dynamics in semiconductor nanocrystals probed by anisotropy measurements

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Colloidal semiconductor nanocrystals (NCs) are promising building blocks for various applications. This is mainly due to the ability to modify their physical and chemical properties by controlling the particles size and shape in the nanometer scale. The inorganic NCs surface is usually covered by an organic ligands shell, which has a crucial role in controlling the size and shape of the NCs during the colloidal synthesis. The properties of the ligand shell also determine the NCs dispersibility in various solvents and matrices and their physical and chemical properties. Although the importance of the ligand shell its exact properties and specifically the effect of the NC size and shape are still not well understood. This is mainly due to the lack of experimental tools that will enable to study the ligand shell in situ. In our research we have uniquely studied the physical properties of the ligand shell on the surface of

spherical quantum-dots (QDs), of various sizes. We have utilized dye molecules that are embedded within the organic ligand layer and adopt its properties to optically study the effective viscosity of the ligand shell. Tracing the reorientation times of the dye molecules we were able to calculate the effective viscosity of the shell. We have found that as the size of the QD decreases (and hence the curvature increases), the effective viscosity of the shell is decreasing. Modifying the physical properties of the ligand shell by changing the shape of the surface is a unique property of NCs. Further investigation of the ligand shell will allow rational design of the surface to achieve desired properties, providing an additional important knob for tuning their functionality.



Anisotropy reorientation measurement for dye molecules bound to the surface of large (red) and small (blue) QDs. The steeper slope for the blue curve indicates faster reorientation and hence lower viscosity for the smaller QDs

COLL 636

Homochiral semiconductor nanohelices

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Chirality at the nanoscale is an emerging and dynamic area of research. The relationship between chiral nanostructures and their chiroptical activities is far from being fully understood. In this work, chiral ligand cysteine capped cadmium telluride nanoparticles (CdTe NPs) were found to spontaneously assemble into homochiral nanohelices. These nanohelices represent a convenient model system to understand

the effects of various helix structural changes on chiroptical activity both experimentally and computationally. Circular dichroism (CD) studies revealed a red-shift in rotatory activity as the nanohelices were formed with increasingly aged NPs. We carried out computer simulations to study how the incident photons interact with the semiconductor nanohelices of various geometries, with thickness of the helix being the most probable cause for the CD red-shift observed experimentally. Heuristic guidelines for the design of chiroptically tunable semiconductor helical nanostructures were formed through computer simulations. Our simulations also shed light on the complexity of nanoscale electromagnetic phenomena involving polarization rotation and offer valuable input for rotatory power optimization. Furthermore, simulated CD spectra matched well the experimental data. These semiconductor nanohelices display broad band rotatory power throughout the UV-vis-NIR range, in addition to a strong chiral anisotropy factor approaching $g=0.01$. The capability of chiral semiconductor NPs to assemble into nanostructures with significantly improved rotatory power will allow for more widespread applications of chiral nanomaterials. NPs were hypothesized to be part of the primordial conditions on Earth. Importantly, this study shows that homochiral superstructures with nearly 100% enantiomeric purity can be formed through cooperative interactions between NPs, which can contribute to understanding the origin of homochirality on Earth. This work advances the current understanding of structure-property relationship for chiral semiconductor nanostructures based on self-organized chiral nanoscale units and provides a precise set of guidelines to tune their optical activity.

COLL 637

Optical and electrical properties of a tube-in-a-tube semiconductor

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Atomically-thick materials such as single-walled carbon nanotubes and graphene are prone to chemical attack because all of the constituent atoms are exposed. Conversely, at increased thicknesses, many of the remarkable properties of these materials are lost. We will describe a novel tube-in-a-tube structure that uniquely combines both surface functionalities and interesting electronic properties. This synthetic semiconductor is created from outer wall-selective functionalization of double-walled carbon nanotubes. Correlated spectroscopy confirms that the covalent modification is selective to the outer wall. The electrical conductivity is well retained due to the intact inner-tube conducting channels. Lacking such channels, single-walled carbon nanotubes and graphene become insulators after similar functionalization. We further demonstrate that this chemically tailored functional structure allows simultaneous attainment of high sensitivity and selectivity in electrical detection of small molecules. The implications of these findings will be discussed from the materials and electronics perspectives.

COLL 638

Counterion-mediated ligand exchange for PbS colloidal quantum dot superlattices

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Colloidal quantum dot (CQD) solids represent a popular topic in the field of emerging photovoltaics for the past decade due to their tunable bandgap, high absorbance and the possibility of solution processing. Exchanging the ligands is a crucial step in the fabrication of high quality CQD solids. Although many molecules have been proposed as capping ligands, the process of ligand exchange itself and the influence on the device properties have not gained enough attention.

In this work, we compare the ligand exchange process in CQD thin films using ammonium, methylammonium and tetrabutylammonium iodide, and shed light to the mechanism of the ligand exchange. We obtain two- and three-dimensional square-packed PbS CQD superlattices with epitaxial fusion of the nearest neighbor CQDs as a direct outcome of the ligand-exchange reaction, and show that the order in the layer can be controlled by the nature of the counterion. Furthermore, we demonstrate that the acidic species (both solvent and counterion) mediate the removal and replacement of the carboxylates bound to lead-chalcogenide surface. A non-acidic counterion eventually leads to higher order, but also poorer carrier transport in the QD thin film due to incomplete ligand exchange. Finally, we show that single-step blade-coating and immersion in a ligand exchange solution such as the one containing methylammonium iodide can be used to fabricate well performing bottom-gate/bottom-contact PbS CQD field effect transistors with record subthreshold swing.

COLL 639

Colloidal synthesis of monodisperse semiconductor nanocrystals through the saturated atomic layer adsorption reaction

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We demonstrate a general strategy for the synthesis of colloidal semiconductor nanocrystals (NCs) exhibiting the size dispersion below 3%. The present approach relies on the sequential deposition of fully saturated cationic and anionic monolayers onto small-diameter clusters, which leads to focusing of nanocrystal sizes with the increasing particle diameter. Each ionic layer is grown through a room-temperature colloidal atomic layer deposition (ALD) process that employs a two-solvent mixture to separate the precursor and nanocrystal phases. As a result, unreacted precursors can

be fully removed after each deposition cycle, preventing the secondary nucleation. By using CdS NCs as a model system, we demonstrated that a narrow size dispersion of 2-3% can be achieved through a sequential deposition of fully-saturated Cd²⁺ and S²⁻ half-monolayers onto starting 2-nm CdS cluster “seeds”. With a negligible dispersion in the thickness of the deposited multilayer shell, the primary contribution to the standard size deviation of grown CdS NCs comes from the size variation in the starting CdS clusters ($\Delta d < 0.2$ nm). In addition to yielding a narrow distribution of nanoparticle sizes, the demonstrated methodology offers an excellent batch-to-batch reproducibility and an improved control over the nanocrystal surface stoichiometry. The present synthesis is readily amenable to other types of semiconductor nanocrystals and is expected to emerge as a viable alternative to traditional hot-injection strategies of the nanoparticle growth.

COLL 640

Investigating the doping of nanocrystals with hydrazine

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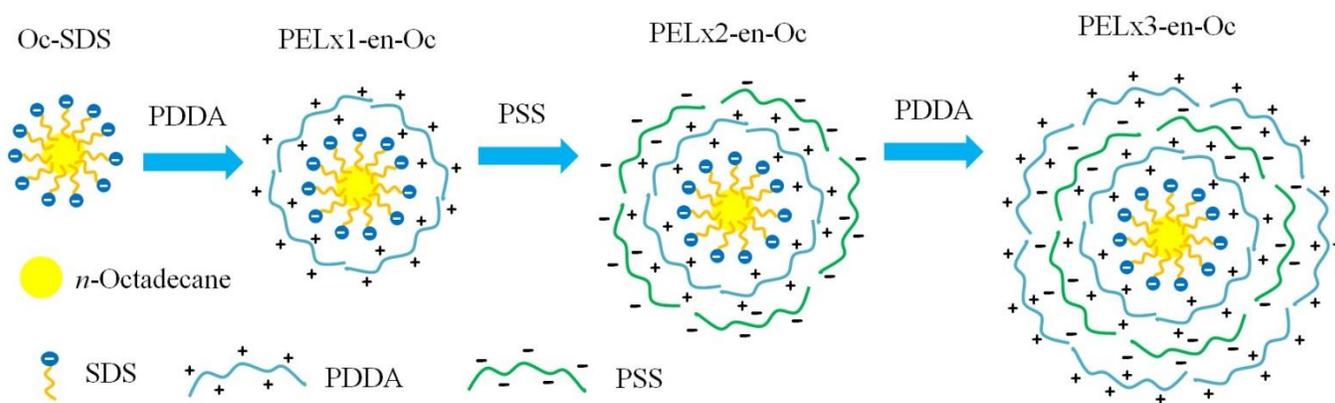
The mobility of the charge carriers plays a significant role in the power conversion efficiency of quantum dot solar cells. The conductivity of a nanocrystal (NC) solid can be improved by decreasing the tunneling barrier between particles, or increasing the intrinsic conductivity. Hydrazine achieves both, but the way it dopes NCs is not well understood. In addition, its effects are transient, thus precluding its use in real-world applications. Here we study the effect of hydrazine derivatives on the doping of PbSe NCs. By varying the electronegativity, affinity and stability of the hydrazine-NC adduct, we hope to engineer a NC solid that is permanently doped. This also enables characterization of the NC thin film to elucidate the mechanism of doping. The NC thin films are characterized by optical absorption, photoluminescence (PL), x-ray photoelectron and ultra-violet photoelectron spectroscopy, attenuated total reflection-infrared spectroscopy. The effect of all treatments on the stability of the device and its conductivity, is observed through field effect transistor measurements.

COLL 641

Effect of polyelectrolyte multilayers shell on thermal properties of *n*-octadecane phase change material nanocapsules

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Encapsulation is an important process for protect phase change materials (PCMs) from the outside environments and prevent leakage and loss of PCMs in frequent phase transition process. The encapsulation of PCMs using polyelectrolyte (PEL) multilayer as capsule shell is a good choice because this method uses a low concentration of non-toxic chemical reagents and low treatment temperature, resulting in cost and energy-saving and eco-friendly process. However, the thickness of PEL multilayer shell and characteristic of PEL layer were considered to play a significant influence on thermal properties of PEL encapsulated *n*-octadecane (PEL-en-Oc) nanocapsules, i.e. latent heat and thermal stability. Therefore, the effect of number of PEL shell layers on thermal properties of PEL-en-Oc nanocapsules was studied using two types of PEL, i.e. poly (diallyldimethylammonium chloride) (PDDA) cationic polyelectrolyte and poly 4-styrenesulfonic acid (PSS) anionic polyelectrolyte. The PEL-en-Oc nanocapsules were prepared by stepwise adding PDDA and PSS solutions into the nanoemulsion of *n*-octadecane, resulting in the formation of PELx1-en-Oc, PELx2-en-Oc or PELx3-en-Oc nanocapsules with single, double and triple shell layers, respectively. The zeta-potential results revealed the successful coating of stepwise assembled PEL on the surfaces of *n*-octadecane droplets, in which the average particle sizes of PEL-en-Oc nanocapsules were in the range of 154 – 204 nm. The increase of number of PEL shell layers could increase the thermal stability of PEL-en-Oc nanocapsules, but decrease the latent heat of *n*-octadecane in nanocapsules. The PELx3-en-Oc nanocapsules with 118 J/g of latent heat of fusion exhibited the highest thermal stability.



Schematic representation of PEL-en-Oc nanocapsules with single, double and triple shell layers

COLL 642

Structural control of self-assembled porous polyelectrolyte films by interaction with specific metal ions

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Layer-by-layer self-assembly (LbL) is one of the most elegant methods to create various functional materials such as electrical conducting, adsorption, optical and porous materials. The previous studies showed that the porous films using LbL were obtained by immersing dense weak- polyelectrolyte films into an aqueous solution with a specific pH value. We described a novel method to fabricate simply the porous polyelectrolyte film with metal ions; a dense structure transformed into the porous structure by immersing in specific metal ion solutions.

The dense polyelectrolyte films composed of poly(allylamine hydrochloride) (PAH) / poly(acrylic acid) (PAA) were formed by the LbL technique. The porous PAH/PAA films with metal ions were obtained by immersing the dense PAH/PAA films in several concentrations of silver or copper acetate aqueous solutions. The pore size of porous PAH/PAA films were reduced with an increasing concentration of metal ion solution. In addition, the porous films with copper ions had the smaller pore size than these ones with silver ions (Figure 1). The porous transition of the novel method was caused by three phenomena: (a) the formation of a new bond between polyelectrolyte and metal ion, (b) subsequent ionic bond disruption and (c) re-formation (Figure 2).

To the best of our knowledge, this is the first report that the pore size of the porous structure was controlled in the range from microscale (1-10 μm) to nanoscale (50-100 nm) by the concentration or types of metal ions among the reports of LbL technique. These porous films with high surface were available for various applications such as adsorption, separation, catalysis, and optics.

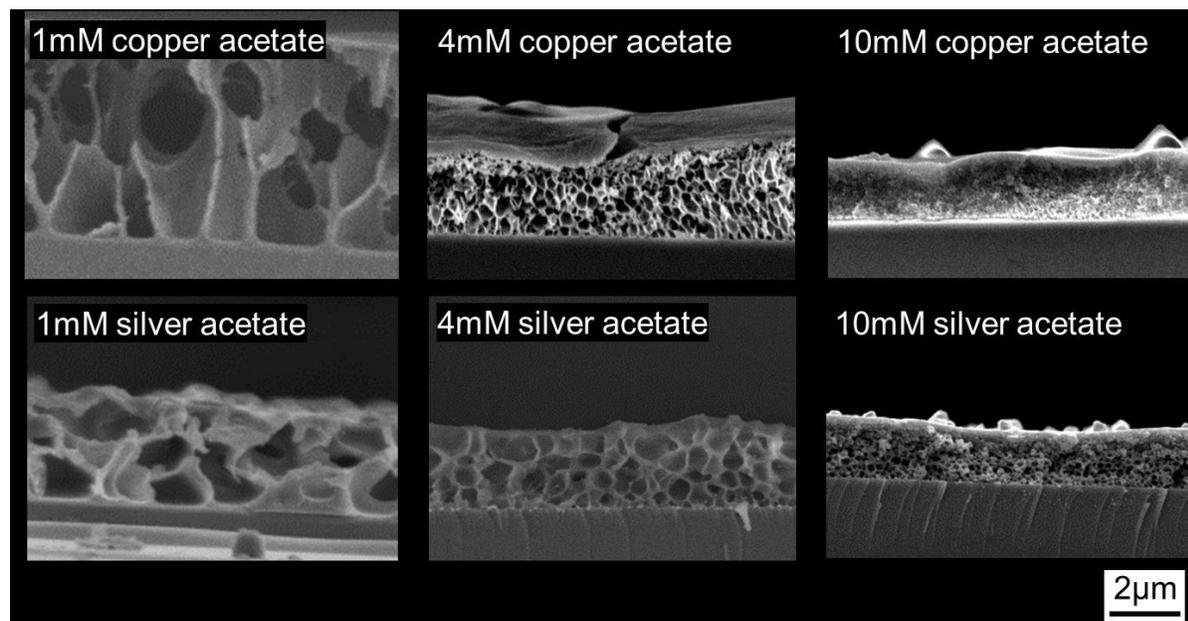
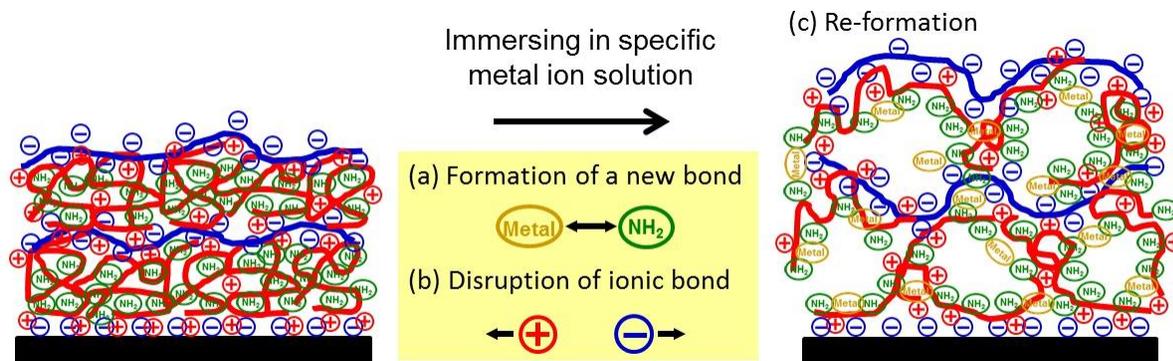


Figure 1. Cross-sectional SEM images of the porous polyelectrolyte films with copper or silver ions.



Scheme 1. Schematic representation of the deduced formation process of the porous polyelectrolyte films through the novel method.

COLL 643

Microwave welding/reinforcing approach at the interface of thermoplastic materials

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As an attempt to address the needs and tackle the challenges in welding of thermoplastic materials (TPMs), a novel process was performed via short-term microwave (MW) heating of a specific composite, made up of conducting polypyrrole nano-granule (PPy NG) coated carbon and catalyst source precursor (ferrocene) fine particles, at substrate polypropylene (PP) dog bone pieces' interface. Upon vigorous interactions between MWs and electromagnetic absorbent PPy NG coating, the energy was transformed into a large amount of heat leading to a drastic temperature increase that was simultaneously used for the instant carbonization of PPy and the decomposition of fine ferrocene particles, which resulted in multi-walled carbon nanotubes (CNTs) growth at the interface. Meanwhile, the as-grown CNTs on the surface conveyed the heat into the adjacent bulk PP and caused locally molten surface layers' formation. Eventually, the light pressure applied at the interface during heating process, squeezed the molten layers together and a new weld was generated. The method is considerably advantageous compared to other alternatives due to; (i) its fast, straightforward and affordable nature, (ii) its applicability at ambient conditions without the need of any extra equipment or chemical, and also (iii) its ability to provide clean, durable and functional welds, via precisely controlling process parameters, without causing any thermal distortion or physical alterations in the bulk TPM. Thus, it is believed that this novel welding process will become much preferable for the manufacturing of next generation TPM composites in large scale, through short-term MW heating.

COLL 644

Two faces of a polyelectrolyte multilayer: Tailoring the structure and the properties

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The interface between a polyelectrolyte multilayer (PEMU) and its substrate has remained unexplored until recently due to the inability of most traditional techniques to access it without destroying the film. To investigate this buried face, multilayers of poly(diallyldimethylammonium) (PDADMA) and poly(styrene sulfonate) (PSS) were assembled on a pH-sensitive substrate (aluminum) and subsequently released by exposure to aqueous alkali (pH = 11). Surface morphology, viscoelasticity and elemental composition of the film/solution and film/substrate interfaces were examined using atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) revealing a substantial difference between the two sides of the PEMU. These results support a previously described model of multilayer growth, where an excess of positive charges remains in the film after assembly. Surface properties of the free-standing films were then manipulated to exert unique characteristics. A capping layer of nafion, a perfluorinated polymer, was adsorbed on top of the hydrophilic PDADMA/PSS film prior to release, to enhance the hydrophobicity of the film/solution interface. The released PEMU, so-called “janus” polyelectrolyte multilayer, showed water-repelling properties on one side, (water contact angle of 95°) while simultaneously exhibiting hydrophilicity on the other side (water contact angle of 34°). Surface analysis using XPS revealed a gradient of fluorine in the multilayer caused by the interlayer diffusion of the fluorinated polyelectrolyte. Finally, the resistance of the nafion capped PEMUs to high salt concentration was tested using Fourier transform infrared spectroscopy (FTIR).

COLL 645

Electrochemically-triggered microgel size modulation

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Microgels are crosslinked polymeric particles consisting of a porous network swollen by a solvent with the ability to undergo often a volume phase transition with respect to environmental changes. Introduction of charges into the microgel network leads to a possible interaction of the polyelectrolyte microgel with oppositely charged counterions based on electrostatic attraction (host-guest interplay). The charge of guest molecules can be changed by various means. Besides light-sensitive counterions,^[1] electrochemically-addressable counterions are of scientific interest since years. For

example, electrolysis of complexes between linear polyelectrolytes and hexacyanoferrates leads to a film formation onto the electrodes,^[2] while the polymer architecture has an influence on these processes. We could demonstrate recently an electrochemically-triggered bulk aggregation of branched macromolecules in combination with redox-active species and simultaneous switching between the unimeric and the micellar/vesicular state.^[3]

We now address thermoresponsive cationic microgels and their influence on the electrochemistry of hexacyanoferrates. Further, we investigate the influence of the counterion guests on the swelling of the microgel hosts. The combination of hydrodynamic voltammetry and electrochemical impedance spectroscopy allowed a distinction between the electron pathways.^[4] In addition, the data strongly suggest the selective uptake of ferricyanide and an encapsulation of the guest molecules inside the microgel network at elevated temperatures. By that, the size of the cationic microgel can be reversibly modulated by electrochemical switching leading to a redox-responsive microgel system.^[5] In addition, there is an increased contribution of direct electron injection into the $[\text{Fe}(\text{CN})_6]^{3-}$ -microgel complex, as seen by impedance spectroscopy.

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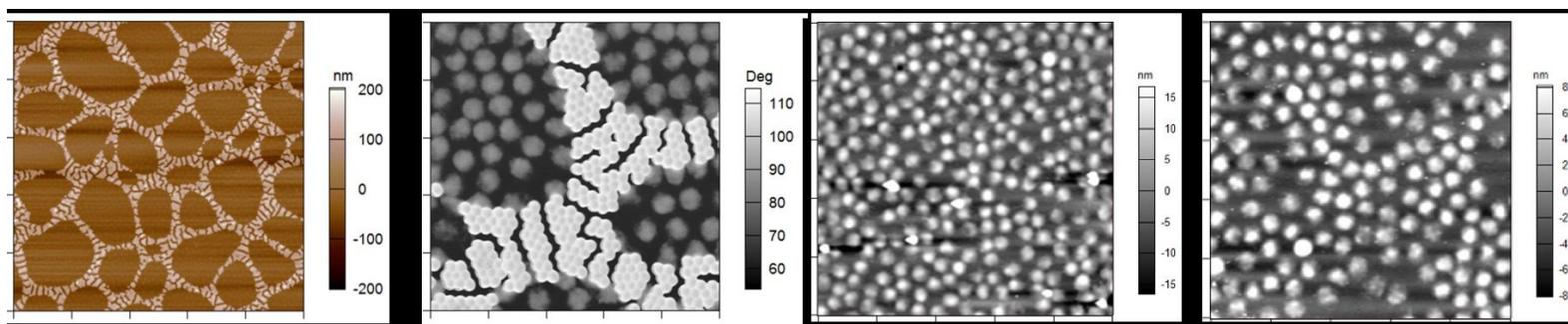
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COLL 646

Tuning the properties of oligo ethylene glycol and poly (*N*-isopropylacrylamide) microgel for future biomedical applications

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We synthesized a series of oligo(ethylene glycol) methyl ether methacrylate (OEGMA) microgel systems with defined size and crosslinking density by tuning the reaction temperature and amount of poly(ethylene glycol) diacrylate (PEGDA) crosslinker. We studied the deformability, surface pattern and degradation of these microgels by Dynamic Light Scattering, Atomic Force Microscope and Resistive Pulse Sensors. Their deformability, translocation through smaller pores and hence the spreading on surface depends on polymer concentration and network flexibility inside the particles. We found



that microgels prepared without any crosslinker exhibit very low crosslinking density which is tunable by reaction temperature. The deformability of self-crosslinked microgel prepared at high temperature is comparable with microgel prepared with 5% PEGDA. We studied how the particle deformability dictates their assembly on functionalized glass surface (Fig. 1 a and b). We also studied their accelerated degradation (Fig. 1 c and d) and found that the rate of degradation not only depends on the amount of crosslinker but also on the extent of chain transfer reaction happened during the synthesis. This study will help us build future microgel-based biocompatible dynamic system with controlled flexibility, porosity and functionality for tissue engineering and drug delivery applications.

Fig. 1: AFM (a) height retrace and (b) phase retrace of a patterned microgel monolayer formed upon sequential deposition of stiff OEGMA microgel with 10% PEGDA and soft OEGMA prepared at 70 °C on an APTMS-functionalized glass substrate. AFM height retrace of 1% PEGDA crosslinked microgel (c) before and (d) after incubation in 3M HCl solution at 50 °C for 9 weeks.

COLL 647

Spiky hedgehog particles with conformal layer-by-layer coatings

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Layer-by-layer (LbL) assembly allows for the production of functional thin films on macroscopically flat surfaces and microscale spherical colloidal particles. By expanding LbL films to more complex colloidal surface geometries featuring high corrugation, one can engineer a new generation of colloids with high dispersion stability, an unusual balance of van der Waals, electrostatic, and other interactions, as well as a diversity of chemical/biological functionalities. In this study, LbL was applied to a spiky colloidal substrate—Hedgehog Particles (HPs). HPs consist of a micron-sized polystyrene core surrounded by nanoscale zinc oxide spikes. The surface corrugation from the spikes leads to reduced aggregation and increased colloidal stability, resulting in the ability to disperse in both organic and aqueous solvents. This property combined with the high surface area of HPs indicates that HPs can have a large impact on the field of catalysis.

Uniform coating of nanocatalysts and other functional materials can be achieved by LbL films, as demonstrated by electron and confocal microscopy. Furthermore, zeta potential measurements confirmed the deposition of alternating charged polymer layers. Additionally, the cross-linking of polymer layers allowed for additional control of film morphology. The rigid zinc oxide spikes can be used as a template and dissolved with acid, leaving behind polymeric spikes. In addition to polymer films, a uniform and homogeneous coating of gold nanoparticles was achieved on the HP spikes. These hybrid HPs are being investigated as a novel catalytic system which can greatly expand on catalysis in hydrophobic solvents.

COLL 648

Strong and tunable wet adhesion with rationally designed layer-by-layer assembled triblock copolymer films

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The wet-adhesion of Layer-by-Layer (LbL) assembled films of triblock copolymer micelles has been evaluated with colloidal probe AFM, opening up yet another application area for block copolymers – as nanometer thin adhesive films with tailored thickness and properties. A network of energy dissipating polymer chains with electrostatic linkages can be built through the LbL assembly of triblock copolymer micelles with long, hydrophobic, low Tg middle blocks and short, charged outer blocks. Four triblock copolymers were synthesized and studied, one pair having poly(ethyl hexyl methacrylate) (PEHMA) and the other poly(n-butyl methacrylate) as middle block. One triblock copolymer with cationic and one with anionic outer blocks was made from each middle block. It has been found earlier that the wet adhesion of an LbL system with poly(allylamine hydrochloride) (PAH) and hyaluronic acid (HA) was 20 times higher than that of bone and collagen. The pull-of force for the PEHMA system studied here was in turn more than 400% higher than that of PAH/HA. This study has shown that the devised concept can yield films with high wet adhesion which could find numerous uses where a nanometer-thin adhesive joint is desired.

COLL 649

Cellulose nanocrystals as additive and reinforcing agent in melt-spinning of polypropylene

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Nanocelluloses have gained major interest as reinforcement for polymers due to their excellent mechanical properties. However, challenge associated with the nanocellulose dispersion hinders the production of composite polymers with expected properties. The purpose of this study is to develop a new nonwoven platform to produce polyethylene and polypropylene composites featuring bio-based materials. These new fibrous and film composites are expected to display improved thermal-mechanical properties when compared to the base materials. In order to enhance the compatibility of hydrophilic CNC with hydrophobic PP, maleic anhydride polypropylene was used as compatibilizer. CNC and NFC used in this work were both commercial grades supplied by the University of Maine. AFM images were obtained to assess the structure of these two types of nanocelluloses. In order to adjust the shear viscosity of PP after the addition of CNC or NFC, their loading was varied in the range between 0.5 to 2.5 wt%. In this new trial, the materbatch was pre-diluted in order to obtain better nanocelluloses dispersion in PP matrices. SEM imaging was used to better understand the structure of PP and the composite fibers. Some physical properties of PP and the composite fibers were determined, including the tensile strength and crystal size/shape. In addition, the thermal properties of the fibers were evaluated as well as the crystallization kinetics.

COLL 650

Stimuli responsive polymer capsules with multiple concentric shells

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Polymeric capsules have been extensively studied by researches for encapsulation of payloads such as drugs, cosmetics, therapeutics, and flavor ingredients. Current techniques for producing capsules (such as via emulsion polymerization) typically result in a polymeric shell of given thickness and composition. Herein, we report a simple approach for creating polymeric capsules with multiple concentric layers, much like the structure of an onion. The thickness of each layer in the shell can be controlled, and more importantly, the chemical composition of each layer can also be varied. For example, one layer can be made from a thermosensitive polymer like poly(N-isopropylacrylamide) whereas the adjacent layer can be composed of a polymer that is responsive to a different stimulus such as pH. In turn, the overall capsule can display responsiveness to multiple stimuli. The presence of multiple layers can also be used to control the release of payloads encapsulated in the capsule core. We have also extended our technique to fabricate non-spherical shapes such as tubes or cylinders with a concentric layered structure.

COLL 651

N-halamines: Antimicrobial surface functionalization of polymers & nanomaterials

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In the fields of healthcare, food processing, and agriculture, vast resources are being directed toward management of microbial contamination risk, yet problems continue to persist. N-halamines offer an effective and safe means for incorporating potent and rechargeable antimicrobial properties into common-touch surfaces. The choice of surface functionalization and conjugation methods, however, can have a significant impact on performance, durability, and cost. New inventions are presented that focus on novel incorporation of N-halamines and their commercial application in polymers, paints, and hard surfaces. Compounds are synthesized as polymeric particles or attached to surfaces using pre-treatment methods such as Layer-by-Layer (LbL) deposition, gas plasma functionalization, silane couplers, and carbodiimide crosslinking chemistry. Characterization is verified using multiple known methods such as Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Dynamic Light Scattering (DLS), X-ray Fluorescence (XRF) and UV/VIS spectroscopy. Commercial scaling-up of the antimicrobial polymeric additives has been achieved through the identification and control of critical process characteristics (CPC's) at the nanoscale level (polymerizing emulsion). Currently, the extent of retention of the antimicrobial properties of N-halamine – based nanoparticles after their application to the explored materials is under investigation.

COLL 652

Interlayer coupling and compositional domain growth in stacked lipid bilayer membrane systems

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The formation and growth of compositional domains within multicomponent lipid bilayer membranes has been experimentally reported in several lipid systems. Recent findings demonstrate further that stacked bilayer membrane systems can exhibit long range interlayer alignment of compositional domains, with an emergent columnar order extending over hundreds of membranes. The average domain size in such systems was found to increase in time as a power law with exponent ~ 0.455 , in apparent discord with the diffusion-limited Ostwald ripening scaling exponent of $\sim 1/3$ reported for single membrane systems. However, the detailed physical mechanism responsible for the intermembrane coupling is not well-understood, nor is the nature of the subsequent

alignment-induced coarsening regime with enhanced scaling exponent.

We combine numerical simulations of an advective diffuse-interface description of multimembrane lamellae with theoretical sharp interface analysis and dynamic scaling arguments to provide a quantitative analysis of the effect of interlayer coupling on domain growth and long range intermembrane alignment. Our description incorporates the effects of thermodynamic intermembrane coupling, membrane/solvent hydrodynamics, intermembrane friction, and lipid diffusion. Three alignment-driven dynamic scaling regimes are identified for diffusion-dominated, advection/interlayer friction-dominated, and advection/membrane viscosity-dominated systems, respectively. The noted experimental systems are shown to be within the advection/interlayer friction-dominated regime, for which we predict a scaling exponent of $1/2$, in good agreement with reported values. We also propose a quantitative measure of domain alignment based on an intermembrane correlation function, and demonstrate that its behavior is closely related with that of the domain scaling.

COLL 653

Engineered nanostructures of lipopolysaccharide triggers rapid morphogenesis among dendritic cells

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Dendritic cells (DCs) are antigen-presenting cells that elicit specific T-cell responses, which offers great promise for anti-tumor therapy. To realize the therapeutic potential, directing DC cells to desired immune-responses is critical. This presentation reports a new means to regulate the DC signaling process, i.e., *via* using nanotechnology. Using a commonly known stimuli for DC, lipopolysaccharide (LPS), the responses, e.g., activation and maturation, can be monitored by measuring the release of cytokines such as TNF- α and IL-6, as well as by visualizing cellular morphology. DCs, upon maturation, evolve from hat shape to dendritic morphology. Five arrays of LPS nanodots were produced, with height of 9.1 nm and diameter of 240 nm. The periodicity of the five arrays ranged from 200, 300, 500, 700, to 1000 nm. Upon interactions with bone marrow-derived dendritic cells (BMDCs) from C57BL/6 mice, the cellular morphology was studied using scanning electron microscopy (SEM) and atomic force microscopy (AFM). As shown in Figure 1, the morphology of mature BMDCs was observed among BMDCs after 1 h exposure to LPS presented by nanostructures, while elongated BMDCs with smooth membrane were observed after 1 h activation by LPS in solution. These observations indicate that LPS nanostructures promote rapid maturation of BMDCs, and that DC activation depends sensitively on the local arrangement of the

ligands, which can be designed and produced using nanotechnology. Parallel cytokine assays confirm this conclusion. This presentation also discusses possible mechanisms for the highly effective stimulation of cells by nanostructures of ligands.

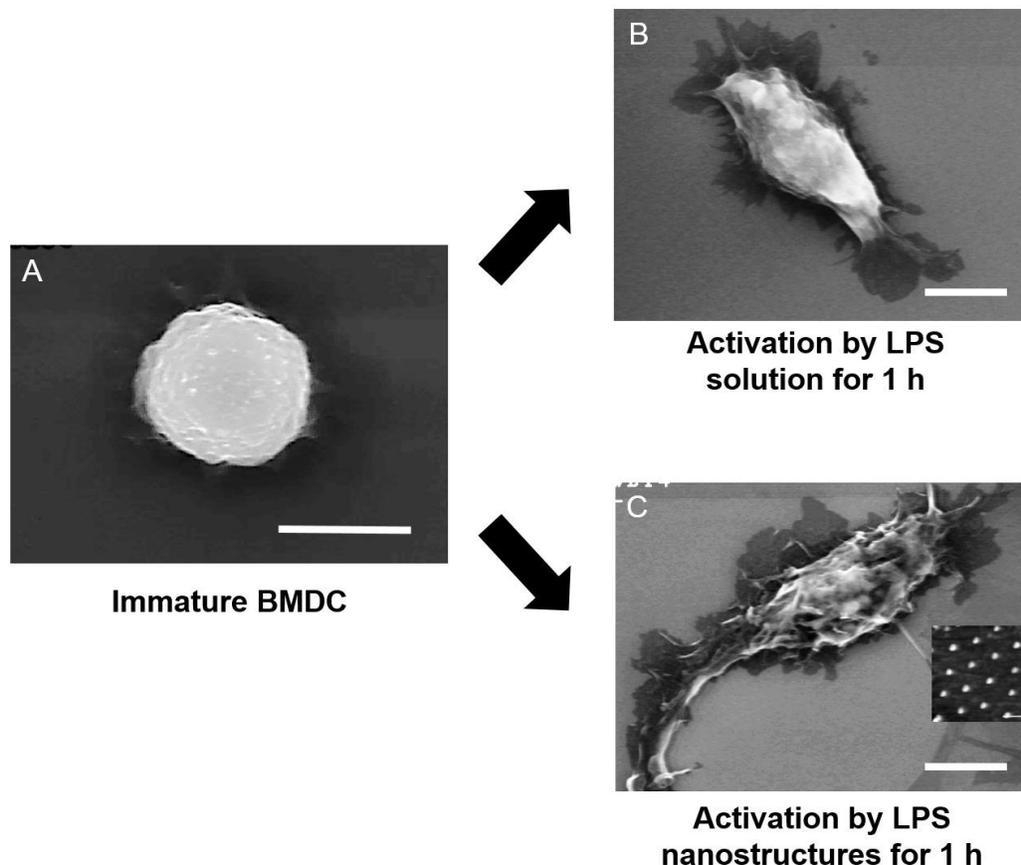


Figure 1. SEM images reveal cellular morphologies of (A) immature BMDC, (B) elongated BMDC with smooth membrane after 1 h activation by soluble LPS, and (C) mature BMDC after activation by LPS nanostructures for 1 h. Inset in C is a characteristic AFM image of LPS nanostructures. Scale bars are as follows: (A)-(C), 10 μm ; inset in (C) 500 nm

COLL 654

Effects of cationic and anionic surfactant concentrations on adsorbed self-assembled micellar structure at graphite surfaces

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In this work, we explore the effects of mixing species of cationic and anionic surfactant on their adsorbed self-assembled structures. Such mixtures often have structures that

differ greatly from those seen in single component solutions, forming vesicles and cylindrical micelles at various concentrations. When mixed, the surfactants also aggregate more easily and have higher surface activities, making their mixtures interesting topics for detergent development. We looked at the structure of micelles comprised of various mixtures of sodium dodecyl sulfate (SDS), dodecylamine HCl (DAH), and sodium palmitate (NaPa) on a graphite surface in water via atomic force microscopy. In images of pure SDS and DAH, it was found that the micelles present at the surface were hemicylindrical in structure, in agreement with previous works on the subject. Increasing surfactant concentration invariably decreased the width of these micellar lines down to a minimum value past the critical micelle concentration. This minimum micellar width was found to be roughly 4.6 nm for SDS and 8.6 nm for DAH within the studied concentrations of 5 to 15 mM solutions. Increasing the concentration of monovalent counterions in solution did not appear to affect this minimum width. When the surfactants were present in mixed solution, however, they displayed new behavior and structure at the graphite surface. Namely, they began exhibiting a fishbone pattern with a great deal of disorder and a large number of grain boundaries. Changing counterion concentration in these surfactant mixtures appears to directly affect the degree of surface disorder, with higher concentrations producing seemingly more compact structures. While the pure solutions of SDS and DAH were studied at concentrations ranging from 5 to 15 mM, their mixture could only be studied in molar ratios between 20:1 and 40:1 due to the presence of milky film. Further work will be done on the effects of both counterion and surfactant concentration on the mechanical properties of these films, such as elasticity and breakthrough force.

COLL 655

Stability of giant vesicles in salinity gradients

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Giant lipid vesicles, the simplest cell-like structures, are topologically closed compartments consisting of a semi-permeable flexible shell consisting of single lipid bilayer and an aqueous core encapsulating femto- to pico-liter quantities of the aqueous phase. Although water equilibrates across vesicular walls between the encapsulated core and the surrounding phase, passive permeation of solutes is strongly hindered. As a result, gradients of solute concentration are readily established. Here, using fluorescence microscopy methods we show that giant vesicles subject to salt (or salinity) gradients become unstable in the presence of glass surfaces: lysing, rupturing, and spreading at the solid surface producing laterally fluid two-dimensional supported lipid bilayers.

Monitoring the vesicle destabilization process using fluorescence microscopy in real-time, we find that the dimensional and morphological transition – from three dimensional

vesicles to two-dimensional lamellar supported membranes – proceeds through an interplay of symmetric and asymmetric rupture. Asymmetric rupture involves the formation of a single pore in the GUV at the contact boundary of a deflated GUV; Subsequent expansion of which drives the dimensional and the morphological transition. This mode of rupture, evident by the appearance of heart-shaped and non-spreading membrane patches at the glass surface inverts the membrane leaflets presenting the inner leaflet at the “top” membrane-water interface and the outer leaflet of the GUV assumes a proximal position at the membrane-substrate interface. The symmetric rupture, which is also evident in our data, involves pore formation at the point of contact between essentially under-formed GUVs and the underlying substrate, by contrast preserves the leaflet order and it is accompanied by lateral spreading, which we observe. Taken together, these results provide a mechanistic explanation for conditions under which membrane patches obtained by rupture of giant vesicles retain or abandon leaflet asymmetry – a fundamental property of membranes of living cells.

COLL 656

Using infrared measurements to probe the structure and local environment of membrane proteins

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It is well known that tryptophan (Trp) plays an important role in anchoring various membrane peptides and proteins into lipid bilayers. In addition, Trp residues are critical towards the self-assembly and function of a number of ion channels. However, the indole ring of Trp lacks a strong and convenient infrared (IR) transition that can be exploited to study the local structure and dynamics of membrane proteins using IR spectroscopy. Herein, we demonstrate that the CN stretching vibration of a nitrile-derivatized Trp analog, 5-cyanotryptophan, is a useful IR probe for this purpose. Specifically, we will discuss, using the transmembrane domain of the influenza A M2 proton channel as an example, how this probe, in conjunction with several linear and non-linear IR spectroscopic techniques, can be used to site-specifically determine the orientation, hydration state, and dynamics of Trp residues in membrane peptides and proteins.

COLL 657

Cholesterol-enriched microdomain formation induced by viral-encoded, membrane active amphipathic peptide

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The α -Helical (AH) domain of the hepatitis C virus nonstructural protein NS5A – anchored at the cytoplasmic leaflet of the endoplasmic reticulum – plays a role in viral replication but the peptides derived from the domain also exhibit remarkably broad-spectrum virocidal activity raising questions about their modes of membrane association. Here, using giant lipid vesicles, we show that the AH peptide discriminates between membrane compositions: In cholesterol-containing membranes, peptide binding induces micro-domain formation. By contrast, cholesterol-depleted membranes undergo global softening at elevated peptide concentrations. Furthermore, in mixed populations, the presence of ~100 nanometer vesicles of viral dimensions suppress these peptide-induced perturbations in GUVs suggesting size-dependent membrane association. These synergistic – composition- and size-dependent – interactions explain, in part, how AH domain might on the one hand segregate molecules needed for viral assembly and furnish peptides exhibiting broad-spectrum virocidal activity on the other.

Work done in partnership with:

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COLL 658

Multivalent presentation enhances the evolution of membrane structure and actin assembly

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Bone morphogenetic protein-2(BMP2), a member of the transforming growth factor- β -super family induces osteogenic differentiation among osteoprogenitor cells and human mesenchymal stem cells. Cartilage oligomerization matrix protein (COMP) is a homopentamer that binds up to 5 BMP2 molecules, potentially presenting it to the receptors on C2C12 cells in a multivalent manner. Our prior investigation indicates that the COMP+BMP2 complex enhances the activity of BMP2 in the context of osteogenic differentiation via the Smad pathway. This presentation provides further mechanistic insight into this enhancement at the molecular and single cell level. Using multimodal and multifunctional approach of atomic force microscopy image, single cell mechanics, and confocal imaging, our investigation reveals that treatment of C2C12 cells with COMP+BMP2 increases the stiffness of the cell membrane and appearance of fiber-like features on the cells. COMP+BMP2 induces the strong presence of actin stress fibers at the basal interface of the cells and the rearrangement and formation of ordered actin filaments on the apical surface to a greater extent when compared to cells treated with the same amount of BMP2 alone. These finding help us understand the mechanism of this enhancement, therefore, demonstrating the ability of COMP to present BMP in a more active configuration to stimulate bone regeneration at lower doses.

COLL 659

Configurable lipid membrane gradients quantify diffusion, phase separations, and binding densities

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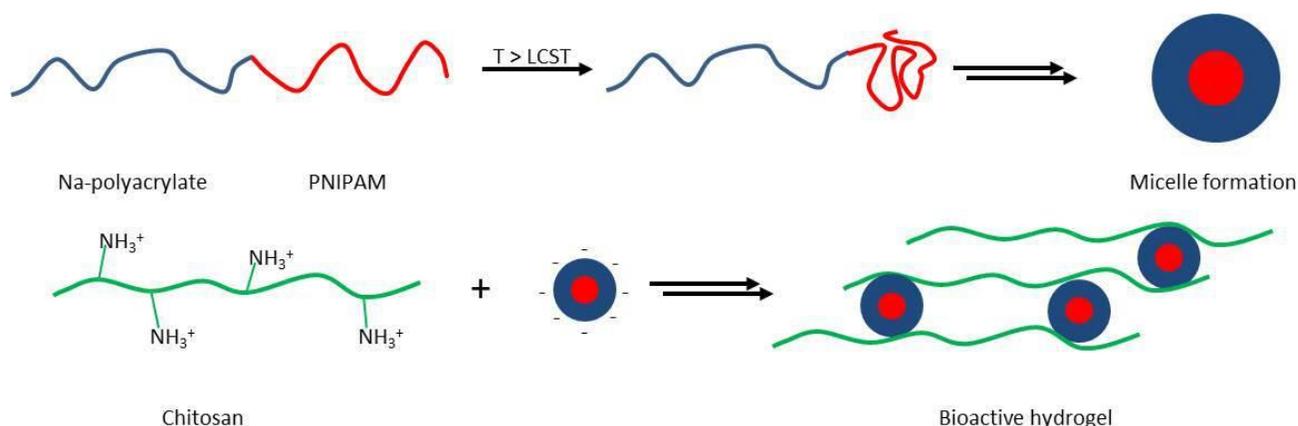
Systematically testing the composition of supported phospholipid membranes typically requires many separate lipid depositions in distinct experiments or bins. Alternatively, we developed a simple and low-cost method to create phospholipid gradients that exhibit a broad range of spatially resolvable compositions. We image these gradients as they relax to equilibrium to reveal diffusion coefficients, phase separation parameters, and protein binding densities as a function of localized lipid mixtures, in single experiments. Compositional gradients are formed by directed self-assembly where rapid-prototyping techniques (i.e., 3D printing or laser-cutting) prescribe supported lipid geometries that self-spread, heal and mix by diffusion. We are currently applying this platform to explore mechanisms of intra-bilayer cholesterol transport. DOI: 10.1039/C5SM02013A, Soft Matter (2015).

COLL 660

Stimuli-responsive hydrogels for treatment of severe limb trauma and controlled drug delivery

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Severe limb trauma is the most common type of battlefield injury. Current technologies are limited in their ability to prevent infection and are difficult to remove from the wound at later stages of treatment, often causing further tissue damage. Therefore, a need exists for new wound-contact materials that incorporate hemostatic, antibiotic drug releasing, and absorptive elements to reduce wound-related mortality and morbidity. A novel thermoresponsive mixture of poly(*N*-isopropylacrylamide)-block-sodium polyacrylate (PNIPAM-*b*-PAA_{Na}) and chitosan was designed to undergo a sol-gel transition around the LCST temperature of PNIPAM, 32-34 °C. This allows for an injectable, drug loaded sol to be locally delivered to the site of severe limb wounds, effecting hemostasis and preventing further infection. The synthesis, characterization, and select *in vitro* characteristics of the gel are presented herein.



COLL 661

Cellulose nanocrystals and closite-Na⁺ clay micro-nano complex formation and its application in drug delivery studies

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In this study we report formation of a micro-nano complex by using cellulose nanocrystals (CNCs) and Closite-Na⁺ (CNa⁺) MMT clay by simple sonication process without any chemical modifications, primarily for drug delivery application. Three

different weight ratios 1:1, 1:2 and 2:1 of CNCs to CNa⁺ clay have been taken for the complex formation. Polarized optical microscopy (POM), X-ray diffraction spectroscopy (XRD) and field emission scanning electron microscopy (FESEM) techniques have been utilized for structural analysis of micro-nano complex. POM and FESEM studies have confirmed the formation of cubic shape micro-nano complex structure in-between CNCs and CNa⁺ clay for the weight ratio 2:1 of CNCs to CNa⁺ clay (Figure 1). Particle size analysis shows the distribution of particle diameter in the range of 70 nm – 120 nm. Interaction between CNCs and CNa⁺ clay due to sonication has been confirmed by Fourier transform infrared spectroscopy (FTIR). The thermal stability of the complex has been analyzed by thermal gravimetric analysis. Fluorouracil, which is an anti-cancer drug has been loaded on the CNC-CNa⁺ complex of weight ratio 2:1 and its release studies have been carried out in detail. Drug release experiments have been carried out in phosphate-buffered saline (PBS) medium and simulated body fluids (SBF), which gave satisfactory results. Kinetic study of drug release has also been carried out to calculate the kinetic parameters of release. Thus the micro-nano complex formed by simple sonication technique in this study by using CNCs and CNa⁺ clay may be utilized in drug delivery area.

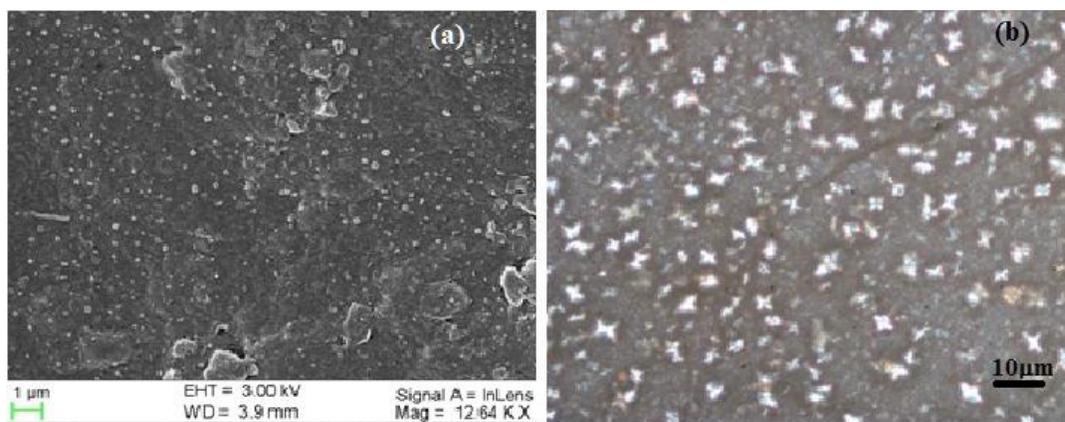


Figure 1: (a) FESEM and (b) POM images of the micro-nano complex cubic shaped CNC: CNa⁺ at weight ratio of 2:1

COLL 662

Titanium dioxide nanoparticles induce oxidative stress

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Titanium dioxide nanoparticles (TiO₂ NPs) are present at high levels in industrial and commercial products such as paints, cosmetics, and food. The resulting human exposure motivates interest in understanding how these NPs interact with cells. In the bloodstream, all NPs are exposed to blood serum proteins that adsorb onto the surface of the NP forming a protein “corona.” This protein layer mediates the interaction

between the NP and the cell. Using gel electrophoresis and proteomic analysis, we first identified the corona of proteins adsorbed on TiO₂ NPs and model carboxylate-modified polystyrene nanoparticles (PS NPs). We then incubated HeLa cells with each NP and serum proteins for 24 hrs. Using a PCR array to screen for changes in oxidative stress-related genes, we identified changes in the peroxiredoxin family of anti-oxidant enzymes for TiO₂-treated cells. This contrasts with the insignificant change in peroxiredoxin levels found in response to PS NPs. Because corona composition remained similar in both NP types, we suggest oxidative stress-related changes are a direct result of the nanoparticle identity.

COLL 663

Mesostructured silica nanorod based fluorescent sensor for highly sensitive and visual detection of dopamine

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Dopamine (DA) is a neurotransmitter which has many important brain and cardiovascular functions. Since dysfunction of DA may be an indication of diseases such as Parkinson's and Alzheimer's disease, its diagnosis is crucial. Here, we present the development of a fluorescent sensor based on colloidal nanoparticles for the simple, sensitive and selective detection of DA. We first synthesized mesostructured silica nanoparticles (MSNs) and encapsulated pyrene as the fluorescent probe in their hydrophobic parts. Nanoconfinement of pyrene inside the MSNs resulted in a bright excimer emission which is centered around 473 nm. Furthermore, pyrene interaction with pore templating surfactant micelles led to the formation of rod-shaped particles with uniform morphology. Nanorods had a thickness around 65 nm and an aspect ratio ranging from 2 to 5.5. The nanorods exhibited good colloidal distribution as well as stable fluorescence in tris-buffer (pH= 8.6) solution where they were incubated with DA during detection measurements. Mesostructured nanorods showed highly sensitive fluorescence quenching against DA which was attributed to the electron transfer from the excited pyrene dimers to quinone; oxidized form of DA. The prepared nanoparticle sensor assay had a practical detection limit of 300 nM and can detect DA concentration up to 25 µM. Electron microscopy images revealed that oxidized dopamine is polymerized around the nanorods in the basic assay leading to the formation of nanorod/polydopamine (PDA) hybrids and enlarged PDA sheets with further increase in DA concentration (> 50 µM). Finally, we demonstrated visual dopamine detection thanks to the strong blue emission of pyrene dimers under UV light. We believe that the reported assay with its simple preparation, sensitivity and selectivity present a promising dopamine sensing platform.

COLL 664

Profiling heterogeneity of circulating tumor cells using multifunctional nanoplatform

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Circulating tumor cells (CTC) are the main vehicles of metastatic relapse and becoming a dynamic prognostic biomarker for oncologists in clinics. Two major barriers for the exploitation of CTC analysis as "liquid biopsy" in clinics are the following: CTCs are highly heterogeneous in nature due to epithelial-mesenchymal transition (EMT) and also they are extreme rare cells. Here we will discuss our recent reports for the development of multicolor nanodots conjugated magnetic nanoparticle based multifunctional fluorescent-magnetic nanoplatform for targeted capturing and fluorescence mapping of heterogeneous CTCs from whole blood sample. Experimental data indicate that multicolor fluorescence nanoplatforms are capable of mapping heterogeneity of circulating tumor cells by accurate capturing and identification of multiple subpopulations of CTCs from blood.

COLL 665

Lateral phase separation in superheated perfluorocarbon nanodroplet monolayers leading to enhanced ultrasound contrast imaging

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This work explored the effect of lateral phase separation of phospholipids on acoustic contrast of perfluorocarbon droplets. Nanodroplets containing a volatile liquid perfluorocarbon core have been studied as ultrasound contrast agents owing to their ability to be vaporized into high-contrast microbubbles in response to high intensity focused ultrasound. These droplets are generally stabilized by a mixture of phospholipids and polymer-lipids that provide both stability and resistance to serum proteins. However, while there have been several studies on the effect of different acoustic parameters on contrast, the effect of the droplet's stabilizing shell has not been studied as extensively. Inspired by previous studies showing lateral phase separation in microbubbles and vesicles, nanodroplets were formulated with a perfluorocarbon core and a shell composed of varying amounts of saturated (DPPC) and unsaturated (DOPC) phospholipids along with cholesterol. The stability of these mixed lipid droplets was confirmed via Nanoparticle Tracking Analysis of particle size and concentration. Because of difficulties in using fluorescence microscopy to measure phase separation on nanodroplets measuring less than 400 nm, lateral lipid phase separation was characterized by FRET analysis and TEM. The effect of the consequent shell composition on phase separation, coexistence, and nature of domain distribution in the

monolayer was thus examined. It was found that, monolayer phase separation led to a distinct increase in acoustic response from the droplets on application of high intensity focused ultrasound by at least one order of magnitude. Droplets containing mixed lipid monolayers were also found to produce a significantly greater and less polydisperse yield than single-component droplets, which could be useful for scaling up preparation protocols. These monolayer-dependent properties may help not only to understand the formulation and behavior of acoustically responsive nanodroplets, they would also aid in tuning the interfacial properties of these contrast agents to obtain desired responses in different biological environments.

COLL 666

Controlled local chemotherapeutic drug delivery through self-assembled peptide amphiphile hydrogels

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Peptide amphiphiles (PA) self-assemble into three dimensional hydrogels which are suitable environment to encapsulate both hydrophobic and hydrophilic drug molecules. PA hydrogels have significant advantages for controlled drug delivery applications due to their high capacity to retain water, biocompatibility, and biodegradability. The drug release through the PA hydrogels can be sustain via local concentration gradient or different environmental factors including pH, temperature and enzymatic activation etc. In this study, we aim to develop injectable and biodegradable self-assembled PA hydrogels which can form three dimensional supramolecular networks at physiological conditions. Doxorubicin which was FDA approved and clinically used chemotherapeutic molecule for breast cancer treatments is selected as a drug molecule and encapsulated within PA hydrogels with 100% efficiency. After the characterizations of the physical and chemical properties of the PA self-assembled PA hydrogels prepared at different concentrations, the release behavior of the drug molecule through the PA hydrogels was studied at physiological conditions; and the diffusion parameters of the drug molecule within the PA hydrogels were estimated using Fluorescence Recovery After Photobleaching (FRAP) technique. Moreover, breast cancer model using 4T1 cancer cell line were developed to test the applicability of doxorubicin encapsulated self-assembled PA hydrogels for breast cancer treatments at *in vivo* conditions.

COLL 667

Probing polymeric nanoparticles with solid perfluorocarbon for *in vivo* imaging

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Perfluorocarbon nanoemulsions have been used for a range of biomedical applications in the past decades, ranging from blood substitutes to contrast agents for imaging. In particular, contrast agents for ^{19}F MRI usually consist of a liquid perfluorocarbon stabilized by a lipid surfactant. However, poor relaxation parameters, chemical shift artifacts and toxicity often hamper the performance of these agents in MRI. Furthermore, the colloidal stability of perfluorocarbon-containing emulsions is relatively low, which may also lead to poor biodistribution and organ accumulation and thus strongly limits additional *in vivo* applications such as drug delivery.

Here we studied the encapsulation of a solid superfluorinated molecular probe, herein called PERFECTA, which shows only a single resonance peak in ^{19}F NMR, in poly-D,L-lactide-co-glycolide (PLGA) nanoparticles. We synthesized the particles using a combination of ultrasonication and solvent evaporation method to form the miniemulsion. Particularly we focus on impact of different parameters on properties of resulting colloids, including the impact of surfactant, oil phase, and sonication energy. Additionally, we studied coencapsulation of PERFECTA with different liquid perfluorocarbons, such as perfluoro-15-crown-5-ether and perfluorooctylbromide. To obtain information on physicochemical properties of resulting colloids we characterized them with different techniques, including electron microscopy (TEM, Cryo-TEM, SEM), dynamic light scattering, X-ray diffraction, zeta-potential measurements and calorimetric methods. Moreover, we quantified amount of encapsulated fluorine by ^{19}F NMR using external and internal standards and carried out relaxation time measurement.

Our results demonstrate how the properties of fluorine-based emulsions can be tuned by changing various parameters during the emulsification process. Thus, we show that PERFECTA-encapsulated particles are promising for imaging with quantitative ^{19}F MRI *in vivo* and can potentially be applied as theranostic agents. Therefore, we are now carrying out studies on coencapsulation of PERFECTA with fluorescent dyes to add an additional imaging modality.

COLL 668

Mixed micelles of chemically modified Pluronic as drug delivery system

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A new strategy to design a multifunctional mixed Pluronic micelle system aiming to overcome weaknesses of normal Pluronic when used as drug delivery systems will be presented. Pluronic are popular drug delivery systems known to form micelles. The specific advantages of Pluronic-based micelles as drug carriers lie in 1) biocompatibility and nontoxicity, 2) feasibility of structural and functional modification, 3) ability to encapsulate water-insoluble bioactive drugs and 4) commercial availability. However,

Pluronic micelles suffer from several weak points which have impeded further applications. Pluronics normally have relatively high CMCs which consequently decrease the micelle stability in human body, leading to micelle disintegration and sudden burst of drug. Additionally Pluronic systems have relatively low hydrophobic drug loading capacity.

By chemical modification of Pluronic, F127 (PEO-PPO-PEO, Mn=12,500 g/mol) and reversed Pluronic, 10R5 (PPO-PEO-PPO, Mn=2000 g/mol) with folic acid and quercetin, respectively, increase the drug loading capability was increased and the CMC was lowered. Folic acid was covalently conjugated to the chain ends of F127 to introduce a cancer cell-targeting functionality. Hydrophobic quercetin (as a combinatory drug for Doxorubicin (DOX)) was anchored to the PPO chain ends of 10R5 to increase interaction with hydrophobic drugs. Colloidal probe AFM further indicated that the adhesion force between DOX coated probe and quercetin anchored Pluronic was approximately doubled compared to the adhesion between DOX and unmodified Pluronic. The release rate of the anti-cancer drug DOX was also lowered and the release time was increased.

COLL 669

Pulsed laser generated gold nanoparticles allow optimization of surface tri-functionalization for their targeted delivery into cancer cell nuclei

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Among the large variety of subcellular organelles, the nucleus remains a significant target for nanoparticles due to the importance of genetic information and transcription machinery residing there. In this presentation, we demonstrate highly efficient and targeted nuclear delivery of gold nanoparticles produced by pulsed laser ablation of a bulk gold target in ultrapure water. This unique pulsed laser ablation (fabrication) process gives access to produce stable naturally negative charged gold nanoparticles avoiding the use of any chemical precursors, reducing agents, and stabilizing ligands. Such chemically pure gold nanoparticles free of stabilizer and surfactants offer an opportunity to optimize surface functionalization of gold nanoparticles with three types of functional ligands, containing poly (ethylene glycol) and two different peptides, for their targeted delivery to nuclei following their internalization into cancer cells. Both optical microscopy and transmission electron microscopy were used to confirm the *in vitro* targeted nuclear delivery of such gold nanoparticles cofunctionalized with both poly (ethylene glycol) and peptides by showing their presence in the cancer cell nucleus. We envision that the methods and findings reported here will accelerate the development of novel diagnostic and therapeutic strategies based on safe and efficient delivery of nanoparticles into cell nuclei.

COLL 670

Impact of amphiphile packing parameter on the drug loading and delivery properties of an anticancer liposomal delivery system

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Liposomes constitute established drug delivery systems (DDSs) for many hydrophobic, hydrophilic and amphiphilic drugs, due to their simplicity, formulation ease and excellent biocompatibility. Irrespective of drug nature, the bilayer composition is of critical importance since it controls the stability, drug loading and release properties of these DDSs.

We will present the interplay of these features in a recently optimized liposomal delivery system for a lipophilic experimental anticancer drug TUSP532 based on lipids and mixtures of lipids with gemini surfactants. The critical role of the packing parameter of amphiphiles used in liposomal formulation(s) on the stability, drug loading and drug release profile of these DDSs will be revealed through a combination of dynamic light scattering and zeta potential measurements, nano-differential scanning calorimetry (nanoDSC) and fluorimetry experiments. We will also present in vitro and ex vivo delivery experiments that will allow the full evaluation of the proposed technology in the detection of colon cancer.

COLL 671

Surfactant effect on synthesis of silica hollow particles by encapsulation of water droplet with perhydropolysilazane in octane/dibutylether mixtures

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Aqueous/oil emulsions with 20 to 100 nm in diameter of narrow droplet size distribution were prepared with NaCl and NiCl₂ aqueous and octane/dibutyl ether mixtures. Span 80 and batyl alcohol were used as surfactants. Perhydropolysilazane, which is a preceramic material of dense silica, was added to the emulsions to encapsulate the droplets. Water in the droplet converted perhydropolysilazane to silica. The diameters of droplet and capsules in solution were measured by dynamic light scattering, and the shape and size of products were observed by transmission electron microscope without staining. The hollow type silica particles with narrow size distribution were successfully synthesized from the emulsions prepared with batyl alcohol. Silica thickness was controlled from 3 nm to 10 nm by varying feed ratio of perhydropolysilazane to aqueous and rate of addition. In contrast, solid silica particles with 28 nm with narrow size distribution were formed with Span 80.

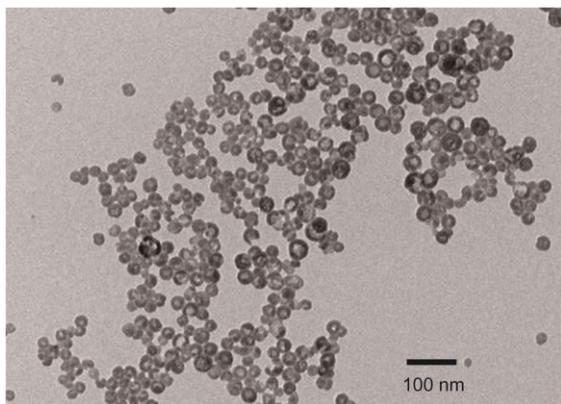


Figure 1 Transmission electron image of silica hollow particles prepared with perhydropolysiazne from NaCl aqueous/(octane/dibutyl ether) emulsion with batyl alcohol.

COLL 672

Solid-state reactivity of nanoparticulate ZnO in templated ZIF synthesis

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In the last decade zeolitic imidazolate frameworks (ZIFs), a subclass of metal-organic frameworks (MOFs), have been rising in popularity due to their diverse topologies, good thermal and chemical stability, and large pore volumes, which could enable their use for gas-storage, separation of gases, and catalysis.¹ However, traditional solution synthesis methods are very energy demanding, they use large quantities of organic solvents and rather expensive inorganic nitrates as starting material, and, above all, are often irreproducible and hard to control, giving mixtures of different ZIF frameworks in often low yields. Mechanochemical alternatives have been proposed, including neat grinding², ion and liquid assisted grinding (ILAG)³, and most recently, accelerated aging⁴.

We explored several different methods for solid-state ZIF synthesis, including neat and liquid-assisted grinding, slurring, as well as a modified accelerated aging procedure. We show that starting from nanoparticulate zinc oxide, and utilizing mechanochemical activation in conjunction with a macrocyclic template, we can reproducibly direct the outcome of ZIF syntheses to frameworks containing a specific structural motif.

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COLL 673

Feasible colloidal approach to produce nanostructured composites to inactivate pathogenic bacteria under visible light conditions

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Water pollution is a serious problem in developing countries due to the presence of organic contaminants and biological species. To solve this issue, our group developed a series of photocatalysts. In this study, a feasible colloidal approach was used to prepare cerium cations (Ce^{4+}) doped titania (TiO_2) composites (CTCs), followed by functionalization using natural product extracts. These CTCs displayed synergistic efficacy to decompose toxic compounds and pathogenic bacteria. Different molar ratios of Ce to Ti were used to form forty formulations of CTCs with tunable structures and sizes. Characterization indicated highly crystalline anatase CTCs were obtained and crystallite sizes can be tuned. The electrokinetic potential reflected the potential difference between the stationary layer of fluid around the solubilized solute and the dispersion medium. The CTCs with smaller diameter exhibited a large negative zeta potential and long-term stability. These CTCs displayed photocatalytic reactivity to decompose the model organic contaminant (methylene blue) under visible light conditions. The CTCs also rapidly destroyed both Gram-negative (*S. marcescens*) and Gram-positive (*M. luteus*) bacteria in low parts per million concentration range. The mechanisms of microbe inactivation can be summarized and hypothesized as three modes: **1)** Lipid peroxidation by direct and indirect interaction via reactive oxygen species; **2)** Disruption of DNA replication and repair due to DNA conformational changes; and **3)** Inhibition of respiratory proteins by promoting dimerization of the enzyme and leading to inhibition of respiration.

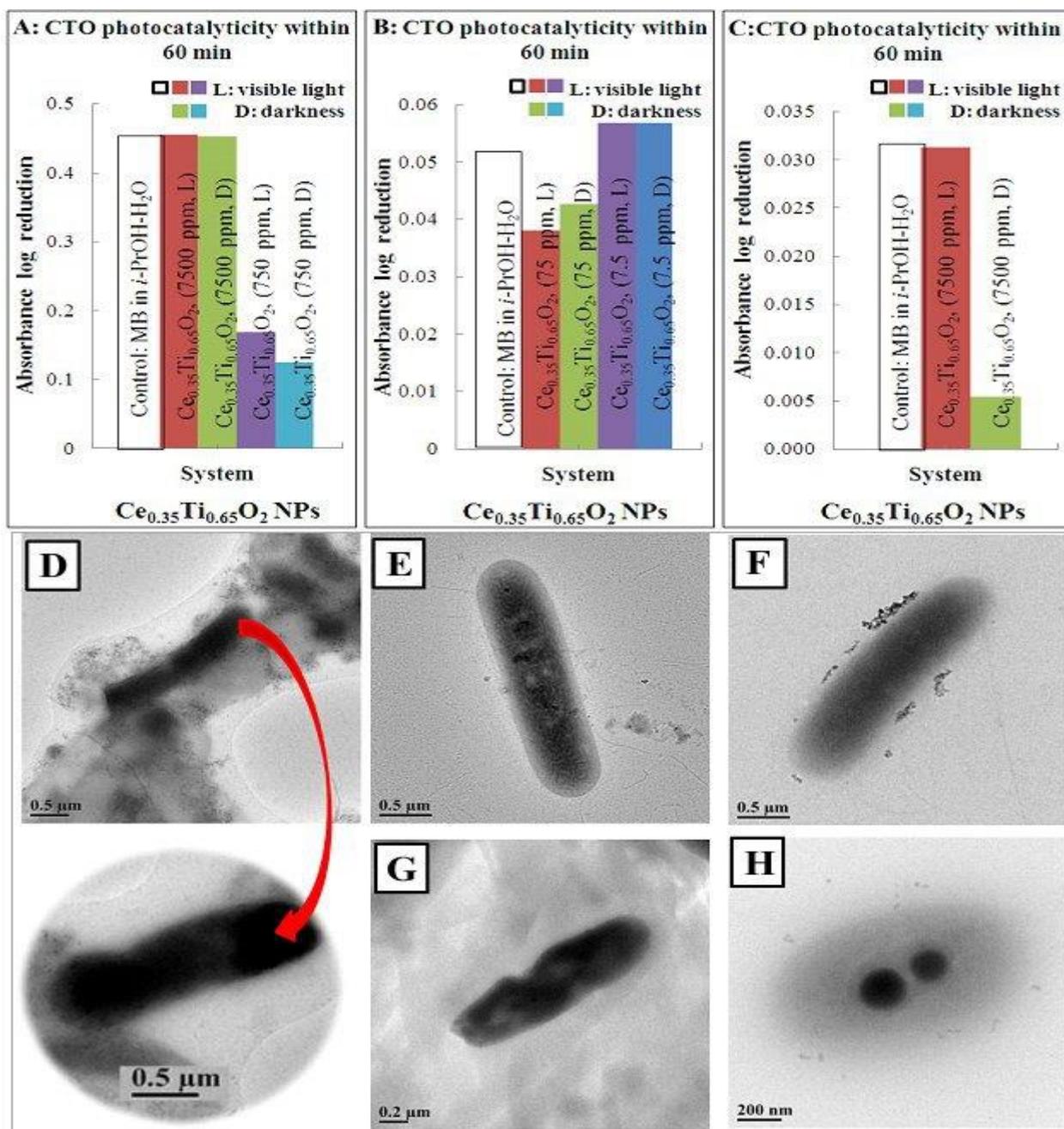


Fig. A-C: The photocatalytic reactivities of CTCs. **Fig. D:** TEM image of *S. marcescens* in varying stages of cell damage from **E** to **H**.

COLL 674

Designed mussel-inspired boat for smart crude oil cleanup

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Superhydrophobic fabric was simply prepared by a novel mussel-inspired strategy at a much lower concentration of dopamine with the aid of folic acid (FA), avoiding the use of any additional nanoparticles. Intriguingly, different from the additional nanoparticles, FA takes the role of structure directing agents for preparation rough polydopamine (pDA) coatings, and such hierarchical structures can be readily controlled by adjusting the FA concentrations or the coating duration. Higher FA concentration is adverse to formation of obvious hierarchical structure because of the inhibition effect of FA on the pDA formation, while appropriate duration of Stage I is indispensable for construction of rough pDA coatings. After octadecylamine (ODA) chemical manipulation, the as-prepared cloth boat with hierarchical structure exhibits excellent superhydrophobicity and the water contact angle and rolling off angle were about 162° and 7°, respectively. Importantly, the superhydrophobic fabric can withstand continuous and drastic 3.5 wt.% NaCl solution rinse and repeated tear with adhesive tape more than 30 times, exhibiting the excellent durability. Moreover, an energy-saving and highly efficient mini boat fabricated by our novel superhydrophobic fabric was innovatively utilized for self-driven oil spill cleanup, which can automatically recycle crude oil spill while float freely on water with the cleanup rate of crude oil spill up to 97.1%, demonstrating great potential in environmental remediation. The novel strategy designed in this study can inspire the fast development of mussel-inspired superhydrophobic materials for applications in various fascinating fields.

COLL 675

Magneto–acoustic hybrid nanomotor: Dynamic actuation and assembly of nanomaterials under complex external stimuli

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Efficient and controlled nanoscale propulsion in harsh environments requires careful design and manufacturing of nanomachines, which can harvest and translate the propelling forces with high spatial and time resolution. Here we report a new class of artificial nanomachine, named magneto–acoustic hybrid nanomotor, which displays efficient propulsion in the presence of either magnetic or acoustic fields without adding any chemical fuel. These fuel-free hybrid nanomotors, which comprise a magnetic helical structure and a concave nanorod end, are synthesized using a template-assisted electrochemical deposition process followed by segment-selective chemical etching. Dynamic switching of the propulsion mode with reversal of the movement direction and digital speed regulation are demonstrated on a single nanovehicle. These hybrid nanomotors exhibit a diverse biomimetic collective behavior, including stable aggregation, swarm motion, and swarm vortex, triggered in response to different field

inputs. Such adaptive hybrid operation and controlled collective behavior hold considerable promise for designing smart nanovehicles that autonomously reconfigure their operation mode according to their mission or in response to changes in their surrounding environment or in their own performance, thus holding considerable promise for diverse practical biomedical applications of fuel-free nanomachines.

COLL 676

Tuning localized surface plasmon resonance wavelengths of nanoparticles by mechanical deformation

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When the size of noble metal nanoparticles is reduced to less than the wavelength of light, the particles intensely absorb and scatter light at wavelengths that depends on the particle size, shape, and local dielectric environment due to Localized Surface Plasmon Resonance (LSPR) modes. Plasmonic particles have been used in a wide variety of sensor and optical device applications including tracers for intracellular transport, immunoassays, and surface enhanced Raman spectroscopy substrates. Controlling nanoparticle shape is essential for tuning these nanoparticles for a given application; however, controlling shape without affecting the particle volume is challenging. Reported here is a simple technique to mechanically alter the shape of silver nanoparticles by mechanically rolling a glass tube over them. This shape change in turn induces a red-shift in the LSPR wavelength of silver nanoparticles. The flattened particles were characterized by both optical and electron microscopy, single nanoparticle scattering spectroscopy, and surface enhanced Raman spectroscopy. AFM and SEM results consistently demonstrate the effect of applied load on silver nanospheres into discs; deformation increases with applied load (0-100 N). Increase in applied load from 0 to 100 N increases the silver nanoparticle diameter and decreases the height. This deformation caused a dramatic redshift in the nanoparticle scattering spectrum and also generated new surface area to which thiolated molecules could attach as evident from the SERS spectrum. The simple technique employed here requires no lithographic templates and has potential for rapid, reproducible, inexpensive and scalable tuning of nanoparticle shape, surface area, and resonance while preserving particle volume. This work was supported by *NIBIB* of the National Institutes of Health under award number R15EB014560-01A1 and *NIGMS* of the National Institutes of Health under award number 5P20GM103444-07.

COLL 677

WSe₂ nanoflower synthesis and application for catalysis

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Layered transition metal dichalcogenides (TMDCs) have recently been subject to intense research by the scientific community, due to the novel electronic properties arising from their structure. With the increasing need for renewable energy power sources, TMDCs that can catalyze the water splitting reaction are of interest to the community. TMDCs such as MoS₂, WS₂, MoSe₂, and WSe₂ are promising earth abundant alternatives to Pt metal. MoS₂ has seen intense research, including for catalysis applications, the other materials less so, especially WSe₂. Previously, WSe₂ has been synthesized via mechanical exfoliation and CVD, but both methods are not easily scaled. Recent work with MOCVD and VLS show potential for scalable mono- and thin-layer WSe₂ and for vertically aligned WSe₂, respectively, but material must still be grown on a substrate and requires high reaction temperatures. The most scalable methods in the literature can form very thin and active WSe₂ layers on a substrate, but the material must be chemically exfoliated before deposition.

In this talk, we will discuss a new synthesis of WSe₂ nanoflowers (NFs) via a substrate-free solvothermal route. We will demonstrate that this material is predominately in the metallic 1T-WSe₂ form without exfoliation and useful for hydrogen evolution catalysis.

COLL 678

Microwave synthesis of colloidal nanozeolite and polymorphism mechanism

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Zeolites are microporous aluminosilicates crystalline materials with enclosed cages and channels of molecular size. With narrow pore size distribution and enclosed catalytic active sites, zeolites find wide applications in catalysis, separation and sensing. Colloidal nanozeolites, compared with conventional micron sized zeolites, have large external surface area (> 100 m²/g) and short diffusion path (< 20 nm), which in principle improves both efficiency and selectivity in catalysis. To synthesize colloidal nanozeolite particles with narrow particle size distribution, clear-solution synthesis method is used, which requires long synthesis time and has low yield. Microwave heating generally has advantages of uniform heating, increased crystallization kinetics and enhanced dissolution of precursor gel. Directly applying microwave heating to clear solution synthesis composition of nanozeolite Y results in the formation of polymorphs of zeolite Y and A.

In this study, clear solution synthesis with a single Al and Si composition that produces both zeolite Y and A polymorphs with microwave heating are studied with electron microscopy. The differences in nuclei structure between zeolite topologies are evaluated. Polymorphism formation mechanism and kinetics are studied. Understanding

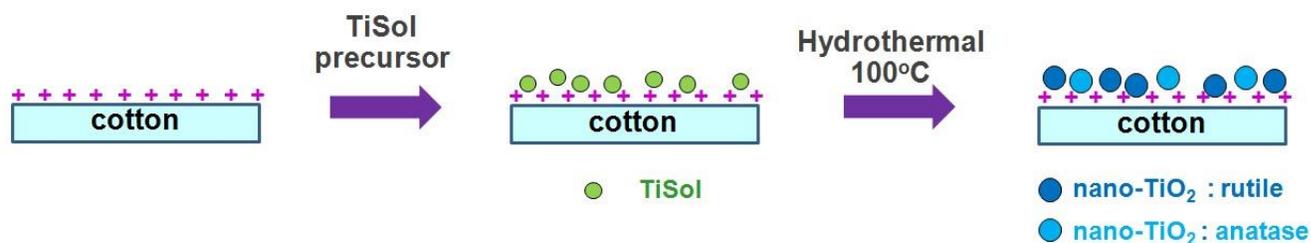
of zeolite crystal polymorphism formation mechanism will direct the rational tuning of synthesis conditions to control crystal polymorphism in material synthesis and explore new zeolite frameworks.

COLL 679

Facile immobilization of nano-TiO₂ on cotton fabrics

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Cotton is natural fiber which possesses comfort, soft touch, durability, water absorbency, breathable and easy maintenance. However, the cotton fabric is extremely susceptible to microbial attack. To overcome this drawback, the nano-TiO₂ was immobilized on the cotton fabrics in order to induce the antimicrobial activity. Firstly, the cotton fabrics were cationized with 3-chloro-2-hydroxypropyl trimethylammonium chloride (CHTAC). A starting precursor sol (TiSol) was prepared by treating an acidic aqueous solution of titanium tetraisopropoxide (TIP) with high intensity ultrasonic processor for 5 min. The surfaces of the cationized cotton fabrics were treated by soaking in the TiSol precursor for 10 min. The surface-treated cotton fabrics were then hydrothermally reacted at 100°C for 1 hour in various reaction media, i.e. H₂O, TiSol in H₂O, NH₄OH and TiSol in NH₄OH. XRD and SEM data revealed that the nano-TiO₂ successfully formed and immobilized on all hydrothermally treated cotton fabrics. The crystalline phases of nano-TiO₂ formed in all reaction media were mixtures of rutile and anatase. It was considered that the TiSol could electrostatically interact with the cationized cotton and acted as nano-seeds for hydrothermal growth of nano-TiO₂ on the fabric surfaces. The growth of nano-TiO₂ in the NH₄OH system was faster than that in the H₂O system. The presence of TiSol in the hydrothermal reaction media could promote the quantity of nano-TiO₂ immobilized on the cotton fabrics. This proposed technique is simple but effectively processes using non-toxic chemicals and low treatment temperature; therefore, it is an environmentally friendly cotton finishing technique.



Schematic representation of facile immobilization of nano-TiO₂ on cotton fabrics

COLL 680

Hydrophobic aluminosilicate aerogel and their composites

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Aluminosilicate aerogels have higher sintering temperature than silicate aerogels. Their mesoporous microstructure can be maintained at temperatures as high as 1200 °C. Aluminosilicate aerogels composites can be fabricated by using ceramic papers, felts or fabrics as reinforcements so that they can be more handleable for high temperature thermal insulation applications. By achieving good adhesion between fiber and aerogel, spallation of aerogel particles can be averted, making them less “dusty” than many state of the art aerogel insulation materials. For many applications, it is desired that the composites be hydrophobic. In the current work, various silanes with hydrophobic groups were used to modify the surface of the aluminosilicate aerogel or aluminosilicate aerogel composites prior to supercritical drying. The resulted aerogels are hydrophobic but still have low density, high porosity, and high surface area. The microstructure structure, alumina phase transformation, and surface area of hydrophobic aluminosilicate aerogel samples after thermal exposure were characterized for comparison with aerogels without hydrophobic modification.

COLL 681

Polymer templated mesoporous frameworks for strain-coupled magnetoelectric composites

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Strain-coupled magnetoelectric composites transfer strain through the interface between a piezoelectric material and a magnetostrictive material. Maximizing this interface should therefore enhance the magnetoelectric coupling in the composite material. Mesoporous frameworks of magnetostrictive cobalt ferrite (CFO) are synthesized through polymer templating methods using sol-gel precursors combined with amphiphilic diblock copolymers. The template and the metal precursors self-assemble into an ordered inorganic/organic composite; pyrolysis of the template leave a stable network of interconnected pores, resulting in a high surface area. These porous frameworks are subsequently filled with piezoelectric lead zirconate titanate (PZT) using atomic layer deposition to create a porous magnetoelectric composite by conformal deposition onto the CFO framework. Upon application of an electric field, strain is transferred from PZT to CFO, modifying the magnetization of the film and thus demonstrating magnetoelectric coupling. ALD allows precise control of PZT thickness, and magnetization measurements show that greater magnetoelectric coupling is achieved when the pores are incompletely filled, demonstrating the importance of mechanical flexibility in magnetoelectric coupling. Solution-phase self-assembly thus

complements vacuum deposition processes in creating complex structures to optimize material properties.

COLL 682

Transport across 5-25 nm in carbon based molecular junctions

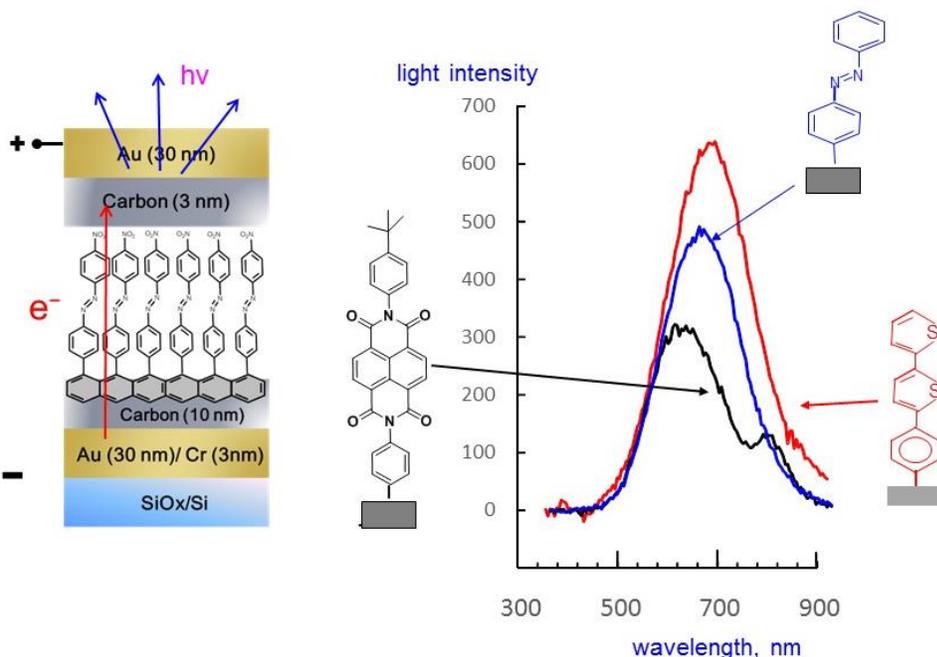
Oleksii Ivashenko², Akhtar Bayat², Amin Morteza-Najaran², Adam Bergren¹, **Richard L. McCreery**², richard.mccreery@ualberta.ca. (1) National Institute for Nanotechnology, Edmonton, Alberta, Canada (2) Univ of Alberta Dept of Chem, Edmonton, Alberta, Canada

We study “all carbon” molecular junctions made by covalent bonding of aromatic molecules to flat, conducting, sp^2 carbon surfaces, then vapor depositing disordered sp^2 carbon to make a conducting “top contact”. Such MJs can be incorporated into electronic circuit consisting of conventional semiconductor components to realize functions not possible with silicon. Electron transport across 1-30 nm differs fundamentally from that in standard semiconductors and thicker organic films, and often involves quantum mechanical tunneling. Light emission by molecular junctions was used to assess the energetics of charge transport in Carbon/molecule/Carbon molecular junctions with molecular layer thicknesses in the range of 2-25 nm. The spectrum of the emitted light is a direct function of the applied bias across the molecular junctions, with tunneling transport resulting in minimal energy changes and emitted photons with a maximum energy of eV_{applied} . For devices with thickness greater than 5 nm the emitted light is lower in energy than eV_{applied} , and the energy loss is a strong function of molecular layer structure and thickness. Detailed analysis of current-voltage behavior and light emission as functions of temperature and molecular structure permit insights into the transport mechanism, which is likely initiated by field ionization of occupied molecular orbitals.

(1) Yan, H.; Bergren, A. J; McCreery, R.; Della Rocca, M. L; Martin, P; Lafarge, P; Lacroix, J. C. Activationless charge transport across 4.5 to 22 nm in molecular electronic junctions, *Proceedings of the National Academy of Sciences* **2013**, *110*, 5326.

(2) McCreery, R; Yan, H; Bergren, A. J. A Critical Perspective on Molecular Electronic Junctions: There is Plenty of Room in the Middle, *Physical Chemistry Chemical Physics* **2013**, *15*, 1065.

(3) Sayed, S. Y; Fereiro, J. A; Yan, H; McCreery, R. L; Bergren, A. J. Charge transport in molecular electronic junctions: Compression of the molecular tunnel barrier in the strong coupling regime, *Proceedings of the National Academy of Sciences* **2012**, *109*, 11498.



COLL 683

Phenyl ring as an electronic design motif: Orientation and coupling

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Accumulated recent evidence reveals a little effect of chemical modifications on net charge transport across molecular junctions. It is attributed to hybridization between the molecular energy levels and those of the contacts, leading to their broadening and shifting. Using a combined computational – experimental approach, we have explored how the chemistry of a tether group affects the energetics of a distal aromatic group (Ar, mostly a phenyl ring), and the net charge transport across metal/monolayer-Si junctions. For monolayers of Ar-X-Si, where X is a hetero-atom, such as O or N, there is a drastic hybridization of the π orbitals with Si states, which is facilitated by the lone-pair electrons on X. [1] Such coupling is efficiently blocked when binding is done via a saturated tether as in Ar-R-Si with R being an alkyl chain. The number of carbons in the saturated R spacer, $n = 1-5$, has a minor effect on the coupling. However, there is a clear odd-even effect of n on the orientation of the phenyl ring, with a prominent effect on barrier height for transport. [2] Finally, we studied a combined system including both X and R, i.e., phenyl-X-(CH₂)₂-Si, with X = O, S or CH₂. Interestingly, in such systems, the nature of X has a little effect on the induced surface dipole, yet the HOMO of the bonded monolayer varies by almost 1 eV depending on X. [3] Overall, this study does show a fine chemical tuning of electronic properties, yet it is a combined result of various factors; saturated spacers are especially effective in buffering the substrate effect.

[1] T. Toledano et al., *J. Electron Spectrosc.* **2015**, ASAP.

[2] T. Toledano, et al., *Langmuir* **2014**, *30*, 13596.

[3] H. Alon, et al., *in preparation*.

COLL 684

What is in a contact? Understanding basic interfacial properties of self-assembled monolayers by engineering substrate roughness

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There is a general assumption, albeit challengeable, that the interfacial properties of self-assembled monolayers (SAMs) are well understood—the premise on which many studies/technologies are based. Due to a large volume of work in SAMs, it has been largely assumed that their wetting (a fundamentally informative property) and related properties are well understood, for example the so-called odd-even effect. Through carefully studies, this talk demonstrates that there exists complimentary limits in substrate surface roughness where either the molecule or capillary forces (or substrate's surface morphology) dominates the surface properties of a functionalized surface. By fabricating surfaces with root-mean-square roughness of 0.18 nm – 3.4 nm, and surveying wetting of probe liquids across a range of surface tensions on n-alkanethiolate SAMs (C10-C16), we observe that a transition occurs at ~1-1.5 nm. We summarize the data in a so-called 'Scarlett quadrangle' that can be used to predict the dominant factor in the study of liquid-SAM interactions. We extend this study to charge transport and engineer the nature of a liquid-metal SAM interface to enhance the contact and hence promote better charge injection into the SAM. A discussion on the effect of engineering the nature of contact in understanding the effect of interfacial vs bulk properties of the SAM on charge transport through large area junctions of the type M-SAM//liquid-metal (EGaIn) will be presented.

COLL 685

Intersection of metals and organics on the properties of molecular-based devices

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The fusion of metals and organics has long been known to produce dramatic electronic effects. In molecular electronics and nanoscale electronics, effects such as valence tautomerism and spin crossover that come from these inorganic-organic “hybrid”

systems are diverse and have strong promise for these and other fields. However, designing and studying electronic devices is a challenge at the nano- to single-molecule scale, and great care must be taken to preserve, observe, and study these effects.

In this talk, I will detail work toward studying the impacts of modifying both organic and inorganic components in several molecular-based inorganic-organic “hybrid” systems on the overall charge and spin transport of devices. First, I will discuss nanoscale devices designed with *meso-to-meso* ethyne-bridged (porphinato)metal oligomers. Solution electrochemical studies show that synthesizing the oligomers with different metal centers modifies the energy levels of the oligomer, a modification confirmed with the molecule on a surface *via* UPS. Metal-molecule-metal junctions created on a surface using nanotransfer printing (nTP) yields evidence of different charge transport properties in different metal centered porphyrins. Finally, I will describe studies of devices incorporating metallic nanoparticles with various organic linkers. This fundamental test bed allows for a framework where impact of both organic and inorganic component can be isolated and tuned, and observations of observed charge and spin transport as a function of device constituency can lead to both understanding of fundamental principles and provide an architecture for observation of more unique transport properties.

COLL 686

Environmental gating of single-molecule circuits

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The proposal to create molecular analogs of circuit components dates back to the work of Aviram and Ratner from 1974,¹ where they suggested using a single molecule as a diode circuit element in giving birth to the field of molecular electronics. This field has advanced tremendously since then; nanoscale single-molecule devices are now also used as test beds for understanding and controlling electron transfer across metal/organic interfaces. Despite the long-standing interest in creating molecular diodes, their experimental realization has been difficult, with only a handful of studies showing rectification at the single molecule level. This is because most designs, such as the Aviram-Ratner model of rectification, rely on the complex interplay between many variables, such as the level alignments of the molecular components and the Fermi level of the metal electrodes. In this talk, I will review the scanning tunneling microscope break-junction technique we use to measure conductance through single molecule junctions² and then present our results illustrating how a high on/off ratio can be achieved using an environmental gating technique.³

1 Aviram, A. & Ratner, M.A., Molecular Rectifiers. *Chem. Phys. Lett.* 29 (2), 277-283 (1974).

2 Venkataraman, L., Klare, J.E., Nuckolls, C., Hybertsen, M.S., & Steigerwald, M.L.,

Dependence of single-molecule junction conductance on molecular conformation. *Nature* 442 (7105), 904-907 (2006).

3 Capozzi, B. *et al.*, Single-molecule diodes with high rectification ratios through environmental control. *Nat Nano* 10 (6), 522-527 (2015).

COLL 687

Stereo-electronic effects on charge transport across large area tunneling junction

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Organic electronics have great potential that rests on the ability to engineer the wave-function through molecular synthesis, and hence properties of the resultant devices. Understanding the mechanism in charge transport through large area tunneling junction, largely based on self-assembled monolayers (SAMs), offers great promise in advancing molecular/organic electronics. Despite the fact that large efforts have been put into understanding the structure-property relations in charge transport, little is known about the effect of dipoles and related stereo-electronic molecular properties on charge transport. Previous work has, however, indicated that the steric orientation of the SAM molecules, or a single moiety, affects the rate of charge tunneling, as demonstrated by the odd-even effect. A reliable physical-organic study on delineating the effect of dipole on charge transport, should entail strategies to minimize steric effects. We, therefore, use thiocarboranes-based SAMs to decouple the two effect of dipoles and steric on the rate of charge transport. The packing density, orientation and thickness of SAMs derived from meta-1-carboranethiolates and meta-9-carboranethiolates on ultra-flat Au are similar. These SAMs, however, have significant differences in the magnitude and orientation of their dipoles, and, therefore, they are ideal candidates to delineate the effect of dipole on charge transport. BY comparing odd-even effect in n-alkanethiolate SAMs and differences in tunneling rates through structurally similar thiocarboranes, we infer that the rate of charge transport through large area tunneling junctions is dependent on the stereo-electronic properties of the SAM.

COLL 688

Controlling charge transport mechanisms in nanoscaled porphyrin assemblies on Au surfaces

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Molecules offer exceptional possibilities for the design of organic electronic components based on the ability to readily tune their electronic states through directed synthetic modifications. However, in the conditions where tunneling is the dominant mechanism of charge transport, the conductivity of the molecules being used become largely insensitive to chemical and structural changes that do not alter the overall length of the junction, limiting the ability to synthetically modulate changes in conductivity in a well-defined fashion. Recently we have been investigating how nearest-neighbor interactions can be used to afford charge delocalization in molecular islands, whereby one can then shift transport out of the tunneling regime and into the charge-hopping regime, which can be more readily chemically controlled. Here, to explore this concept, the transport properties of a series of porphyrin thiols Au(111) have been investigated using scanning tunneling microscopy (STM). For isolated molecules (placed in a background of a dodecanethiol matrix), the tunneling efficiency and I-V behavior was found to be dominated by through bond tunneling, dictated by the alkyl tether used to attach the molecules to the surface. However, when the porphyrin thiols were driven to aggregate on the surface into nanoscaled islands of ca. 5 – 10 nm in dimension, this was found to result in sufficiently reduced charge confinement energy as to facilitate the transition from a purely tunneling mechanism to a charge-hopping mechanism, illustrating the impact of molecular aggregation and nearest-neighbor interactions on the charge transport of molecular assemblies, and demonstrating the effectiveness of using such aggregates to achieve single-electron transport characteristics. Directing such assemblies into pre-designed architectures however still represents a significant challenge. Here, to further control the dimensionality and organization of such assemblies, combinations of nanofabrication (using electron beam and scanning probe lithographies) and click-chemistry have been employed to enable the construction of controlled assemblies. The fabrication and assembly process along with the corresponding changes in the observed electronic properties of the assembled island will be discussed.

COLL 689

Size-dependent measurements with spatially confined nanoclusters of porphyrins using conductive probe atomic force microscopy

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Protocols were developed for nanopatterning porphyrins i.e. nanorods and nanodots on Au(111) using immersion particle lithography. Porphyrins with and without a central metal ion, 5,10,15,20-tetraphenyl-21H,23H-porphine (TPP) and 5,10,15,20-tetraphenyl-21H,23H-porphine cobalt(II) (TPC) were patterned as surface test platforms for conductive probe-atomic force microscopy (CP-AFM). A film of silica mesospheres was used as a surface mask to prepare patterns of nanopores within an alkanethiol matrix film. When the surface mask of mesospheres was rinsed away, a periodic arrangement of nanopores is produced. The uncovered circular areas within the nanopores are

exposed gold substrate. The nanopores within a methyl-terminated alkanethiol matrix were filled by immersing the sample in a solution of porphyrins. By controlling the concentration and immersion interval, nanorods or nanodots of porphyrins were generated. Individual nanostructures of porphyrins were spatially isolated into well-defined, nanoscale arrangements directed by a template film of the thiol monolayer prepared with particle lithography. Regular geometries with defined spacing can be reproducibly generated for surface test platforms on Au(111). Surface structures of porphyrin nanorods and nanodots exhibited differences in dimensions at the nanoscale, which enabled size-dependent measurements of conductive properties. The conductivity along the horizontal direction of the nanorods was evaluated using CP-AFM. Changes in conductivity were measured along the long axis of nanorods. The TPP nanorods exhibited conductive behavior of a rectifier. The TPC nanorods exhibited profiles that are typical of a semi-conductor. The conductivity in the z-direction was measured for test platforms of porphyrin nanodots formed by TPC or TPP, exhibiting semi-conductive I-V curves. Wire-like conductive I-V curves were detected with cobalt-coordinated TPC nanodots. The applicability of particle lithography will be demonstrated for preparing surface platforms for the measurement of conductive properties at the nanoscale. Fundamental knowledge of the conductivity of porphyrins at the nanoscale is applicable for the manufacture and testing of molecular devices.

COLL 690

Interfacial electron-transfer processes at diamond-aqueous interfaces

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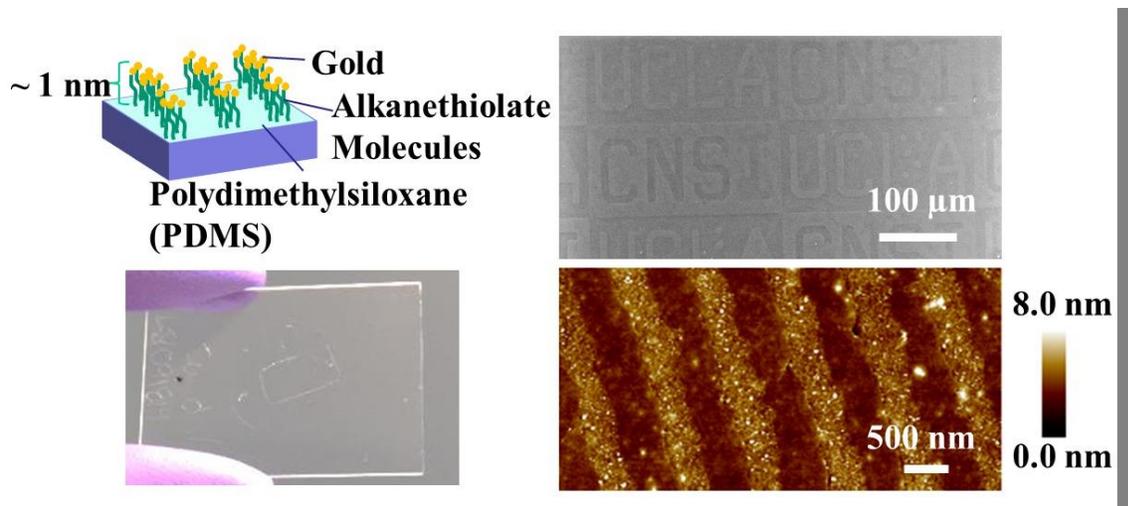
Diamond is uniquely suited as an electrode material for electronic application in aqueous media because of its extraordinary chemical and electrochemical stability. Inexpensive boron-doped diamond substrates can be readily functionalized with a range of redox-active molecules, including catalysts, with the resulting adducts having excellent electron-transfer rates and stability. The remarkable electron-transfer rates at functionalized diamond electrodes arise in part from the inherent disorder of molecular layers on diamond surfaces, and the resulting conformational flexibility that ensues. Diamond's negative electron affinity can also be leveraged to aid in photochemically activating reduction reactions via direct emission of electrons; in this case the surface functionalization of diamond plays a critical role by controlling the barrier at diamond-aqueous interfaces. By introducing surface dipoles and/or positive surface charges, the electron emission can be substantially enhanced and used to initiate formation of solvated electrons, atomic hydrogen, and other highly reactive species. Here I will discuss some of the factors that influence interfacial electron-transfer processes at functionalized diamond surfaces, and how an understanding of these processes can be used to enhance diamond's application in electrochemical and photoelectrochemical conversion processes.

COLL 691

Chemical fabrication of patterned transparent gold-coated polydimethylsiloxane

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We present a straightforward, contact-based, strategy to functionalize and to pattern polydimethylsiloxane (PDMS) with atomically thin gold over square millimeter areas. The pattern features span hundreds of nanometers to hundreds of microns. Functionalization depends on a recently discovered contact-based chemistry, chemical lift-off lithography (CLL), where PDMS first conformally contacts a gold surface with self-assembled hydroxyl-terminated alkanethiols, then removes molecules and gold from the surface upon separation. We have devised a suite of fabrication and characterization tools to pattern flat PDMS via CLL and to visualize these patterned features, which do not measurably influence the optical transparency or flexibility of the PDMS. We visualize the patterns directly through peak-force atomic force microscopy and scanning electron microscopy. We then demonstrate the chemical functionality of the lifted-off gold on PDMS through a simple DNA hybridization assay. Thiolated single-stranded DNA probes bind to the lifted-off regions on the PDMS, and the pattern becomes visible in fluorescence microscopy when the probes bind to their dye-labeled target strands. Compared with common strategies for patterning PDMS, the CLL mechanism is chemically selective, straightforward, replicable at ambient conditions, and enables nanometer to millimeter feature sizes. Further, this study forms the basis on which to interrogate the optical, electrical, and chemical properties for the morphologies of the ultrathin gold produced here.



Top left: Schematic of the hybrid material. Bottom left: Photograph of a substrate - the material is optically transparent. Top right: Scanning electron micrograph patterned PDMS with feature sizes of ~10s of microns. Bottom right: Atomic force micrograph of patterned PDMS with 350 nm wide lines.

COLL 692

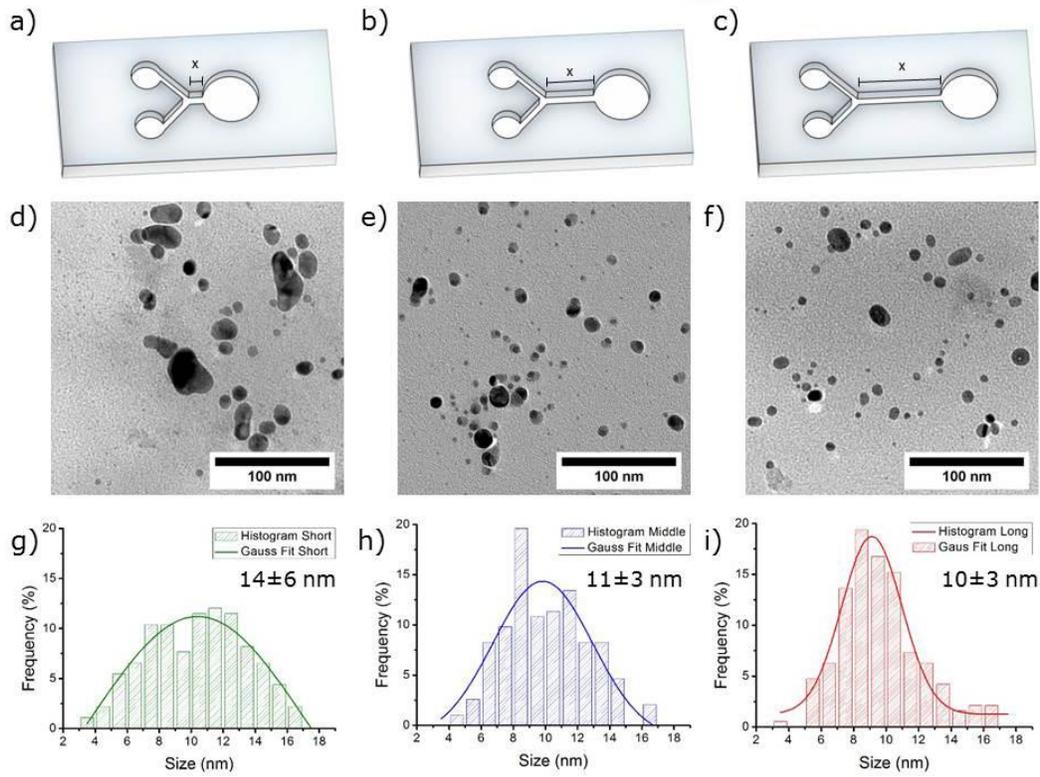
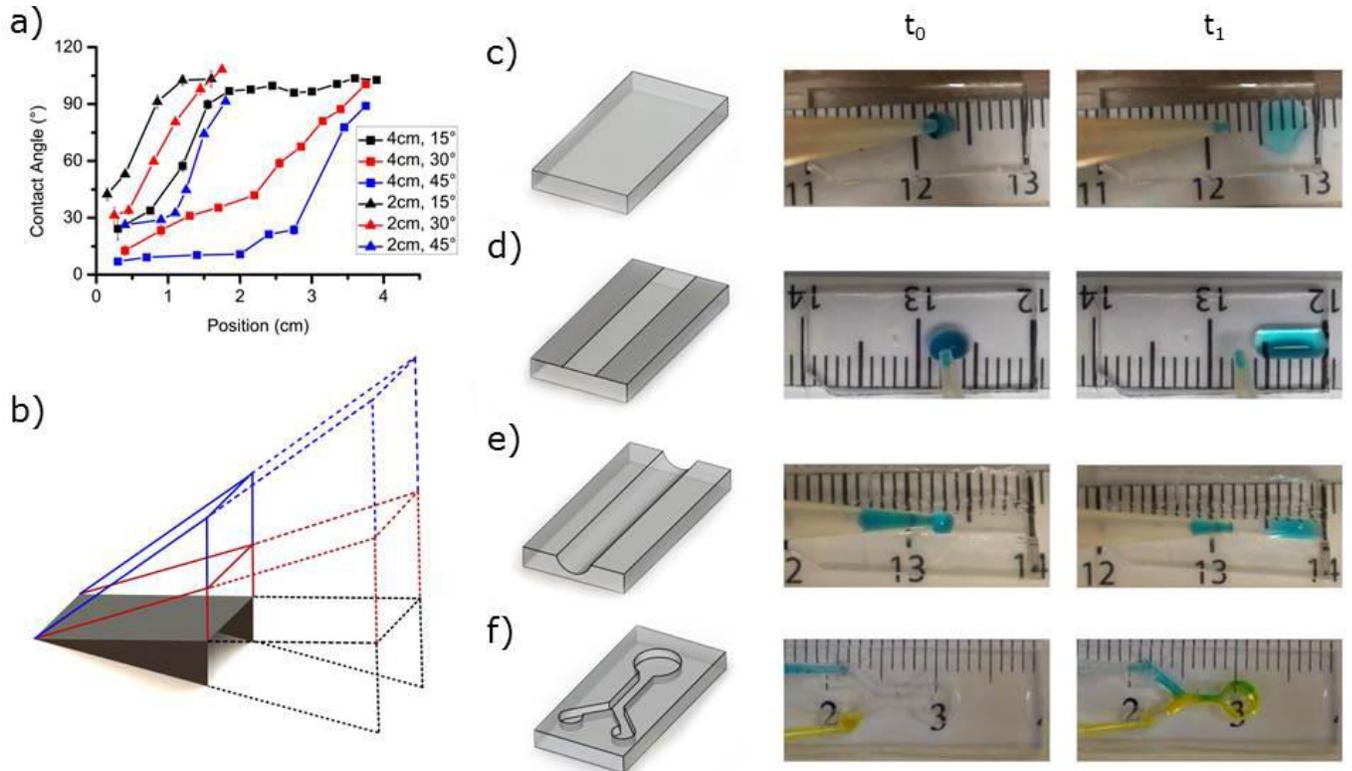
Directed autonomic flow: Functional motility fluidics

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Multiple interesting systems like anti-fogging and lab-on a chip devices as well as DNA microarrays and microfluidic chips have liquid dynamics as the most important working component. Surface wettability has a main influence on liquid dynamics at solid-liquid interfaces. Surface gradients in wettability are known to be able to drive liquid motion without the need of an external force. These gradients need to be precisely designed, which is labor-intensive and expensive. Therefore, a new cheap and easy way to create a surface gradient in wettability is presented in this project. Where moving droplets, since they were first discovered by Whitesides et. al.,^[1] were limited by side effects like spreading, here a new approach for functional autonomous liquid motion is shown. Using Polydimethylsiloxane (PDMS) in combination with air plasma shielded with a metal mask (Fig. 1b), leads to surface wettability gradients ranging from 25° up to 110° in static water contact angle (Fig. 1a). This droplet movement was utilized to create directed and controlled water movement on different PDMS-surfaces and channels (Fig.1c-f). This controlled movement was used to create a chemical fluidic motility chip, enabling silver nanoparticle synthesis as a model reaction in a chip solely based on autonomous movement of two droplets. The size distribution of the resulting nanoparticles could be controlled by the channel length of the mixing chip, which can be linked to the mixing time of the solutions (Fig.2).^[2]

[1] M. Chaudhury, G. Whitesides, *Science* **1992**, 256, 1539

[2] P. T. Kühn, B. S. de Miranda, P. van Rijn, Adv. Mater. 2015, DOI 10.1002/adma.201503000.



COLL 693

Supramolecular engineering: Applications to molecular recognition and biocatalysis

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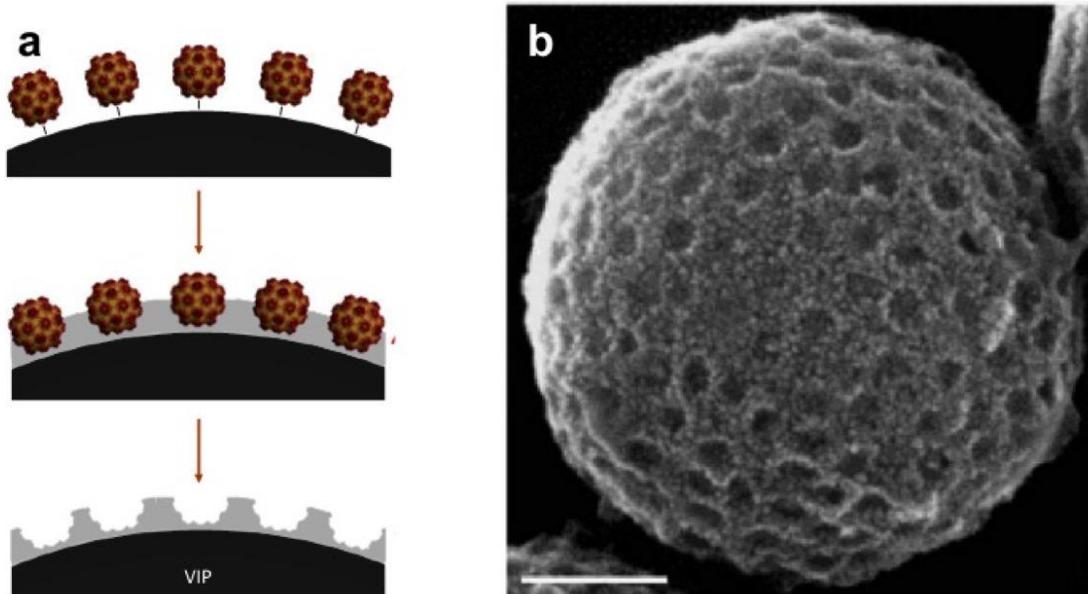
In nature, various organisms are endowed with the ability of producing intricately patterned and hierarchically structured inorganic matter with a meticulous proficiency. As those materials often exceed the performances of their artificial counterparts, mimicking their biosynthesis offers new opportunities to develop a wealth of novel engineered (nano)materials.

In the first part of the lecture will be discussed the design of nanomaterials able to specifically recognize viruses using a surface-imprinting strategy.^{1,2} We demonstrate the formation of a chemical imprint, comparable to the formation of biosilica, due to the template effect of the virion surface on the synthesis of the recognition material (Figure 1).

In the second part will be discussed a novel and versatile strategy that allows the design nanobiocatalysts using an approach also based on the assembly of silane building blocks at the surface of natural enzymes. This method allows for drastic stabilization of the shielded natural biocatalyst with regard to chaotropic stresses (temperature, pH, solvent, urea, protease, surfactant).

The final part of this lecture will be dedicated to a novel supramolecular strategy that allows the stable yet reversible immobilization of functional biocatalysts on solid surfaces (e.g., filtration membranes).³

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2. Cumbo, A.; Lorber, B.; Corvini, P. F.-X.; Meier, W.; Shahgaldian, P. *Nat. Commun.* **2013**, *4*, 1503
3. Moridi, N.; Corvini, P. F.-X.; Shahgaldian, P. *Angew. Chem., Int. Ed.* **2015** (10.1002/anie.201507020)



General synthetic scheme of surface virus-imprinting (a); Scanning electron micrograph of a virus-imprinted silica nanoparticle (b). Scale bar represents 100 nm.

COLL 694

Shear banding in drying films of colloidal nanoparticles

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Drying suspensions of colloidal nanoparticles exhibit a variety of interesting strain release mechanisms during film formation. These result in the selection of characteristic length scales during failure processes such as cracking(1) and subsequent delamination. A wide range of materials (e.g., bulk metallic glasses) release strain through plastic deformations which occur in a narrow band of material known as a shear band. For the first time, we demonstrate that drying colloidal films also exhibit shear banding(2).

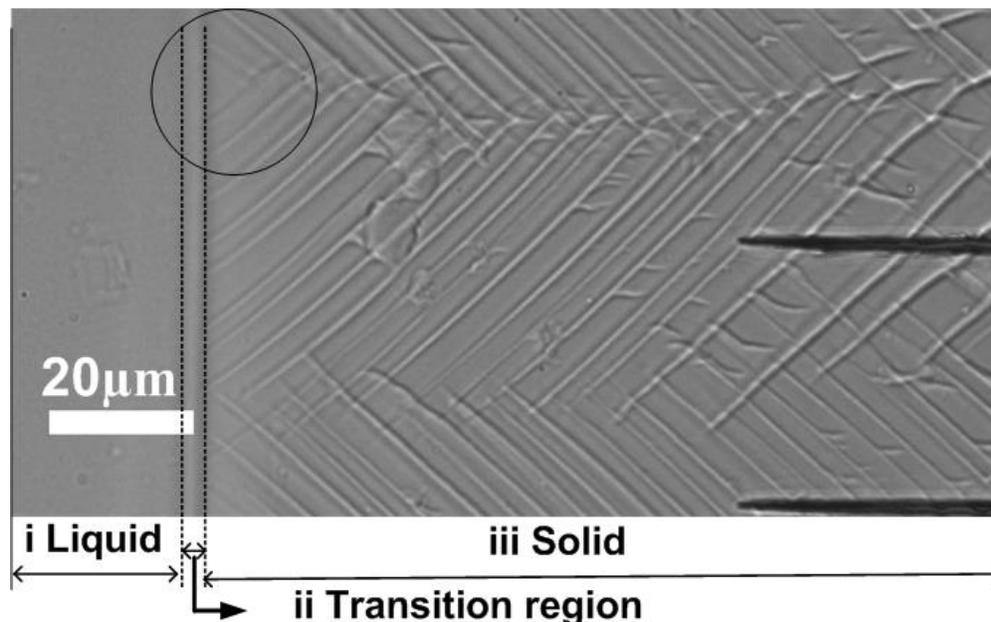
Bands are observed to form a small distance behind the drying front and then to propagate rapidly at $\sim 45^\circ$ to the direction of drying. The combined observations suggest that the critical shear rate (related to the film yield stress) controls the ratio of bandwidth to band spacing, which depends on particle size, salt concentration and the evaporation rate of the colloidal suspension. We also show that below the critical drying rate, the ratio obeys a simple Lever rule.

To study the cause of shear band formation, we measured the local deformations in the early stages of drying using fluorescent tracer particles. The measurements were used to show that the existence of shear bands is linked to the compaction of particles perpendicular to the drying front. The spacing of shear bands was also found to be strongly correlated with the characteristic length scale of the compaction process. These combined studies elucidate the role of plastic deformation during pattern

formation in drying films of colloidal nanoparticles.

Reference

1. Singh KB & Tirumkudulu MS (2007) Cracking in drying colloidal films. *Phys Rev Lett* 98(21).
2. Yang B, Sharp JS, & Smith MI (2015) Shear Banding in Drying Films of Colloidal Nanoparticles. *Acs Nano* 9(4):4077-4084.



COLL 695

Biomolecule triggered shape transformation of hybrid hydrogels

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Many hydrogels have been designed to undergo a change in 3-D shape in response to an external trigger such as pH and temperature. For example, self-folding hydrogel sheets have been created, where an initial flat sheet curls up into a folded shape under the action of the above triggers. Such self-folding behavior is inspired by the morphological changes exhibited by plant leaves. These types of structures have potential applications in biosensing, drug delivery and tissue engineering. For further developing these hydrogels for applications, it is necessary to expand the range of triggers to include unconventional solutes. For example, can gels be made responsive to low concentrations of enzymes or other proteins, or to small molecules such as glucose or fructose? Moreover, can we endow gels with high specificity, where the

response occurs only with a particular biomolecule? Towards this end, we present an approach based on hybrid hydrogels, wherein two or more hydrogels with distinct chemical formulations are combined into the same gel and covalently bonded at interfaces. Utilizing photolithographic techniques, we pattern a biopolymer derivative within our hybrid gel films. In the presence of an enzyme that degrades the biopolymer, regions within the gel undergo differential swelling. As a result, differential stresses are generated within the film leading to its buckling and folding to form a specific shape. We demonstrate that our technique can be successfully used to create structures such as tubes, helices and other complex structures. Importantly, the shape change occurs even in the presence of low concentrations of enzyme.

COLL 696

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 been the default anodic and cathodic fuel cell catalyst, which makes resulting fuel cell devices less efficient due to Pt poisoning and slow kinetics for the oxygen reduction reaction (ORR). Recent work in our laboratories has shown that a block copolymer template-directed synthesis of mono- and bimetallic nanoparticle catalysts is an attractive method for preparing high performance fuel cell catalysts. The content of this presentation will describe our investigation of the underlying principles for prescribing the size, spacing and composition of nanocatalysts that can be isolated from self-assembled block copolymers loaded with metallic anions 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 catalyst 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.

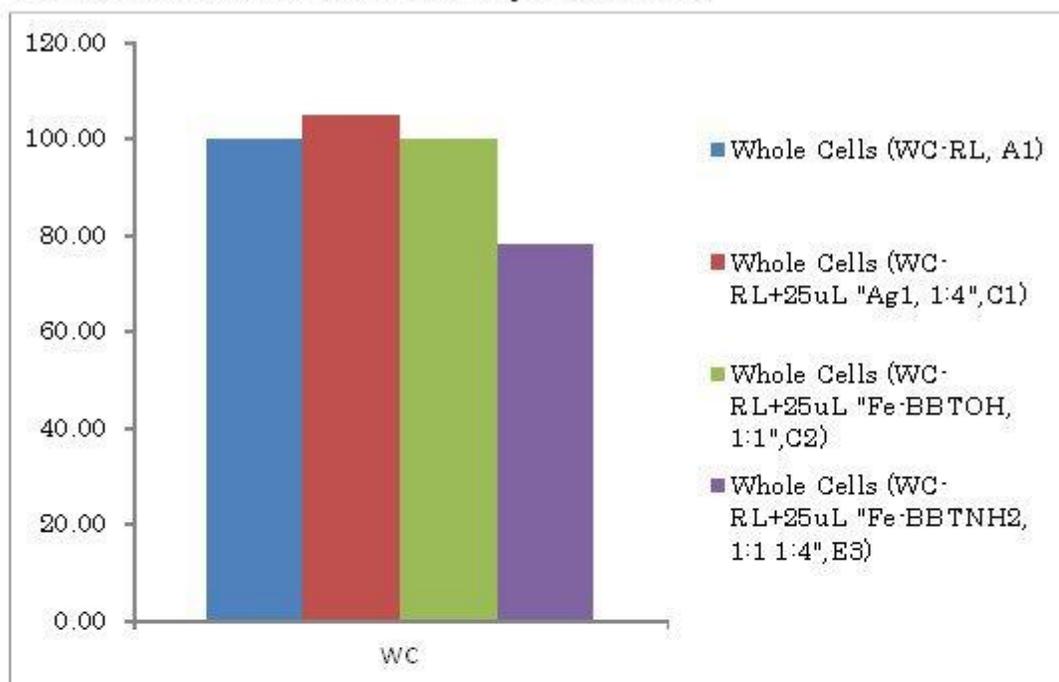
COLL 697

Cytotoxicity of metal-organic frameworks derived from wet-chemistry approach

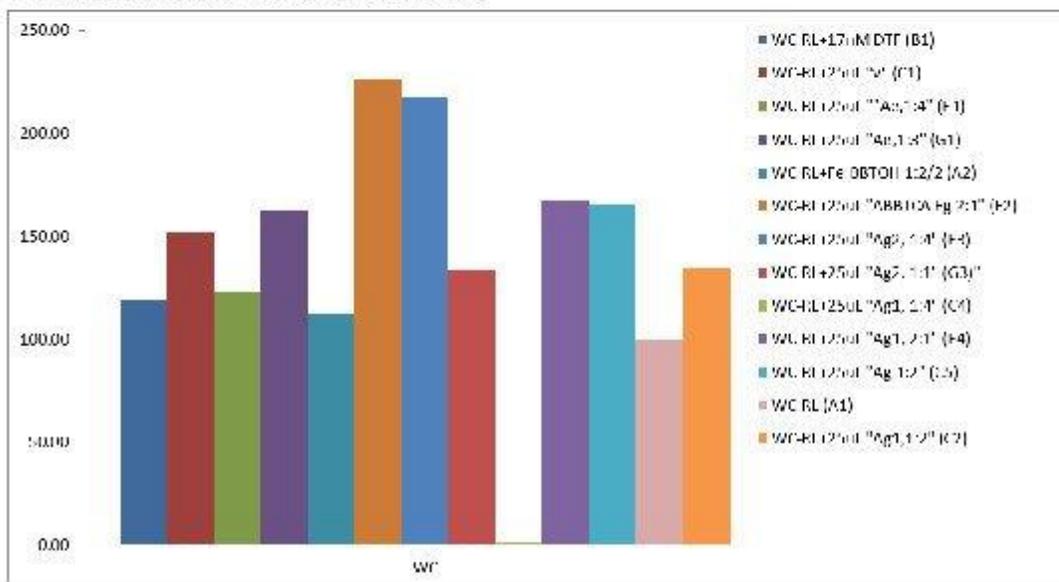
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Metal-organic frameworks (MOFs) are the crystalline compounds obtained by complexing various metal ions and ligands. The MOFs were evaluated for cytotoxicity using lactate dehydrogenase (LDH) assay on retinal pigment epithelium (RPE) whole cells. The assay was compared and contrasted between control and test samples. The control samples were potassium ferrocyanide, sodium nitroprusside, and carbonyl cyanide-4-(trifluoromethoxy)phenylhydrazine (FCCP). The parameters were production of RPE cellular nitric oxide (NO) levels using a NO-specific fluorescent dye (labelled DAF-FM) and LDH levels over an 8 h period. When various MOFs were compared, three clusters were observed, showing different toxicity level. The small NO values suggest that the MOFs are not causing stress, allowing the cell to produce NO, as a messenger for a number of biochemical pathways, such as apoptosis. The high values resulted from some MOFs indicated that they act as electron acceptors in a similar manner to nitrite and facilitate the reduction of nitrite to NO. They may cause cellular stress, allowing NO to signal caspases to start apoptosis. The mitochondrial potential was examined using a positively charged dye that accumulates within the membrane maintaining a negative mitochondrial membrane potential (MMP). A comparison of the MMP values indicated that the majority of MOFs had higher than control values, suggesting the membrane was intact and functional. Collectively, these results suggests that the MOFs are not cytotoxic but soluble in biological fluids, simulated using PBS and under specific circumstances. We infer the MOFs can generate reactive oxygen species, modification of active heme groups of respiratory enzymes and disruption of the electron transport chain through redox chemistry as electron acceptors.

A: Measurement of LDH Activity Difference



B: Measurement NO difference



A: Measurement of Lactate dehydrogenase (LDH) activity Difference; B: Measurement of nitrogen monoxide (NO) difference.

COLL 698

Application of reactive amphiphilic clay nanogels for removal of toxic cationic dye and heavy metals water pollutants

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The present work aims to reduce the water surface tension using dispersed organophilic clay minerals to increase the adsorption water pollutants (organic and inorganic) into the clay galleries. Therefore, sodium montmorillonite (Na-MMT) was functionalized with amphiphiles based on crosslinked nanogel polymers of N-isopropylacrylamide (NIPAm), acrylic acid (AA), acrylamide (AAm), N-isopropylacrylamide, 2-acrylamido-2-methylpropane sulfonic acid (AMPS) sodium 2- acrylamido-2-methylpropane sulfonate (Na-AMPS), acrylamide (AAm) and acrylamidopropyl)trimethylammonium chloride solution (APTAC) using surfactant free technique. The chemical interactions between nanogels and Na-MMT and their chemical structure were confirmed by FTIR analysis. The intercalation and exfoliation of Na-MMT were confirmed by wide-angle X-ray diffraction. The morphology of Na-MMT nanogel composites was investigated by TEM analysis. The adsorption capacities of the prepared Na-MMT nanogels for methylene blue dye, cobalt and nickel cations from water were investigated. The data indicated that the Na-MMT nanogels reduced the surface tension of water and efficiently remove dye and metal ions from water.

COLL 699

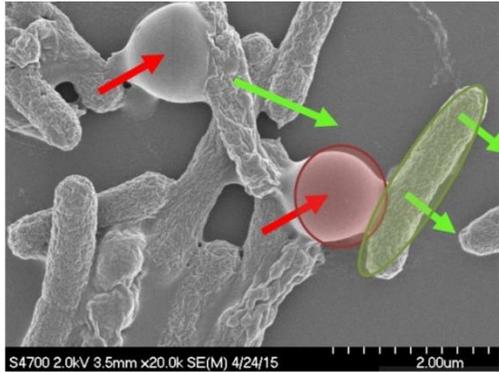
Enhancing chemical adsorption and biodegradation using bioreactive phenyl-functionalized silica gels

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Phenyl-functionalized silica gels comprised of hydrophobic microspherical patches with adhered biodegrading bacteria were developed. The resulting bio-gels showed enhanced chemical adsorption and biodegradation properties. Silica gels with increasing phenyl alkoxide content were characterized using fluorescence measurements, confocal and scanning electron microscopy. Efficiency of adsorption and biodegradation was assessed using a model hydrophobic pollutant, the herbicide atrazine, and an *E. coli* strain expressing atrazine chlorohydrolase. The phenyl doped silica gels contained spherical hydrophobic patches increasing in size and abundance as a function of phenyl content introduced. These materials exhibited a 6-fold enhancement of atrazine adsorption over a non- functionalized silica gel and a 4-fold selectivity of the substrate (atrazine) over the product (hydroxylatrazine). Moreover, biodegradation rates of atrazine increased almost five-fold at 75% phenyl alkoxide content. Similar trends were observed for other triazines, such as fluoroatrazine and additional pesticides, such as parathion. SEM and confocal images suggest that the increase in activity is due to increasing bacterial adherence to the phenyl-silica gel; this creates a unique configuration where the hydrophobic microspheres act to sequester hydrophobic chemicals from water and allow facile transfer of the desired chemicals to the adhering non-viable bacteria.

Phenyl functionalized bio-silica gel

Enhanced adsorption of substrate to hydrophobic microspheres



Increased degradation by adhered bacteria

COLL 700

Morphic atomic switch networks for beyond: Moore computing architectures

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The fulfillment of Moore's law of an exponential growth of transistor density has been pushed to the limit within the past decade. Processing units have reached a turning point in their capability to scale in performance with increasing transistor densities. Contemporary processors ubiquitously follow the Von Neumann architecture – computation where data storage and computing function separately. Despite increased transistor densities, the ability to successfully transfer and communicate information between elements is limited by the transfer rate of connections - the von Neumann bottleneck. Development of highly interconnected devices provides a solution to this bottleneck by redistributing the information traffic into several branches thereby resolving the exchange between elements several times faster. However, this multithreading tactic suffers from limited fabrication techniques to resolve features in the sub-10 nm scale and increased noise with decreasing feature size. Here, we have developed a device using CMOS compatible technologies as a platform for hybrid-CMOS architectures and novel computation through a combination of controlled fabrication techniques with spontaneous nanowire formation. We propose the use of an

atomic switch network (ASN) of interconnected Ag₂S inorganic synapses with characteristics of a complex system ideal for maximal information transfer and memory storage.



A SiO₂ substrate with patterned copper posts (a) was prepared then submerged in a 50 mM solution of silver nitrate, undergoing electroless deposition and diffusion limited aggregation to produce nanowire networks shown in (b). A reversible pinched hysteresis I-V curve was observed with the application of an alternating voltage sweep. Figure (d) shows the power-spectrum of the ASN under a constant voltage input and decayed as a power-law $t^{-\sigma}$ $\sigma = 0.7$ which indicated that the ASN operated as a complex system

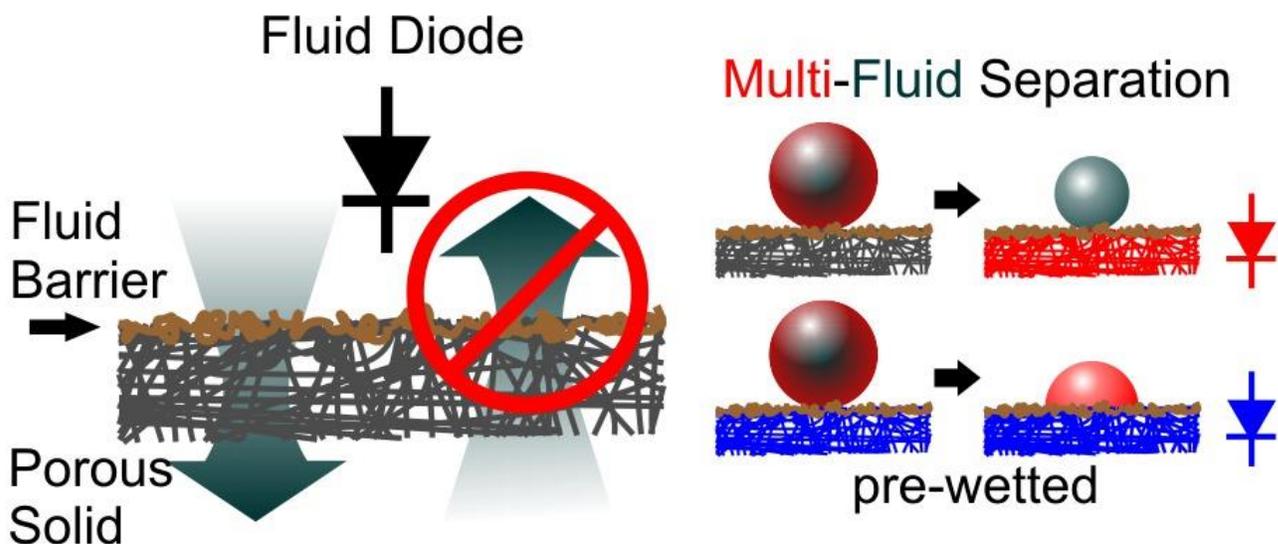
COLL 701

Diodic fluid flow rectification with low surface energy fluids

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Fluid management is a critical concern in industry, many fluids have much lower surface energies than water and therefore require unique material solutions. A mechanism is presented, for the unidirectional control of low surface energy flow analogous to the electronic diode. In electronics, diodicity is determined by high resistance in one direction with low resistance in the other. A fluid diode is capable of permitted fluid flow under negligible pressures in the forward orientation, with much higher resistance pressures in the reverse orientation. The mechanism has been previously presented using superhydrophobic coatings on porous media to rectify water flow, but is confirmed for lower surface energy oils in the current work. The work makes use of substrates with varying well-defined porosity to illustrate the dependence of Laplace pressure on the underlying mechanism, made possible by a combination of low surface energy fluorinated coatings and specific coating morphology. In addition, the diodic

performance can be shown to make possible the separation of multi-component fluid mixtures, for fluids having surface energies well below that of water (< 72 mN/m).



COLL 702

Adsorption properties of novel silica gel sorbents surface-functionalized with salicylhydroxamic acid-attached polystyrenes for quercetin

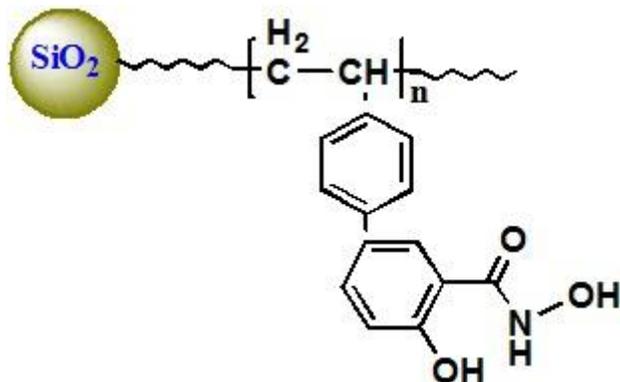
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Flavonoids are a diverse group of polyphenolic compounds present in plants, which contain a 15-carbon flavone skeleton. They can generate particular interest with regard to human health effects including antioxidant activities, cancer prevention, and so on.¹ Therefore, the extraction and separation of flavonoids have attracted much attention of researchers. In this contribution, a novel silica gel sorbents surface-functionalized with salicylhydroxamic acid-attached polystyrenes (SHA-PS/SiO₂, as shown in Scheme 1) was prepared. And its adsorption property for quercetin was studied. It is shown that SHA-PS/SiO₂ possesses strong adsorption ability for quercetin. The saturated adsorption amount reaches 452.13 mg/g, which is much higher than that in the literatures, such as PMAA/SiO₂ 98.22mg/g, ADS-5 48.69 mg/g, DM-130 resins 39.5 mg/g. Quercetin is a flavonoid containing a ketone carbonyl and multiple phenolic hydroxyl groups. So, a conventional hydrogen bond is formed between the hydroxamic acid groups and phenolic hydroxyl groups on the surfaces of SHA-PS/SiO₂ and the phenolic hydroxyl groups in quercetin, while π -type hydrogen bond is generated between the hydroxamic acid groups and phenolic hydroxyl groups on the surfaces of SHA-PS/SiO₂ and the conjugated aromatic rings in quercetin. In addition, π - π stack is

produced between the aromatic rings on the surfaces of SHA-PS/SiO₂ and the conjugated aromatic rings in quercetin. As a result of combined action of two types of hydrogen bond and a kind of π-π stack, SHA-PS/SiO₂ possesses very strong physical adsorption for quercetin. Obviously, quercetin has potential application value in the extraction and separation of flavonoids.

Scheme 1.

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Scheme 1. Structure of SHA-PS/SiO₂

COLL 703

Lowering the barrier to C-H activation using Pt/Cu single atom alloys

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Activation of C-H bonds in alkanes has been a challenge to chemists as these molecules are relatively inert due to strong localized C-C and C-H bonds. Nevertheless, researchers have pursued many ways to break C-H bonds as this activation enables the synthesis of a variety of different chemicals from simple hydrocarbons through carbon coupling reactions. In this work, we use a surface science approach to model C-H activation on a Cu(111) surface using methyl iodide. Methyl iodide is known to decompose to produce methyl groups and iodine atoms on Cu(111) below 200 K. The methyl groups are then stable on the surface up until 450 K, at which temperature they decompose to form a number of products including methane, ethylene, ethane, and propylene. The rate limiting step to forming these products is the activation of one of the C-H bonds in the methyl group to produce surface bound hydrogen and methylene. Pt(111) is also able to activate the C-I bond in methyl iodide, but methyl groups on this surface only produce methane, hydrogen, and surface bound methylene groups at 290 K. While the barrier to C-H activation is lowered on Pt compared to Cu, the Pt surface is

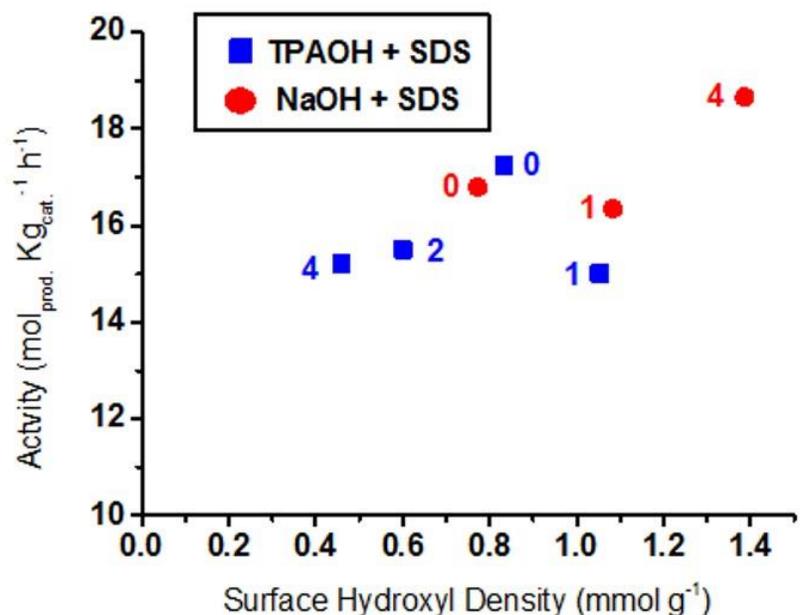
unable to perform carbon coupling reactions. Inspired by these previous results, we fabricated surfaces consisting of 1% Pt in the Cu(111) surface. At this concentration, Pt exists as single, isolated atoms substituted into the Cu(111) lattice. These *single atom alloys* exhibit synergistic chemistry and yield the desirable properties of each of the two pure metal surfaces. They are able to produce carbon coupling products like pure Cu, but are able to activate the C-H bond necessary to begin these reactions at 340; 110 K cooler than on Cu(111). Increasing the concentration of Pt further decreases the temperature necessary to activate C-H bonds, but also decreases the amount of carbon coupling products formed as the surface becomes more similar to Pt(111). Single atom alloys therefore provide an ideal model catalyst for the decomposition of methyl iodide, allowing for more facile activation of the C-H bond than pure Cu while also producing the desired coupling products, which Pt(111) is unable to do.

COLL 704

Surface modification of basic sites on MgO by varying surfactant and precipitating agent concentrations

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Magnesium oxide (MgO) as a solid, strong base has shown potential as a catalyst and as a catalyst support. We have attempted to maximise the catalytic potential of this oxide via magnesium hydroxide prepared under hydrothermal conditions with NaOH or *tetra*-propyl ammonium hydroxide as precipitating agents and a common surfactant; sodium dodecyl sulphate (SDS). This was then calcined to form magnesium oxide and subsequently used as a base catalyst in a Knoevenagel condensation reaction (benzaldehyde and ethyl cyanoacetate). Analysis of nitrogen adsorption indicated that in general surface areas could be improved by adding SDS, however, close to the critical micelle concentration of SDS (1-2 mmol) surface areas dramatically decreased. Concurrent adsorption of benzaldehyde through its C=O group on Mg²⁺ sites and adsorption of ethyl cyanoacetate via H-bonding to O²⁻ sites will improve the catalytic activity. SDS can influence the crystal growth of the forming Mg(OH)₂ in the presence of NaOH; such that the surface is more suitable to such condensation reactions. The highest activity of ca. 18 mol of product per Kg cat per hour was achieved over a catalyst precipitated by NaOH with 4 mmol of SDS added (Fig. 1). According to NMR analysis of the MgO surface hydroxyl density, increasing the surfactant concentration resulted in an increase of basic -O²⁻ sites with NaOH precipitated Mg(OH)₂. Conversely, the combination of TPAOH and SDS resulted in materials with a lower density of hydroxyl sites. This approach may find wider application in other catalytic reactions where fine control of basic surface sites is desirable.



Catalytic activity as a function of surface hydroxyl density of MgO catalysts precipitated with either NaOH or TPAOH and varying concentrations of SDS (values in mmol).

COLL 705

Photoinduced actuation of aqueous solutions containing a photoresponsive surfactant

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Photoresponsive surfactants have interfacial properties that can be controlled by light irradiation with specific wavelengths. Active changes in the surface tension facilitate manipulating liquids based on the Marangoni effect. In this paper, we have reported the photoinduced actuation of aqueous solutions containing a light-responsive surfactant (C4AzoTAB) with an azobenzene group. Surface tension measurements of the aqueous C4AzoTAB solutions revealed that the surface tension for *cis*-C4AzoTAB was higher than that of *trans*-C4AzoTAB within a specific range of surfactant concentrations. Thus, ultraviolet (UV) light irradiation of the aqueous *trans*-C4AzoTAB solution increases the surface tension. When UV light is irradiated on only one side of an aqueous *trans*-C4AzoTAB solution in a quartz glass tube, the surfactant solution moves toward the UV-irradiated side. The aqueous *cis*-C4AzoTAB solution moves in the opposite direction under visible light irradiation. Notably, for UV-induced actuation, the surface tension during *trans*-*cis* photoisomerization changes at only one edge of the fluid. The actuation velocities are related to the magnitude of the UV-induced change in the surface tension of the aqueous C4AzoTAB solution. The photoinduced actuation is caused by changes

in the Laplace pressure as the surface tension is varied by light irradiation. Overall, the light energy is converted to the kinetic energy of the actuation through the change in the surface tension of the surfactant solution by *trans-cis* photoisomerization of the surfactant.

COLL 706

Nanotribology of a catechol-functionalized alkane with terminal chain branching

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A bio-inspired system was studied where the terminal chain branching found in fatty acids naturally present on hair and wool was combined with a catechol group as the hydrophilic moiety to mimic the adhesion strategies found in mussel proteins. Atomic force microscopy (AFM) was used to study the adhesion and nanoscopic friction of monolayers of a catechol-functionalized branched alkane, 4-[(18S)-18-methyleicosyl]benzene-1,2-diol, formed by Langmuir-Blodgett deposition on silicon oxide, mica, and polydimethylsiloxane (PDMS) substrates. Measurements were done in ambient air and in dry N₂ gas. In dry N₂, the friction of these monolayers was low and the adhesion was well described by van der Waals interactions. In ambient air, the adhesion and friction showed a stronger hysteresis and different friction responses at low and high loads. The results will be discussed in view of possible bonding to the substrate and lateral cross-linking in the monolayer.

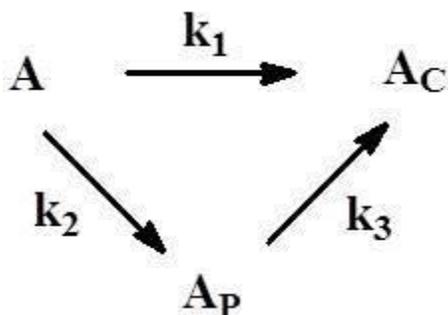
COLL 707

Use of chemical kinetics to examine spreading sessile drop behavior on solid surfaces

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Contact-line motion of liquid drops on a solid surface has received attention for some time. This is due to the large number of applications where the phenomena of drop spreading on solid surfaces is important. Researchers applied kinetic modeling simulations to characterize the spreading dynamics in the contact-line vicinity. However, many of these studies do not consider the disjoining forces involved in attracting fluid components to the surface. Furthermore, actual experimental data is rarely used, such as contact angle (CA) variation with time, to simulate proposed theory to experiment. In this discussion a kinetic scheme (indicated below) is used to simulate experimental CA-time data. In the scheme, A, is the liquid adsorbate, which competitively adsorbs via weak interactions to a surface site forming a state, A_p, or a strong interactive adsorption to a surface site forming state, A_c. (These rate constants values of occupation are represented by k₁, k₂, k₃. (k₃ follows Cassie-Baxter and Wenzel models). (These data

follow purely exponential and multiphase behavior of the CA-time data. The differential equations derived from this scheme were solved to fit the data. (The algorithm solves the differential scheme for the rate constants of occupation via a Simplex to locate the global minimum and a Levenberg-Marquardt algorithm to refine the constants.) Furthermore, these constants are related to energy barriers of adsorption of liquid to the solid surface with respect to, A_c and A_p , (temperature variation as experimental parameter). A number of liquid-solid surface combinations were examined involving printing and other concerns using this analysis. The values of the constants and adsorption energies correlated with molecular properties of the fluid and solid component(s). Also, coalescence (mottling), is explained by the scheme. The rate constants values rationalize the Arrhenius /non-Arrhenius behavior with molecular temperature variations of the surface.



COLL 708

Probing interfacial chemical reaction and surface interactions of electrochemically active galena mineral surface using atomic force microscope

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The interfacial electrochemical processing as a cost-effective and environment-friendly technique finds wide application in many engineering processes, such as mineral froth flotation. In this work, electrochemical atomic force microscope (EC-AFM) was employed to modulate the interfacial electrochemical reaction and simultaneously probe the evolution of surface characteristics (i.e., morphological changes and surface forces) of electrochemically active galena mineral surfaces at the nanoscale. The in situ topographic imaging demonstrates the homogeneous electrochemical oxidation across the mineral surface, leading to noticeable surface roughing at the potential of 0 V and more pronounced surface roughing at higher potentials (e.g., 0.3 and 0.45 V). The direct force measurements with an OTS functionalized AFM tip show that the magnitude of attractive hydrophobic interaction increased with increasing the applied potential from -0.7 to 0.45 V due to the enhanced surface hydrophobicity, which agrees well with

contact angle measurements. Fitted with the extended Derjaguin–Landau–Verwey–Overbeek (DLVO) theory by including the effect of hydrophobic interaction, the decay length of hydrophobic interaction was found to rise from 0.7 to 1.3 nm with increasing the potential from -0.7 to 0.3 V; while the continued increase of the potential to 0.45 V had a negligible effect. The electrochemical oxidation at 0 V is believed to be the formation of metal-deficient lead sulfide; while the oxidation at 0.45 V arises from the formation of elemental sulfur that is further confirmed by cryo-XPS. The results provide insights into the basic understanding of the interfacial properties and surface interaction mechanisms on electrochemically polarized mineral surfaces at the nanoscale, and the methodology can be extended to many other interfacial electrochemical processes.

COLL 709

Specific ion effects at the silica nanoparticle-electrolyte interface: Quantifying the structure of the electrical double layer

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The structure of the electrical double layer has been debated for well over a century, since it mediates colloidal interactions, regulates surface structure, controls reactivity, sets capacitance and represents the central element of electrochemical supercapacitors. The surface potential of such surfaces generally exceeds the electrokinetic potential, often substantially. Traditionally, a Stern layer of non-specifically adsorbed ions has been invoked to rationalize the difference between these two potentials; however, the inability to directly measure the surface potential of dispersed systems has rendered quantitative measurements of the Stern Layer potential, and other quantities associated with the Outer Helmholtz Plane, impossible. Here we use X-ray photoelectron spectroscopy (XPS) from a liquid microjet to measure the absolute surface potentials of silica nanoparticles dispersed in aqueous electrolytes. We quantitatively determine the impact of specific cations (Li^+ , Na^+ , K^+ , and Cs^+) in chloride electrolytes on the surface potential, the location of the shear plane and the capacitance of the Stern layer. We find that the magnitude of the surface potential increases linearly with hydrated-cation radius. Interpreting our data using the simplest assumptions and most straightforward understanding of Gouy-Chapman-Stern theory reveals a Stern layer (bounded by the Outer Helmholtz Plane) whose thickness corresponds to a single layer of water molecules hydrating the silica surface, plus the radius of the hydrated cation. We end by discussing the effect of electrolyte concentration on the surface potential, zeta potential, surface charge density and the thickness of the Stern layer.

COLL 710

Structure of zirconium(IV) hydroxide materials for chemical warfare agent decomposition

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Commercially available zirconium(IV) hydroxide materials have shown high activity towards decomposition of chemical warfare agents (CWAs), particularly for VX (O-ethyl S-(2-diisopropylamino)ethyl methylphosphonothioate).¹ The activity is known to arise from the presence of acidic / basic bridging and terminal hydroxyls, but more detailed fundamental understanding of Zr(OH)₄ activity remains limited as only general structural and compositional features are known. This is due in part to the amorphous nature of these porous nanoparticle aggregates. Furthermore, Zr(OH)₄ structural properties and activity towards CWAs vary depending on preparation and environmental conditions. Generally, Zr(OH)₄ complexes are formed in acidic solutions and can undergo condensation polymerization to form amorphous colloids and sol-gels. In this work, we systematically examine structural details of Zr(OH)₄ complexes with increasing molecular weight to understand how short range order, defects, and hydroxyl substituents vary with the extent of polymerization and particle aggregation. In particular, we identify representative structural elements for use in theoretical calculations to model reactions with CWAs, enabling comparison with experiments. Results presented include analysis by TEM, XRD, AFM, FTIR, Raman, and molecular dynamics calculations.

¹ Bandoz, et al., *J. Phys. Chem. C* 2012, 116, 11606

COLL 711

Surface profile exploration of thin film auto-stratification with atomic force microscopy

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Thin films dried from colloidal suspensions have wide applications, such as paint and varnish. To meet the requirements of emerging applications such as energy and electronic device, a multifunctional coating is necessary. Instead of multi-step deposition methods, a cost-effective single step method is preferred to save time and reduce cost. When mixed together, particles with different size or charge will segregate vertically upon drying. In this work, the effects of Peclet number, humidity and volume fraction on the thin film surface profile were examined with atomic force microscopy (AFM). Image analysis was performed to analyze the results from AFM. The results showed that there was a dependence of volume fraction and Peclet number ratio on the surface structure

of the thin films. On the surface of thin films, the volume fraction of big particles decreased with increasing Peclet number ratios and increasing volume fraction of big particles. The effect of humidity on the surface profile of thin film was not obvious. The results were compared to literatures with systems of different particles and sizes. We concluded that the surface structures of thin films could be controlled by controlling the Peclet number ratios and volume fractions of each content. The results are promising in creating a cost-effective single-step method for paints, vanishes and coatings in different fields.

COLL 712

Adsorption of Cu^{2+} from aqueous solution on *Irvingia gabonensis* biomass: Kinetics and thermodynamics studies

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Irvingia gabonensis (dika nut) (DN) was treated with acid in order to enhance its adsorption potential. Acid treated DN (ADN) was characterized by Fourier transform infrared (FTIR) spectroscopy, Brunauer–Emmett–Teller (BET) surface area analysis and scanning electron microscopy (SEM). The adsorbents was found to have characteristic functional groups such as –OH, C-N and C=O. SEM revealed that acid treatment resulted in the development of several pore sizes. ADN was subsequently utilized for the uptake of Cu^{2+} from aqueous solution and optimum adsorption was obtained at pH of 5.5. While multilayer adsorption dominated the uptake of Cu^{2+} onto ADN (R^2 value for Freundlich isotherm = 0.9937), monolayer adsorption and adsorbate-adsorbate interactions also played a major role in Cu^{2+} removal. The maximum monolayer adsorption capacity (q_{max}), obtained from the Langmuir adsorption isotherm was 103.09 mg g^{-1} . The pseudo-second-order kinetics model was observed to fit the adsorption data. Adsorption process was influenced by solution pH, temperature, agitation speed and temperature. Negative values of gibbs free energy suggest that the sorption process was spontaneous and feasible. Highest desorption efficiency (67.65 %) was recorded using CH_3COOH as eluent. Desorption eluent and energy of adsorption obtained from D-R isotherm model suggests that uptake of Cu^{2+} onto ADN was chemical in nature.

COLL 713

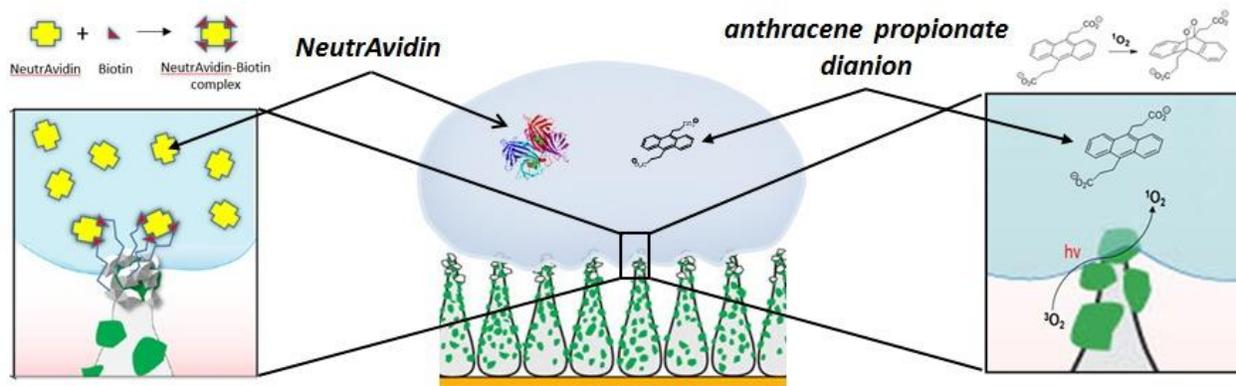
Reactions in Individual droplets on a superhydrophobic surface: Effect of convection

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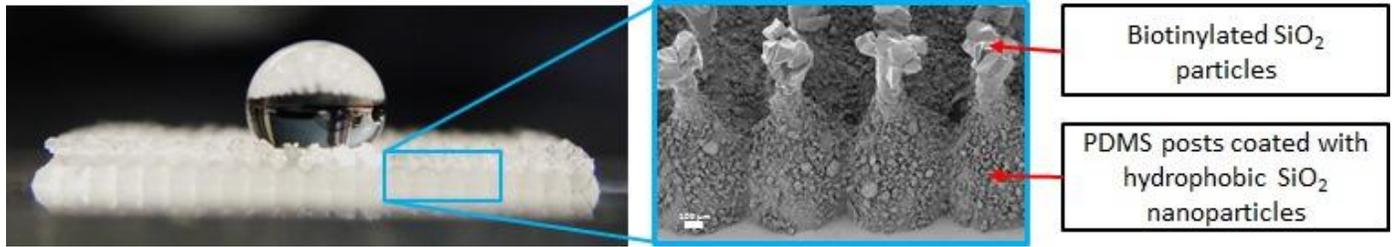
On a superhydrophobic surface, an aqueous droplet can maintain its quasi-spherical shape without wetting the surface. This geometry creates a nearly isothermal micro-scale container in which chemical reactions and analysis can be conducted using small volumes ($<10\ \mu\text{L}$) of reagents. Due to their small size and thermal isolation from the substrate, convection in these droplets is suppressed and so mixing within these micro-containers occurs only by diffusion. In this paper, we present a method to induce, control and quantify convective mixing within small size droplets poised on multifunctional superhydrophobic surfaces.

We prepared superhydrophobic surfaces using a 3D printing process to create arrays of PDMS posts onto which functionalized nanoparticles were partially embedded. On these surfaces, an aqueous droplet was placed and imaged using a high speed camera to quantify convection. By modifying the functionality of the nanoparticles, two reactions were studied. In one system, singlet oxygen was generated by illuminating sensitizer particles such that singlet oxygen was generated at the solid-liquid interface. Anthracene dipropionate dianion dissolved in the drop trapped the $^1\text{O}_2$ and the concentration change was measured by UV spectroscopy. In a second system, the protein binding interaction between NeutrAvidin (dissolved in the droplet) and biotin (bound to the surface) was quantified using a fluorescently labeled protein. The binding profile was plotted as a function of time, and the kinetic rate constant was calculated. By comparing the rates with and without convection, we show that the reactions are limited by diffusion in static droplets and that convection leads to significantly higher reaction rates.



Schematic of the two reactions studied at liquid-solid interface.

Schematic of the two reactions studied in droplets on functionalized superhydrophobic surfaces.



Side view of a 10 μ L water droplet on a functionalized superhydrophobic surface; inset shows SEM image of PDMS posts with particles partially embedded into the surface.