

COLL 1

Surface science of molecular catalysis and integration of the three fields of catalysis: Heterogeneous, homogeneous, and enzyme

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Our aim focuses on a climate change research program to convert greenhouse gases, carbon dioxide (CO₂) and methane (CH₄) to high quality fuels (methanol and hydrogen). CO₂ hydrogenation can be carried out using copper, cobalt and manganese oxides in recent publications [1,2]. The oxidation of methane to methanol can be achieved by using only the active site of the enzyme (PMMO), which consists of two copper atoms and an imidazole molecule [3]. We discovered that metal nanoparticles that are smaller than one nanometer (40 atoms) have electronic structures of the oxidation states of ions. For example, platinum or gold becomes Pt²⁺ and Pt⁴⁺ and Au²⁺ and Au⁴⁺ and rhodium Rh³⁺. These small size ions can carry out homogeneous catalytic reactions if they are stabilized by dendrimer polymers.

COLL 2

Identifying single-atom catalysts for CO oxidation from density functional theory

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Due to their activity and cost effectiveness, atomically dispersed transition metals are highly desirable catalysts. In addition, their uniform active sites enable high selectivity. However, sintering into larger particles is thermodynamically favorable in the absence of strong metal–support interactions. Using density functional theory, we study the stability of atomically dispersed transition metals on different support materials and their activity toward CO oxidation.

We find that the late transition metals Pd and Pt bind strongly to oxygen vacancies of MeO (Me = Fe, Mg, Mn, and Ni), and that their atomic dispersion is thermodynamically favorable at low metal loadings. The resulting single-atom catalysts enable CO oxidation with barriers as low as 40 kJ/mol. The intrinsic barriers were found to depend primarily on the nature of the transition metal.

These findings are in good agreement with previous experimental work on Pd₁/MgO_x catalysts that enable CO oxidation at 260 K. However, the Pd₁/MgO_x catalyst is deactivated after the first oxidation step, as it leads to a metastable PdO/MgO_x species, which can heal the O vacancy. Without the vacancy, nanoparticle formation is thermodynamically favorable. Due to their lower oxygen vacancy formation energies, reducible oxide supports are predicted to be more resistant to sintering. Thus, the anion vacancy formation energy of the support is an important parameter for the stability of anionic single-atom catalysts, while their activity depends primarily on the

nature of the transition metal atom. These atomistic insights can be used to design even more stable single-atom catalysts for CO oxidation at low temperatures.

COLL 3

Single-site catalysts by metal-ligand complexation at surfaces: From model systems in vacuum to high-pressure catalysis on oxide supports

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A grand challenge in heterogeneous catalysis is to achieve high levels of selectivity by controlling the chemical uniformity of metal catalyst sites at surfaces. Our group is working to apply principles of on-surface metal-organic redox assembly to develop a new approach to this problem. Metal-organic coordination complexes at surfaces hold promise for selective chemical function, but there is a limited understanding of the chemical reactivity of these systems. The studies in our lab include both ultra-high vacuum surface analysis and reaction testing in flow or batch reactors at high pressure and elevated temperature. Each type of study contributes valuable information to advance new catalyst design. In vacuum studies, we are able to screen metal-organic complexes and their chemical activity on model supports using scanning tunneling microscopy, X-ray photoelectron spectroscopy, and high-resolution electron energy loss spectroscopy. For example, V-tetrazine complexes show activity for O₂ activation with very high selectivity for a single V-oxo product. On high surface area oxide supports, X-ray absorption spectroscopy (especially fine-structure analysis), transmission electron microscopy, and X-ray photoelectron spectroscopy allow us to characterize the formation of metal-organic redox complexes and to verify their single-site character. We have demonstrated excellent catalytic activity for some hydrosilylation and hydrogenation reactions and demonstrated that the single-site character of the catalysts is maintained after the reaction.

COLL 4

Interactions of methane on and near high-temperature liquid surfaces

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Molecular adsorption on liquid surfaces in motion introduces unusual and interesting aspects of surface chemistry. Dehydrogenation of methane on high temperature liquid metals and salt surfaces is studied to facilitate the pyrolysis of methane to produce molecular hydrogen and solid carbon. In a liquid environment the carbon may be readily separated and removed continuously allowing processes for the carbon dioxide-free production of hydrogen from natural gas. The turnover frequency of methane on metal alloys is observed to strongly depend on the alloy composition. The relative reactivities

were investigated by density functional theory (DFT) and *ab initio* molecular dynamics (AIMD) simulations and the experimental observations correlated to charge transfer between the alloying elements. A similar approach was used to understand the observed methane reactivity differences observed in monovalent and polyvalent halide molten salt surfaces. The catalytic liquid surfaces are found to facilitate both complete dehydrogenation, and the production of methyl radicals to increase the gas phase methane decomposition. The results have pointed to possible applications of high temperature liquids for transforming natural gas into molecular hydrogen fuels without carbon oxides.

COLL 5

2-Propanol dehydration on single-facet-dominant TiO₂ (101) and (001) nanopowder catalysts

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Two anatase titania model catalysts, with preferential exposure of (101) and (001) facets, were synthesized and studied for 2-propanol dehydration. A series of microscopic and spectroscopic techniques including X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), ammonia temperature program desorption (NH₃-TPD), diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and chemical titration were employed to correlate the structure properties of the model catalysts to their catalytic performances. Based on selective site poisoning titration using 2,6-di-tert-butyl pyridine, surface Lewis acid sites were found to be active for 2-propanol dehydration. Surface species present during steady-state reaction were probed using temperature-dependent DRIFTS and used to construct model surface structures to describe the elementary steps of 2-propanol dehydration using density functional theory (DFT). DFT simulations demonstrated that on both anatase surfaces, 2-propanol dehydrates via concerted E2 elimination pathways, but with different initial states and thus also different intrinsic activation barriers. Molecular 2-propanol dehydration dominates on TiO₂ (101) while on TiO₂ (001), 2-propanol simultaneously converts to more stable 2-propoxide before dehydration, which then requires higher activation energies for E2 elimination. These DFT simulated results are consistent with reaction kinetics measurements; the latter also demonstrated that the (101) model catalyst is more active. However, the minority facets on the (001) model catalyst likely play important roles in the dehydration chemistry, causing uncertainties in the interpretation of the kinetics data.

COLL 6

Applying low temperature titration for determination of metallic sites on active oxide supported catalysts

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Chemisorption-titration, as a surface sensitive analysis method, is widely applied for direct measurement of specific surface area of metallic clusters on heterogeneous catalysts. However, on active oxide supports, the products yield of this method is strongly affected by the exchanging of oxygen between the support and the titration gases. In this study, Pt and Cu based catalysts are used as the source for metallic sites characterizations through isothermal titration experiments within a wide temperature range. Pt/Fe₂O₃ catalysts were characterized using CO oxidation and Cu/CeO₂ catalysts were characterized using N₂O decomposition. The titration products are CO₂ and N₂ respectively. Detailed measurements requires instant online mass spectroscopy characterization and temperature control from subzero to room temperatures, for this purpose an online micro reactor is developed and applied for quantitative products calibration. For both series of catalysts, MS signal are also measured on pure metallic powder and calibrated with commercial chemisorption measurement system. The temperature dependence of both total titration products from the supported samples reveals that for each catalyst, there are narrow subzero temperature windows that the titration products are only related with metallic sites. The results provides an approach towards an one-step chemisorption-titration procedure for measurement of dispersion on active oxide supported catalysts, which is a possible benchmark that bridges fundamental model catalysts and industrial applied catalysts in performance evaluation.

COLL 7

Catalysis with metal phosphides: Synthesis, properties, and reactivity

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Metal phosphides (e.g. Ni₂P, MoP, Fe_xNi_{2-x}P) have attracted substantial interest as the active phase in a new class of catalysts for a number of conventional and renewable energy applications. The synthesis and properties of metal phosphide catalysts will be reviewed, with particular attention given to the preparation of nanoscale particles on a range of metal oxide supports. Catalysis by metal phosphides for hydrotreating reactions (hydrodesulfurization (HDS), hydrodenitrogenation (HDN)) will be discussed, as will new findings for reactions important in renewable energy processing.

COLL 8

Failure modes in quantum dot bioimaging agents: It's all about the coating

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Quantum dots (QDs) were introduced over 20 years ago as revolutionary agents for bioimaging. As semiconductor nanoparticles with narrow emission wavelengths, broad excitation spectra, large optical cross sections, and tunable fluorescence, it was believed that QDs would rapidly replace organic molecular dyes in fluorescence imaging. However, more than 20 years after the publication of seminal papers in this area, this has not occurred. For the last several years, we have explored mechanisms of QD failure in the preparation processes for bio-imaging, including transfer to the aqueous phase and bio-conjugation. We have evaluated QDs sold by commercial vendors, as well as those synthesized via common routes, and the transfer processes used to solubilize organic QDs in the aqueous phase. Here, we will discuss the two most significant problems that we have identified with biological QDs: oxidation and loss of colloidal stability, in the context of the two most common QD coating strategies: interdigitated amphiphilic polymer passivation and micelle encapsulation. We have identified clear links between the QD coating method, colloidal stability, and susceptibility to oxidation. We will also discuss the current state of the art in QD coatings, and potential paths forward to QDs with sufficient precision and repeatability for clinical use.

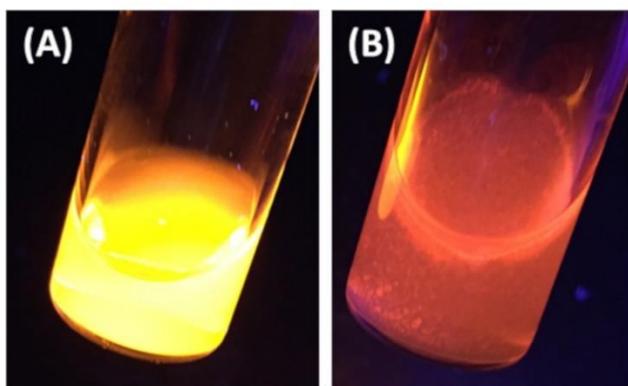


Figure 1: Commercial aqueous QDs in water (left) and 2-(N-morpholino)ethanesulfonic acid (MES) buffer. QDs precipitate in MES commonly used for bioconjugation protocols.

Measuring the absolute photoluminescence quantum yield of colloidal nanoparticles with multipoint method

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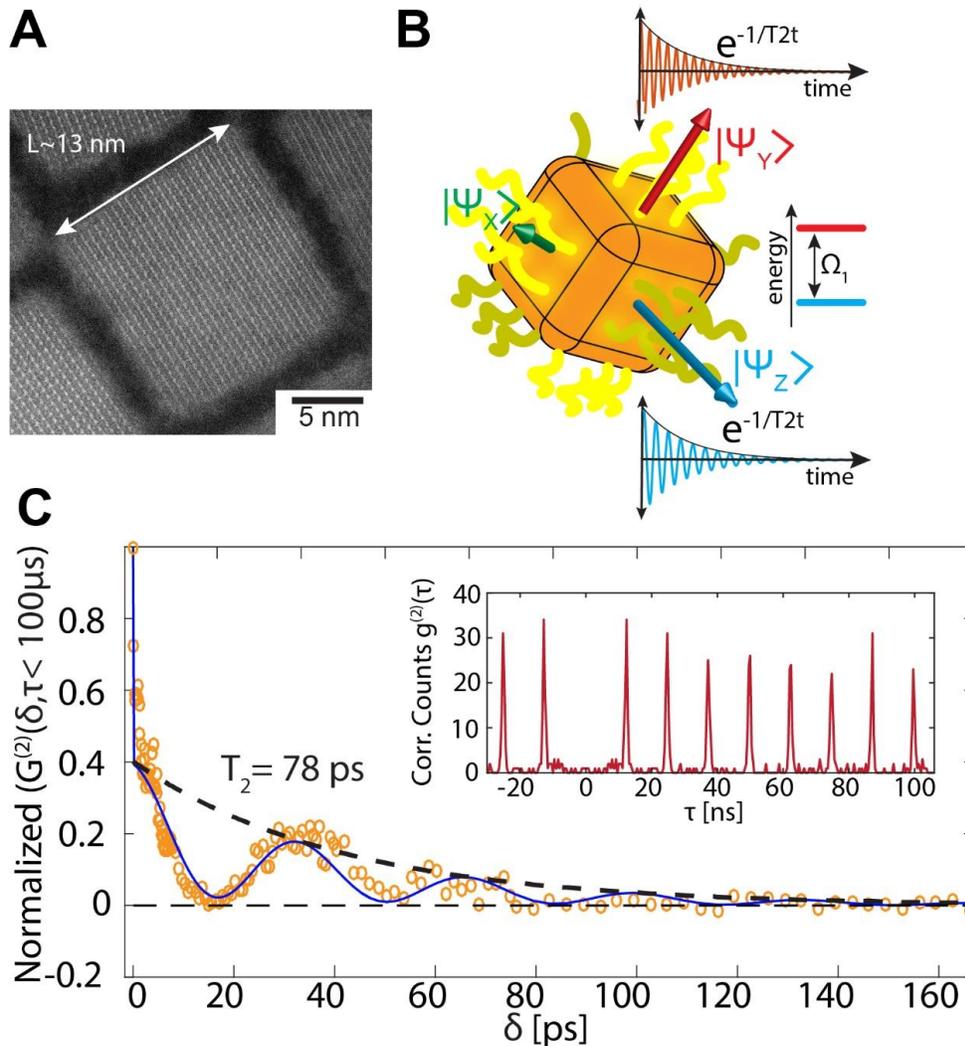
Photoluminescence quantum yield (PL QY) is one of the most important properties of luminescent materials. The best method for absolute PL QY measurement so far is recognized as using the optical integrating sphere system. However, measuring the absolute PL QY in high accuracy and stability is still challenging. Herein, both the experimental setup and analytical method for PL QY measurement are systematically studied. Two sets of absolute PL QY measurement systems based on two different integrating spheres have been built and optimized in two aspects, i.e. the light path and cuvette holder. A rationally designed cuvette holder has been fabricated using 3D printing technology. For quantum dot solution samples with constant PL QYs in a wide range of concentrations, a multi-point measuring method is developed. By plotting the remaining excitation photon number after absorbed versus the emission photon number for a series of quantum dot solutions with various concentrations, PL QY can be calculated as the absolute value of the slope of the linear fitting of the experimental data points. The reliability of the multi-point method can be evaluated by the fitting deviation. The R^2 of the linear fitting of more than six points reaches 0.999 for CdSe/CdS core-shell quantum dots. Comparing to the commonly used single-point method, multi-point method has much lower system error and higher repeatability. The PL QYs of the standard dyes, such as Rhodamine 6G and Nile Red, determined using the new method is found to be in good agreement to the values reported in literature. For the quantum dots with small Stokes shift or with weak-binding ligands, the PL QY would reduce at very high or low concentrations. The multi-point method with a series of quantum dot concentrations could be used to evaluate the self-absorption effect and the desorption of ligands on the surface of colloidal quantum dots. The concentration gradient method for PL QY measurement introduced here can be further used for quantitatively studying the ligand dynamics of colloidal quantum dots.

COLL 10

Colloidal perovskite quantum dots as scalable emitters of coherent single photons

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The development of practical optical quantum technologies requires the reproducible and scalable production of single quantum emitters with long optical coherence times that can be readily integrated with devices[1]. Here, we demonstrate the superior optical properties of chemically-made, colloidal lead halide perovskite quantum dots (PQDs)(Fig. **A**) as single emitters. Using photon-correlation Fourier spectroscopy at low temperatures, we find that PQDs exhibit long optical coherence times and small exciton fine-structure splittings (Fig. **B**, **C**)[3]. The long coherence and short radiative emission lifetimes (210 ps) renders the PQD emission linewidth near the Fourier transform limit. Moreover, we show that spectral diffusion is drastically reduced compared to other colloidal quantum dots and that the majority (50-80%) of photons is emitted coherently. The fraction of coherent photons is already comparable to silicon vacancy centers in diamond as often-used emitters in quantum photonics. We further take steps towards improving the low-temperature stability and reducing inhomogeneity with the synthesis. Our results suggest that, while all other colloidal quantum dot materials suffer from prohibitively incoherent emission, PQDs can be explored as sources of indistinguishable single photons that can be processed from solution onto virtually any substrate and easily coupled with hybrid nano-photonics components like waveguides or plasmonic gap cavities. The talk concludes with our efforts to integrate PQDs into 2D-heterostructure devices capable of emitting single photons of electrically-tunable color, a first step towards the realization of PQD-based quantum light sources.



COLL 11

Colloidal quantum dots-based nano-heterostructures for solar fuel generation

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Direct conversion of sunlight to fuels using photocatalytic processes has long been explored as one of the most promising sustainable approaches. The two widely investigated processes are hydrogen generation via water splitting and carbon dioxide to hydrocarbon fuel conversion. Neither of these technologies has yet gone beyond laboratory scale research due primarily to problems such as low process efficiency and

poor stability of photocatalysts. While the photocatalysts in the form of colloidal quantum dots possess tremendous potential in boosting the solar to fuel conversion efficiency due to their unique properties provided by the zero dimensional geometry, most materials investigated so far have not shown sufficient robustness in sustaining the photo-assisted redox reactions for a long time. Nevertheless, some new materials and strategies emerging currently raise hopes. For example, we recently used quantum dots of boron nitride, a stable wide band gap material, in association with titania nanotubes, another stable material, for photoelectrochemical hydrogen generation. Our work demonstrated that the nano-heterostructure formed by the two materials could absorb and convert light more efficiently to charges for redox reactions in a significantly broader energy range than the individual materials. The advances in using this nano-heterostructure approach for the performance enhancement of photocatalysts used for solar fuel generation will be discussed in this presentation.

COLL 12

Impact of spacers on controlling the optical properties of silicon quantum dots: Fluorescein dyad

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The unique properties of silicon quantum dots (SQDs), such as their unique optical properties, low toxicity, and ease of surface functionalization have made them great candidates for various biological and optoelectronic applications. Unfortunately, the low quantum yield, unstable photoluminescence, and poor colloidal stability of SQDs hindered their wide applicability. Herein, we report the synthesis of four assemblies of SQDs (1.6 – 1.8 nm average diameter) functionalized with fluorescein dye through isothiocyanate (-NCS) and carboxylate (COO) spacers to produce the dyads Am-SQD-FI, DiAm-SQD-FI, Urea-SQD-FI, and SiF. The photophysical results showed that the interaction between SQDs and Fluorescein chromophores in the dyads Am-SQD-FI, DiAm-SQD-FI, and SiF is mainly proceeding through photoinduced electron transfer at different rates, while energy transfer was confirmed to be the predominant process in the dyad Urea-SQD-FI. Furthermore, the utilization of the isothiocyanate spacer in the dyads led to a significant improvement in the quantum efficiency of SQDs (up to 65%) and extended their photostability for a year. The nature of the spacer played a key role toward directing and controlling the optical properties of SQDs. To demonstrate the suitability of the functionalized SQDs for bioimaging, the four dyads were examined for fluorescent imaging of human bone cancerous U2OS cells.

COLL 13

Noble- and heavy-metal-free colloidal semiconductor branched frame photocatalyst

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The design and construction of semiconductor-semiconductor heterojunctions is one of the key factor for photocatalysts. The nano frames (nano couples) are emerging materials with unexplored functions [1]. On the other perspective, the noble- and heavy-metal free colloidal semiconductor rod offer an environmental free and low cost idea to achieve high efficient photocatalysts as water splitting [2]. From those point of view, the assembly of new types of frame heterostructures have promising values in photocatalysis application. The heterojunctions play a crucial in a highly efficient charge collection and separation which improve the capability of photocatalysis and provide a brand new strategy in design of photocatalyst.

COLL 14

Colloidal carbon dots for solar technologies

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The conversion of the solar radiation in electric power represents a promising opportunity to address the increasing demand for clean energy, while decreasing the environmental impact caused by excessive CO₂ emissions from fossil fuels. Colloidal nanocrystals (NCs) have been widely investigated in recent decades due to their unique optical, electrical properties and various applications in solar technologies. Among these NCs, colloidal carbon dots (Cdots) are regarded as promising candidates for realizing solar harvesting devices. Cdots are the latest addition to the carbon nanoallotropes family and they are exclusively composed of non-toxic elements, such as nitrogen, carbon and oxygen. They can be easily synthesized in large quantities by solvothermal method. Their main advantages, compared to conventional semiconducting quantum dots (QDs), is the non-toxicity, environmental friendliness, low-cost and simple preparation using abundant carbon based feedstock.

Herein, different type of Cdots with different surfaces functionalization and optical features are prepared. In particular their absorption and emission spectra are tuned in the Visible/Near infra-red range. Their ability to inject charges in different materials, such as TiO₂ and Graphene Oxide, is systematically investigated in order to understand the role of the different surface functionalization in the charge transfer mechanism. Based on these results and thanks to the excellent opto-electronic properties of the Cdots; carefully chosen Cdots are then employed in different roles: as photosensitizer for wide-band gap semiconductors, as charge transport layer to realize high efficient perovskite solar cells and also as luminophores for metal-free large-area luminescent solar concentrators (LSC).

COLL 15

Investigating nucleation and growth kinetics of indium phosphide quantum dots in a continuous flow reactor

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Colloidal quantum dots (QDs) with versatile solution processability are generating new opportunities in multiple areas including photovoltaics, imaging, solid-state lighting and displays. Predominantly studied cadmium chalcogenides based QDs exhibit high toxicity and hence, in recent years the interest of industry and academia has shifted towards alternate heavy-metal free materials. Majority of the work reported in the literature has focused on QD synthesis using small-scale conventional batch synthesis approach, that limits precise control over reaction conditions – precursor injection, heating rates, temperature, and pressure. As an alternate synthesis approach, continuous flow synthesis offers two-fold advantage: (i) better control over reaction parameters, thus improving the tunability of size, shape, and composition of QDs in a reproducible manner; and (ii) a viable platform for investigating nucleation and growth of QDs.

This presentation will focus on design and implementation of a modular flow reactor setup for synthesis of monodisperse InP QDs. Our unique flow reactor platform allowed the synthesis of InP/ZnSeS core-shell quantum dots exhibiting 67% QY with ability to tune the emission wavelength by simply varying the process parameters (flow rates, temperature and concentration) at different stages. The flow reactor platform also allowed mechanistic investigation of InP QD growth using aminophosphines precursors. Our results show that the presence of excess zinc source shifts equilibrium between two active species involved in the precursor conversion reaction. To further investigate the InP flow chemistry, we developed a dual-stage strategy that enables heating of the precursor streams, first to the nucleation temperature and then a rapid quenching of precursors to the growth temperature (all within 1.5 seconds), thus allowing spatial separation of nucleation and growth. The application of dual-stage reactor platform allowed tuning both the nucleation and growth parameters independent of each other as an additional synthesis knob. A comparison with conventional batch synthesis, and single stage flow synthesis approach further confirms the advantage of spatially-separated nucleation and growth strategy for size-focused growth of InP QDs.

COLL 16

HgCdSe/HgS/CdZnS colloidal quantum wells with bright short-wave infrared light emission

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There has been a growing interest in bright short-wave infrared (SWIR; 1000-1700 nm) light emitters for their unique applications in biomedical imaging and optoelectronics. Previous studies have shown that core/shell quantum dots (QDs) such as PbS/CdS/ZnS and InAs/CdSe/CdS can emit bright, stable, and wavelength-tunable SWIR lights. However, these QDs showed high QYs (up to 80%) only in a part of SWIR window (1000-1100 nm) and in organic solution, otherwise QYs dropped significantly (lower than 30%). To address these limitations, we engineered a new SWIR nano-emitter by synthesizing CdHgSe/HgS/CdZnS colloidal quantum wells (QWs), which can exhibit bright emission across the whole SWIR region in both organic solution and water. Our SWIR QWs were synthesized via multi-step colloidal reactions to (1) prepare CdHgSe core via a partial Cd-to-Hg cation exchange on CdSe QD surface, (2) grow HgS emitting layer with controlled thickness over CdHgSe core to tune the SWIR wavelength, and (3) add CdZnS passivating layer to enhance QY and photostability (**Figure 1(a)**). Photoluminescence (PL) measurements showed that our SWIR QWs can emit bright, narrow (FWHM 150-300 nm) SWIR emission tuned between 1050 to 1550 nm. Moreover, absolute photoluminescence QY measurements confirmed that our SWIR QWs can exhibit much higher QYs than previous QDs in both organic solution and in water after encapsulating with amphiphilic polymer (**Figure 1(b)**). Furthermore, we could make bright AC-driven SWIR LEDs covering full SWIR spectrum operating at much lower threshold voltage than visible ones by using our SWIR QWs. We expect that our SWIR QWs would find various future applications including bright SWIR probes for deep tissue biomolecular imaging and non-invasive medical imaging and active layers for flexible SWIR LEDs.

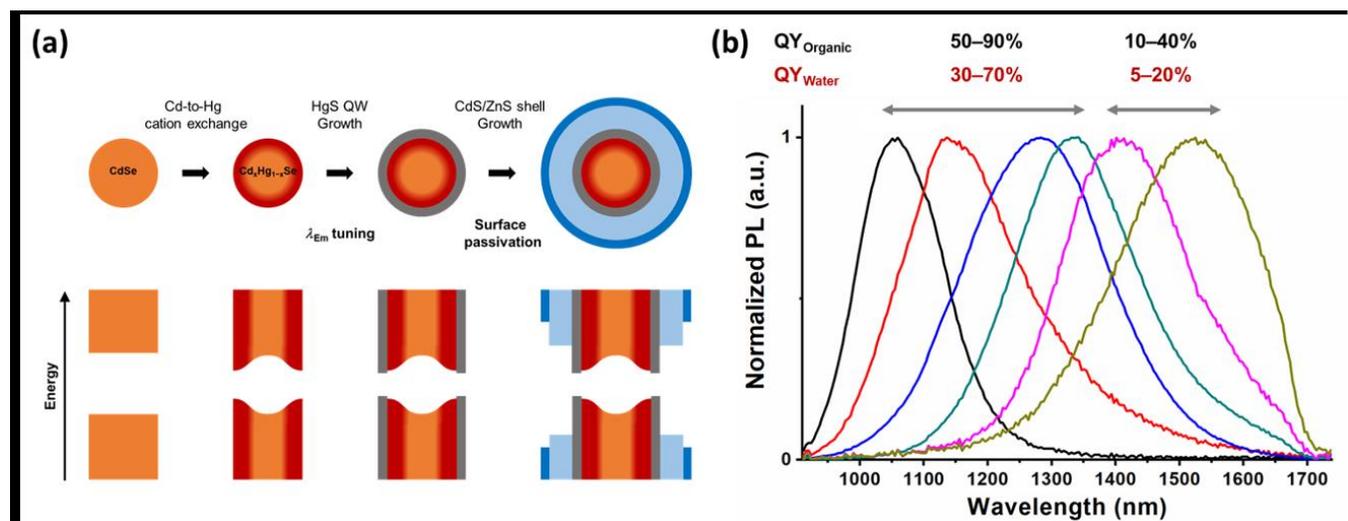


Figure 1. (a) Schematic of SWIR QW synthesis and corresponding energy band diagrams. (b) PL spectra and measured absolute QYs of SWIR QWs.

COLL 17

On the confined orientational motions of dyes diffusing in surfactant templated cylindrical silica mesopores

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Single molecule emission polarization (SMEP) measurements are used along with single molecule (SMT) data to better understand the confinement of dye molecules diffusing within one-dimensional (1D) surfactant templated silica mesopores. Mesoporous silica films are prepared by spin casting silica sols templated by cetyltrimethylammonium bromide on microscope coverslip surfaces. The films are loaded with any one of several different dye molecules during preparation. Cationic, anionic, and uncharged perylene diimide dyes are employed, as is the strongly solvatochromic dye Nile Red. The films are subsequently imaged on a widefield fluorescence microscope under a water-ethanol vapor atmosphere that mobilizes the molecules. Fluorescence videos acquired simultaneously in two orthogonal polarizations reveal that all dyes investigated were orientationally confined, diffusing in a highly aligned state within the cylindrical mesopores. Quantitative SMEP measurements show that the level of orientational confinement depends on the length of the hydrocarbon tails attached to the perylene diimide core and whether the dyes are uncharged, cationic, or anionic. The SMT data reveal that confinement of the dye molecules to individual silica mesopores is also dependent on dye charge. While studies employing the dye Nile Red indicate that the uncharged hydrophobic dyes are most likely confined to central regions within the pore-filling surfactant micelles, SMT data obtained from charged dyes suggest that some (i.e., anionic dyes in particular) locate near the charged surfactant-silica interface and can more readily cross between neighboring mesopores. The results of these investigations afford an improved understanding of mass transport phenomena in the tightly confined spaces of surfactant-filled silica nanopores and will have an impact on the applications of these and related materials in chemical separations and catalysis.

COLL 18

Multicomponent diffusion in mesoporous materials evaluated via diffusion NMR: Guest/host interfacial transport

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Nuclear magnetic resonance (NMR) diffusometry is a powerful tool for measuring dynamics of multi-component mixtures. In guest-host systems comprised of mixed fluids and solids, the short transverse relaxation times and decreased resolution complicate the interpretation of the experimental results resulting in a lack of published data on guests in nanoporous solid hosts. Here, the pulsed field gradient (PFG) technique is utilized to reveal chemically-specific diffusion coefficients in mixed fluids intercalated within solid hosts. Mesoporous glasses and zeolites with 2D or 3D channels were utilized and diffusion coefficients at different loadings are evaluated. Furthermore, the effect of pressure on the transverse relaxation times and the NMR spectra were investigated. These diffusion coefficients are analyzed to evaluate guest/host interfacial transport. The outcomes of this work will help with the rational design of stimulation fluids.

COLL 19

View of confinement from the perspective of water molecules, as observed by Overhauser dynamic nuclear polarization

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Overhauser Dynamic Nuclear Polarization (ODNP) isolates the translational motion of water near a selectively placed spin label, and reads out the result through variable enhancement of NMR (Nuclear Magnetic Resonance) signal. ODNP does not rely on higher-order spectroscopic effects, requires only a simple, versatile, and non-perturbative labeling strategy, and functions seamlessly in opaque, viscous, and other “dirty” systems. These methods have included earlier studies (by the speaker and coworkers) of protein and lipid systems under crowded conditions, and the surprising observation that surface hydration water is not perturbed by protecting osmolytes. While ODNP has been applied to a variety of biological systems, as well as polymer systems, it still possesses many fundamental capabilities and a flexibility that remain largely untapped. ODNP should serve as an excellent tool for understanding water confinement and the role it plays in a vast range of applications, from the binding of proteins to syntheses inside reverse micelles. Rigorous studies, however, hinge on the development of techniques that can properly map out the behavior of surface and confined water across different compartments and phases in highly heterogeneous and/or porous materials. Emphasizing reverse micelles as model systems, we describe our progress towards measurements in highly phase-heterogeneous and confined systems and we include comparisons to molecular modeling simulations. By integrating ODNP with modern NMR relaxometry techniques, we facilitate its deployment in truly heterogeneous systems such as the reverse micelle. We pursue careful temperature-

dependent studies that will reveal the activation energy of translational motion of water at different locations adjacent to the surfactant vs. centered in the reverse micelle. We will discuss how these studies translate to a broader understanding of systems involving confined water.

COLL 20

Infiltration of polymers into disordered nanoparticle packings: Polymers under extreme nanoconfinement

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Capillary rise infiltration (CaRI) is a new method of fabricating polymer nanocomposites with extremely high fractions of nanoparticles (> 50 vol%). In CaRI, highly filled composites are formed by thermally annealing a bilayer of polymer and nanoparticle, which induces imbibition of polymer into the interstices of the nanoparticle packing. The chain dimension of the polymer, which depends on its molecular weight, can be comparable to or greater than the average pore size of the nanoparticle packing; thus this system provides a powerful platform to study the effects of extreme nanoconfinement on the transport and thermomechanical properties of polymers. I will share our current understanding of the transport phenomena and glass transition of polymers under such nanoconfinement using a combination of experimental and computational approaches.

COLL 21

Quantitative measurement of nanoconfinement effects on molecular transport and chemical reaction with a core-shell mesoporous particle

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Theoretical studies with simplified model systems and ensemble experimental measurements have shown that molecular transport and chemical reactions in nanoconfined environments are largely different compared to those in bulk solution. Here we design a well-defined platform with catalytic reaction centers confined in the end of nanopores with controlled lengths to study the *in situ* dynamic behavior of molecular dynamics and catalytic processes under nanoconfinement at the single-molecule and single-particle level. Variable single molecular mass transport behavior reveals the heterogeneity of the confined environment in the nanopores. The combination of the unique model nanomaterial and the single-molecule imaging technique paves the way to understand the fundamental nanoconfinement effects for catalysis and separations.

Water permeation behavior thorough vertically-aligned carbon nanotube array/polymer composite membranes: Effect of temperature

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Water transport through carbon nanotube (CNT)-confined spaces has recently attracted considerable attention in the context of application to filtration and molecular gatekeeping. The molecular dynamic simulations predict the formation of a variety of water structures and phase transition behaviors in CNTs, which depend on the CNT diameter, pressure, and temperature. In contrast, very few studies have focused on experimental investigations with liquid water.

This study experimentally investigates the temperature dependence of pressure-driven liquid permeation through a membrane composed of a vertically-aligned double-walled carbon nanotube (VA DWCNT) array composited with poly(paraxylylene). We prepare a membrane with CNT inner diameter of 3.9 nm, which exhibits no water permeation below the critical temperature of 26 °C, after which water permeability is first observed and increases with temperatures > 26 °C. Further, the critical temperature decreases to 18 °C when the CNT inner diameter increases to 6.0 nm. The observed water permeation in the CNT-confined space exhibits activation energy transitions around 36 °C (Figure 1), which suggests that the confined water molecules in CNTs exhibit plural ordered structures.

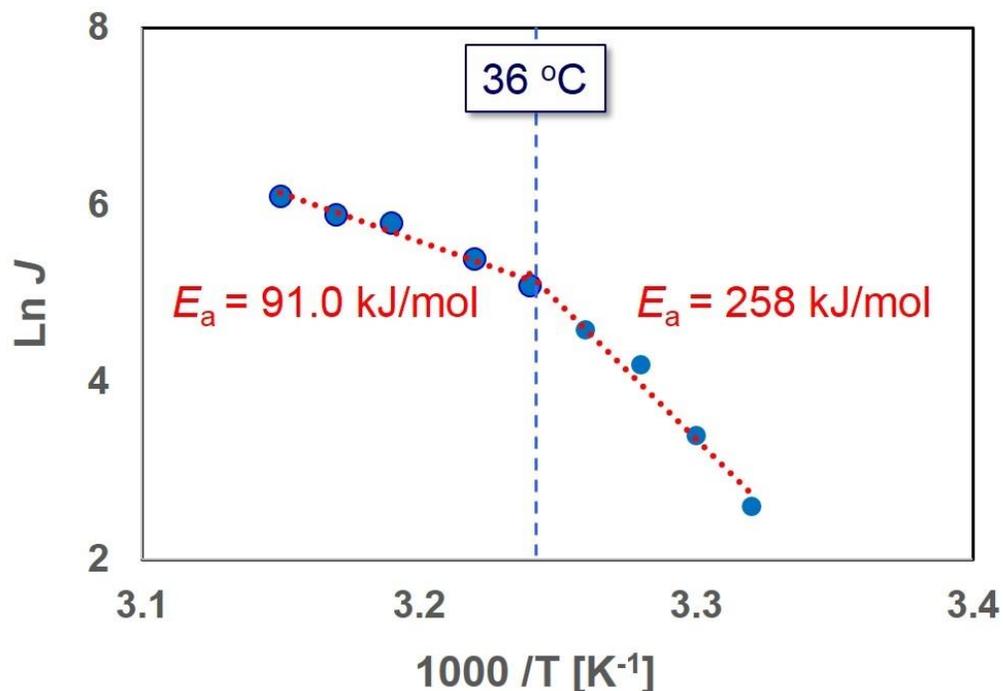


Figure 1 Arrhenius plot of water flux through vertically-aligned double-wall carbon nanotube array/polymer composite membrane.

The activation energy for water transport, E_a [kJ/mol], is calculated by the Arrhenius equation: $J = A \exp(-E_a/RT)$, where, J [g/m²h], A , R , and T represent the water flux, frequency factor, ideal gas constant, and absolute temperature, respectively.

COLL 23

Dielectric constant of interfacial water over charged interfaces

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Second harmonic generation measurements of charged aqueous interfaces are presented. The results are consistent with a dielectric constant point estimate considerably below that of the bulk value. Specific applications to oxide/water, lipid membrane/water, and porous membrane/water interfaces are discussed.

COLL 24

Exploration of the nanomedicine-design space with high-throughput screening and machine learning

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Only a tiny fraction of the nanomedicine-design space has been explored, owing to the structural complexity of nanomedicines and the lack of relevant high-throughput synthesis and analysis methods. In this presentation, a methodology for determining structure–activity relationships and design rules for spherical nucleic acids (SNAs) functioning as cancer-vaccine candidates will be discussed. First, ~1,000 candidate SNAs on the basis of reasonable ranges for 11 design parameters that can be systematically and independently varied to optimize SNA performance were identified. Second, a high-throughput method for making SNAs at the picomolar scale in a 384-well format was developed, and then a mass-spectrometry assay was used to rapidly measure SNA immune activation. Third, machine learning was used to quantitatively model SNA immune activation and identify the minimum number of SNAs needed to capture optimum structure–activity relationships for a given SNA library. Our methodology is general, can reduce the number of nanoparticles that need to be tested by an order of magnitude, and could serve as a screening tool for the development of nanoparticle therapeutics.

COLL 25

Machine learning-driven design of nanomaterials: Ingredients for success

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Data-driven capabilities such as machine learning (ML) are rapidly growing in popularity in materials science and chemistry, but several prerequisites are crucial for repeatable success with these methods. We will walk through an end-to-end case study in which ML is applied to accelerate the design of nanomaterials, and focus attention on several enabling aspects such as experimental setup, data processing, and data management.

COLL 26

Nanoinformatics in drug delivery: Matching drugs to carriers

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Designing nanomedicines for targeted drug delivery often requires complex preparation steps involving both supramolecular self-assembly and multiple chemical modifications. These processes are generally difficult to predict, execute, and control. The relatively new field of nanoinformatics uses machine learning and data mining to facilitate preparation processes and drug selection. I will present methods to predict successful formulations of hydrophobic kinase inhibitor molecules based on their molecular

structures. In addition, I will propose additional methods to optimize formulations for drugs that are not predicted to form stable nanoparticles.

COLL 27

caNanoLab: Enhancing retrieval and sharing of cancer nanotechnology data

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Though some nanomedicines have progressed to the clinic and are now in regular use, the field of cancer nanomedicine still has much to gain from investment in basic nanoparticle science. To address this, the National Cancer Institute (NCI) in conjunction with a team at Leidos Biomedical Research have developed a database designed for the needs of the nanomedicine community, known as caNanoLab.

The US NCI cancer Nanotechnology Laboratory (caNanoLab) data portal is an online nanomaterial database that allows users to submit and retrieve information on well-characterized nanomaterials available for clinical translation, including composition, *in vitro* and *in vivo* experimental characterizations, experimental protocols, and related publications.

The database structure is based on characterization assays required for clinical regulatory review performed by the Nanotechnology Characterization Laboratory (NCL) using a model informed by standards such as the NanoParticle Ontology (NPO) and ISA-TAB. The curation of nanotechnology information is accomplished by selecting relevant publications, manually extracting reported text and data, submitting extracted information into caNanoLab and converting to ISA-TAB-Nano files to enable data exchange.

The caNanoLab team strives to build a community of users to enhance the quality of submitted data. The first step in this effort has been to build a network of data coordinators who act as the representatives from each Alliance for Nanotechnology in Cancer program (Alliance) awardee, now expanding to include coordinators from the National Institute of Environmental Health Sciences (NIEHS) Health Implications Research (NHIR) Consortium. The caNanoLab team is also working with other groups to develop data standards and guidelines for data submission and sharing including community-based programs such as the NCI Nanotechnology Working Group (Nano WG) and the National Nanotechnology Initiative (NNI).

caNanoLab is unique among nano data curation and collection initiatives because of its cancer translational focus, as well as the depth of data and metadata held for each sample. It is also home to standardized characterization protocols from the NCL, made available to the public. Though the primary focus is to curate information about cancer nanomedicines, the content of caNanoLab is relevant to the broader biomedical

research field with interests in the use of nanotechnology for the development of diagnostics and therapeutics.

COLL 28

Synthetic closed-loop smart insulin patch

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The closed-loop drug delivery strategies have proven to be a practical tool for homeostatic regulation, by tuning drug release as a function of biosignals relevant to physiological and pathological processes. Among them, a glucose-responsive closed-loop insulin delivery system mimicking the function of pancreatic cells holds great promise to improve quality of life and health in people with diabetes. In this talk, I will introduce our ongoing efforts in developing formulations and related devices for glucose-responsive insulin delivery. I will first discuss the transdermal microneedle patches integrated with glucose-sensitive components for self-regulated insulin delivery tested on both mice and pigs. I will further introduce integration of beta cells and microneedle patch loaded with the synthetic “glucose-signal amplifier” for releasing insulin with a glucose-responsive manner. In addition, synthetic beta cells with vesicle fusion-mediated mechanism for glucose control will also be presented.

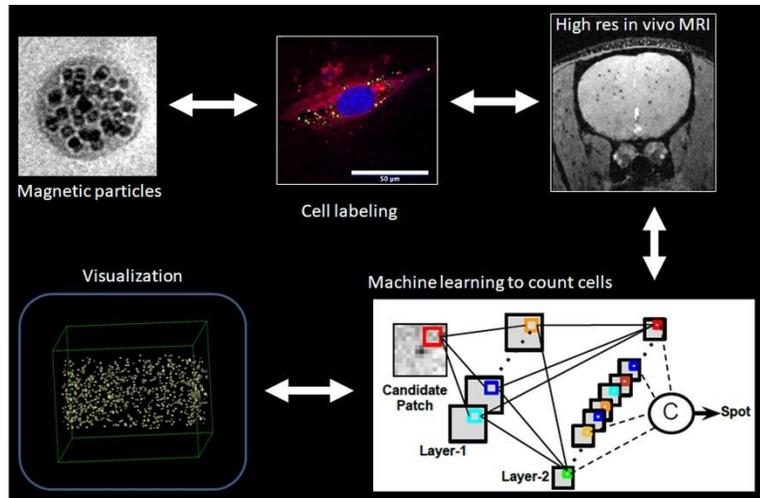
COLL 29

Nanoinformatics as a driver for nanoparticle synthesis and biomedical imaging paradigms in MRI and CT

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The process by which we develop new biomedical imaging paradigms in molecular and cellular imaging has changed. What once used to begin with new chemistry and biology – probe development and disease models – now begins with data analysis and informatics, working backwards to inform how we design and perform our experiments. In molecular and cellular MRI and CT imaging, data analysis methods guide nanomaterial properties and imaging paradigms, including material composition and methods for in vivo delivery of nanoparticles and therapeutics. For MRI, our laboratory has been using machine learning for intelligent and automatic in vivo detection of transplanted cells in MRI. The deep convolutional neural network (CNN) architecture we employ to enumerate transplanted cells by MRI requires discrimination of individual cells by MRI, which in turn prescribes the delivery methods for magnetically labeled cells, ultimately dictating the composition of the magnetic nanoparticles themselves. For

multi-color CT, our material decomposition data analysis scheme drives experimental procedures, requiring specific methodologies for nanoparticle synthesis and incorporation into targeted imaging probes and CT-visible tissue engineered scaffolds.



Dynamic interplay along the entire experimental path for MRI-based cell tracking of magnetically labeled cells showing how visualization and data analysis can drive early experimental steps of particle synthesis, cell delivery and imaging.

COLL 30

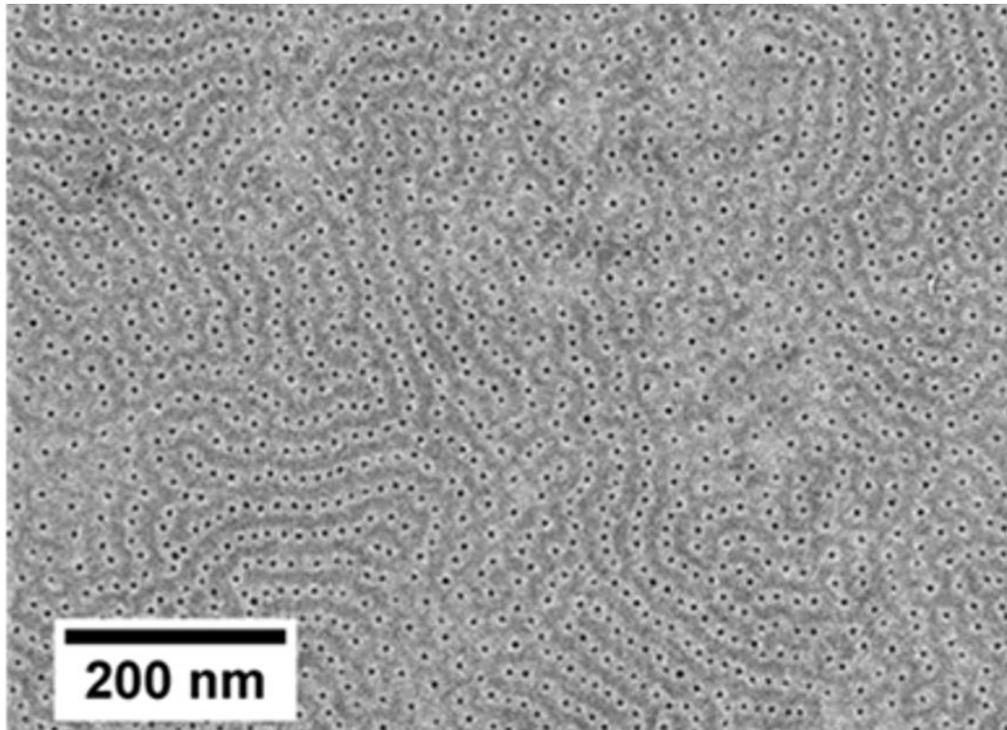
Controlled assembly of block copolymer coated nanoparticles in 2D-arrays

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The defined assembly of functional nanoparticles in polymer matrices is highly desirable for the development of next-generation electrical, optical, memory, and energy conversion devices. Currently, the lack of a precise control of nanoparticle positions, distances, and ordering in polymeric matrices is a severe barrier for many nanotechnology applications. Furthermore, the controlled and stable incorporation of nanoparticles into block polymer matrices remains difficult, because nanoparticles are thermodynamically immiscible with polymers leading to problems of macrophase separation already at small nanoparticle volume fractions.

We systematically investigated PbS-, ZnO-, Fe₂O₃-, and Cu₂ZnSnS₄-nanoparticles coated with PS-PI block copolymer ligands of different molecular weights. We show that

the direct self-assembly of block copolymer coated nanoparticles leads to thermodynamically stable, highly loaded and highly ordered nanocomposites. It enables the incorporation of exactly one nanoparticle per unit domain, and allows precise control of the inter-particle distance at the nanometer scale. We find that the direct coupling of nanoparticle and block copolymer self-assembly leads to new ordered morphologies with locally 2-, 3- and 6-fold rotational symmetry, that have not been reported and are otherwise difficult to access. Our studies demonstrate that the nanoparticle/domain size ratio and the grafting density are the two most important factors that control the type of block copolymer domain structure and the inter-particle distance. The method opens the way to the controlled preparation of well-defined complex nanoparticle arrays in polymer matrices with domain-selective localization such that ordered binary or ternary nanoparticle arrays can be achieved as would be necessary e.g. for scintillation materials.



TEM-image of ordered PbS-nanoparticle stripe arrays in a PS-PI block copolymer matrix.

COLL 31

Molecular design strategies for creating liquid crystals forming gyroid nanostructures and their advanced functions

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Gyroid structure is a unique cubic structure having 3D periodicity and continuity. The use of gyroid structures has a great potential to be a way for creating new functional materials with advanced and special properties. One of an advantageous strategy for creating gyroid structures with a nanometer lattice is to use self-organization of liquid crystals. Liquid-crystalline molecules forming gyroid structures are categorized as bicontinuous cubic liquid crystals. To date, we have developed a variety of bicontinuous cubic liquid crystals. Through these studies, we have constructed our original molecular design principles for bicontinuous cubic liquid crystals (Figure). One is molecular design based on amphiphilic zwitterions, which is advantageous for creating a 3D continuous gyroid minimal surface with proton conductive ability. Another is lyotropic liquid-crystalline systems containing amino acid ionic liquids as solvents, which is effective for controlling self-assembly of amphiphiles. Third is to employ atropisomers to induce helices. In the presentation, we will talk about these molecular design principles and show some specific functions of these liquid crystals forming gyroid nanostructures.

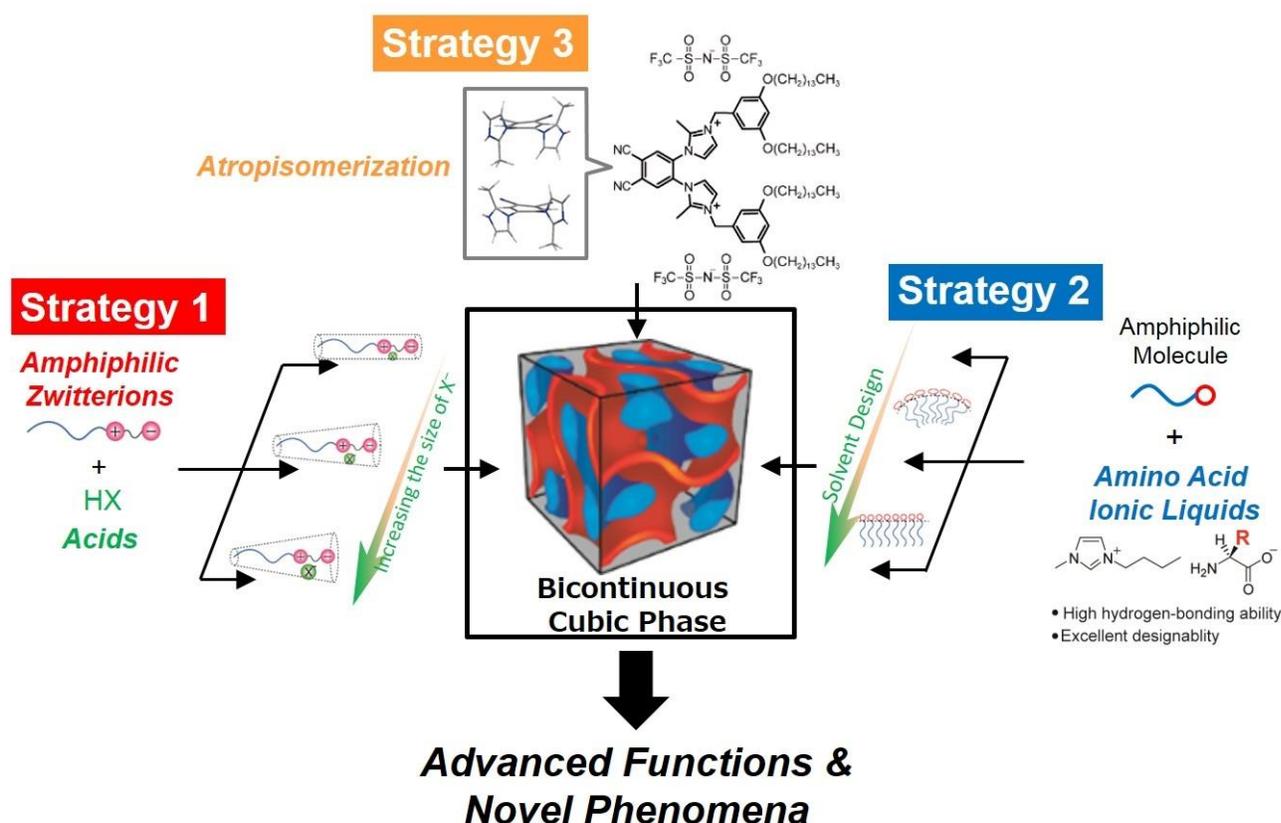


Figure. Our molecular design strategies for creating gyroid structured bicontinuous cubic phases.

COLL 32

Controlling orientational orders in self assembly of quantum dot gold heterostructural nanocrystals

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The self-assembly of nanocrystals into ordered superlattices is a powerful strategy for the production of functional nanomaterials. The assembly of well-ordered target structures, however, requires control over the building blocks' size and shape as well as their interactions. While much progress has been made assembling nanocrystals with homogeneous composition into different superlattices, high-quality multicomponent nanocrystals and their ordered assemblies are rarely reported. Besides, controlling the relative orientations of nanocrystals in those lattices also remains a challenge. We combine experiments with computer simulations to study the self-assembly of two unique quantum dot-gold (QD-Au) heterostructural nanocrystals (HNCs), namely heterodimers and satellites. Assembly of the heterodimers results in a superlattice with long-range orientational alignment of dimers while the assembly of satellites results in a close-packed superlattice with pronounced orientational orders. Molecular dynamics simulations of a coarse-grained model suggest that anisotropic interactions between the QD and Au is responsible for superlattice formation. In the case of satellites, we also demonstrate experimentally that the degree and type of orientational alignment can be controlled by changing ligand populations. This study provides guidance for the design and fabrication of nanocrystal superlattices with enhanced structural control and potential optoelectronic properties.

COLL 33

Controlled self-assembly of conjugated block copolymers driven by π - π interactions

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Block copolymers have attracted much attention in recent years as they can be used as building blocks to fabricate ordered nano-/micro- architectures, which possess potential applications in many fields. They have play vital roles in the researches of polymeric supramolecular self-assembly. We combine conjugated fluorescent blocks poly (phenylene vinylene) (PPV) and flexible corona blocks poly (2-vinyl pyridine) (P2VP) to build rod-coil type amphiphilic diblock copolymers PPV-*b*-P2VPs with strong fluorescence emission. With the help of the driven force of π - π interactions, instead of normally used crystallization, electrostatic interaction and crosslinking, nano-/micro-supramolecular fluorescent architectures of the copolymers were obtained by dissolving-cooling-aging process. The scales of the uniform structures could be controlled by the block length ratio of the copolymer, the concentrations of the growing solutions and other environmental factors. By modifying the alkyl side chains of PPV blocks and changing corona blocks, the regular morphologies of the obtained structures, including ribbons, scarfs, squares, diamonds, spiral towers and so on, could be transformed from one-dimensional (1-D) to three-dimensional (3-D). In addition, since the conjugated PPV blocks possess the semiconductor properties, the interesting electrical performance of individual 2-D assembly architecture has been investigated.

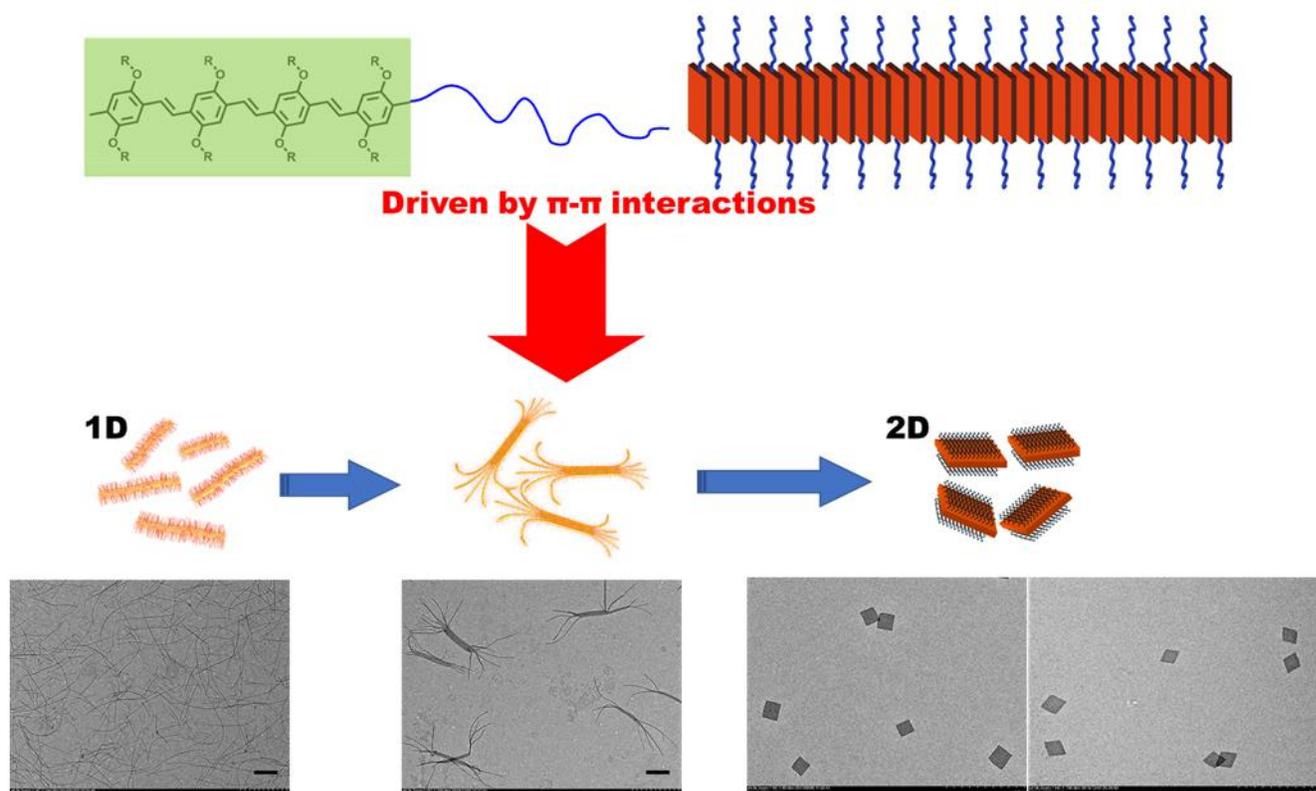


Figure 1. The 1D/2D micelle systems driven by π - π interactions.

COLL 34

Exerting control over random media by directed self-assembly for optical applications

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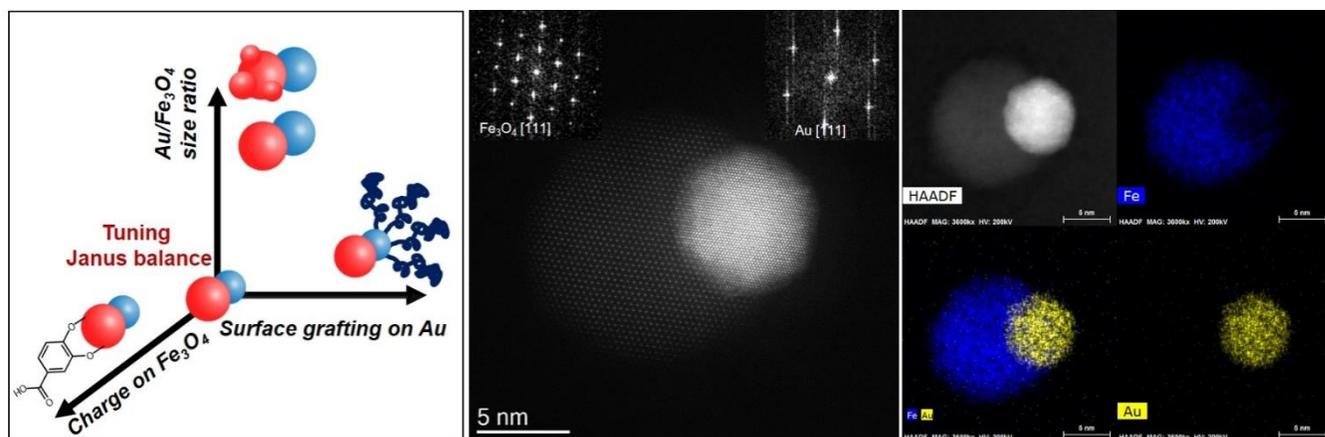
Traditionally, disorder present in optical systems introduces intolerable defects and negatively impacts performance through unwanted scattering. However, strategically implementing electric-field directed self-assembly methods to dynamically control disordered particle assemblies can be used to elicit favorable optical responses. Reconfigurable control over aspects of particle populations such as particle orientation, location, and number density enables tuning and enhancement of the optical response in a broad array of optical phenomena such as lensless imaging and random laser systems. Here we demonstrate the versatility and utility of exploiting disorder in our particle assemblies to control light scattering.

COLL 35

Synthesis and self-assembly of Janus dumbbell nanocrystals

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We designed a novel Janus nanocrystal platform to control the self-assembly of nanoparticles in aqueous solutions by balancing the hydrophobic and hydrophilic moieties. Janus Au-Fe₃O₄ dumbbell nanocrystals (< 20 nm) were synthesized with the hydrophobic ligands coated on the Au lobe and negatively charged hydrophilic ligands coated on the Fe₃O₄ lobe. We systematically fine-tune the lobe size ratio, surface coating, external conditions and even additional growth of Au nanocrystal domains on the Au lobe of dumbbell nanoparticles (Au-Au-Fe₃O₄) to harvest self-assembly structures including clusters, chains, vesicles and capsules. It was discovered that in all these assemblies the hydrophobic Au lobes preferred to stay together. The strong interparticle plasmonic coupling displayed a red-shift in surface plasmon resonance, with larger structures formed by Au-Au-Fe₃O₄ assembly extending into the near-infrared region. Self-assembly of Janus dumbbell nanocrystals can also be reversible under different pH values.



COLL 36

Surface-directed, DNA-programmed crystallization of nanoparticles

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The programmability of DNA makes it an attractive structure-directing ligand for the assembly of nanoparticle superlattices with unique structure-dependent physical phenomena. While DNA base pairing has enabled the development of materials with nanometer-scale precision in nanoparticle placement and independent control over particle size, lattice parameters, and crystal symmetry, manipulating the macroscopic shape of the lattices remains challenging. By pairing this “bottom-up” assembly method with “top-down” lithographic techniques and assembling nanoparticle superlattices on a patterned substrate, complete control over crystal size, shape, orientation and unit cell structure can be realized. The key challenges in developing this technique are to first understand how different design factors affect the assembly process in this broken-symmetry system that is assembled at an interface, and subsequently develop structure-property relationships that correlate the above mentioned design parameters with the resulting overall material structure. Here, we examine both at-equilibrium deposition processes capable of generating single crystals with well-defined shapes, as well as post-deposition annealing to transform disordered particle arrangements into crystalline arrays. Using a combination of X-ray diffraction and electron microscopy techniques, both surface morphology and internal thin film structure are examined to provide an understanding of the mechanisms of particle crystallization under conditions where crystal growth is anisotropic due to a boundary condition. This novel method for controlling particle assembly draws several strong analogies to traditionally atomic epitaxy/heteroepitaxy, providing a useful tool for understanding thin film growth processes. As a result, we are able to realize 3D architectures of arbitrary domain

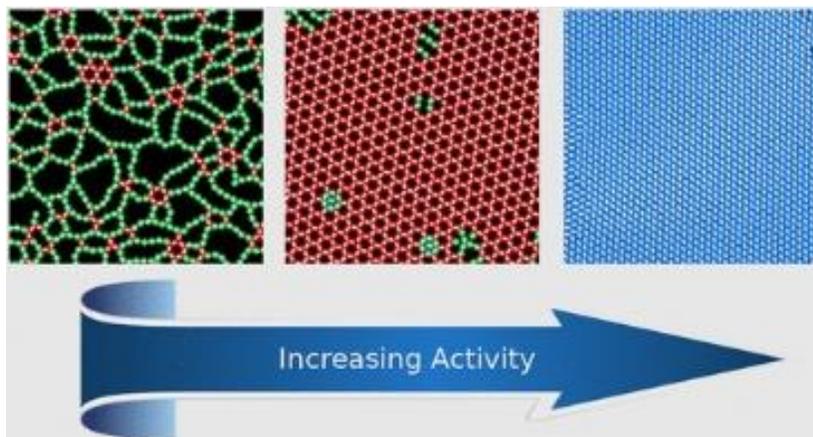
geometry and size, thereby making materials with unprecedented precision across multiple length scales.

COLL 37

Activity-enhanced self-assembly of a colloidal kagome lattice

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In this talk, we describe a method for the enhanced self-assembly of triblock Janus colloids targeted to form a kagome lattice. Using computer simulations, we demonstrate that the formation of this elusive structure can be significantly improved by self-propelling or *activating* the colloids along the axis connecting their hydrophobic hemispheres. The process by which metastable aggregates are destabilized and transformed into the favored kagome lattice is quite general, and we argue this *active* approach provides a systematic pathway to improving the self-assembly of a large number of colloidal structures.

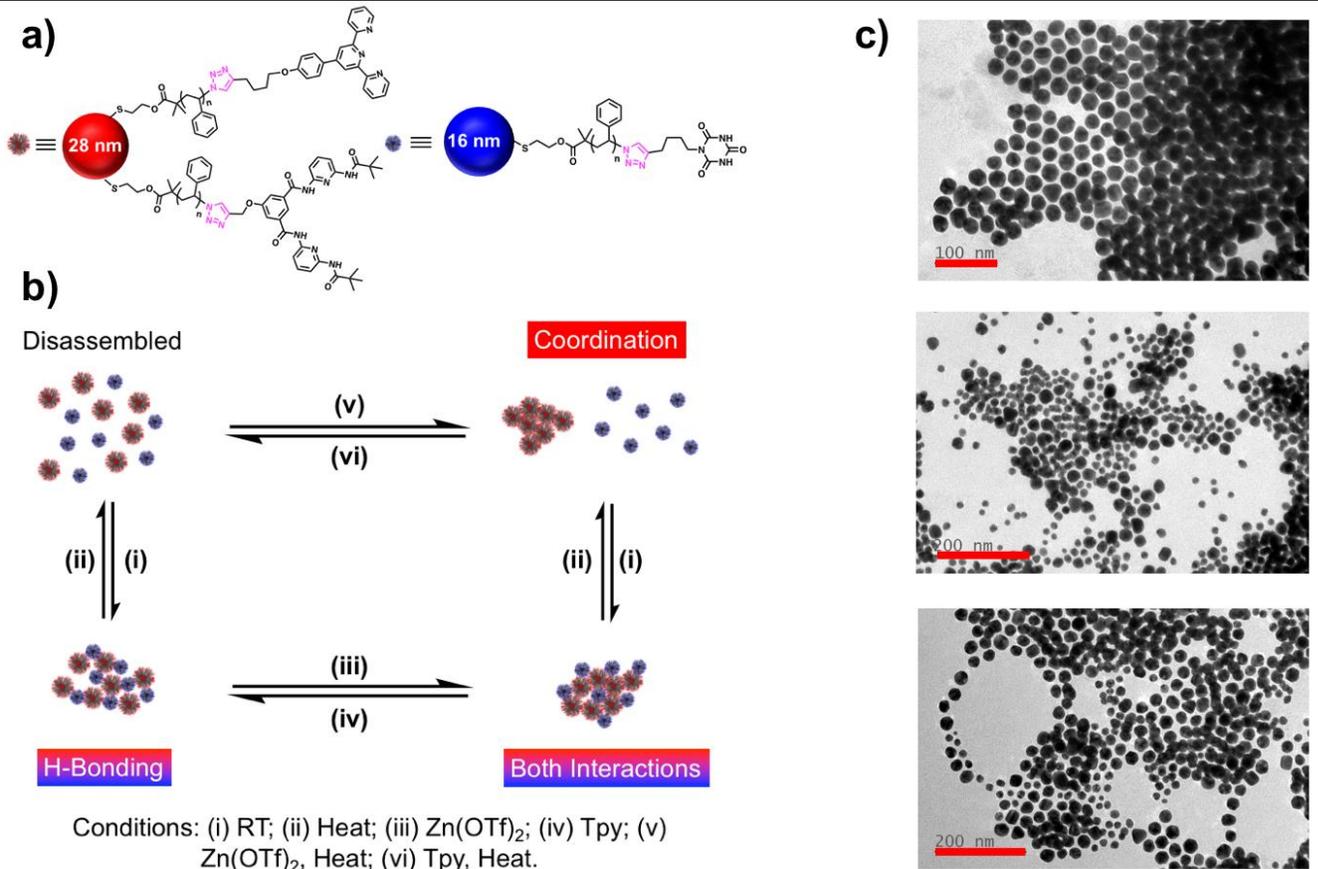


COLL 38

Multi-stimuli responsive nanocomposite tectons

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“Nanocomposite tectons” (NCTs) are a type of hybrid building block consisting of a nanoparticle (NP) core functionalized with dense monolayer of polymer chains terminating in supramolecular recognition groups, where the interactions between these groups drive the assembly of the NCTs into hierarchically ordered structures. Importantly, the fact that these interactions can be tuned separately from the composition of the NPs and polymers enables independent control over the chemical make-up and spatial organization of the assembled structure. However, while NCTs have significant potential in the development of unique polymer nanocomposite materials, major challenges to be addressed include developing strategies to (i) fine-control the degree of NCTs’ aggregation, so that a single NCT structure can express different assembly behaviors and (ii) use the NCT assemblies as a platform to perform more complicated chemistry. The ability to use different supramolecular recognition moieties to drive NCT assembly would potentially be a major step towards these goals, as different stimuli (solvents, pH, temperature, etc.) could be used to control NCT interactions. Additionally, the ability to use multiple orthogonal supramolecular interactions simultaneously would enable the development of more sophisticated NCT architectures (e.g. selective control over different NCT sets within a large mixture). Here, we present a rationally designed NCT system, where employing multiple recognition motifs (hydrogen bonding Hamilton wedge/cyanuric acid pairs, and terpyridine ligand and metal ion complexes) allows NCT assembly to be tuned by multiple external stimuli including temperature, small molecules, pH, and light. Moreover, we show that by taking advantage of the formation of these NCT assemblies, it is possible to perform hydrazide/aldehyde based dynamic covalent chemistry between Au NPs and consequently obtain covalently linked Au NP assemblies in a fast and efficient manner.



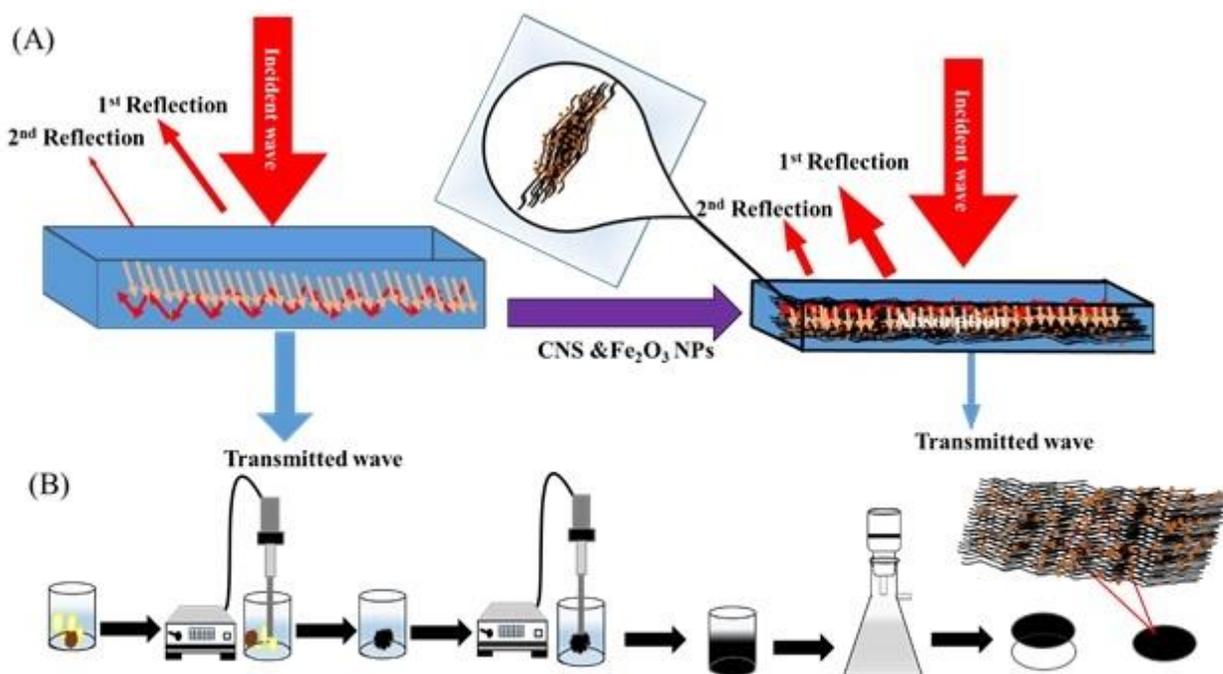
COLL 39

Thin carbon nanostructure mat with high electromagnetic interference shielding performance

Hammad Younes¹, hammad.younes@ku.ac.ae, **Amal Al Ghafer**², **Ahmad Bani Younes**³. (1) Civil Infrastructure and Environmental Engineering, Khalifa University, Abu Dhabi, United Arab Emirates (2) Mechanical and Material Engineering,, Khalifa University, Abu Dhabi, Abu Dhabi, United Arab Emirates (3) Aerospace Engineering, San Diego State University, San Diego, California, United States

The electromagnetic interference (EMI) pollution problem has led to an increasing interest in the development of lightweight materials for effective SE. This paper presents a facile approach for the fabrication of flexible, ultrathin, foldable, rollable, and highly conductive carbon nanostructures (CNS)-based mats. CNS epoxy, CNS-Fe₂O₃ nanoparticles (NPs) heterojunction mats and clean CNS mats of various thickness made of CNS flakes 300–350µm long and of various width have been

fabricated and tested for the SE application. Thinner CNS mats are found to have higher electrical and thermal conductivity. On the other hand, thicker CNS mats are found to have better SE performance, which reveals that thickness has a more profound impact on SE than electrical conductivity. Incorporation of the $\gamma\text{-Fe}_2\text{O}_3$ in the CNS mass provides magnetic properties and greatly improves the SE of the mats. Also, the uniform distribution of $\gamma\text{-Fe}_2\text{O}_3$ NPs increases the absorption of incident waves, which improves the overall shielding (SE_{All}). Thus, the SE_{All} performance improved from 47.1dB for the clean CNS mat to 60.29dB with the incorporation of $\gamma\text{-Fe}_2\text{O}_3$ NPs. Furthermore, the use of the epoxy to fabricate the CNS mats has significantly improved the mechanical properties of the CNS mats, but it reduced the SE performance by hindering the absorption of the electromagnetic waves.



COLL 40

Novel self-assembling drugs for amino-acid delivery system

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Amino acids are not only constituents of proteins such as muscles and enzymes, but also important molecules responsible for various physiological responses in living organisms. For example, arginine is involved in angiogenesis and apoptosis induction by NO production as a substrate of nitric oxide synthase (NOS). Ornithine is involved in the metabolism of ammonia by the ornithine cycle in the liver. Despite the amino acids exhibit various physiological actions like this, they are hardly taken into the blood even by oral administration because of their high water solubility, and they are metabolized extremely rapidly, which makes effective utilization difficult. Based on poly(ethylene glycol) (PEG) -polypeptide block copolymer, we have improved the bioavailability of amino acids by their self-assembly and developed the effective utilization of amino acids. For example, we have found that mixing of hydrophilic poly (ethylene glycol) -b- poly (L-arginine) with oppositely charged chondroitin sulfate (CS) forms a stable polyion complex self-assembly. This poly(L-arginine) based self-assemble drug accumulate in tumor via tail vein injection of tumor bearing mouse and generate nitric oxide in tumor environment, which caused NO level dependent effects. In this talk, I will summarize the material design and the effect to several disease model.

COLL 41

Hyperloaded poly(2-oxazoline) micelles as personalized drug carriers for brain tumors

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Polymeric micelle (PM) drug carriers were invented a quarter of century ago. 1 Today nearly a dozen of drug formats based on PM undergo clinical trials and one product, Genexol-PM, a PM paclitaxel, was approved for cancer therapy in South Korea. 2 The value proposition of PM drugs includes increased drug solubility, passive distribution and targeting to disease sites. Poly(2- oxazoline) PM display unprecedented high loading with respect to insoluble drugs. 3 This PM platform has been validated for more than 20 very poorly soluble active pharmaceutical ingredients (APIs) of different classes. It has demonstrated potential to increase treatment efficacy of cancers by using high-dose therapy and shown superiority in treatment of tumors in animal models. 4 Systemic therapies for brain tumors are complicated by dose-limiting extraneural toxicity, serum protein binding and restricted blood-brain barrier (BBB) permeability. For patients with SHH-subgroup medulloblastoma, SHH-pathway inhibition may be more effective and less toxic than

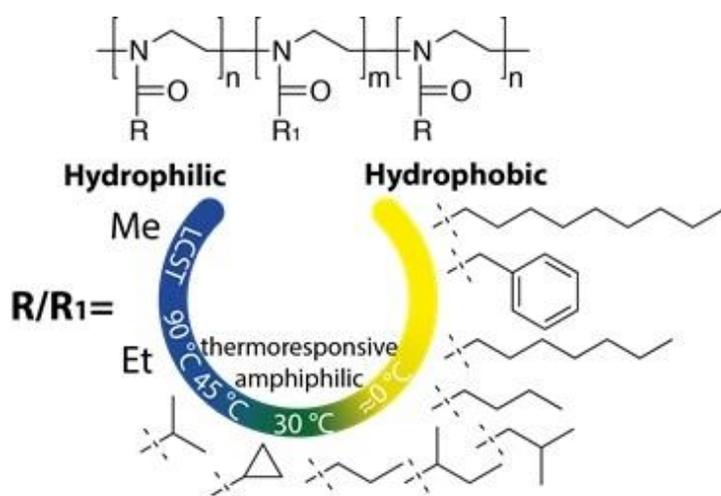
current non-targeted therapy. However, vismodegib, which effectively targets SHH-driven basal cell carcinoma, has limited benefit for patients with SHH-driven medulloblastoma. Formulating vismodegib in poly(2-oxazoline) micelles (POx-vismo) improved delivery and efficacy, using medulloblastoma-prone hGFAP-Cre/SmoM2 (G-Smo) mice for a preclinical model. Compared to conventional vismodegib (c-vismo), POx-vismo increased maximum tolerated dose (MTD), tumor:serum ratio and penetration to brain and tumor. Our results show the potential for POx-vismo to improve medulloblastoma treatment, demonstrating the potential for poly(2-oxazoline) micelles delivery to make failed brain tumor treatments newly effective.

COLL 42

Effects of the polymer corona on the drug loading in ultra-high drug loaded poly(2-oxazoline)/poly(2-oxazine) micelles

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Poly(2-oxazoline) and poly(2-oxazine) based micelles show a highly diverse and structure-sensitive solubilization behavior for hydrophobic molecules and drugs. Notably, these systems seem to strongly contradict the common wisdom, like-dissolves-like. In fact, the polymers with a minimal hydrophilic/hydrophobic contrast are much typically found to be more successful in solubilizing molecules of ultra-low water solubility. In addition, the hydrophilic corona can exert a significant influence on the drug loading and formulation stability. Our results show that the interactions between polymer and drug which govern drug encapsulation and formulation stability are much more complex than previously thought.



COLL 43

Drug-loaded polymer scaffold parameters on treatment of postsurgical glioblastoma

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Glioblastoma (GBM) is the most common primary brain tumor. Even with the current standard of care, which includes surgical resection, radiation, and chemotherapy, the median survival for GBM patients' remains 12 - 15 months. Because approximately 90% of tumors recur within 2 cm of the original tumor, implanting drug loaded scaffolds after surgical resection remains a promising strategy to delay or prevent local GBM recurrence. The only FDA-approved polymer implant for interstitial drug delivery for GBM, Gliadel, has afforded minimal improvement in combatting GBM recurrence, in part due to its poor drug release profile. Here we explored the use of acetalated dextran (Ace-DEX), a polymer with tunable degradation rates, as a drug delivery platform for optimizing interstitial therapy to combat GBM. Ace-DEX scaffolds with wide range of drug release rates were fabricated by tuning parameters such as drug loading, solvent system, and Ace-DEX degradation rate. Scaffolds were then evaluated in two clinically relevant murine models of GBM: (1) GBM surgical resection and recurrence to replicate the positive tumor margins often left behind during surgery and (2) a contralateral hemisphere model, which allowed us to evaluate therapeutic effect of drug penetration to tumor deposits more distant from the resection cavity. We found that optimal release rate differed depending on tumor location. In the GBM model of resection and recurrence, a combination of scaffolds with fast and slow drug release rates resulted in significantly improved survival compared to individual release rates of fast and slow. However, in the contralateral hemisphere model, the fast drug releasing scaffold outperformed slow. These results highlight the substantial impact of scaffold parameters on therapeutic efficacy in interstitial GBM therapy.

COLL 44

Chemical transformations of nanostructures

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Chemical transformations often bring unusual morphological and compositional changes to nanoscale structures. In this presentation, we review typical examples of

chemical transformations including those induced by ion exchange, the nanoscale Kirkendall effect, and the galvanic replacement reactions. When nanocrystals are made to undergo chemical transformations, there are often accompanying, large mechanical deformations and changes to overall particle morphology. These effects can constrain the development of multi-step synthetic methods through loss of well-defined particle morphology and functionality. Here we also discuss surface protection may allow preservation of overall particle morphology despite large volume changes during their chemical transformation. The surface protected conversion strategy represents a general self-templating method for nanocrystal synthesis and can be applied to the chemical conversion of nanostructures of many morphologies (spheres, rods, cubes, and plates) and compositions (hydroxides, oxides, and metal-organic frameworks).

COLL 45

Immobilized metal nanoparticle catalysts for energy applications

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Recently, we have successfully immobilized a number of metal nanoparticles (NPs) on different supports, which have been used for various applications, especially for energy.^{1,2} Metal NPs have been immobilized to graphene and porous carbons using different methods, which have been used for catalytic dehydrogenation of chemical hydrides such as ammonia borane, hydrous hydrazine and formic acid.² Metal nanoparticles have been immobilized to MOFs via various approaches, which exhibit excellent catalytic performances for various reactions.¹ Porous carbons have been synthesized by using MOFs as templates/precursors and the resultant carbons display high specific surface areas and excellent electrochemical properties as electrode materials for electric double-layered capacitor (EDLC) and as catalysts and catalyst supports for various reactions.³ Super-long single-crystal cobalt-organic framework (Co-MOF) nanotubes have been synthesized and carbonized to produce hierarchical dendrites with carbon nanofiber trunks and carbon nanotube branches, which exhibit excellent electrocatalytic activity for oxygen reduction reaction (ORR), and exceptional applications in rechargeable Zn–air batteries. “Quasi-MOFs” have been prepared by controlled deligandation of MOFs, which have a transition-state structure between porous MOFs and metal oxides and exhibit dramatically enhanced catalytic performance. This talk will discuss the catalytic and energy applications of immobilized metal nanoparticles.

COLL 46

Phase engineering of novel nanomaterials

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In this talk, I will summarize the recent research on the phase engineering of nanomaterials in my group. It includes the first-time synthesis of hexagonal-close packed (*hcp*) Au nanosheets (AuSSs) on graphene oxide, the first-time synthesis of 4H hexagonal phase Au nanoribbons (NRBs), the synthesis of crystal-phase heterostructured 4H/*fcc* Au nanorods, the epitaxial growth of metals with novel phases on the aforementioned Au nanostructures, and the synthesis of amorphous/ crystalline hetero-phase Pd nanosheets. In addition, the first-time synthesis of 1T'-MoS₂ and 1T'-MoSe₂ crystals have been achieved. Moreover, the phase transformation of transition metal dichalcogenide nanomaterials during our developed electrochemical Li-intercalation method will also be introduced. Interestingly, the lithiation-induced amorphization of Pd₃P₂S₈ is also achieved. Currently, my group focuses on the (crystal) phase-based properties and applications in catalysis, surface enhanced Raman scattering, waveguide, photothermal therapy, chemical and biosensing, clean energy etc., which we believe are quite unique and very important not only in fundamental studies, but also in practical applications. Importantly, the concepts of crystal-phase heterostructures and hetero-phase nanomaterials are proposed.

COLL 47

Designing highly durable core@shell electrocatalysts

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Seed-mediated co-reduction is a versatile synthetic route to strain-engineered core@shell electrocatalysts with alloyed surfaces. This presentation will highlight the generality of this synthetic approach by showing that Pt-M alloyed surfaces can be deposited on seeds, with the Pt-M identity, Pt-to-M ratio, and overall shell thickness being precisely tuned. These synthetic levers, in turn, allow for catalyst activity to be optimized. Moreover, by comparing alloyed surfaces deposited on random alloy and intermetallic seeds of the same composition, we show that the crystallinity of the core impacts catalyst durability to provide sustained performance and minimal leaching of the non-noble metals from the catalyst surface. This enhanced durability is shown with several catalysts and is likely a general feature enabled through the use of intermetallic cores.

COLL 48

Selective chemical transformations on ordered surfaces of intermetallic nanoparticles

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Intermetallic compounds, solid-state mixtures of two or more metal components, possess both modified crystal structures and altered surface geometric/electronic

structures that could lead to superior catalytic properties in chemical transformations. Intermetallic compounds are structurally more stable than random alloys because the formation of the ordered structure is driven by thermodynamic. Only a very small portion of them have been studied for application in heterogeneous catalysis, given there are more than 10,000 reported intermetallic compounds of different compositions and structures. Herein, we will discuss the synthesis strategy and catalytic properties of monodisperse intermetallic nanoparticles of different compositions. With the proper adjustment of the composition, we found that intermetallic nanoparticles are robust catalysts for hydrogenation, oxidation, and coupling reactions with enhanced activity, selectivity, and stability. Intermetallic nanoparticles are unique catalysis platforms that are important for both fundamental research and industrial applications.

COLL 49

Tailoring cooperative metal-support interfaces for catalysis

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Understanding the cooperative interactions of metals with active supports is essential to controlling their catalytic activities and reaction pathways. These interfacial interactions can be achieved through two mechanisms: interfacial charge redistribution and interfacial restructuring. In the last few years, a number of advances have been made by our research team toward tuning the metal-support interactions. The success of our approach capitalizes on nanoconfined spaces (e.g., confined interface restructuring), complex oxide supports (e.g., perovskite oxides), and 2D material edge sites (e.g., boron nitride), demonstrating that uniquely strong interfacial interactions and cooperativities between nanoparticles and supports can emerge through judicious structural choices of metals and supports. This presentation will focus on the following three synergistically linked research activities: (1) sacrificial strong metal-support interactions, (2) “intelligent” metal-support interactions, and (3) charge-flow metal-support interactions. The interconnections among the above three metal-support interactions will be also discussed.

COLL 50

Phase-controlled synthesis of colloidal metal nanocrystals

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A new parameter built upon the crystal structure or phase has recently emerged as an attractive knob for engineering the catalytic properties of metal nanocrystals. For metals crystallized in a close-packed structure with a packing efficiency of 74%, one can obtain either a cubic close-packed (*ccp*) or a hexagonal close-packed (*hcp*) phase, with

the *ccp* phase also corresponding to a face-centered cubic (*fcc*) lattice. The sole difference between *ccp* and *hcp* phases lies in the positions taken by the third layer of atoms, corresponding to stacking sequences of “ABCABC...” and “ABABAB...”, respectively. In this talk, I will discuss how to engineer the phase of colloidal metal nanocrystals using two different approaches: control of reduction kinetics and template-directed synthesis. I will also highlight some of the new catalytic properties enabled by metal nanocrystals in the unconventional phases.

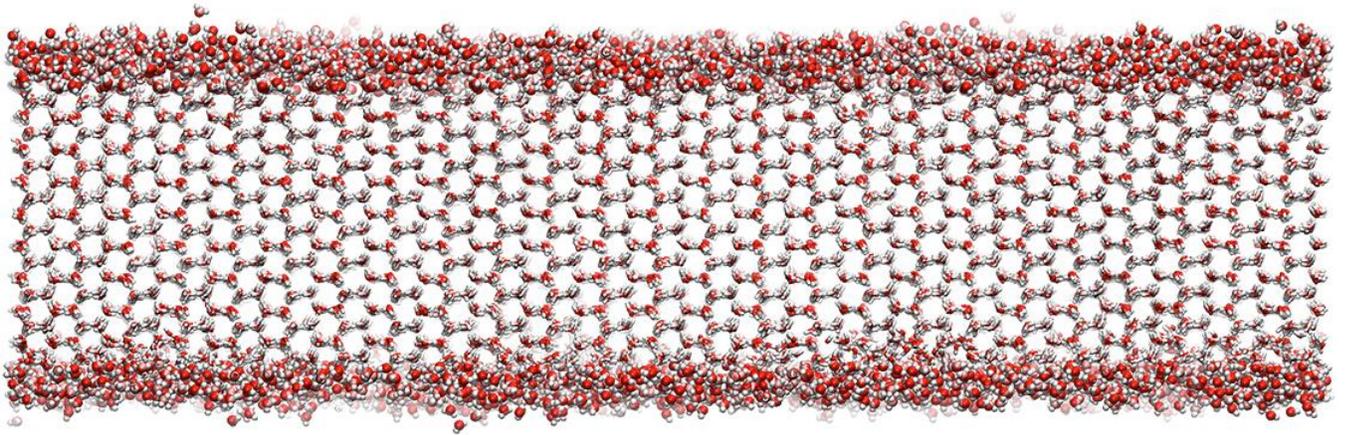
COLL 51

Why is ice slippery? Simulations of solid-liquid friction and the shear viscosity of the quasi-liquid layer on ice

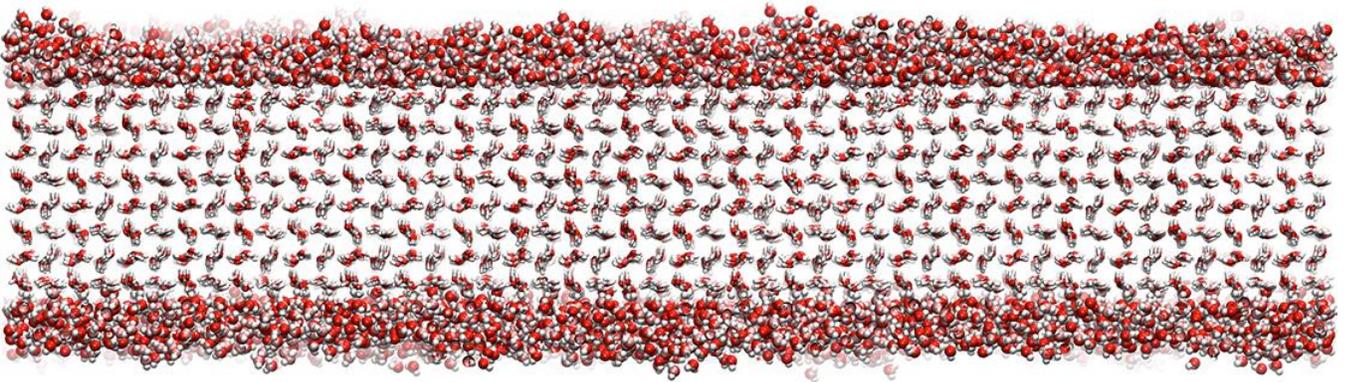
J D. Gezelter, gezelter@nd.edu. Chemistry & Biochemistry, University of Notre Dame, Notre Dame, Indiana, United States

The temperature and depth dependence of the shear viscosity (η) of the quasi-liquid layer (QLL) of water on ice- I_h crystals was determined using simulations of the TIP4P/Ice model. The crystals display either the basal {0001} or prismatic {10-10} facets, and we find that the QLL viscosity depends on the presented facet, the distance from the solid / liquid interface, and the undercooling temperature. Structural order parameters provide two distinct estimates of the QLL widths, which are found to range from 6.0-7.8 Å, and depend on facet and undercooling temperature. Above 260 K, the viscosity of the vapor-adjacent water layer is significantly less viscous than the solid-adjacent layer, and is also lower than the viscosity of liquid water.

Simulations of solid / liquid friction at ice / water interfaces also suggest that the surface density of solid to liquid hydrogen bonds directly correlates with interfacial friction. When the basal {0001}, prismatic {10-10}, pyramidal {20-21}, and secondary prism {11-20} facets of ice are were drawn through liquid water, the interface is in negative slip conditions. Careful treatment of friction in this regime will be discussed, and the friction of these interfaces is found to be invariant to the shear rate and direction of shear relative to the surface features, but highly dependent on the density of solid to liquid hydrogen bonds, which does depend strongly on surface features of the four facets.



Prismatic



Basal

COLL 52

Ice-rubber friction mechanisms

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Driving on ice is a rather delicate exercise due to the poor adherence of tire on ice. In this context of road safety improvement under severe climatic conditions, it becomes necessary to precisely study and investigate the sliding contact between rubber and ice and to identify the key mechanisms governing the tribological behavior of the rubber-ice contact.

A multi-scale strategy was chosen in this work, from the scale of apparent surface area to the scale of groups of asperity contacts, in order to understand the effect of adhesion and of thermal heating of the contact on the rubber/ice friction. The KOR1 tribometer, developed in LTDS, was used to perform ice/rubber friction experiments over four decades of sliding velocities, under an initial loading of 10N. The contact was simultaneously visualized and measured by means of a camera with a resolution of 5x5 mm². A cooling system was designed in order to maintain the contact zone at a negative temperature, down to -20°C, for several hours, independently of the external temperature and humidity conditions. In parallel, an ice-manufacturing unit was designed to produce a repeatable transparent vertically grown ice disc. Rubber/ice friction experiments were performed. Each measurement was repeated three times for each sliding velocity. The friction behavior was analyzed at the macro and micro scales for temperatures ranging from -15°C to -2.5°C on rubbers with various mechanical properties and glass transition temperature. Thanks to the visualization of the real contact area, it was possible to measure the interfacial shear strength of rubber/ice contact.

The rubber-ice friction as a function of the sliding velocity formed a bell-shaped curve classically observed for rubber friction. The higher the temperature, the lower the friction coefficient. In the 'high velocity' range, the thermal effects cannot be neglected. The modeling of the mean contact temperature, T_c , suggested the initiation of melting on the ice surface at 0.1 m/s regardless of the environmental temperature, T . This phenomenon controlled the transition of friction regime. The values $(T_c - T)/(T_m - T)$, where T_m is melting point of ice calculated for each temperature collapsed onto a master curve. The existence of this master-curve implies that the interfacial shear stress within the contact can be analytically predicted as function of the sliding velocity, temperature and viscoelastic properties of the rubber.

COLL 53

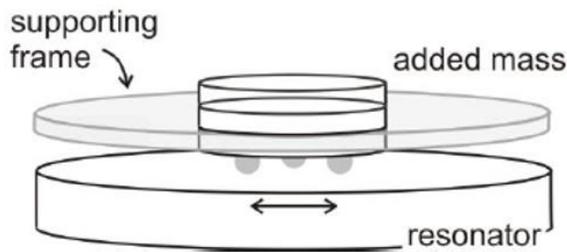
Partial slip takes time

Diethelm Johannsmann, *johannsmann@pc.tu-clausthal.de*, Frederick Meyer. Institute of Physical Chemistry, Clausthal University of Technology, Clausthal-Zellerfeld, Germany

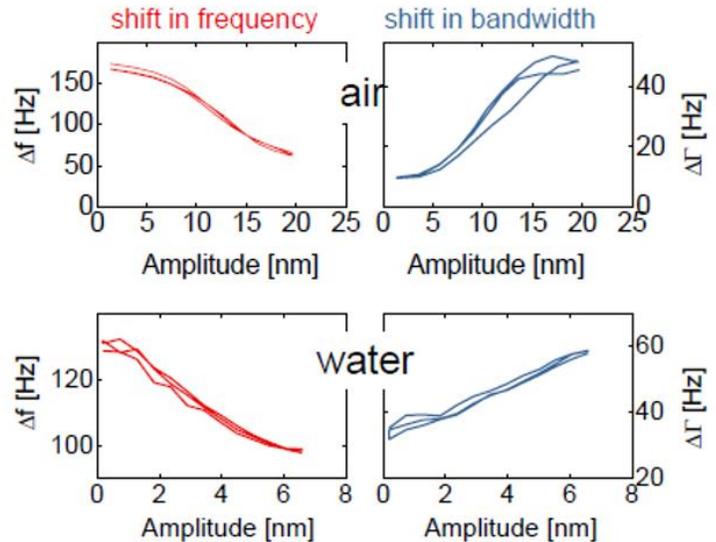
Slip and partial slip under conditions of reciprocating motion have been studied on time-scales ranging from microseconds to seconds. The technique employed was the quartz

crystal microbalance (QCM), which was employed as a high-frequency tribometer (applying oscillatory displacements in the range of a few nanometers). The QCM surface is brought into contact with spheres (dry and in aqueous environments). As long as linear mechanics holds, the frequency increases in proportion to the stiffness of the sphere-plate contact. As one increases the amplitude, partial sets in at the edges of the contact. The apparent contact stiffness decreases, while the dissipated energy (as extracted from the resonance bandwidth) increases. Also, partial slip (of following the Cattaneo-Mindlin scenario) leads to third harmonic generation (THG), meaning that the stress is no longer a harmonic function of time.

The amplitude of the third-harmonic signal is much lower than what is expected based on the reduced apparent contact stiffness (as extracted from the amplitude-dependence of the resonance frequency and the resonance bandwidth). This disproves the Cattaneo-Mindlin picture. A sliding ring evolves over many periods of oscillation. Experiments undertaken in air and water are compared.



A quartz resonator is brought into contact with spheres of various size and composition. As the oscillation amplitude increases, the frequency decreases and the bandwidth increases, which is a consequence of partial slip. There also is third-harmonic generation, albeit much less than expected.



COLL 54

Relating dermal friction to water and skin moisture content

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Shear forces acting on the skin are an important cause for tissue trauma, such as pressure ulcers. These shear forces that develop in the contact with a counter surface, such as clothing, bedding or a prosthetic liner is strongly related to the amount of water present in the contact, however, the exact relationship between moisture and frictional behaviour is unclear. This is partially because friction is not a material parameter and thus strongly depends on a range of other system characteristics, and partially because 'skin moisture' is not unambiguously defined and is typically measured in an indirect way. In this work we present friction experiments that were conducted on in vivo human skin using woven textile samples. By controlling the temperature and the humidity of the environment, we show an increased friction at both increasing temperature and humidity. The observed effects were more pronounced at warmer and more humid environments, meaning there is a clear link with the absolute amount of water available in the 'tribosystem'. Following this, we investigated interpersonal differences by combining in-vivo skin-textile interaction experiments with in-vivo FTIR measurements. The observed spectra indicate that both the moisture content and the characteristics of skin sebum play an important role, with positive correlations found between moisture and friction, and skin sebum viscosity and friction. We conclude that spectroscopy techniques can be used as a tool to predict individuals with 'naturally high friction' and may be at risk of developing skin trauma.

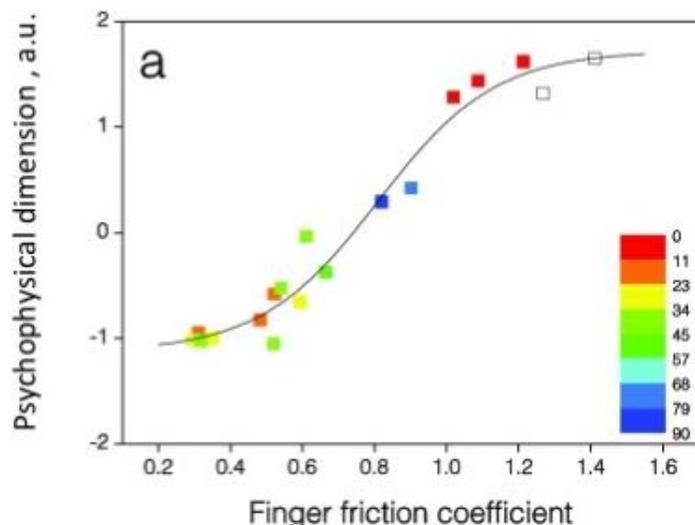
COLL 55

Psychotribology: How friction, materials properties, and age influence tactile perception

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Like taste, touch requires an intimate contact of the "object", material or stimulus with the body. Recent measurements from our group show how the contact of fingertip skin with surfaces depends on moisture, topography and surface chemistry – as well as elastic modulus. The physical and psychophysical methodology is described, and the logic behind our conclusions as to how we perceive fine textured surfaces is explained.¹

In addition to understanding how the material properties of a surface influence our perception of it, the role of aging and the material properties of the skin are also addressed, together with the reasons for reduced tactile perception amongst the elderly.



COLL 56

Structure of water inside thin polysaccharide films

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Polymer coatings play a fundamental role in imparting surfaces with macroscopic features such as feel, tack, wetting or resistance to biofouling or mechanical scratch. Because different techniques (dip-coating, spin-coating, bar-coating) can be used to create a polymer coating on a surface, each leading to different polymer conformations, understanding quantitatively how macroscopic surface properties relate to how the polymer was deposited, remains a challenge. The question becomes particularly thorny with very thin coatings - as confinement effects start modifying the very conformation of a polymer - and even thornier with thin hydrophilic coatings - as they absorb water from the atmosphere or a flow they are exposed to. In such confined geometry, how do the well-known thermodynamics principles of polymer-solvent mixture apply? How important are the details of the structure of the hydrophilic polymer, such as its molecular weight, its chemical nature? These questions are relevant in all the everyday-life examples where a hydrophilic polymer is used in minute quantities to modify a substrate's macroscopic properties. From cationic polymers deposited on hair from

shampoos to modify their feel and ease of combing, to amphoteric copolymers deposited on hard surfaces to facilitate their drying, we are exposed, all day long, to ultra-thin hydrophilic polymer layers that provide macroscopic properties that make our life easier.

In this work, we present how thin films of guar, a plant-based polysaccharide, behave in the presence of water, on the whole range from ca. 0 to 95%RH. We systematically vary film thickness (10-200 nm) and molecular weight (20 Kg/mol to several millions), as well as different chemical modifications of guar, and combine x-ray and neutron reflectivity, spectroscopic ellipsometry and polarization modulated infrared reflection-absorption spectroscopy, to quantitatively resolve how water organizes, structurally and spatially, inside said films. We find that water molecules show depletion close to the substrate and enrichment close to the interface with humid air in films as thin (or thinner) than the radius of gyration R_g of the guar macromolecules used, yet show a close-to-homogeneous spatial distribution in films significantly thicker than R_g , thereby evidencing how confinement may affect the very structuration of a hydrophilic polymer/water system, hence their macroscopic properties, in particular wetting, lubrication and tack.

COLL 57

Macroscale water-based superlubricity achieved by PDMS under boundary lubrication regime

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The tribology of soft materials has been attracting continuous research interest due to its similarity to the human body. The friction behavior between a glass ball and a flat poly(dimethylsiloxane) (PDMS) disk is studied. Ultrahigh coefficient of friction (COF) (COF~1) under pure water lubrication is observed for its intrinsic hydrophobicity. However, whether it increases or decreases the pH of the water, the COF dramatically decreases and superlubricity (COF~0.005) is achieved at low velocity in both acidic and alkaline environments. Stribeck curve obtained by changing the velocity confirms the boundary lubrication regime. Silicate generated in alkaline environment is considered to be responsible for the low friction state. Increased hydrophilicity in acidic environment is proposed to be responsible for the ultralow friction state, which is further connected with the increased hydration force. The results suggest potential applications for adjustable friction performance across three orders of magnitude.

COLL 58

Supramolecular nanostructures with capacity to mimic or bind proteins

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One of the grand challenges for science in this century is to create strategies to regenerate parts of the human body in order to achieve longer “healthspans”. Synthetic and bioactive nanostructures can play critical roles in regenerative biology if they are designed to activate receptors in cell signaling or to amplify signaling by proteins such as growth factors. Ideally such systems should have a short half-life and trigger critical biological events that will eventually result in regeneration. This lecture will describe a broad platform of supramolecular nanostructures built with a toolbox of peptides, peptide amphiphiles, glycans, and nucleic acids that exhibit various forms of dynamic bioactivity toward neural or musculoskeletal cells. In one example these systems bind proteins and this way enhance their biological activity, leading to the regeneration of musculoskeletal tissues with minimal amounts of protein. In a second example peptides displayed by the nanostructures activate important receptors that are critical to the survival and function of neural cells or the proliferation of different types of cells.

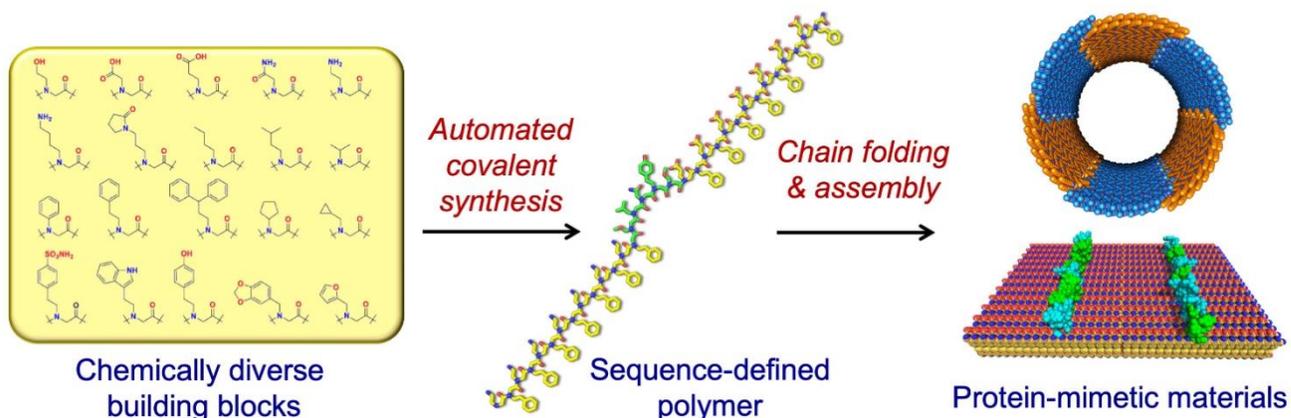
COLL 59

Hierarchical folding and assembly of protein-mimetic nanomaterials

*Sunting Xuan, Andy I. Nguyen, **Ronald N. Zuckermann**, rnzuckermann@lbl.gov. Molecular Foundry, Lawrence Berkeley National Laboratory, El Cerrito, California, United States*

In order to mimic the complex architecture and function of proteins with synthetic materials, we need to copy the way Nature build them. We need a modular approach to synthesize sequence-defined, non-natural polymer chains that spontaneously fold and assemble into precise three-dimensional structures. Here, we use peptoid polymers, prepared by automated solid-phase submonomer synthesis, to create bio-inspired, information-rich polymer chains in exceptionally high yield. We use fundamental lessons gleaned from the world of protein structure, along with computational modeling, to design and engineer a variety of well-defined protein-mimetic nanostructures. We show by AFM, cryo-TEM and X-ray scattering, that we can form helices, nanosheets and nanotubes, whose structures can be precisely engineered to introduce protein-like functions.

Molecular Folding Science



Hierarchical folding of non-natural polymers into protein-like architectures, requires at least two fundamental steps: linking chemically-diverse monomers into a precise sequence, followed by folding and self-assembly of the chain into a well-defined 3D structure.

COLL 60

Peptide assembly at interfaces templated by striped phases of amphiphiles

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Some of the most complex peptide assembly in nature is carried out using the lipid bilayer as a foundation for controlling local chemical environment. The bilayer provides well-defined nonpolar regions, as well as controlling the locations of specific functional groups in the membrane periphery. The noncovalent interactions between amphiphiles in the bilayer also enables amphiphiles to be displaced, enabling expansion of growing peptide structures in the membrane. While amphiphiles form standing phases in the cell membrane, they can also be assembled to form striped phases on materials such as graphene and highly oriented pyrolytic graphite (HOPG). In the striped phase, the alkyl chains extend horizontally across the substrate, creating a surface that looks like a repeating cross-section of a lipid bilayer, with 1-nm-wide stripes of functional headgroups alternating with 5-nm-wide stripes of hydrophobic alkyl chains. We will discuss experiments and simulations illustrating that striped phases represent a means of controlling assembly of peptides and amino acids at interfaces, both utilizing the stripes of functional headgroups, and using the amphiphiles as a displaceable template that balances alkyl-alkyl and alkyl- π interactions on the aromatic substrate.

COLL 61

Multicomponent coordination self-assembly toward hierarchical supramolecular nanocolloids for efficient photodynamic therapy

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Supramolecular nanocolloids have been extensively explored as drug delivery carriers in antitumor therapy with the aim to improve therapeutic efficiencies as well as decrease side effects. Such therapeutic benefits rely on efficient delivery of drugs to tumors and consequent release of drugs from the carriers under tumor microenvironments. Especially, burst release of drugs in tumors is highly important for specific therapeutic methods, such as photodynamic therapy. However, it is still challenging to construct supramolecular nanocolloids to fulfill the demand of integrating robust blood circulation and targeted burst release. Herein, we propose a multicomponent coordination self-assembly strategy that shows great potential in rational design of hierarchical supramolecular nanocolloids for proving therapeutic efficiencies in photodynamic therapy. Inspired by the multicomponent self-organization of polypeptides, pigments, and metal ions in metalloproteins, hierarchical supramolecular nanocolloids are facily constructed by using metal-binding peptides, photosensitizers, and metal ions as the building blocks. The resulting nanocolloids have uniform sizes, well-defined nanosphere structures, and high loading capacities. Importantly, the nanocolloids are highly stable in blood, leading to prolonged blood circulation and enhanced tumor accumulation. In tumor microenvironments, which possess lower pH values and higher glutathione levels, the nanocolloids show ultrasensitive responses, reasonably due to the combination and cooperation of coordination and non-covalent interactions. Hence, efficient tumor ablation was demonstrated by using the nanocolloids as photodynamic nanoagents. Based on the fact that many antitumor drugs contain metal-binding groups, multicomponent coordination self-assembly is expected to be explored as a versatile and efficient strategy for developing next-generation, smart nanomedicines.

COLL 62

Predictive modeling of bionanomaterials from picometers to micrometers

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The development of functional materials continues to involve extensive trial-and-error studies while rational understanding and design using modeling and simulation play an increasing role thanks to more accurate models and affordable computing resources. This talk describes simulation techniques and capabilities at the 1 to 1000 nanometer scale related to the Interface force field (IFF) to understand recognition and assembly of metal, oxide, and biomineral nanostructures for various applications. We will discuss different mineral surfaces and interactions with organic compounds, implications on nanocrystal growth and morphology, as well as rules of molecular recognition and self-assembly derived from simulations. Specific adsorption and assembly of peptides and

macromolecules on metallic and oxide/hydroxide nanostructures will be described according to measurements and simulations, including predictions in chemical accuracy and guidance in designing new commercial products. Applications to low dimensional materials, catalysts, hydrogels, and therapeutics will be discussed. The realistic representation of polar chemical bonding, specific surface chemistry, and electrolyte composition using IFF also supports accurate reactive simulations up to the large nanometer scale with heuristic inputs from quantum mechanics and experiment.

COLL 63

Synthesis and applications of peptoid-based crystalline nanomaterials

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In nature, biomolecules (e.g. proteins and peptides) play significant roles in the assembly of hierarchical structures and delivering sequence-specific functions ranging from photosynthesis, to molecular separation, selective ion transport, and tissue mineralization. Inspired by nature, many sequence-defined molecules have been designed and exploited for bio-inspired synthesis of nanostructured functional materials. Among them, peptoids have received particular attention because they combine advantages from both biopolymers and bulk polymers.

In this presentation, I will report my group's recent progress in the synthesis and applications of peptoid-based crystalline nanomaterials, including self-repairable nanomembranes,¹ highly stiff and dynamic nanotubes,² and flower-like fluorinated nanoparticles.³ Our results show that peptoid-peptoid interactions play critical roles in the peptoid assembly and can be tuned through peptoid side-chain chemistry. Supramolecular interactions (e.g. π - π stacking or fluorine-fluorine interactions) among peptoid side chains are the main driving forces that lead to the formation and stabilization of highly-ordered superstructures. We further demonstrated that a broad range of functional groups, including chromophores, can be precisely incorporated and patterned within these crystalline nanomaterials, leading to the development of biomimetic materials tailored to specific applications (e.g. live cell imaging, drug delivery, molecular sensing and water purification).

COLL 64

Peptide-modulated self-assembly of photosensitive nanocolloids for antitumor phototherapy

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Self-assembly is ubiquitous at various length scales throughout biology and is a key process of life. Inspired largely by biological systems, self-assembly has been developed as a dominant technique towards creation of complex synthetic systems. However, how to achieve controlled self-assembly of functional structures towards biomimetic fabrication and biomedical application by key small biomolecules such as peptides and porphyrins remains a remarkable challenge. In this presentation, we will show how simple dipeptides and even amino acids can be used to tune self-assembly of photosensitive nanocolloids with well-defined nanostructures and flexible functions as a future nanomedicine towards antitumor photodynamic and photothermal therapy (Figure 1). Due to advantages of easy availability, structural simplicity, and functional flexibility of simple peptides, such delivery systems based on co-assembly with photosensitive drugs on themselves will provide a new alternative pathway for enhanced antitumor efficacy.

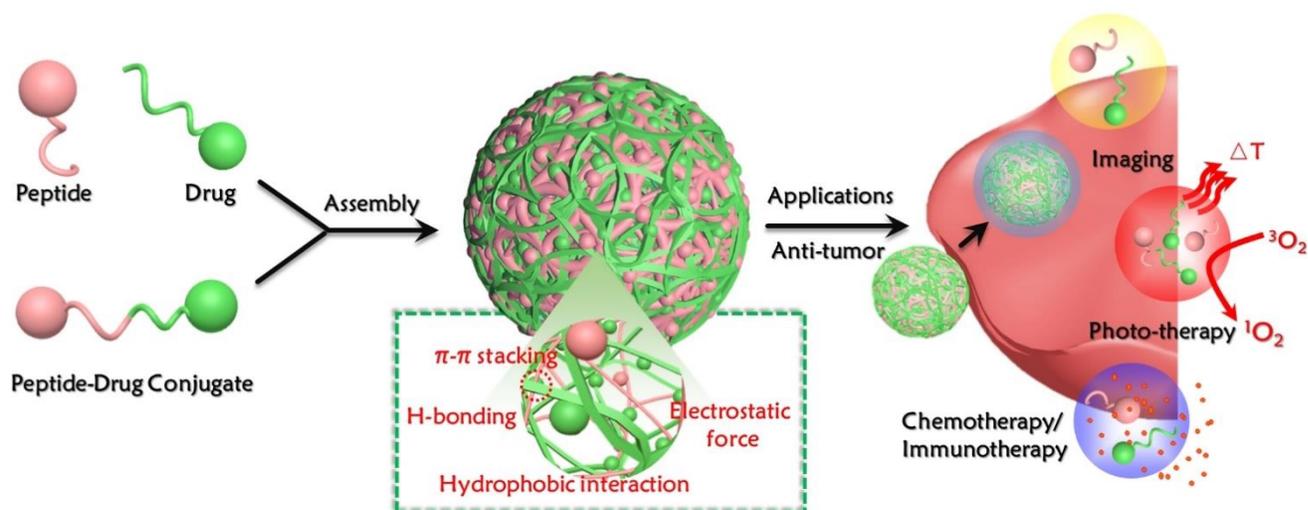


Figure 1. Schematic illustration of constructing assembled nanocolloids, the interactions for structure formation, and applications towards antitumor PDT and PTT therapy.

COLL 65

Hierarchically assembled three-dimensional array materials composed of virus-like particles (VLPs)

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Virus capsids are elegant examples of biomolecular structures hierarchically assembled from a limited number of protein subunits. Here we demonstrated the bio-inspired modular construction of materials with three levels of hierarchy using virus-like particles (VLPs). The first level of hierarchy is the formation of catalytically active VLPs through directed enzyme encapsulation concurrent with VLP assembly. This was achieved by exploiting a capsid formation process involving two types of subunit proteins, coat proteins (CPs) and scaffolding proteins (SPs). Cargo proteins such as enzymes can be directed inside of VLPs through genetic fusion with SP. The second level of hierarchy is the assembly of these VLP building blocks into ordered three-dimensional arrays. This was achieved through electrostatic interaction between negatively charged VLPs and positively charged linker molecules. Ordered VLP arrays with face-centered cubic (FCC) lattices were formed at an optimal solution ionic strength at which proper balance between attractive and repulsive interaction between the building blocks was realized. We demonstrated that an array, constructed from two populations of enzyme packaged VLPs, exhibited a coupled two-step catalytic conversion for isobutanol synthesis from α -ketoisovalerate *via* isobutyraldehyde. Assembly conditions can be finely tuned by manipulating the surface charge of VLPs. This leads to implementation of the third level of hierarchy into the arrays. Two populations of VLPs were selectively assembled with spatial control over each population within the array resulting in construction of a core-shell array with an FCC structure (Fig 1). Furthermore, we recently adopted a coarse-grain computational method to model the higher order assembly of these VLPs. Effective feedback between computational model and experimental verification can lead to the design of hierarchically organized VLP arrays with desired functionalities in a predictable manner.

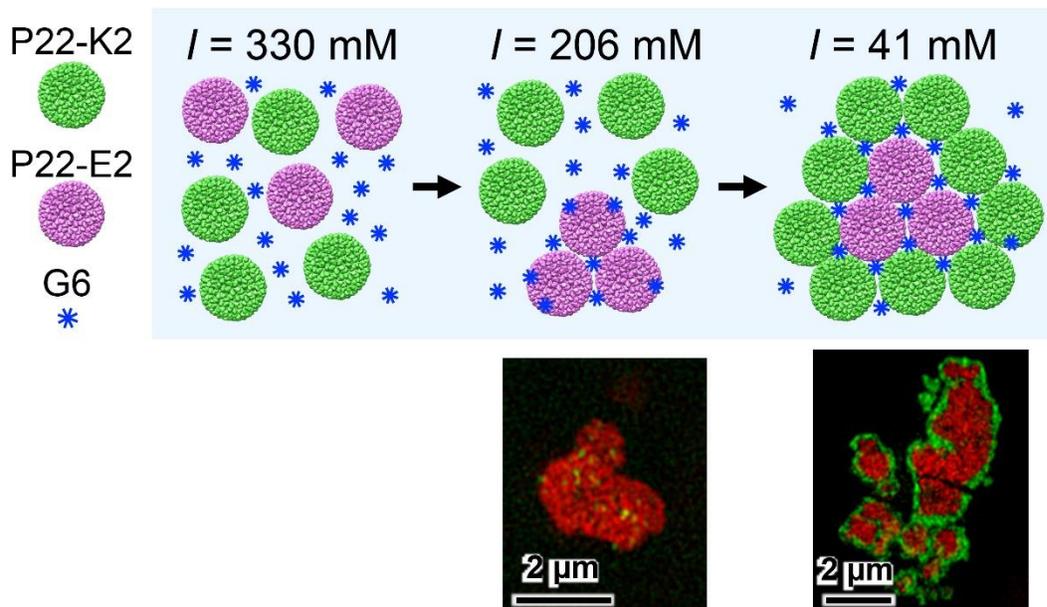


Fig 1 Ordered core-shell array assembled from two populations of VLPs (P22-K2, P22-E2) and a linker (G6) *via* modulating ionic strength (I) of solution

COLL 66

Two-step model for liquid-liquid phase separation in therapeutic antibody solutions

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Aqueous two-phase system formation is the macroscopic completion of liquid-liquid phase separation, a process by which aqueous solutions demix into two distinct phases. Concentrated liquid formulations of therapeutic antibodies are susceptible to phase separation, which compromises their stability. The mechanism of phase separation, however, has remained elusive because the temperature-dependent kinetics is cumbersome to measure. Herein, we overcome the problem of rapidly obtaining kinetic data by capturing dark-field images of protein-rich droplet suspensions as a function of time along a linear temperature gradient. These studies indicate that the kinetics of aqueous two-phase system formation is largely governed by the ability of proteins to dissociate from protein-rich droplets. We quantify the apparent activation energies for this dissociation and for droplet coalescence. Under certain conditions, we observe the formation of kinetically trapped gels that arrest phase separation. This work proposes a simple two-step mechanism for liquid-liquid phase separation that may help in formulating stable biopharmaceuticals and understanding the phase behavior of biological and colloidal systems.

COLL 67

Reactions in confined space: Can surface science contribute?

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Understanding reactions in confined space¹ is a topic of considerable interest in a variety of fields, as for example catalysis with zeolites, reactions involving membranes, and even such broad topics as “origin of life” where phenomena as deep sea black smokers may be related to confined spaces on sulfide surfaces. We have designed a system where a Ru(0001) surface works as a catalyst and may be covered by a silica bi-layer, which only weakly – through dispersive forces – interact with the metal surface leaving a space of ca. 1nm to carry out reactions, which in turn may be compared with the same reaction without the membrane present.² We study the oxidation of H₂ to

water by diffusing H_2 through the ring openings in the silica layer toward atomic oxygen adsorbed at the Ru(0001) surface.³ We use a LEEM/PEEM instrument designed in our laboratory to follow the reaction in operando. The experimental work is underpinned by theoretical calculations.⁴ Details will be discussed in the presentation.

COLL 68

Computational approach to determine entropy of adsorbates in catalytic reactions

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Adsorbed species and surface chemistry plays an important role in a large range of applications and technologies, especially in catalysis and electrocatalysis, separations, and device fabrication through film growth. Due to its technological relevance, a tremendous effort has been made worldwide to determine and predict reactions rates and selectivity for networks of elementary surface reactions through microkinetic modeling. These models depend on accurate predictions of reaction rates and equilibrium constants both which depend on enthalpy and entropy of adsorbates. We have developed an easy to implement method to calculate entropy of adsorbates using standard DFT approaches. This model joins the two limiting cases for adsorbates on a surface, the 2D ideal lattice gas model and the 2D ideal gas model, making it valid over large temperature range and for a verity of adsorbates. To verify this model, density functional theory was used to calculate adsorbate entropies of four different adsorbate species and found to agree well with experimental results. This method has been implemented into free computational tools, ASE and CatMAP, making it widely available.

COLL 69

How water improves the selectivity of preferential oxidation of CO in the presence of excess H_2 over Au/TiO_2

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Preferential oxidation (PrOx) of CO is a promising energy efficient alternative to CO methanation for purifying H_2 streams from steam reforming processes. With high-purity H_2 being the desired product, the obvious challenge is to find a catalyst that readily oxidizes CO, but does not burn H_2 . Through integrated experimental and computational studies we have produced evidence suggesting that O_2 and H_2 activation over Au/TiO_2 catalysts occurs at the metal-support interface (MSI).^{1,2} The activation of O_2 on

Au is assisted by support protons originating from hydroxyl groups or weakly adsorbed water molecules. In contrast, H₂ dissociation across the MSI occurs heterolytically resulting in a Au-hydride and a proton on the oxide support.

The accessibility and strength of proton accepting/donating sites on the titania support can be tuned by controlling the amount of water in the reaction feed. Water adsorbs weakly on the titania support and near the MSI, where it increases the local proton concentration. This is beneficial for O₂ activation and, in turn, for CO oxidation on Au. Conversely, the increased proton concentration and the screening of basic support sites by water impede the heterolytic H₂ activation at the MSI. Given the opposing effect of water on CO and H₂ oxidation it is possible to achieve very high PrOx selectivity with standard supported Au catalysts by simply tuning the partial pressure of water and maintaining ca. 1 monolayer of weakly adsorbed water on the support.

COLL 70

Heterolytic H₂ cleavage and water-assisted hydrogen spillover on single palladium atoms supported on Fe₃O₄(001)

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Single-atom catalysts (SACs) have recently attracted great attention due to their ultimate metal efficiency and the promise of novel properties. However, at the atomic level, little is known about their stability, interactions with the support, and mechanisms by which they operate. In hydrogenation reactions, the mechanisms of many critical steps such as hydrogen activation and spillover are far from understood. Here, we employ a combination of scanning tunneling microscopy and density functional theory and demonstrate that on a model SAC comprised of single Pd atoms on Fe₃O₄(001), H₂ dissociates heterolytically between Pd and surface oxygen. The efficient hydrogen spillover allows for continuous hydrogenation to high coverages which ultimately leads to the lifting of the Fe₃O₄ reconstruction and Pd reduction and destabilization. Water plays an important role in reducing the hydrogen diffusion barrier, thereby facilitating the redistribution of hydroxyls away from Pd. Our study demonstrates a distinct H₂ activation mechanism on single Pd atoms in contrast with Pd nanoparticles and corroborates the importance of charge transport on reducible support away from the active site. Computational studies yield detailed insight into the activity of different transition metals.

COLL 71

Control the reactions on surfaces

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The control of reactions toward the formation of targeted products on surfaces is always challenging but of great importance in many fields such as heterogeneous catalysis and on-surface synthesis. In order to achieve this goal, atomic level understanding of the mechanisms of the reactions occurred on the surfaces is the key. In this presentation, I will report a few examples from our recent studies of organic reactions on surfaces, including the Ullman, Glaser and Sonogashira couplings as well as Bergman cyclization reactions. These studies were performed under ultra-high vacuum (UHV) conditions using a combination of scanning tunneling microscopy (STM) and high-resolution synchrotron-based photoemission spectroscopy (HRPES). I will show that by tuning the dynamic and kinetic parameters such as the different substrates, substrate temperature, annealing procedure and reactant concentration, etc, we are able to control the surface reactions toward the designed pathways to some extent.

COLL 72

Parahydrogen-induced hyperpolarization on ordered surface of intermetallic nanoparticles

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Parahydrogen induced hyperpolarization of molecules can significantly enhance their nuclear magnetic resonance (NMR) signal intensity, thereby reducing needed sample quantities and instrument cost. These benefits have rendered parahydrogen induced hyperpolarization a promising research direction for magnetic resonance image (MRI) as well as other NMR-based structure/dynamics characterization techniques. We have discovered that intermetallic PtSn, an ordered alloy formed by 1:1 stoichiometry of Pt to Sn, can selectively catalyze the symmetry-breaking pairwise addition of a parahydrogen molecule to a C=C bond in propene, inducing the hyperpolarized proton signal in propane. Pairwise selective addition can be achieved if hydrogen molecules do not undergo dissociative adsorption on the catalyst surface. Pt alone is not a good catalyst for pairwise addition because H₂ readily dissociates to produce H ad-atoms that freely diffuse on its surface. On the other hand, PtSn can effectively prevent the dissociation of the hydrogen molecules and lead to high pairwise addition selectivity. Moreover, we have discovered that Pt₃Sn, another member of Pt-Sn intermetallic family, can hyperpolarize water using parahydrogen in a remarkable process that we refer to as SWAMP (Surface Waters Are Magnetized by Parahydrogen).

COLL 73

Selective oxidation of acetaldehyde to acetic acid on Pd–Au(111) bimetallic surfaces

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Acetic acid is a widely employed reactant in the chemical industry and it is also used as a food ingredient. Here, we report a new pathway for the gas-phase selective oxidation of acetaldehyde to acetic acid on the Pd–Au(111) heterogeneous model catalyst. On an oxygen precovered Pd–Au surface, acetaldehyde is selectively oxidized to acetic acid from 250 K to 340 K. Using vibrational spectroscopy, the formation of acetate species is detected from 160 K to 260 K on this surface, which is a widely known adsorbate derived from acetic acid on metal surfaces. With higher Pd coverages, the acetaldehyde is less selectively oxidized to acetic acid and near 375 K, CO₂, H₂O, CH₄, and H₂ are evolved, evidence for the decarboxylation of acetate. In our density functional theory calculations, we confirm that the relative energy difference between the acetate state and the decarboxylated state decreases as Pd ensemble size increases.

COLL 74

Surface reactions of complex molecular systems: From supported graphene to hydrogen storage molecules

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X-ray photoelectron spectroscopy (XPS or ESCA) is a versatile tool to investigate chemical reactions on surfaces. At third generation synchrotron radiation facilities, such as BESSY II in Berlin, XPS can be performed in situ with high resolution during adsorption or during heating. From the binding energies of the adsorbate and substrate core levels, detailed quantitative information on the chemical composition, chemical state and adsorption sites can be derived. In this presentation, two examples will be addressed. The first concerns the chemical properties of supported graphene or h-BN on metal surfaces, including the growth of metal clusters with a small size distribution on lattice-mismatched graphene Moire-layers and corresponding reaction studies. The second example addresses the adsorption and reaction of liquid organic hydrogen carriers (LOHCs) like octahydroindole or dodecahydro-N-ethylcarbazole, on metal surfaces. Hydrogen storage in LOHCs is a possible future technology to circumvent the challenges in energy storage.

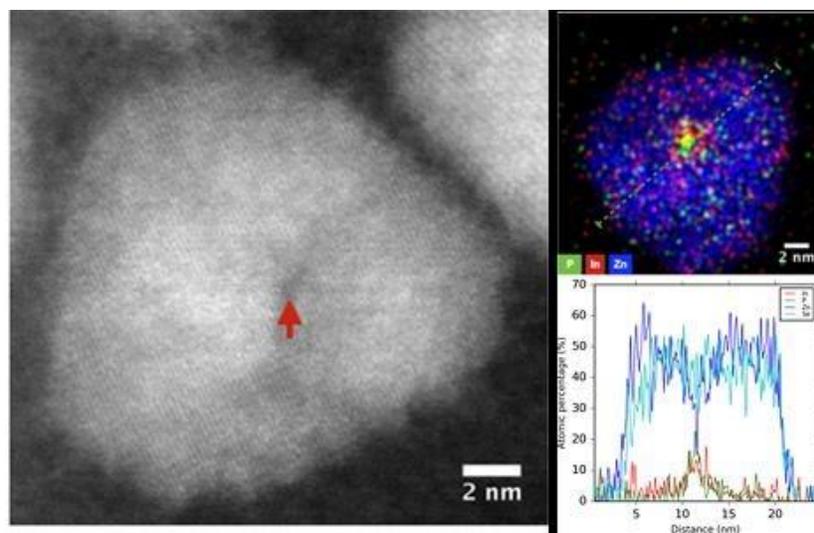
COLL 75

Impact of shell imperfections in colloidal quantum dots

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The synthesis of colloidal core/shell nanocrystals has continually progressed to the point of true commercial-scale production. However, long term stability in ambient or aqueous conditions remains a significant challenge. This is especially the case for emergent, cadmium free nanocrystal systems, such as InP, which are utilized commercially only under stringent air and moisture free encapsulation. To improve long term ambient stability, the simple idea of growing thick epitaxial shells to passivate surface trap states and isolate the charge carriers creates new challenges as a result of increased lattice strain. Strain-induced dislocations at the core/shell interface have long been suggested as the major reason for lower fluorescence quantum yields in thick-shelled quantum dots. Unfortunately, directly characterizing these defects is difficult in nanocrystal systems compared to their bulk-epitaxial counterparts. To elucidate the impact of shell morphology and shell defects on the performance of colloidal quantum dots, we are utilizing a correlation strategy which allows for the interrogation of the single particle fluorescence dynamics and the atomic structure of the same quantum dot. This strategy has enabled the study of dark, non-emitting sub populations and has highlighted the effect of nanocrystal charging on the ensemble quantum yield. Correlation data will be presented which show the physical location of subtle and often overlooked surface defects in seeded CdSe/CdS nanorods and determine the charge carrier recombination mechanism and the type of blinking observed. Further, HRTEM, STEM-EDS and aberration-corrected STEM images of thick shelled InP/ZnSe and graded alloyed CdZnSeS/ZnS nanocrystals will be presented revealing further insight into the true physical structure of the shells and the need for improved synthetic strategies.



HRSTEM and STEM-EDS of a thick shelled InP/ZnSe quantum dot with a shell defect highlighted.

COLL 76

Linker-free deposition of Au nanoparticles from a Au colloid

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Commercially available, citrate-stabilized gold nanoparticles are attractive engineering materials for a variety of applications given their unique and tunable properties. Their size-dependent optical properties, surface plasmon resonances, fluorescence, electrical properties and easily functionalized surface has spawned research in fields ranging from biological sensors to electronic devices. Typically, these Au colloids are adhered to a surface using a polyelectrolyte linker. This polyelectrolyte linker prevents direct contact of the Au nanoparticles with the underlying surface and can adversely affect the desired properties. In our application, this polyelectrolyte linker was found to prevent an epitaxial connection between a resulting Si nanowire and the underlying Si substrate. We examine the effects of deposition time and Au colloid size on agglomeration and nanoparticle density. Initially, longer deposition times increases the density of Au nanoparticles on the surface; however, the density eventually plateaus. Agglomeration too increases with deposition time and plateaus as well. In order to increase Au nanoparticle density on the surface and minimize agglomeration, we used multiple, short-timed deposition cycles which tended to increase the density without significantly increase the agglomeration of the Au nanoparticles.

COLL 77

Modulating ferroelectric response in colloidal semiconductor nanocrystals through cation exchange

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Ferroelectrics are a class of materials that exhibit unique electronic behavior that has the potential to revolutionize energy storage and random-access memory design. Their polar, non-centrosymmetric crystal structure results in inherent piezoelectric and pyroelectric properties and can therefore be used for energy harvesting applications. CdSe nanocrystals are ubiquitous in nanoscience and, unlike their bulk counterparts, can be deposited through spin-coating, spray-coating, reel-to-reel printing, and ink-jet printing onto flexible substrates at low temperatures. In our studies, ferroelectric behavior arose through a room-temperature cation exchange of semiconductor

nanoparticles. Because cadmium selenide and cadmium sulfide quantum dot syntheses have been thoroughly studied, cation exchange synthesis grants access to control over many precisely defined shapes, sizes, and compositions of ferroelectric nanoparticles. Additionally, synthesis of ferroelectric nanoparticles using cation exchange of highly studied quantum dots yields the possibility of improved stability of ferroelectric nanoparticles. Cation exchange reactions were performed on colloidal nanocrystals using metal chloride salts. The atomic percent of exchange cation was determined using STEM-EDS and ferroelectric properties were measured using a Sawyer-Tower circuit. Variation in exchange cation identity and atomic percent allows for control over ferroelectric properties. The ability to tune the structure and ferroelectric response of nanostructures offers a broad range of applications for these ferroelectric nanoparticles formed through a simple room-temperature cation exchange synthesis.

COLL 78

First-principles modeling of photoluminescence of colloidal nanostructures

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Colloidal semiconductor nanostructures demonstrate favorable tuning of the optoelectronic properties facilitated by quantum confinements. The interpretation understanding and optimization of experimental features and trends in photoluminescence of nanostructures is often guided by computational modeling at atomistic level. Two important factors provide contribution to efficiency, quantum yield, and lineshape of PL signal in photoexcited colloidal nanostructures: (a) cascading process of cooling of hot carriers, due to dissipation of electronic excitation energy to lattice vibrations and (b) distribution of transition energy and oscillator strength in an ensemble, also related to exciton-to-phonon coupling, providing quantitative way to assess thermal broadening of the PL lineshape. [1] The first principles modeling demonstrated correlation between temperature and PL lineshape of Si-quantum dots [2]. The radiative and nonradiative relaxation and multi-exciton processes in MAPbI₃ quantum dots are all found to be affected by quantum confinement, that positively affects PLQY. [3] For quantum dots composed of heavy elements, such as CsPbBr₃ colloidal quantum dots, the spin-orbit interaction found to provide additional splitting between transitions energies of states involved in PL and affect rates and efficiencies of the PL. [4] Deviation of nanoparticles from spherical shapes towards elongated nanorods and nanowires provides specific spectral signatures, especially for materials that carry indirect gap feature in bulk form.

COLL 79

Shortwave infrared highly emissive nanostructures derived from Cd/Hg chalcogenide platelets

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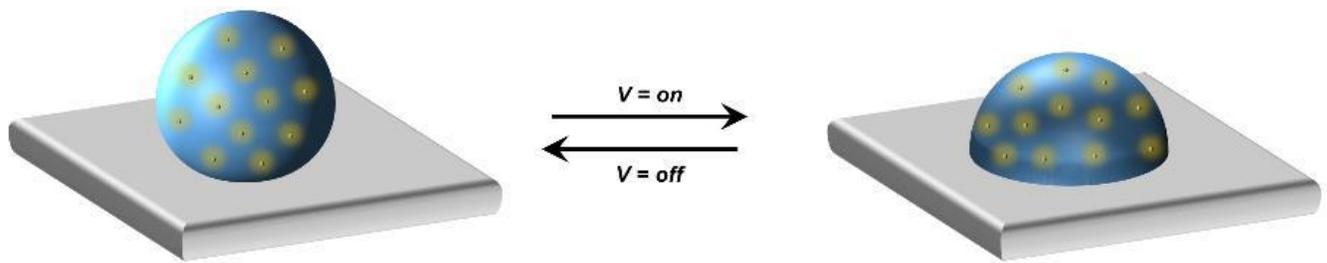
Materials that absorb and emit beyond the bandgap of silicon have many potential uses, from biomedical imaging to novel optoelectronic architectures. We report bright (>30% QY) tunable shortwave infrared (SWIR) emission from Hg/Cd chalcogenide nanoplatelets. Through modification of ligand coverage we tune this emission from 1 -2 microns, while retaining quantum confined HgTe absorption features. This creates a large intrinsic stoke shift between absorption and emission, associated with exciton self trapping. Broadly speaking, these nanocrystals reveal the non-trivial role of ligand coverage and surface dominated properties of 2D nanocrystals. We will show that these unique NCs may be useful as a luminescent concentrator of visible light into telecom wavelengths.

COLL 80

Influence of quantum dot and nanomaterial composition on aqueous and non-aqueous digital microfluidics

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The actuation of droplets on surfaces is very critical for various microfluidic, nanofluidic and optofluidic applications. Electrowetting represents an attractive technique to manipulate fluids on surfaces and has gained interest in smart optics, electronic paper, and energy harvesting applications. The unique spreading characteristics of nanofluids (fluid –containing nanoparticles) are very appealing for fluid actuation on surfaces. We will present our work firstly, on the electrowetting of nanofluids based on quantum dots (CdSe/ZnS and InP/ZnS), ferroelectric (BaTiO₃) and metallic (Ag) nanoparticles synthesized in aqueous and non-aqueous media. We show that nanoparticle surface chemistry, composition, concentration and dispersion media are key parameters in nanofluid actuation on dielectric surfaces. Secondly, this interesting phenomenon will also be demonstrated in an electrowetting-based OpenDrop digital microfluidic platform in which the actuation voltages differ significantly depending on the medium and nanoparticle composition.



Nanofluid actuation through the application of voltage

COLL 81

Controlling carrier polarization in plasmonic semiconductor nanocrystals

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Degenerate semiconductor nanocrystals with tunable localized surface plasmon resonance (LSPR) have attracted significant attention in recent years due to their unique optoelectronic properties. Unlike noble metal nanoparticles, colloidal plasmonic semiconductor nanocrystals have LSPR frequencies tunable in the infrared region, which makes them appealing for terahertz imaging, heat-responsive devices, and surface-enhanced infrared spectroscopic measurements. Besides expanding the LSPR frequency range, plasmonic semiconductor nanocrystals could potentially bring about numerous other opportunities related to single-phase plasmon-exciton interactions. However, non-resonant nature of the LSPR and exciton in semiconductor nanocrystals has been a major obstacle toward realizing such opportunities. In this talk I will discuss the results of our recent work on the structure and composition dependent plasmonic properties of colloidal semiconductor nanocrystals. I will particularly focus on generating robust excitonic splitting in degenerately-doped transparent metal oxide nanocrystals, enabled by non-resonant plasmon-exciton coupling in an external magnetic field. This phenomenon allows for controlling carrier polarization in semiconductor nanocrystals using circularly polarized light. Possible applications of these intrinsically multifunctional colloidal nanocrystals for new energy-efficient electronic and quantum information technologies will also be discussed.

COLL 82

High temperature digestive ripening and size focusing of semiconductor nanocrystals in ligand-saturated solutions

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Digestive ripening (DR) represents a powerful strategy for improving the size homogeneity of colloidal nanostructures. It relies on the ligand-mediated dissolution of larger nanoparticles in favor of smaller ones and is often considered to be the opposite of Ostwald ripening. Despite its successful application to size-focusing of metal colloids, digestive ripening of semiconductor nanocrystals has received little attention to date. Here, we explore this synthetic niche and demonstrate that ligand-induced ripening of semiconductor nanocrystals exhibits an unusual reaction path. The unique aspect of the DR process in semiconductors lies in the thermally activated particle coalescence, which leads to a significant increase in the nanocrystal size for temperatures above the threshold value ($T_{th} = 200\text{--}220\text{ }^{\circ}\text{C}$). Below this temperature, nanoparticle sizes focus to an ensemble average diameter just like in the case of metal colloids. The existence of the thermal threshold for coalescence offers an expedient strategy for controlling both the particle size and the size dispersion. Such advanced shape control was demonstrated using colloids of CdS, CdSe, CsPbBr₃, and CuZnSnS₄, where monodisperse samples were obtained across broad diameter ranges. We expect the demonstrated approach to be extended to other semiconductors as a simple strategy for tuning the nanoparticle morphology.

COLL 83

Synergistic approach towards understanding the mechanistic behavior for eradication of superbugs using multifunctionalized nanoplatforms

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Despite numerous superior disinfection/advanced sterilization methods being available in modern clinical settings to control the deadly superbugs infections, the sensitive detection, early in vivo diagnosis and complete removal of superbugs infections are still the major challenges. Functional carbon-based materials such as, graphene oxide, oxidized carbon nanotube and carbon dots have become rising stars with high interest in the scientific community due to their unprecedented tunable properties such as high mechanical strength, excellent photostability, biocompatibility, highly tunable photoluminescence (PL), exceptional multiphoton excitation, ease to be conjugated with biomolecules, chemical inertness, cost effectiveness and their ability to serve as effective carriers for drug delivery. For example, Graphene oxide based ultrathin porous membranes exhibit exceptional molecular permeation properties which have many applications in water purification by the disinfection of pathogen bacteria, specifically methicillin-resistant *Staphylococcus aureus* (MRSA) and multidrug resistant superbugs. Aptamer-modified two-dimensional graphene oxide nano-sheets can be used for multicolor targeted bio-imaging of antibiotics resistant bacteria (MRDB) in the first and the second biological transparency windows. Three dimensional (3D) porous membrane produced by attaching **nisin (polycyclic antibacterial peptide)** identify, effectively separate, and completely disinfect MRSA pathogens from contaminated water. A number of multi-functionalized nanoplatforms were synthesized for the selective

detection as well as rapid and efficient killing (~100%) of the multi-drug resistant superbugs within a few minutes. We will discuss the detailed mechanism insight the sequestration and eradication process and how to tune the limit of sensitivity as well as effectiveness. This material would be great promise for use in clinical settings.

COLL 84

Linking interfacial protein dynamics to macroscale elutions

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Our long-term objective is to link the micro/nanoscale mechanisms underlying chromatographic separations to the macroscale observable of an elution curve via an expanded stochastic theory. I will report on our recent efforts to incorporate competition and 3D dynamics within a molecular dynamics simulation. In addition I will discuss recent developments to achieve phase engineering during fluorescence super-resolution microscopy.

COLL 85

Single-molecule spectroscopy study of crowding-induced protein spontaneous denature and crowding-perturbed unfolding-folding conformational fluctuation dynamics

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The effects of molecular crowding on protein folding-unfolding processes are of importance for understanding protein function and structure dynamics in living cells. The enhancement of protein stability as a result of reduced entropic effect in the presence of molecular crowding is well understood both experimentally and theoretically. However, due to the complexity and interplay between various interactions existing in an equally favored environment of protein folding and unfolding conformational dynamics, such simple reduced entropic enhancement model does not suffice to describe protein folding conformational dynamics under a protein crowding condition. In this talk, we report our observation on that single protein molecules spontaneously denature into unfolded proteins and folding-unfolding fluctuations in solution of crowding reagent. We have identified such the protein dynamics involves in a combined mechanism of polymer-polymer interaction, entropic effects, and protein solvation dynamics. We characterize the protein folding-unfolding dynamics by using single-molecule spectroscopy to obtain detailed molecular dynamic scale information on the protein folding-unfolding conformational fluctuation dynamics. Our findings suggest that the complex unfolding dynamic processes are spontaneous denature of single protein molecules induced by molecular crowding effect which has been elusive for analysis in ensemble-averaged measurements.¹ We have also studied the protein spontaneous ruptures under AFM tip

compressive force manipulations.^{2,3} Furthermore, the energy needed for the spontaneous unfolding is at the biological accessible force fluctuation level, which suggests a strong implication of significant human health relevance and importance. The new knowledge of the inhomogeneous protein unfolding processes can serve as a step forward to a mechanistic understanding of human diseases associated with molecular crowding, protein aggregates, fibril formation as well as gene translational regulation processes typically under molecular crowded local environment.

COLL 86

Superresolution (fcsSOFI) imaging of porous polymer support and active control of protein dynamics

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Confinement of proteins at the porous chromatographic support leads to anomalous confined diffusion. Molecular level understanding and control over such complex dynamics are needed for predictive applications. Cross-linked hydrogels made of stimuli-responsive polymers provide unique control over their physio-chemical properties by spatial and chemical transformation with environmental changes. These stimuli-driven transformations generate a dynamic heterogeneity of hydrogels' physio-chemical properties and are the driving forces behind their underlying surface chemistry. Characterizing Nanoscale structure and dynamics at crowded environments under ambient conditions is challenging with traditional techniques, such as AFM. Fluorescence correlation spectroscopy combined with Super-resolution Optical Fluctuation Imaging (fcsSOFI) is ideal to understand the complex dynamic behavior of proteins and characterize porous polymer surface. Herein, we use fcsSOFI and single particle tracking to understand the dynamics of a model protein lysozyme on the dual stimuli-responsive (pH and temperature) hydrogel surface and inside the hydrogel pores. Lysozyme shows variable reversible surface dynamics on the poly-N isopropylacrylamide hydrogel surface and nanopores. Also, chemical heterogeneity of the surface and geometrical confinement dictates the dynamic hopping behavior of proteins at the complex nanogel surfaces. The single molecule picture of these complex processes and active control of protein dynamics will inspire better bottom-up design strategies with other stimuli-responsive polymers for various applications including, but not limited to, separation science and biomedical sciences.

COLL 87

Cadherin cluster formation in two dimensional confinement

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Single molecule tracking of cadherin extracellular domains on supported lipid bilayers revealed the density-dependent formation of oligomers and clusters due to *cis*-interactions, which were virtually eliminated by mutating a putative *cis* (lateral) binding interface. At low cadherin surface coverage, wild-type (WT) and mutant cadherin diffused rapidly, consistent with the motion of a lipid molecule within the supported bilayer. Although the diffusion of mutant cadherin did not change appreciably with surface coverage, the average short-time diffusion coefficient of WT cadherin slowed significantly above a fractional surface coverage of ~ 0.01 , and a detailed analysis of molecular trajectories suggested the presence of a broad distribution of cadherin cluster sizes. Since *cis*-interactions have not been successfully detected between cadherin in homogeneous solution, these findings suggest that *cis*-interactions are strongly influenced by two-dimensional confinement.

COLL 88

Reversible nanobubble surface modifications form protective surface layers at solid/liquid interfaces

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Surface-templated nanobubbles were studied for their ability to provide protective coatings for protein stabilization. Nanobubbles are stable gas pockets measuring tens of nm in height and up to thousands of nm in diameter that can form at solid-liquid interfaces such as glass surfaces that are used to store protein therapeutics; the denaturation of which can lead to protein deactivation or aggregation.

To study the effect of surface chemistry on nanobubble stability, glass surfaces were functionalized with copolymer brushes containing mixtures of hydrophobic and hydrophilic segments, exhibiting static water contact angles (CA) ranging from 10 to 75°. On methylated glass, dissolution and redeposition of nanobubbles resulted in reformation in mostly the same locations, consistent with the contact line pinning hypothesis. However, for copolymer-stabilized surfaces the presence of stable nanobubbles was correlated with global surface wettability, rather than local topography. Nanobubbles appeared to be stable when the surface exceeded a critical water CA of 50-60° for polymers containing carboxyl or sulfobetaine groups, respectively, as hydrophilic side chains. The critical CAs were insensitive to the identity

of the hydrophobic segments.

The behavior of proteins on the nanobubbles was examined using single-molecule total internal reflection fluorescence (SM-TIRF) microscopy combined with intramolecular Förster Resonance Energy Transfer (FRET). To study protein conformational dynamics, nitroreductase (NfsB) labeled with FRET dyes was prepared by engineering NfsB with noncanonical amino acid substitution and subsequent dye conjugation. Next, nanobubbles formed by a solvent exchange method were imaged using reflection brightfield microscopy, permitting the observation of spatial co-localization of nanobubbles and NfsB adsorption. Virtually all (96%) of NfsB molecules that interacted with nanobubbles remained folded, whereas less than 50% of NfsB molecules remained folded in the absence of nanobubbles, either on unmodified silica or methylated glass surfaces. Ensemble-average fluorometer TIRF experiments were consistent with the SM observations. We hypothesize that nanobubbles reduced protein damage by specifically passivating strongly denaturing topographical surface defects. As such, the nucleation of nanobubbles on surfaces has potential important implications for designing anti-fouling surfaces as well as for stabilizing therapeutic proteins during storage.

COLL 89

Impact of confinement and crowding on the kinetics of enzyme encapsulated in virus-like particles

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Enzymes make an excellent choice for biocatalysis in industrial applications, due to their ability to carry out complex reactions under mild reaction conditions. However, they are easily denatured with changes in surrounding conditions, therefore it is crucial to stabilize their structure and function to retain their activity for longer periods. This can be achieved through their immobilization or encapsulation into a matrix. Encapsulation of enzymes into confined spaces such as virus-like particles (VLPs), liposomes, and polymerosomes, are shown to protect them from environmental assault and allow us to study their behavior without any interference from other molecules. The encapsulation, however, modulates the activity of enzyme when compared with the free enzyme. Macromolecular crowding, resulting from the high-density packaging of enzymes inside these caged systems, confinement-induced denaturation or self-association, and slower diffusional mobility of enzymes and substrate molecules are used in conjunction to rationalize the outcome of enzyme encapsulation. We have developed a methodology that has allowed us to control the amount of packaging and the degree of packing density of enzymes inside the VLPs (derived from P22), thereby allowing us to dissect the role of confinement and crowding onto these enzyme systems. Additionally, morphogenesis of P22 VLPs offer cages with different porosities that have allowed us to determine the involvement of diffusion controlled enzyme kinetics. This work will highlight the motivation that led to the development of this methodology, followed by its utilization to tease out underlying phenomenon responsible for the modulation of

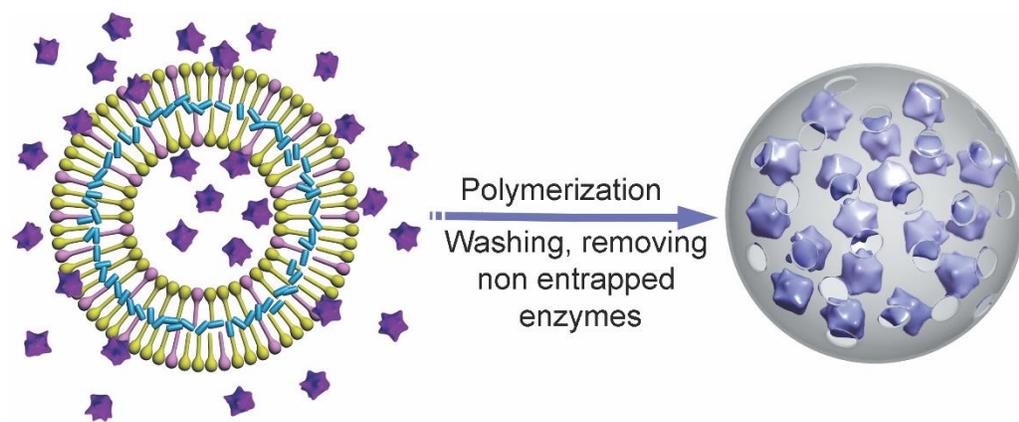
enzymatic rates. We anticipate that this study will help us engineer nanoreactors with better performance and catalytic efficiencies, thus making them more suitable for nano-technological and industrial applications.

COLL 90

Manipulating biological systems with polymer chemistry: Encapsulating enzymes

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Polymer-based nanocapsules of tunable size have been synthesized using a temporary scaffold made of self-assembled surfactant molecules, and a polymerization method initiated by mild heat. In the current project, this synthesis method was chosen to encapsulate enzymes as it was anticipated that the enzymes would survive the mild conditions. The encapsulation of enzymes is desirable because it is hypothesized that a) the confined space of a capsule and the addition of an inert crowding agent will increase the stability of an enzyme, b) the encapsulation will create a microenvironment that is amenable to manipulation to regulate the activity of entrapped enzymes, and c) the controlled permeability of the capsules will enable complex reactions. Initial results indicated that a surfactant-based scaffold system was not viable given the denaturing interaction of charged surfactant molecules with enzymes. Instead, lipids were employed as the scaffold system as they are neutral in charge and will not denature the enzymes, but will still form the necessary bilayer. However, the sensitivity of liposomes to their microenvironment has presented a new set of obstacles. The challenges of interfacing polymer chemistry with biological systems will be discussed.



Representation of synthesis with cationic surfactant vesicles spontaneously forming in the presence of hydrophobic monomers that load into the bilayer and enzymes that are entrapped in the aqueous space inside, followed by polymerization and removal of non-entrapped enzymes.

COLL 91

Experimental and computational search strategies for function in the peptide sequence space

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Life's diverse molecular functions are largely based on only a small number of highly conserved building blocks – the twenty canonical amino acids. These building blocks are chemically simple, but when they are organized in three-dimensional structures of tremendous complexity, new properties emerge. The talk will summarize our recent efforts in the directed discovery of functional nanoscale systems and materials based on these same amino acids, but that are not guided by copying or editing biological systems. We will discuss complementary approaches of searching the sequence space to explore sequence–structure relationships for assembly, reactivity and complexation, namely: (i) strategic editing of short peptide sequences; (ii) computational approaches to predicting and comparing assembly behaviors. These approaches give rise to guiding principles on controlling order/disorder, reactivity and, ultimately, humidity responsiveness by peptide sequence design.

COLL 92

Combinatorial targeting for phenotypic targeting

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Tight control on the selectivity of nanoparticles' interaction with biological systems is paramount for the development of targeted therapies. However, the large number of synthetically tuneable parameters makes it difficult to identify optimal design "sweet spots" without rational guiding principles. Here we address this problem combining super-selectivity theory (SST) with analytical models from soft matter and polymer physics into a unified theoretical framework. Starting from an archetypal system, a polymersome functionalised with targeting ligands, we use our model to identify the most selective combination of parameters in terms of particle size, brush polymerisation degree and grafting density, as well as tether length, binding affinity and ligands number. We further show how to combine multivalent interactions into multiplexed systems which act holistically as a function of the density of more than one receptor type, so as to achieve binding only when multiple receptors are expressed above a threshold density. We show that theory can be used to effectively fit experimental data and hence confirming its suitability. We thus propose the design of "bar-coding" targeting approach that can be tailor-made to unique cell populations enabling personalised therapies.

COLL 93

Transitioning to predictive analysis for nanoparticle biocorona studies

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The pronounced proliferation of studies characterizing the nanoparticle protein corona in the past 10 years has led to significant advances in understanding the formation of the layer of proteins sorbed to nanomaterials in a biological environment and their role in cellular recognition, uptake, and toxicity. Through this work, drivers for protein corona formation have become clear, including the discovery that the protein population on the surface of nanoparticles is dependent upon features of the particle, proteins, and reaction conditions. To limit the need for costly and time-consuming LC-MS/MS proteomics characterization of every protein corona, we present a random forest classification approach to model experimental LC-MS/MS proteomics datasets characterizing protein corona populations. The model serves as a step toward defining the most influential mediators in defining the population of proteins in the corona. To support expanded modeling efforts in this area, we will also comment on guidelines to establish best practice in methodology and in reporting for studies characterizing the protein corona. With a breadth of strong experimental datasets, protein corona studies will improve in reproducibility and benefit from expanded modeling efforts. As we begin to meet the grand challenge of predicting the protein corona surrounding nanoparticles, we can further improve targeted nanomedicines and safe-by-design nanomaterials.

COLL 94

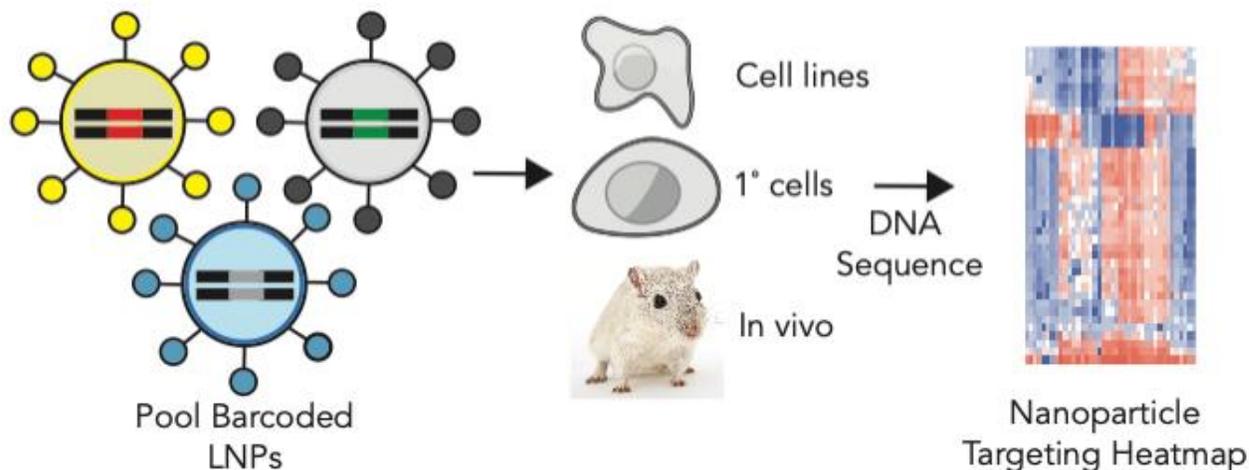
Rapidly identifying nanoparticles for *in vivo* RNA and gene editing using DNA barcoding

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RNA-based drugs can turn on (or off) any gene in the genome. However, whether the drug is made out of siRNA, mRNA, lncRNA, or CRISPR, all RNA therapies are limited by one problem: drug delivery.

Chemists can design thousands of distinct nanoparticles to deliver RNA. However, after nanoparticles are synthesized, they are tested in *in vitro* systems which do not have a liver, kidney, spleen, immune system, pulsatile blood flow, or other factors that affect nanoparticle delivery *in vivo*. To test thousands of nanoparticles *in vivo*, we designed a series of increasingly advanced DNA barcoding platforms. We can now quantify how over 300 nanoparticles functionally deliver mRNA or siRNA into up to 30 cells from a single mouse. These platforms combine high throughput chemistry, *in vivo* RNA

delivery, DNA deep sequencing, and bioinformatics. Since 2016, we have generated nearly 200,000 *in vivo* drug delivery datapoints, and developed a customized bioinformatics pipeline to iteratively ‘evolve’ nanoparticles that target new cell types in the spleen, liver, and bone marrow. Our data demonstrate that DNA barcoded LNPs can elucidate fundamental questions about *in vivo* nanoparticle delivery, and identify nanoparticles for *in vivo* gene therapies.



COLL 95

Learning to predict single-wall carbon nanotube-recognition DNA sequences

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In this work, we demonstrate the applicability of machine learning methods to discovery of special DNA sequences that recognize partner single-wall carbon nanotubes (SWCNT). DNA/SWCNT hybrids have enabled many applications because of their special ability to disperse and sort SWCNTs by their chirality and handedness. Much work has been done to discover recognition sequences which recognize specific chiralities of SWCNT, and significant progress has been made in understanding the underlying structure and thermodynamics of these hybrids. Nevertheless, *de novo* prediction of recognition sequences remains essentially impossible and the success rate for their discovery by search of the vast ssDNA library is very low. Here, we report an effective way of predicting recognition sequences based on machine

learning analysis of existing experimental sequence data sets. Multiple input feature construction methods (position-specific, term-frequency, combined or segmented term frequency vector, and motif-based feature) were used and compared. The transformed features were used to train several classifier algorithms (logistic regression, support vector machine and artificial neural network). Trained models were used to predict new sets of recognition sequences, and consensus among a number of models was used successfully to counteract the limited size of the data set. Predictions were tested using aqueous two-phase separation. New data thus acquired was used to retrain the models by adding an experimentally tested new set of predicted sequences to the original set. The frequency of finding correct recognition sequences by the trained model increased to >50% from the ~10% success rate in the original training data set.

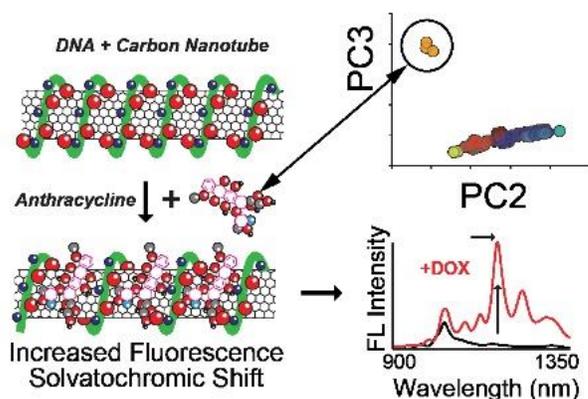
COLL 96

Chemometric analysis of nanosensor libraries for developing short-wavelength infrared optical probes for anthracyclines

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Polymer-functionalized single-walled carbon nanotubes (SWNTs) are a promising new class of short-wavelength infrared (SWIR) fluorescent nanomaterials for non-invasive, *in vivo*, biomolecular imaging. The adsorbed polymer-phase can impart specific molecular recognition, whereby analyte binding can be monitored by measuring the resulting modulation of SWNT fluorescence. Currently, methods for screening new nanosensor-target pairs involve searching for broad changes in fluorescence intensity without capturing subtle changes in the information-dense emission spectra. Herein, we demonstrate rapid and quantitative analysis of fluorescence emission collected from chirality-mixed SWNT nanosensors prepared from a library of polymers and phospholipids screened against a panel of >40 biological targets. Using a distance metric calculations and multivariate approaches, including hierarchical clustering and principal component analysis, we readily identify nanosensors that respond to different small-molecule targets. These chemometric approaches enable the identification of nanosensor-analyte 'hits' and signaling modalities—such as wavelength-shifts—that are optimal for translation to biological imaging. Analytes inducing similar responses, e.g. catecholamines, are grouped by hierarchical clustering and correlate with intrinsic chemical properties, demonstrating that our approach enables classification of nanosensor-target interactions. We identify and characterize a new nanosensor exhibiting a fluorescent red-shift upon exposure to the chemotherapeutic anthracycline doxorubicin and demonstrate its tissue compatibility for imaging doxorubicin in mouse muscle tissue. Our results highlight the benefit of techniques in exploratory data

analysis and data mining for nanosensor discovery and motivate future studies to elucidate the details of chemical interactions involved in hybrid nanomaterial systems.



COLL 97

Development of targeted nanomedicines facilitated by nanoinformatics

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Therapy based on personalized medicine has become a leading strategy to treat cancer. Small molecule drugs such as kinase inhibitors, which target key effectors of cancer signaling pathways, constitute a major component of this strategy. This class of inhibitors inhabits a diverse chemical space, however, making it difficult to develop nanomedicines against the wide set of precision drug targets. We are developing machine learning processes to predict and facilitate the encapsulation of diverse drug classes into nanoparticles based on the molecular structures of the drugs. We devised quantitative structure-nanoparticle assembly prediction models to identify and validate electrotopological molecular descriptors as highly predictive indicators of nano-assembly and nanoparticle size. The resulting nanoparticles selectively targeted kinase

inhibitors to caveolin-1-expressing RAS-driven human colon cancer and autochthonous liver cancer models to yield striking therapeutic effects while avoiding dose-limiting toxicities. This work enables the computational design of nanomedicines based on quantitative models for drug payload selection.

COLL 98

Seeded growth and cation exchange strategies for the synthesis of complex multi-component nanoparticles

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Multi-component nanoparticles offer unique opportunities to combine different properties in a single construct, enabling both multi-functionality and the emergence of new synergistic functions. Synthesizing such multi-component nanoparticles requires simultaneous control over size, shape, composition, and structure, as well as interfaces and spatial arrangements. We have been developing two complementary strategies for synthesizing multi-component nanoparticles, and this presentation will highlight new capabilities in each of these areas. The first approach involves heterogeneous seeded growth, where interfaces and asymmetry are introduced by sequentially growing new nanoparticles off of the surfaces of existing nanoparticles. Complex hybrid nanoparticles of a growing number of materials, configurations, and morphologies can now be synthesized. The second approach involves sequential partial cation exchange reactions, where interfaces and asymmetry are introduced by compositional modifications that are made within an existing nanoparticle. A growing library of complex heterostructured metal sulfide nanoparticles can now be rationally designed and then readily synthesized.

COLL 99

Molecular programming the phase determination of colloidal nanocrystals with dichalcogenide precursors

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We were the first to demonstrate that colloidal oxide and chalcogenide nanocrystals could be synthesized using one general reaction scheme by simply varying a common dichalcogenide precursor (R-E-E-R; where E = O, S, Se, Te and R = *t*Bu, Bn, Ph, etc.). This is the only precursor that can function as a common transfer reagent for *all* of the group VI elements through tellurium. Dichalcogenides have proven to be effective precursors for a very wide variety of colloidal nanocrystals, including many previously undiscovered metastable phases. Along these lines, we recently leveraged the tunability of dichalcogenide precursors to allow for molecular programming of the resulting nanocrystal phase. We demonstrated that the C–Se bond strength of the

dichalcogenide precursor is phase determining for CuInSe₂ nanocrystals, with stronger C–Se bonds leading to a metastable wurtzite-like phase that is kinetically persistent. This talk will discuss these results and the extension of this concept to the molecular programming of other metastable phases of multinary chalcogenide nanocrystals.

COLL 100

Quantum dot design strategies for accurate molecular imaging in cells and tissues

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Quantum dots have been used for more than 20 years as labels for nucleic acids and proteins in cells and tissues, but early variants exhibited limitations in stability, physical dimensions, and optical tunability that hindered widespread adoption and standardized use. This talk will describe how early challenges have largely been overcome through rigorous studies of probe design principles to allow high-fidelity molecular labeling and single-molecule imaging. New technologies include photophysical engineering processes to precisely control light emission flux independently from wavelength, new polymer coatings to shrink the hydrodynamic size from 30 to less than 10 nanometers while maintaining long-term stability and precise bioconjugation, and image analysis tools to quantify absolute molecular stoichiometries in living and fixed biospecimens. The Smith Lab at Illinois is applying these new nanomaterials to quantitatively analyze signal transduction processes at the single-cell level, to image dynamic processes of receptors in living cells, and to count nucleic acids in tissues. This talk will further describe additional developments that are needed to overcome remaining barriers to widespread adoption and commercialization.

COLL 101

Metal-tipped CdSe@CdS tetrapods: Enhanced solar energy conversion and fuel generation enabled by precision nanoscale syntheses and Interface engineering

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Heterostructured II-VI semiconductor (SC) nanocrystal materials continue to be attractive platforms for the study of compositional, structural, and energetic factors that control the efficiencies of photoinduced charge separation, and surface-sensitive redox pathways that can lead to energy storage fuels like hydrogen, as well as improved PV performance. Design rules developed in the last two decades point to the need for asymmetric nanomaterial constructs which can drive vectorial separation of photoexcited electrons and holes, and allow for band-edge energetics local to reaction sites that can

drive relevant redox reactions. In my work, new synthetic methods to access unique monodisperse CdSe@CdS tetrapod photocatalysts (TP-PCs) at scale (>1g isolated) and high yield (>95% TP) have been developed, allowing precise control over energetics (Type-I versus quasi-Type-II heterojunctions) by CdSe seed size control. These materials are of interest to energy and fuel applications due to large absorption cross sections (from four W-CdS “arms”), inherent self-assembly, and the presence of a central, hole-localizing CdSe seed. Ultrafast spectroscopic studies on these materials have confirmed control over energetics (Type-I vs. quasi-Type-II heterojunctions), which are vital to planned catalysis experiments. New measurement science approaches for the characterization of in-situ band-edge energies of these materials have been developed, enabling unique quantification of efficiency robbing trap states, and study of their mitigation through surface passivation. Synthetically challenging asymmetric functionalization of these TP-PCs with a single noble metal tip at the end of one of four arms has been achieved, driving vectorial separation of photoexcited electrons. In the proposed oral-presentation, these efforts will be discussed, along with ongoing efforts to efficiently extract surface local holes at the TP arm vertices via novel interface engineering, and the use of hydrogen/oxygen evolution experiments to quantitatively probe the effects of these structural modifications on photoinduced charge separation, towards the design of an optimized overall water splitting catalyst.

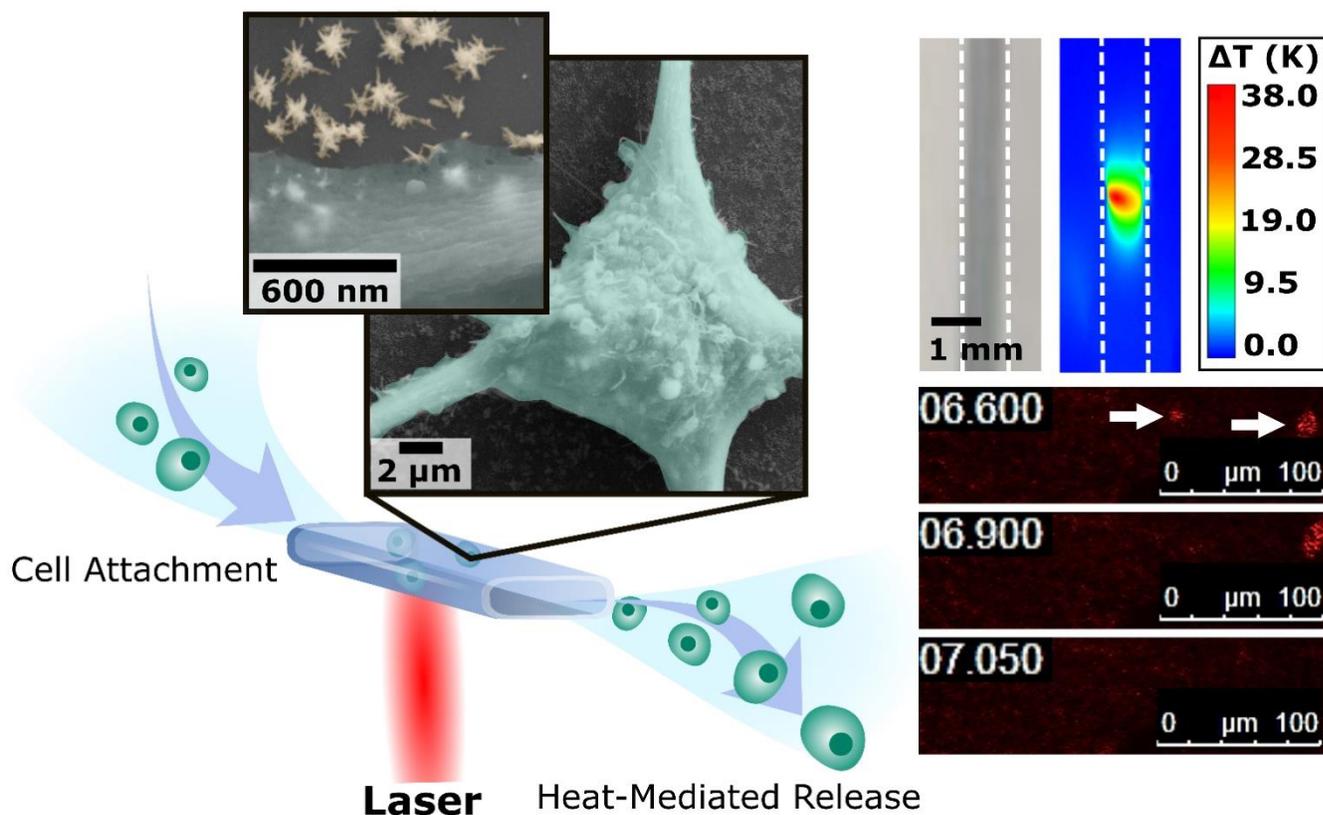
COLL 102

Soft-release of captured cells via plasmonic gold nanostars

Gail Vinnacombe¹, vinnacombe@chem.ucla.edu, **Naihao Chiang**¹, **Liv Heidenreich**¹, **Yuan Hu**², **Isaura Frost**¹, **Yao Gong**¹, **Derek Inouye**¹, **Timothy Fisher**², **Leonardo Scarabelli**¹, **Paul S. Weiss**^{4,1}, **Steven J. Jonas**^{3,5}. (1) *Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California, United States* (2) *Samueli School of Engineering, University of California, Los Angeles, Los Angeles, California, United States* (3) *Eli & Edythe Broad Center of Regenerative Medicine and Stem Cell Research, University of California, Los Angeles, Los Angeles, California, United States* (4) *California Nanosystems Institute, University of California, Los Angeles, Los Angeles, California, United States* (5) *Children's Discovery and Innovation Institute, University of California, Los Angeles, Los Angeles, California, United States*

Gold nanostars (AuNSTs) are ideal for integration with microfluidic technologies targeting biological applications due to their shape, high surface area, extinction in the near-infrared, and biocompatibility. We have developed a robust and simple microfluidic method for the direct growth of anisotropic AuNSTs on the internal walls of glass microcapillaries with high surface density and uniformity. The synthesis was optimized to yield AuNSTs with high anisotropy and surface area for optimal light-to-heat conversion upon laser irradiation. The temperature generated within a AuNST-modified microfluidic capillary was measured at variable laser power and in “flow” and “no-flow” conditions, where we found that heat generation is more localized under flow conditions and can be further controlled with varying laser power. Additionally, we performed simultaneous measurement of capillary temperature and surface-enhanced Raman

spectroscopy (SERS) of molecules bound to the AuNSTs, which enabled correlation of macroscale heating with the nanoscale environment. Finally, the capability of the platform for controlled localized heating was used to explore hyperthermia-assisted detachment of cells adhered to the capillary walls. Ultimately, the primary goal of this work will be to apply these devices for cell-sorting applications, such as cancer cell isolation from blood.



COLL 103

Colloidal ReO_3 nanocrystals: Extra rhenium d-electron instigating a plasmonic response

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In this presentation, we will describe a solution based synthesis of nanocrystals (NCs) of rhenium (VI) oxide (ReO_3) which exhibit localized surface plasmon resonance (LSPR) typical of metals and/or degenerately doped semiconductors. Metal oxides are

often semiconductors with moderate to wide band gaps and one way of introducing charge carriers is through extensive doping. However, the presence of an extra d-electron in the outer electron shell of the rhenium (VI) ion leads to partial filling of the conduction band and manifests in its characteristic metallic conductivity and optical properties. The colloidal synthesis of these NCs follow an ether based reduction of a Re(VII) precursor to the Re(VI) oxide, different from the usual lysis of the metal alkylcarboxylate precursor by a nucleophile like water, alkylamines or alkyl alcohols. The primary reason for this departure is the availability of a range of oxidation states for Re (+2 to +7) and a careful control of this was necessary to obtain the NCs of interest, coupled with unavailability of suitable Re(VI) precursors. The as-prepared NCs exhibit an LSPR optical response in the visible-near-infrared region which imparts an intense blue-green coloration to their solutions. The as-prepared NCs were surface terminated by hydroxyl moieties with additional stabilization in nonpolar solvents offered by L-type coordination by dioctyl ether molecules. The facile removal of the L-type ligands simply by washing with polar solvents enables ease of switching between solvents of choice for transferring these NCs to various substrates. The metallic nature of these NCs was further confirmed by Hall effect measurements on their films. Owing to the visible range LSPR, these metallic ReO₃ NC films can serve as excellent surface enhanced Raman scattering (SERS) sensing substrates as demonstrated for rhodamine 6G as the probe molecule. Further, these NC films could undergo reversible phase transformation under electrochemical Li-cycling with concomitant changes in the optical response, as demonstrated by spectroelectrochemical measurements.

COLL 104

Dielectric environment effects on doping efficiency in PbSe nanostructures

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Doping, as a central strategy to control over free carrier type and concentration in semiconductor materials, suffers from the low efficiency at the nanoscale. Especially in systems with high permittivity and large Bohr radii such as lead chalcogenide nanostructures, the doping efficiency is extremely low (~1%). One of the possible cause is the significant dielectric constant (ϵ) mismatch between the nanostructure and its surrounding media. We study the dielectric confinement effect on the doping efficiency of Pb, In and Se in lead chalcogenide nanostructures, utilizing the platform of PbSe nanowire field effect transistors (FETs). By increasing the ϵ of the surrounding medium, the free carrier concentration and the calculated doping efficiency for n-type (Pb/In) and p-type (Se) dopants increases with a given number of dopants. Ultimately, the doping efficiency can be enhanced by >10 fold with barely any dielectric confinement. Mathematically, a modified *Delerue's* equation is applied to describe the doping efficiency in PbSe NWs with different dielectric environments, which agrees with our experimental data both from NW arrays and single NW devices. Through single NW

FET's temperature dependent characteristics, we further extract ionization energy of Pb in PbSe NW, consistent with the theoretical calculation.

COLL 105

Gelation of plasmonic metal oxide nanocrystals by polymer-induced depletion attractions

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Gelation of colloidal nanocrystals emerged as a strategy to preserve inherent nanoscale properties in multiscale architectures. However, available gelation methods to directly form self-supported nanocrystal networks struggle to reliably control nanoscale optical phenomena such as photoluminescence and localized surface plasmon resonance (LSPR) across nanocrystal systems due to processing variabilities. Here, we report on an alternative gelation method based on physical internanocrystal interactions: short-range depletion attractions balanced by long-range electrostatic repulsions. The latter are established by removing the native organic ligands that passivate tin-doped indium oxide (ITO) nanocrystals while the former are introduced by mixing with small polyethylene glycol (PEG) chains. As we incorporate increasing concentrations of PEG, we observe a reentrant phase behavior featuring two favorable gelation windows; the first arises from bridging effects while the second is attributed to depletion attractions according to phase behavior predicted by our unified theoretical model. Our assembled nanocrystals remain discrete within the gel network, based on X-ray scattering and high-resolution transmission electron microscopy. The infrared optical response of the gels is reflective of both the nanocrystal building blocks and the network architecture, being characteristic of ITO nanocrystals' LSPR with coupling interactions between neighboring nanocrystals.



COLL 106

***In vivo* nucleic acid delivery systems for therapeutic targeting of multiple myeloma-microenvironment interactions**

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Multiple Myeloma (MM) is an incurable hematologic cancer characterized by the accumulation of abnormal plasma cells within bone marrow. We and others have shown that the bone marrow niche itself, specifically bone marrow endothelial cells (BMECs), provides the “soil” supportive of MM cell (the “seeds”) homing, colonization, and proliferation in marrow. Specifically, extracellular cyclophilin A (CyPA) secreted by BMECs promotes signaling changes in MM including enhanced expression of CD147, the receptor of CyPA, which enhances proliferation and homing of MM cells. Thus, inhibition of CyPA secretion from BMECs provides a potential therapeutic strategy via disrupting physical interactions between MM and the bone marrow niche. Herein, we have developed the first controlled release technology to deliver nucleic acids to the bone marrow microenvironment *in vivo*, as a paradigm-shifting MM therapy which disrupts interactions between MM and the marrow niche. We engineered novel lipid-polymer hybrid (PLH) gene delivery materials consisting of dendrimers conjugated to

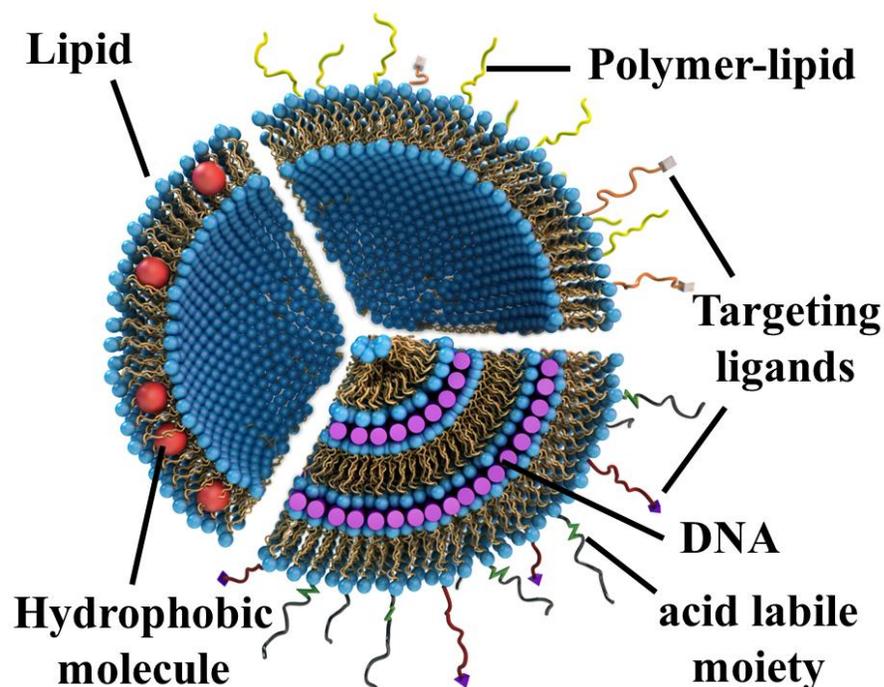
epoxide-terminated lipids. These materials, in combination with polyethylene glycol (PEG)-lipid conjugates and siRNA, assembled into NPs via microfluidic mixing. Through screening of a small library of materials we identified a NP formulation that induces potent gene silencing (~80%) of a target BMEC gene (Tie2) in bone marrow *in vivo*. NPs induced rapid RNA uptake in BMECs *in vivo* within 30 min, demonstrated using multiphoton intravital imaging of mouse BM. Cell populations targeted were primarily BMECs, with minimal RNA uptake in immune cells that reside in BM, identified using flow cytometry. We then screened a library of CyPA siRNAs *in vitro*, and identified a CyPA siRNA candidate that induced potent CyPA gene knockdown (~90%) at low dosages (10 nM) in BMECs *in vitro*. To assess if NP siCyPA treatment can be exploited therapeutically in animal models of MM, mice were treated with siCyPA NPs once per week (dose: 1.0 mg/kg). Strikingly, treatment of mice with NPs silencing CyPA largely reduced progression of MM in mice *in vivo*. Collectively, we have developed the first nucleic acid delivery technologies to therapeutically target MM and its interactions with the bone marrow niche *in vivo*. We envision that our microenvironment-targeted approach can be combined with chemo- and immunotherapies used in the clinic.

COLL 107

Functionalized cationic lipid systems for the delivery of nucleic acid and small molecule therapeutics

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Liposomes are the most widely studied synthetic carriers worldwide for nucleic acid (NA) and drug delivery applications. Cationic liposomes (CLs), in particular, are relatively safe vectors used in ongoing clinical trials. We present ongoing efforts to study and optimize surface-functionalized PEGylated CL–DNA nanoparticles (NPs), including novel approaches to overcome the key barrier of endosomal escape and fluorescence microscopy colocalization with members of the Rab family of GTPases, which has revealed NP pathways and interactions with cells. NP surface functionalization, achieved through custom synthesis, is intended to overcome cell targeting and internalization barriers to delivery faced by NPs designed for *in vivo* applications. We will further discuss recent studies of CL-based NP carriers of paclitaxel. Paclitaxel is an important hydrophobic cancer drug but its poor water solubility poses challenging formulation problems that have not been adequately solved. Our work seeks to establish a mechanistic understanding of the relation between structure and physicochemical properties of the NP and PTXL delivery efficacy, leading to optimized cytotoxicity against human cancer cells.



COLL 108

Machine-learning approach for *in silico* prediction of lipid-based nanoparticles self-assembly

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The self-assembly of lipid-based nanoparticles is a complex process, which is influenced by a number of system-related variables.

In this work, we carried out a systematic *in silico* study to investigate the influence of different parameters (size of the system, relative ratio of the components, nature of the lipids, etc.) on the outcome of the self-assembly process using coarse-grain molecular dynamics simulations. We evaluated 30 lipids belonging to 5 different families, with variability on charge, nature of polar head, length and insaturation of the hydrophobic tail, etc. The results were converted into a machine-readable format and evaluated using different machine learning algorithms for the ability to develop robust predictive models. The strengths and the limitations of each model will be highlighted, as well as their potential applications in modeling the drug delivery process.

COLL 109

Development of gene therapies with novel tropisms by high-throughput *in vivo* screening of lipid nanoparticles

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RNA- and DNA-based drugs can specifically turn any gene on or off. However, whether the drug is made out of siRNA, mRNA, Zinc Finger Nucleases, CRISPR, or others types of DNA / RNA, all genetic drugs are limited by one universal problem: drug delivery. When injected, DNA and RNA drugs tend to accumulate in the liver. Non-liver delivery remains a significant problem. Engineers and chemists have designed thousands of chemically distinct nanoparticles to deliver these drugs to target tissues. After synthesizing these chemically diverse nanoparticle ‘libraries’, the nanoparticles are typically screened *in vitro*. However, *in vitro* conditions typically lack an immune system, kidney, spleen, pulsatile blood flow, and other factors that affect the nanoparticle *in vivo*. For example, we recently compared how 400 different nanoparticles delivered genetic drugs *in vitro* and *in vivo*; we found no correlation.

We therefore reasoned that a method to rapidly screen thousands of nanoparticles directly *in vivo* would allow us to rapidly and efficiently discover nanoparticles with novel tropisms. To this end, we developed a series of increasingly advanced DNA barcoded nanoparticle systems. Here we report three such systems that can (1) measure hundreds *in vivo* nanoparticle biodistribution with 100,000,000x more sensitivity than fluorescence, (2) quantify how hundreds of nanoparticles functionally deliver mRNA to dozens of cell types in a single mouse, or (3) quantify how hundreds of nanoparticles functionally deliver siRNA to dozens of cell types in a single mouse.

Finally, we describe a bioinformatics pipeline to iteratively use these large datasets in order to ‘evolve’ LNPs with new tropisms. Using these new assays and new analytical pipeline, we have identified LNPs that deliver different many types of therapeutic RNAs to new cell types *in vivo*.

COLL 110

Tailoring HDL mimetics for *in vivo* delivery of mRNA

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Recent advances in the development and optimization of nucleic acid-based therapeutics utilizing messenger RNA (mRNA) successfully harness the body’s own cells to produce and deliver therapeutic protein molecules. As mRNA molecules are inherently unstable and difficult to deliver *in vivo* due to their physicochemical properties, current efforts in realizing the full potential of this technology have been focused on enhancing the *in vivo* delivery and *in situ* protein expression. We have successfully engineered reconstituted high-density lipoproteins (termed nanolipoprotein particles, NLPs) to deliver self-amplifying mRNA constructs *in vivo*. These discoidal, nanometer-sized particles are an attractive delivery system as they are safe, non-

immunogenic, and amenable to multiple routes of delivery. Also, their size and surface chemistry are readily tailored, enabling facile optimization of the delivery system's physicochemical properties. NLPs have been successfully used as *in vivo* delivery platforms for vaccine applications, whereby adjuvant and subunit antigen components elicit superior *in vivo* effects when co-localized and delivered on the NLP platform. To tailor NLPs for *in vivo* delivery of large nucleic acids molecules, a panel of NLPs formulated with a wide range of cationic lipids, apolipoproteins, and assembly constituents were screened. Cationic NLPs successfully complexed with RNA Replicons encoding luciferase, provided measurable protection from RNase degradation, and enhanced mRNA *in vivo* expression efficiency. The NLP complexation of the mRNA and *in vivo* transfection efficiency were further enhanced by modulating the type and percentage of cationic lipid, the ratio of cationic NLP to replicon, and by incorporating additive molecules. Our current interests are to elucidate the correlation of NLP composition, NLP-RNA structure, and *in vivo* efficacy to allow the rational design of a highly potent *in vivo* delivery platform that can be used as a universal mRNA delivery technology.

COLL 111

RNAi therapeutics delivered

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Synthetic small interfering RNAs (siRNAs) are potent inhibitors of gene expression; these agents act through the natural RNA interference (RNAi) pathway. Although much hope and speculation regarding the therapeutic potential of RNAi began soon after the discovery of the pathway there have been challenges in realizing this potential, most related to difficulties in efficient delivery into the cells of specific organs or tissues. To deliver siRNAs into liver hepatocytes, we have developed a three-pronged approach with the goals of enabling delivery to hepatocytes after both intravenous and subcutaneous administration. These methods include chemical modification of siRNAs, lipid nanoparticle (LNP) formulation of siRNAs, and multivalent *N*-acetylgalactosamine (GalNAc) conjugation of siRNAs. The LNP strategy with a partially chemically modified siRNA resulted in the first RNAi therapeutic approved by the US FDA in 2018. This drug, ONPATTRO[®], is used to treat polyneuropathy in patients with hereditary ATTR amyloidosis. The approval of ONPATTRO[®] paves the way for a whole new class of RNA-based medicines. Several GalNAc-conjugated siRNAs are currently performing well with promising outcome in the ongoing advanced clinical trials.

COLL 112

Low temperature selective oxidation of methane using unsupported gold-palladium colloidal catalysts

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Methane is the main component of natural gas and a by-product from oil refining and chemical processing. It is therefore desirable that novel technologies and infrastructure are developed to convert methane into value-added chemicals. Direct conversion to oxygenated products is highly desirable but challenging owing to its chemistry.

Currently, primary utilization of methane takes place via indirect routes involving production of synthesis gas which is highly energy intensive. Direct conversion to methanol at low temperatures is an atom-efficient method for utilization.

One strategy for catalyst design involves spatial separation of the oxidation reaction and the active-site regeneration, thus closing the catalytic cycle. However, this requires use of preformed reactive oxygen species, with many systems requiring highly acidic media like Periana catalyst which uses sulfuric acid for oxidation. Conceptually similar is the use of zeolite catalyst with hydrogen peroxide as oxidant. Hydrogen Peroxide can also be synthesised *in situ*, hence creating a catalytic system for methane oxidation. Gold-Palladium catalysts have been shown to be highly effective for the direct synthesis of hydrogen peroxide. It has been shown that supported AuPd and AuPdCu catalyse the low temperature oxidation of methane in liquid phase.

In this work, gold-palladium colloidal catalysts are shown to be active for the oxidation of methane in water at 50°C using hydrogen peroxide as the oxidant. Activity and selectivity of these nanoparticles are compared with those of supported catalysts prepared by sol-immobilization. The effect of supporting the nanoparticles is investigated, specifically its effect on peroxide decomposition. EPR studies show that these reactions proceed via a radical mechanism. These colloidal catalysts involve use of a stabilizing ligand, which afford a greater particle size control with narrow particle size distribution (2-5 nm). The reaction is shown to be highly selective towards the primary oxygenated products namely methyl hydroperoxide, methanol and formic acid, with highest selectivity towards methyl hydroperoxide. Over-oxidation leads to formation of carbon dioxide. With time on line studies and optimization of the reaction conditions, primary oxygenate selectivity of *ca.* 90% can be achieved. Catalyst preparation, characterization and effect of reaction conditions will be discussed.

COLL 113

Probing surface sites on metal/alloy nanocatalysts in gas-phase catalytic oxidation reactions

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Engineering metals and alloys at the nanoscale constitutes an increasingly-important pathway for the design of catalysts in a wide range of catalytic reactions. A key challenge is the ability to control and tune the surface catalytic sites. This presentation describes recent findings in probing the surface sites of metal and alloy nanoparticles in catalytic oxidation reactions of different molecules in the gas phase (e.g., CO, propane, toluene, etc.). In-situ techniques such as diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and in-situ synchrotron high-energy XRD coupled to pair distribution function (HEXRD/PDF) analysis, were employed to probe the atomic-scale surface sites and phase properties of noble metal and low-noble-metal content alloy nanoparticles on different metal oxide supports in the catalytic reactions. The catalytic properties depend strongly on the nano-engineering parameters. Implications for the design and preparation of active and robust nanocatalysts for sustainable energy and clean environmental reactions will also be discussed.

COLL 114

Designing oxide-based nanomaterials for energy applications

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Recently we have focused on the architecture engineering of oxide-based nanomaterials for their applications to lithium ion battery, fuel cell electrocatalysis, and photocatalysis. We reported the first demonstration of galvanic replacement reactions in metal oxide nanocrystals, and synthesized hollow nanocrystals of various multimetallic oxides including $\text{Mn}_3\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$.¹ We report a simple synthetic method of carbon-based hybrid cellular nanosheets loaded with SnO_2 nanoparticles.² These oxide-based nanomaterials exhibited very high specific capacity and good cyclability for lithium ion battery anodes. We designed hollow anatase TiO_2 nanostructures composed of interconnected ~5 nm-sized nanocrystals, which individually reach the theoretical lithium storage limit and maintain a stable capacity during prolonged cycling.³

We present a synthesis of highly durable and active electrocatalysts based on ordered fct-PtFe nanoparticles and FeP nanoparticles coated with N-doped carbon shell.^{4,5} We designed and synthesized highly active and stable Fe-N-C catalyst for oxygen reduction reaction.⁶

We report on the designed synthesis of highly active TiO_2 photocatalysts incorporated with single copper atoms (Cu/TiO_2) that exhibit reversible and cooperative photoactivation process, and enhanced photocatalytic hydrogen generation activity.

COLL 115

Structure-function properties of electrocatalysts at nanoscale

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Electrochemical devices such as fuel cells, electrolyzers and batteries rely on processes that need to provide satisfactory energy density in order to be used in applications for transportation; however, a major challenge lies in the insufficient activity and durability of materials that are currently employed in real world applications. These limitations inevitably lead to a lower operating efficiency of the devices, which highlights the need for development of more active and durable materials. Consequently, the majority of research efforts are placed on the materials design and synthesis aiming to improve their efficiency. It has been found that properties such as surface structure, surface and subsurface composition are determining electronic properties and have distinguished roles in defining the functional properties of these materials. The *material-by-design-approach*, would be used here as an example to emphasize the transfer of the knowledge obtained from the well-defined systems towards tailor-made real-world catalysts at nanoscale. Special emphasis will be placed on utilization of multimetallic systems that could provide additional benefits by bringing together highly diverse constituents to alter and tune both catalytic activity and durability.

COLL 116

Nanoparticles for oxygen in heterogeneous catalysis and electrocatalysis

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Modern processes for chemical transformations rely heavily on the catalysts made of nanoparticles. Many of these transformations involve oxygen species, which are of particular importance in chemical, petrochemical and energy industries, ranging from chemical production, such as epoxidation and automobile exhaust treatment, to the electrocatalysts for fuel cells and metal-air batteries. In this presentation, I will focus on the design of surface structures of metal nanoparticles (Pt, Cu, and their alloys) for catalytic reduction of oxygen both thermally and electrocatalytically. I will also discuss cases for the development of ternary oxygen evolution reaction catalysts, such as pyrochlores ($A_2B_2O_7$). Local structure-catalytic property relationship will be discussed. The conditions that favor the dynamic control of surface compositions will be presented and their important contributions to the optimal catalytic activity and selectivity will be analyzed under the reactive conditions. Our results point to the direction that both thermodynamic and kinetic factors need to be taken into consideration in the design of high-performance catalysts.

COLL 117

Plasmonic circular dichroism of Janus nanoparticle emulsions

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Chiral nanostructures have been attracting extensive interest in recent years primarily because of the unique materials properties that can be exploited for diverse applications. Recently, we show that gold Janus nanoparticles, with hexanethiolates and 3-mercapto-1,2-propanediol segregated on the two hemispheres of the metal cores (dia. 2.7 ± 0.4 nm), could self-assemble into emulsion-like, hollow nanostructures in both water or organic media, and exhibited apparent plasmonic circular dichroism (PCD) absorption in the visible range. This was in contrast to individual Janus nanoparticles, bulk-exchange nanoparticles where the two ligands were homogeneously mixed on the nanoparticle surface, or nanoparticles capped with only one kind of the ligands. The PCD signals were found to become intensified with increasing coverage of the 3-mercapto-1,2-propanediol ligands on the nanoparticle surface. This was accounted for by the dipolar property of the structurally asymmetrical Janus nanoparticles, and theoretical simulations based on first principles calculations showed that when the nanoparticle dipoles self-assembled onto the surface of a hollow sphere, a vortex was formed which gave rise to the unique chiral characteristics. The resulting chiral nanoparticle emulsions could be exploited for the separation of optical enantiomers, as manifested in the selective identification and separation of D-alanine from the L-isomer, as well as directional functionalization of the nanoparticles that may endow the individual nanoparticles with select chirality.

COLL 118

To pNP or not to pNP? Broader scope study of nitrophenol reduction with noble metal nanoparticles

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In addition to the broad environmental implications associated with the removal of toxic nitroaromatics from industrial effluent, their catalytic reduction, and particularly that of paranitrophenol (**pNP**) has emerged as a benchmark model for quantifying catalytic activity of metal nanoparticles. This process is either the main focus, or a component of hundreds of scientific studies/publications in the field of heterogeneous catalysis every year. Here we present a series of noble metal nanoparticles immobilized on amorphous carbon (**Au@C**, **Ag@C**, **Pt@C** and **Pd@C**). All materials show competitive catalytic activity over **pNP**, amino-substituted nitrophenols (**ANPs**) and azo dyes. However, by testing all materials synthesized over a broader substrate scope (more than just the common **pNP**) with added functionalities reveals inconsistencies in the prognosticating ability of the ubiquitous **pNP** model reaction. This begs the question, are we missing out on potentially superior catalysts by relying on this oversimplified protocol? By incorporating variably substituted **ANPs** into the substrate scope and averaging performance, the resulting rank of catalyst activity more accurately reflects activity

trends when applied to other reducible functionalities, such as -N=N- groups in azo dyes.

COLL 119

Controlling acid diffusion rate into gold nano-particle doped silica-based sol-gel material

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The silica-based sol-gel materials were prepared with various gold nano-particles ranging from 5 nm to 100 nm in diameter. Due to degradation of gold colloidal particles under strong acidic condition, the interaction of gold nano-particles with an acid could be monitored by a drastic red shift of SPR (Surface Plasmon Resonance) band. The rate of shift was converted to the diffusion rate of acid. The effect of the diffusion rate of aqueous acid solution was examined as a function of sizes of encapsulated gold nano-colloidal particles. The analytical fit concluded that the maximum rate was found at 15 nm of gold colloid. On the other hand, 60 nm gold colloid was expected to almost stop the acid diffusion. It was speculated that the surface of these gold colloids was homogeneously surrounded by the silica gel homogeneous layer, resulting in avoiding direct interaction with the acid and the surface of gold colloid. The size of 60 nm was estimated to be a close match of the average size of the cavity, which homogeneously covers the surface of the gold colloidal surface.

COLL 120

Friction on graphite in the presence of adsorbates: Physical and chemical effects on the basal plane and at step edge defects

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Water and other adsorbates present at sliding interfaces affect friction measured across a range of length scales. This effect is particularly significant at the nanoscale, where friction can vary by orders of magnitude depending on the environment. Frictional variation is due to both chemical and physical effects, since adsorbates can physically change the size and morphology of the contact interface as well as chemically interact with the contacting bodies to alter how they slide relative to one another. The presence of adsorbates is particularly evident at surface defects on layered materials, such as step edges on graphite, where friction can increase dramatically relative to the superlubricity observed on a basal plane. Here, we use reactive molecular dynamics simulations to study how water and other adsorbates affect atomic-scale friction on both the basal plane of graphite as well as at the ubiquitous step edges. The simulations capture termination of the step edge and probe as well as chemical reactions and interactions that occur during sliding, which then enables us to isolate the physical and chemical factors that determine friction.

COLL 121

Experiments and simulations of the humidity dependence of friction: Role of interfacial contact quality

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Water can have a strong effect on friction and adhesion. In this talk, we explore the nanoscale origins of this effect. First, we will review prior literature using atomic force microscopy (AFM) to study these nanoscale effects. We observe that condensed water changes friction between silica surfaces from a naturally velocity-strengthening behavior (friction increasing with sliding speed) to velocity-weakening behavior. We will then discuss new results using AFM and Grand Canonical Monte Carlo atomistic simulations to study a tetrahedral amorphous carbon (ta-C) probe sliding against highly oriented pyrolytic graphite (HOPG) at relative humidities ranging from <1% to near saturation. Friction varies with humidity in a non-monotonic manner such that water acts as a lubricant only above a threshold humidity; below that threshold, water increases friction substantially relative to dry sliding. A non-monotonic dependence of adhesion and friction on humidity for single asperity interfaces has previously been attributed to the humidity-dependent properties of the water meniscus that forms at the contact. Here we show that the non-monotonic friction behavior is explained by the quality of the contact between the water and the substrate and tip, quantified by the number of water molecules in the interface and their registry with the HOPG surface atoms. Furthermore, hysteresis in how friction varies with humidity is explained by the larger energy barrier for surface desorption of water molecules compared to adsorption.

COLL 122

Friction and mechanochemical reactivity of 2D nanomaterials

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Control of friction and wear is a ubiquitous challenge in numerous machined interfaces ranging from biomedical implants, to engines, to nano- and micro-scaled electromechanical systems (MEMS) devices. Central to developing boundary lubrication schemes for such applications is how to reduce wear at the rough surfaces of such surfaces, where nanoscaled asperities dominate the interfacial contacts that can lead to wear. The robust mechanical properties and general chemical inertness of two-dimensional (2D) nanomaterials, such as graphene and MoS₂, has made them of interest as friction modifiers. While single layer graphene and MoS₂ can readily adapt to surface structure on the atomic scale, when deposited on substrates with nanoscopic roughness of ~ 10 nm rms (as is common in many machined interfaces) a conformal coating generally cannot be fully formed, due to competition between adhesion to the

substrate nanoscopic asperities and the bending rigidity of the material. This often leaves a mixture of supported and unsupported regions which respond differently to applied load, with spatial variations in mechanical properties and chemical bonding. Increased strain in these materials on rough surfaces has also been seen to increase their chemical reactivity. Here, we describe a combination of AFM nanomechanical, confocal Raman microspectroscopic and near field IR scattering studies of graphene and MoS₂ on silica surfaces with controlled nanoscopic roughness, to examine how this impacts their frictional properties, and alters their electronic properties and chemical reactivity, where strain dependent reactions can be driven by applied forces. Studies of MoS₂ on metal surfaces, such as Au(111) will also be described, where even within single layer MoS₂, varying phases of the MoS₂ are found to occur.

COLL 123

Lubricated friction at surface nano-defects

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The lubrication properties of nano-confined liquids control many natural and industrial processes. The diffusion of molecules and ions at interfaces, the functioning of our joints, and the efficiency of engines all hinge on the behaviour of a nano-confined lubricant. It is estimated that 25% of the energy consumed worldwide is lost to friction leaving significant scope for improvement.

Part of the problem comes from our lack of understanding of lubricated friction at molecular level, especially near surface singularities such as chemical and topographical defects.

Here, we use Atomic Force Microscopy to build a functional picture of two model lubricated systems down from single molecule details and up to molecular group effects (~100 nm). In aqueous systems, we show that the hydrogen bond network created by nanoconfined water at the interface with solids induces a glassy-like behaviour that dominates lubrication. Single metal ions act as lubricants by reducing the elasticity of the nano-confined liquid and the magnitude of the hydrodynamic friction. The measured friction force can be quantitatively described by a thermally activated process whereby the moving ions break the hydrogen bonds with surrounding water. This picture breaks down at high salt concentrations due to ion-ion interaction and jamming effects. In contrast, organic lubricants, such as squalane, affect lubrication in an indirect manner, through their conformational relaxation dynamics. This in turn depends on the proximity of local surface singularities.

The experimental results, complemented by molecular dynamics simulations, offer a molecular-level basis for the understanding of tribological problems on multiple spatial scales.

COLL 124

Mechanisms underlying lubrication of faults

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The friction between two adjacent tectonic plates under shear loading may dictate seismic activities. To advance the understanding of the mechanisms underlying the frictional strength of fault rocks, we investigate the frictional characteristics of calcite in aqueous environment. Our friction-force measurements on single-asperity contacts at the nanoscale have revealed a prominent decrease in friction at sufficiently high loads and slow sliding velocities. This is a direct result of the significant reactivity of calcite in an aqueous medium under high pressure, a phenomenon called pressure-solution facilitated slip. During pressure solution, the dissolved mineral and water at the contact act as a very effective aqueous lubricant, which leads to a significant reduction of the coefficient of friction. We also have extended these studies to investigate the effects of the brine composition over a wide range of geologically relevant concentrations. The fluid chemistry is shown to play a critical role in the frictional response of calcite due to the ion-specific and pH-sensitive reactivity of carbonate rocks, but the results also depend on the applied stress.

In addition to this, we have investigated the effect of the fluid composition on both the pressure solution and the frictional response of multi-asperity calcite contacts to account for the effect of contact aging. For that purpose, we have extended our surface forces apparatus to measure the deformation of calcite plates of micrometer thickness (to quantify the dissolution rate) while friction is concurrently measured. The findings of these studies are combined and their contribution to the understanding of mechanisms underlying the frictional strength of calcite in presence of aqueous solutions is discussed. Furthermore, the results of this nanoscale study are extrapolated to the carbonate of carbonate faults in the presence of a reactive fluid and they contribute to advance the fundamental knowledge of induced seismicity at geological scale.

COLL 125

Energy barriers and the temperature-dependent friction of MoS₂

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A model for the temperature-dependence of the friction in MoS₂ has been developed which relies upon the heights of energy barriers to characterize the molecular pathways of MoS₂-flake sliding. Here we present atomistic calculations that show changes to these barriers in the presence of water and oxygen, two major environmental contaminants affecting the friction.

COLL 126

Probing and understanding elementary steps in tribochemical reactions

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The discipline of tribology investigates the effects of mechanical forces during sliding, including energy dissipation, wear, and chemical reactions. The effect of applied stress on the rates of mechano- or tribochemical reactions is described using the Bell model where the stress-induced reaction rate varies as $\exp(\sigma\Delta V^\ddagger/k_B T)$, where σ is the applied stress, k_B is the Boltzmann constant, T the absolute temperature and ΔV^\ddagger is a proportionality constant known as the activation volume and the meaning of the activation volume is not well understood. However, obtaining a detailed molecular understanding of the way in which an external force modifies reaction rates requires knowing the elementary steps for a simple model reaction pathway.

Strategies for measuring reaction pathways and their kinetics are illustrated using a model tribochemical reaction consisting of the gas-phase lubrication of copper by dimethyl disulfide. Two stress-activated elementary-step reactions are identified. The first is the tribochemical decomposition of adsorbed methyl thiolate species, that form rapidly by dimethyl disulfide reacting with copper, to form gas-phase hydrocarbons and chemisorbed sulfur. In a second stress-induced reaction, surface sulfur is transported into the subsurface region of the copper. This process causes an increase in oxidation state of copper, and the creation of vacant surface sites that allows the tribochemical reaction cycle to continue.

The mechanism of shear-induced methyl thiolate decomposition is investigated theoretically using first-principles quantum calculations to obtain an estimate of the value of the activation volume. The results are compared with those for the rate of stress-induced decomposition of methyl thiolate species on a Cu(100) single crystal substrate measured by atomic force microscopy in ultrahigh vacuum.

COLL 127

Ambient-pressure friction force microscopy studies on ultrananocrystalline diamond films: Effect of environment on nanoscale friction

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We report the effect of the atmosphere on nanoscale friction of ultrananocrystalline diamond (UNCD) films using ambient-pressure atomic force microscopy (AP-AFM). The UNCD films were prepared using the microwave-assisted chemical vapor deposition (CVD) method with a mixture of argon and hydrogen gas. The UNCD films exhibit excellent mechanical hardness and a low coefficient of friction similar to single-crystal diamond. To investigate the effect of the environment, various kinds of gases (e.g., O₂, N₂ and H₂O) were dosed via a gas manifold to the AFM chamber. The operation

pressure of the AFM chamber ranged from 1×10^{-9} mbar to one atmosphere. We observed that the oxygen gas resulted in an increase in the friction force. We carried out ambient-pressure X-ray photoelectron spectroscopy to check the effect of oxygen on the chemical states of the UNCD. In the C 1s spectrum, we found that the UNCD was oxidized by 200 mTorr of oxygen. Additionally, the frictional behavior when under oxygen showed reversibility after evacuation. While oxygen was responsible for friction enhancement, nitrogen did not affect the tribological properties (e.g., friction and adhesion). Furthermore, we found that water vapor reduced the friction of the UNCD films. Dissociated water molecules passivate diamond materials acting as a lubricant and friction decreased because of passivation. Friction measurements at various gas conditions would help increase the fundamental understanding of the role of the atmosphere on atomic-scale friction and adhesion.

COLL 128

Heterodimer assembly from *de novo* repeat protein structures

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Highly specific and orthogonal oligomers have broad applications in synthetic biology. In stark contrast to DNA origami, a protein-based molecular toolkit that enables LEGO-style molecular assembly remains elusive. Helical fragments that twist into coiled-coils have been the workhorse for decades, and recent advances in protein design have facilitated the creation of new helical bundles with unprecedented specificity and stability. Nonetheless, the monomeric components based on coiled-coils often cannot be expressed in isolation, which greatly limits their application. As an alternative, we investigate the utility of repeat protein structures for heterodimer assembly. By designing stable toroid structures *de novo*, we hope to develop a novel molecular platform that meets the requirements of general molecular assembly.

COLL 129

Functional protein assemblies by chemical design

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Proteins represent the most versatile building blocks available to living organisms or the laboratory scientist for constructing functional materials and molecular devices. Underlying this versatility is an immense structural and chemical heterogeneity that renders the programmable self-assembly of proteins an extremely challenging design task. To circumvent the challenge of designing extensive non-covalent interfaces for controlling protein self-assembly, we have endeavoured to use chemical bonding strategies based on fundamental principles of inorganic and supramolecular chemistry. These strategies have resulted in discrete or infinite, 1-, 2- and 3D protein architectures

that display high structural order over large length scales (yet are dynamic/adaptive and stimuli-responsive) and possess new emergent functional, chemical and physical properties. In this talk, I will present some of the synthetic protein assemblies constructed in our laboratory.

COLL 130

Reconfigurable hybrid colloids: Using solid-binding proteins to control nanoparticle assembly and disassembly

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Solid binding proteins are genetically engineered chimera that incorporate one or more combinatorially-selected solid-binding peptide (SBP) at defined locations of their framework. These macromolecules are powerful tools to study the fundamentals of biotic-abiotic interactions because they allow for SBP presentation within solubilizing and structurally defined contexts. They are also useful to control inorganic morphogenesis and to assemble hybrid architectures that harness the “built-in” function and topology of the host scaffold. The development of solid-binding proteins that support the dynamic reconfiguration of hybrid materials has however proven more challenging. I will describe here how we used a combination of theory, simulations, mutagenesis and experiments to develop a detailed understanding of how a silica-binding peptide called Car9 interacts with silica surfaces, how we exploited this knowledge to build solid-binding proteins that support repeated cycles of silica nanoparticle assembly and disassembly upon small changes of pH, and how we rationally tuned the characteristics of these hybrid aggregates by manipulating solution conditions, particle size, host scaffold identity, and SBP sequence.

COLL 131

Nucleation pathway selection yields morphologically diverse two-dimensional protein crystals at solid-liquid interfaces

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The enormous diversity of functions necessary to sustain living systems has necessitated the evolution of equally expansive catalogs of unique protein architectures, each individually tailored to fulfill a particular role. Though individual polypeptide chains adopt a striking number of well-defined 3D structures, it is their ability to hierarchically self-assemble into multicomponent complexes which considerably broadens the scope and complexity of their structural and functional capabilities, making them desirable

targets for a broad range of applications, including sensing, catalysis, and therapeutics. Clearly, the directed organization of molecular building blocks into synergistic complexes is a powerful tool for fabricating designer materials and nanoscale machines with advanced capabilities. However, general design rules which dictate protein self-assembly across scales remain undetermined, though numerical simulations have furnished predictions based on geometric considerations and relative interaction strengths.

Here we present an experimental realization of such a system. Using *in-situ* atomic force microscopy measurements, we have characterized the surface-templated self-assembly of a square-shaped protein ($^{C98}\text{RhuA}$) at mineral-water interfaces into three distinct crystal morphologies not observed for 2D $^{C98}\text{RhuA}$ crystals grown unsupported in solution, including a metastable phase which only persists under specific solution conditions. Furthermore, we can selectively promote the formation of each specific surface-grown crystal morphology by systematically varying solution concentrations of $^{C98}\text{RhuA}$ and KCl, and find that crystallization can occur through both classical and non-classical growth mechanisms. Finally, we employ a semi-quantitative thermodynamic analysis of protein-protein and protein-surface interactions to delineate the contributions of each interface to the selected pathways and underlying multidimensional crystallization free-energy landscape, experimentally validating the rich crystallization behaviors predicted by theory from a single building block.

COLL 132

Nanomaterials for nervous regeneration

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Peptidic biomaterials have been receiving great interest because of their easiness of scale-up production, absence of pathogen-transfer risk, biomimetic properties, nanostructured morphology and customization potential for each specific tissue engineering application. However, their proper usage requires the understanding of the several phenomena taking place at different scale-levels during self-assembling. In this presentation, focused on the nanotech advancements in the field of nervous regeneration, we will see some multi-disciplinary researches and advances toward the regeneration of nervous tissues. This will bring us from molecular dynamics to cross-linking and electro-spinning of self-assembling peptides, from 3D neural stem cells cultures to *in vivo* testing.

COLL 133

Polymer particles for bio-nano interactions and cancer therapy

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Polymer particles with tunable physicochemical properties (e.g, size, shape, stiffness, and responsiveness) have demonstrated their high potential for targeted drug delivery to improve therapeutic efficacy with reduced side effect.¹ This presentation will focus on the assembly of polymer particles composed of polypeptides or proteins for theranostics. Imaging reagents (e.g., magnetic resonance imaging reagent) and anti-cancer drugs (e.g, cisplatin drug) can be encapsulated into the particles and be delivered to tumors for imaging-guided cancer treatment, where chemotherapy, photothermal and photodynamic therapies are involved to improve the therapeutic efficacy. In addition, stealthy and targeted polymer particles via the mesoporous silica templating method and their interactions with biological barriers for drug delivery will also be presented.² Specifically, polymer particles mainly composed of poly(ethylene glycol) (PEG) result in long circulation time and avoid non-specific accumulation of PEG particles in spleen and liver.³ Surface modification of PEG particles with targeting molecules (e.g., antibody) can improve the specific cell targeting while retaining the stealth property of PEG particles.⁴ Our studies are aimed to obtain detailed knowledge of complex bio-nano interactions and potential application of polymer particles in combined cancer therapy.

COLL 134

Phospholipid self-assembly-based artificial cells

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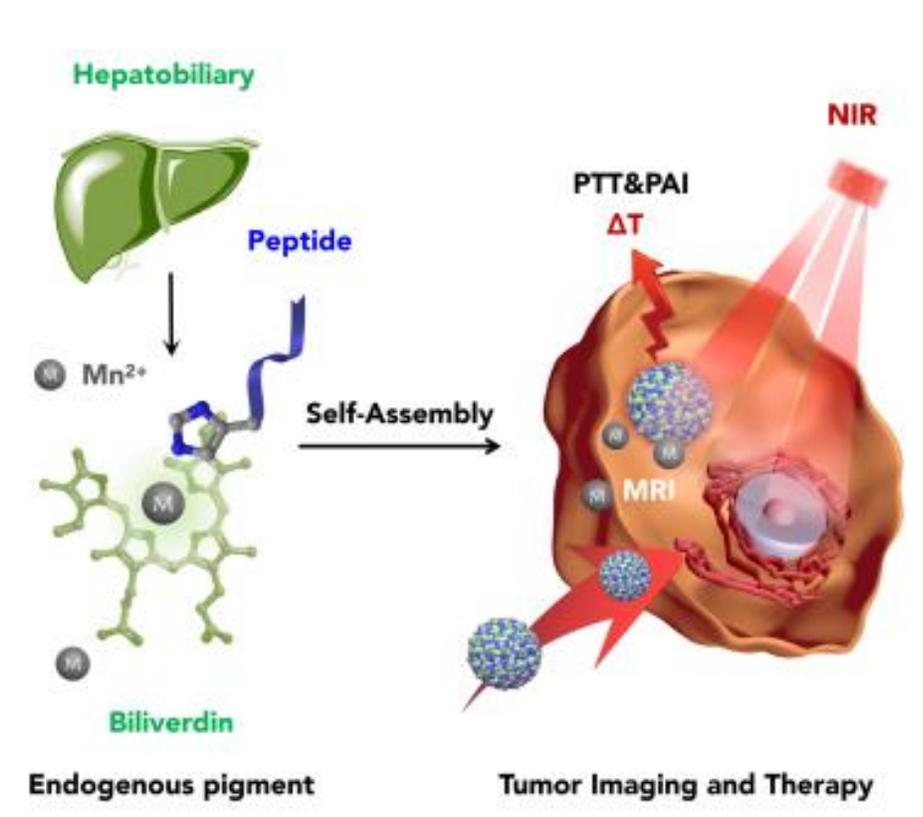
Life begins from cells. Artificial cells, as simplified cell models, can be used to study their structure and function. They also help to establish the link between living and nonliving systems, which provides the theoretical clues for the origin of life. The spherical membrane structures for cell membrane mimick are well studied; however the common membrane morphology in cell is cisternae stacks. They are found in organelles including grana, endoplasmic reticulum, and Golgi apparatus. The grana-like cisternae stacks were assembled to mimick grana functions. The cisternae stacks can reversibly compress and expand, similar to the 'breathing' property of natural grana. This cisternae structure provides advanced cell model, and the clues for the stable mechanism of cisternae stacks. Artificial endoplasmic reticulums with helical structures were also fabricated with the addition of charged lipids into the lipid membranes. The other recent progresses on lipid based artificial cells will also be presented.

COLL 135

Self-assembling endogenous biliverdin as a versatile near-infrared photothermal nanoagent

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Photothermal nanomaterials that integrate multimodal imaging and therapeutic functions provide promising opportunities for noninvasive and targeted diagnosis and treatment in precision medicine. However, the clinical translation of existing photothermal nanoagents is severely hindered by their unclear physiological metabolism, which makes it a strong concern for biosafety. The utilization of biliverdin (BV), an endogenous near-infrared (NIR) absorbing pigment with well-studied metabolic pathways, to develop photothermal nanoagents with the aim of providing efficient and metabolizable candidates for tumor diagnosis and therapy is demonstrated. BV nanoagents with intense NIR absorption, long-term photostability and colloidal stability, and high photothermal conversion efficiency can be readily constructed by the supramolecular multicomponent self-assembly of BV, metal-binding short peptides, and metal ions through the reciprocity and synergy of coordination and multiple noncovalent interactions. BV nanoagents selectively accumulate in tumors, locally elevate tumor temperature under mild NIR irradiation, and consequently induce efficient photothermal tumor ablation with promising biocompatibility. They can serve as a multimodal contrast for tumor visualization through both photoacoustic and magnetic resonance imaging. BV has no biosafety concern, which offers a great potential in precision medicine by integrating multiple theranostic functions.



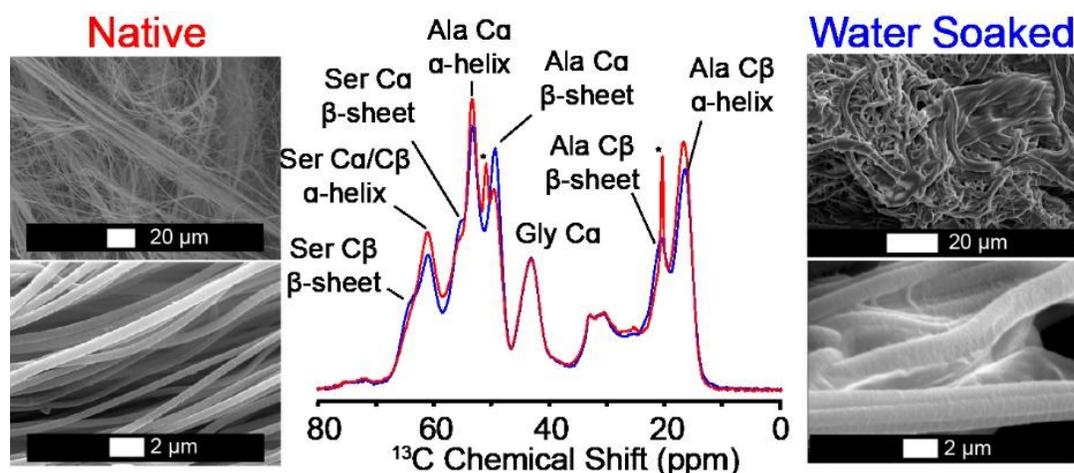
BV nanoagents for multimodal tumor imaging and NIR photothermal tumor ablation.

COLL 136

Water-induced β -sheet crosslinking of α -helix rich spider prey-wrapping silk

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Due to its high strength (~700 MPa) and impressive extensibility before breaking (~60-80%), orb-weaving spider aciniform (AC) prey-wrapping silks are actually the toughest of the spider silks but are remarkably uncharacterized. When stored in the gland AC silk protein is highly helical, adopting a compact “beads-on-a-string” hierarchy with no evidence of β -sheet secondary structure. Our previous results indicate that native AC silk fibers is a α -helix rich coiled-coil / β -sheet hybrid nanofiber, and that conversion of disordered or helical domains to β -sheet aggregates is surprisingly minimal. In this work we demonstrate through solid-state NMR, FTIR and SEM techniques that native AC silks exhibit a remarkable water-induced cross-linking. These physical changes are correlated to an increase in β -sheet content from Ala, Ser, Gly and Gln residues, and additionally we observe a clear unfolding of Val- and Leu-rich domains from coiled-coil regions. We hypothesize that exposure to moisture provides disordered regions and semi-stable coiled-coil motifs the necessary degrees of freedom to access lower-energy β -sheet aggregates. We think this cross-linking behavior is an evolutionarily-adapted trait that benefits the spider during extra-oral digestion and feeding. As the spider feeds, digestive fluids are regurgitated onto her prey. The moisture-exposed prey-wrapping silk bundles are fused together through water-induced β -sheet crosslinking, collapsing the inter-fiber space and becoming more rigid, thereby squeezing and further crushing the prey-package. In addition to their intriguing ecological implications, these findings should be of significant interest to polymer engineers and materials chemists; using water as a solvent to convert malleable, flexible and tough protein-based materials into rigid cross-linked sheets may prove instrumental to developing biomaterials tailored for defense, biomedical and space exploration applications.



COLL 137

Tuning metal (hydr)oxide composites via functionalized polymers

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High surface area metal (hydr)oxide nanopowders have inherently high defect site populations. The reactivity of metal (hydr)oxide nanopowders, such as zirconium hydroxide, strongly depends on these poorly-understood defect sites. Controlling or modulating defect sites to direct chemical reactions have implications ranging from highly selective catalysis and low-cost reactive composite materials to improved energy storage. This work shows that polymerization of various monomers with metal (hydr)oxide nanopowders can modify the defect sites and alter the material's surface reaction chemistry. We explore the tuning of defects by functionalizing the polymer with electron donating and withdrawing moieties to disrupt the local electronic structure and drive new chemistry. A suite of analytical tools including *operando* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), X-ray photoelectron spectroscopy (XPS), and probe molecules such as carbon monoxide were used to investigate changes to the local defect structure in real-time. From this work, a porous polymer composite material with tailored properties for chemical decontamination was conceptualized and demonstrated.

COLL 138

Interactions of ascorbic acid on copper for fuel cell applications

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Some fuel cells are supplied with renewable alternative fuels such as Ascorbic Acid (AA) given that they can be used in biological systems while hydrogen and other common fuels cannot. The development of fuel cells with polyalcohols like AA involve different types of catalysts for electro-oxidation. A recent study by Haan et al. [1] demonstrated that the catalytic activity of palladium-copper alloys was shown to have faster oxidation rates of polyalcohols when the majority of the alloy consisted of copper (Cu). This research computationally explores the intermolecular interactions of AA with Cu. The adsorption potential energy (APE) of each of the four AA stereoisomers adsorbed onto Cu were calculated using density functional theory. L-ascorbic acid had the highest APE of -1.34 eV followed by Isoascorbic acid, D-ascorbic acid and lastly Erythorbic acid with the lowest APE of -1.06 eV. The AA molecule was separated into its two major pieces to understand its principle modes of adsorption: ethylene glycol (EG) and 3,4-dihydroxyfuran-2(5H)-one (DHF). DHF resulted with an APE of -0.86 eV and EG had an APE of -0.45 eV. This study will report on the surface-molecule interactions between AA and Cu to elucidate the role of chirality in fuel cell fuels.

COLL 139

Quantifying sorption and diffusion in polymeric materials: Experimental results and high fidelity modeling

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Quantifying the sorption and diffusion of vapors and gases in diverse types of materials is important to several industries and over a wide range of applications including adsorption and separation technology, materials designed as barrier materials (e.g. polymeric protection layer on photovoltaic cells), and predictions of material outgassing in sealed systems over long durations (e.g. space and satellites, weapon systems, etc). Key parameters include the rate of diffusion, the sorption capacity, and the sorption mechanisms. Understanding these phenomena, and capturing them in a model, allows for predictions of material performance in realistic shapes and dimensions over the life of a system. Here we demonstrate our experimental and modeling capabilities to characterize and quantify sorption and diffusion of vapors and gases in materials. Our experiments can include dynamic vapor sorption and dynamic gas sorption as measured via gravimetric analysis of milligram to gram sized samples. By incrementally stepping up the vapor concentration, or gas partial pressure, we can monitor the sample mass uptake as a function of time to parameterize our dynamic sorption-diffusion model. Our physics based numerical model is a triple-mode sorption model that is coupled to a Fickian diffusion model; the three sorption modes are Henry's absorption, Langmuir adsorption, and pooling. Our initial experiments are performed with quasi-1-dimensional samples and the data is used to parameterize the models. With this numerical model, one can then predict the sorption and diffusion in more complex, 3-dimensional parts to accurately model the behavior of real articles and systems. By also measuring 3D shaped samples in our gravimetric analysis instruments, the model can be validated.

Here we will discuss results from 1D and 3D experiments and our sorption-diffusion numerical model simulations on polymeric materials.

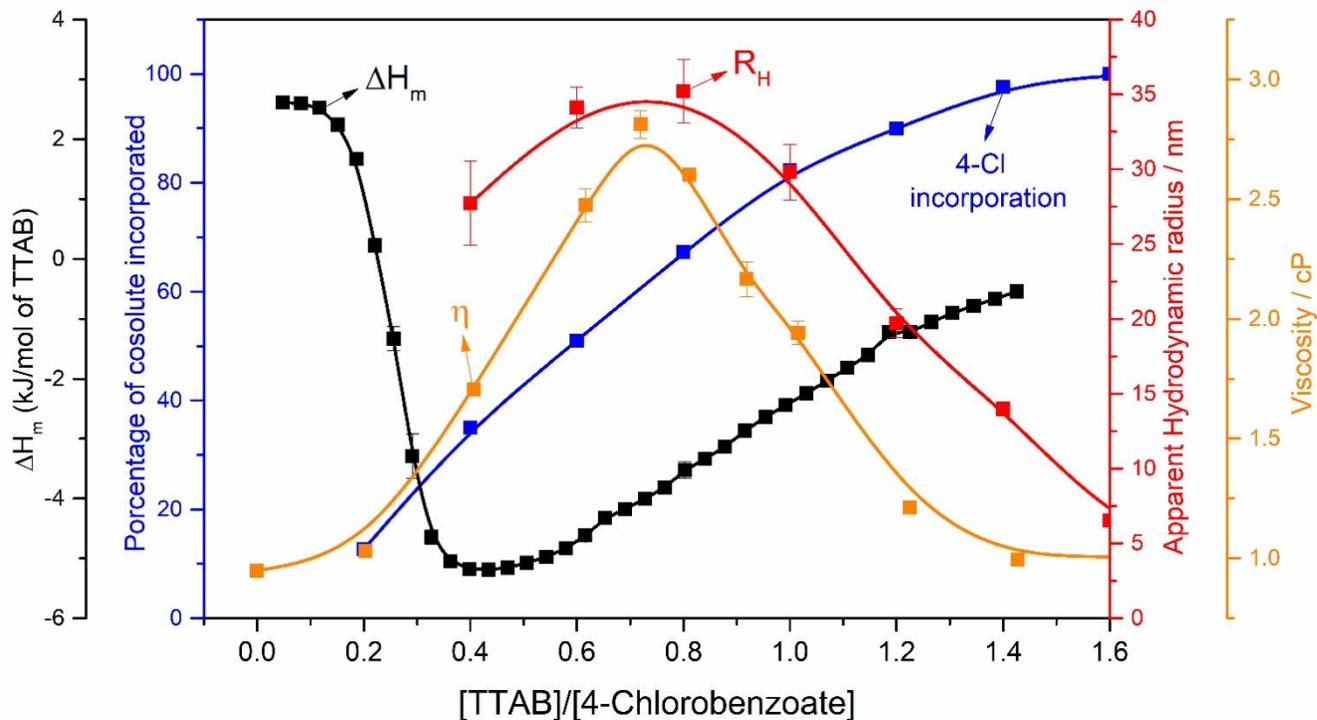
COLL 140

Formation of wormlike micelles with tetradecyltrimethylammonium bromide and 4-halogenbenzoates

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Wormlike micelles (WLM) are elongated self-assembly structures that can reach hundreds of nanometers in length and solutions containing WLM has wide applications in various fields, such as drug delivery, enhanced oil recovery, rheology control, drag reduction agents and many home care, personal care and cosmetic products. Its formation is based on noncovalent interactions such as hydrophobic, electrostatic screening, π - π stacking, hydrogen bonding among others. The elongated structures are dynamic and they are continuously breaking and recombining. The formation of wormlike micelles in aqueous solution with a cationic surfactant is highly favored in the presence of hydrotropes such as derivatives of benzoate. In this study, we used tetradecyltrimethylammonium bromide (TTAB) and 4-halogen benzoates, such as 4-fluorobenzoate, 4-chlorobenzoate, 4-bromobenzoate, and 4-iodobenzoate, to form the wormlike micelles in aqueous solution and understand the implications that the change of the halogen atom brings for the formation of wormlike micelles.

Besides that, the calorimetry profile of this type of aggregate is not fully understood and by comparing the results obtained by isothermal titration calorimetry with rheometry, dynamic light scattering, ^1H chemical shift and diffusion coefficient in nuclear magnetic resonance and cryogenic transmission electron microscopy, it is possible to propose a possible interpretation for the calorimetric profile.



COLL 141

New finds about the mechanism of wormlike micelle formation involving a cationic surfactant and salicylate

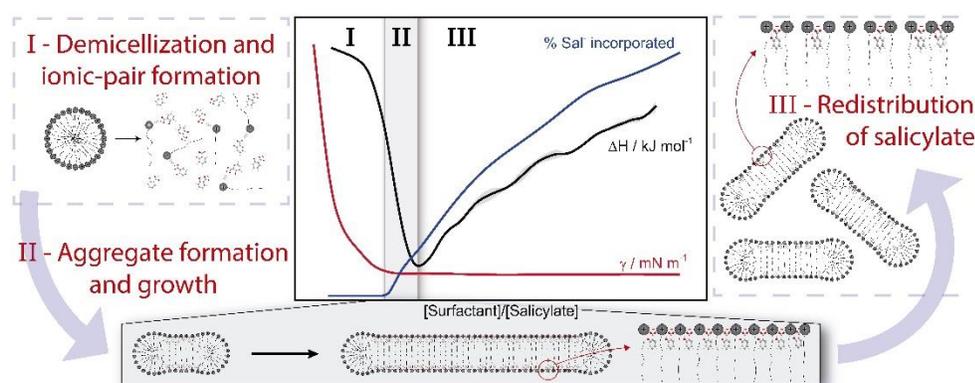
Renato N. Nunes de Souza, nunesrenato90@gmail.com, Manazael Z. Jora, Luis Gustavo T. Duarte, Teresa D. Atvars, Edvaldo Sabadini. Physical Chemistry, University of Campinas, Campinas, São Paulo, Brazil

Isothermal titration calorimetry (ITC) is a technique based on the controlled titration of a solution into a cell, and it can be used to monitor self-assembly processes. Previously, the titration of tetradecyltrimethylammonium bromide (TTAB) in sodium salicylate (NaSal) was studied, and the resulting enthalpogram was separated into three different parts, corresponding to different processes. These three parts were associated with the formation of mixed micelles, followed by the fusion of these micelles into wormlike micelles, at a specific $[TTAB]/[NaSal]$ ratio, and then the decrease in length of such type of aggregates as the concentration of TTAB increased.

Herein, we present a comparative study that was carried out with solutions containing TTAB and NaSal in different molar ratios in order to investigate the structural variations throughout the enthalpogram. The techniques used in the investigations were ITC, time-resolved emission spectroscopy and surface tensiometry. It is possible to observe

considerable variation in the properties studied at a specific surfactant concentration of 0.4 mmol L^{-1} , which corresponds to a molar ratio [TTAB/NaSal] of 0.35, lower than in previous studies. We propose that the formation and growth of wormlike micelles occurs by a very cooperative process in this concentration range, lower than what was previously proposed, without a preliminary mixed micelle state, once no evidence of mixed micelles was seen.

In addition, we propose a simple model which allow us to estimate the proportion of the species TTAB and salicylate that are present in the structure of the aggregate based on the preexponential factors obtained through spectroscopy. Moreover, thermodynamic parameters were investigated using the ITC experiments in different temperatures to study the spontaneous formation and growth of wormlike micelles.



Scheme of the formation and growth of wormlike micelles and then, the salicylate redistribution. The variation of the structures of the aggregate is compared to the properties obtained by ITC, tensiometry and time-resolved emission spectroscopy.

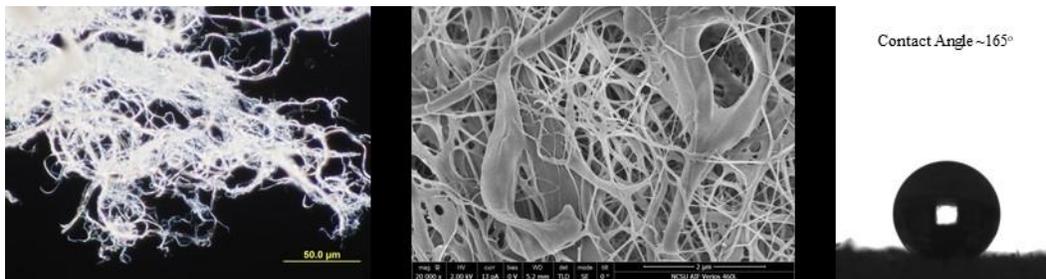
COLL 142

Functional superhydrophobic and icephobic coatings made of new biomimetic "gecko leg" soft dendritic colloids

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We will report how coatings and nonwovens with outstanding superhydrophobic and icephobic properties can be made from novel types of polymer particles with controlled morphologies and interactions. First, we will introduce the synthesis of a new class of particles named soft dendritic colloids (SDCs). These particles are hierarchically structured, with a branched corona of nanofibers spreading out in all directions. They are nanomanufactured by multiphasic polymer precipitation under intensive shear. The

nanofiber corona around these "gecko leg" particles endows them with extraordinary strong adhesion to almost any surface and to each other, and enables unique structure-forming abilities. These particles exhibit the phenomenon of "contact splitting", which is displayed in the remarkable adhesion of gecko feet. The morphological similarity of the SDCs to the gecko lizards' setae endows the SDCs with excellent dry adhesion and cohesion properties. The hierarchical surface roughness resulting from the overlapping SDC micro- and nanofibers allows the facile formation of superhydrophobic and superhydrophilic coatings depending on the properties of the polymer used. The adhesion of SDC coatings to substrates can be further improved both through the addition of a poly(dimethyl) siloxane (PDMS) binder and by creating bicontinuous networks of SDCs composed of different polymers. The addition of a PDMS binder and formation of bicontinuous SDC networks modify the surface roughness and contact angle of the SDC coatings and lead to improvements in durability, wettability, and anti-icing properties, including increased ice nucleation time and decreased ice adhesion strength. The new class of functional coatings can find applications in numerous industrial and consumer products.



COLL 143

Removing fine solids suspended in oil media through wettability modification and water-assisted agglomeration

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Removing fine solids suspended in oil media is required in many chemical and environmental engineering processes with ever-increasing demands on improving product quality and meeting waste management standard. In oil industry, removing fine solids from organic solvent-diluted bitumen is required to achieve high-quality oil products, which however, remains a challenging issue. In this work, a two-step agglomeration method has been developed to destabilize bitumen-coated silica particles in cyclohexane by modifying their surface wettability using an amphiphilic copolymer poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol)

(PEG-PPG-PEG), and then introducing a small amount of water to trigger the agglomeration of the particles. The performance of the two-step agglomeration process was evaluated through sedimentation tests, and the underlying physical interaction mechanisms were investigated using atomic force microscope (AFM) and quartz crystal microbalance with dissipation monitoring (QCM-D) techniques. The results suggest that PEG-PPG-PEG can strongly adsorb to the bitumen-coated silica surface to reduce its hydrophobicity, thereby tuning the interactions between the silica surface and added water drops from repulsion to attraction in cyclohexane, as confirmed by surface force measurements using drop probe AFM. Accordingly, the two-step method achieves high initial settling rate (ISR) and low content of residual solids in the supernatant simultaneously. Batch settling tests with addition of only water, PEG-PPG-PEG or PEG-PPG-PEG aqueous solution were also conducted, whose performances were found much less desirable in comparison with the two-step approach. This research work provides useful insight into the development of effective approaches for destabilization and removal of suspended fine solids in oil media in many related chemical and environmental engineering processes.

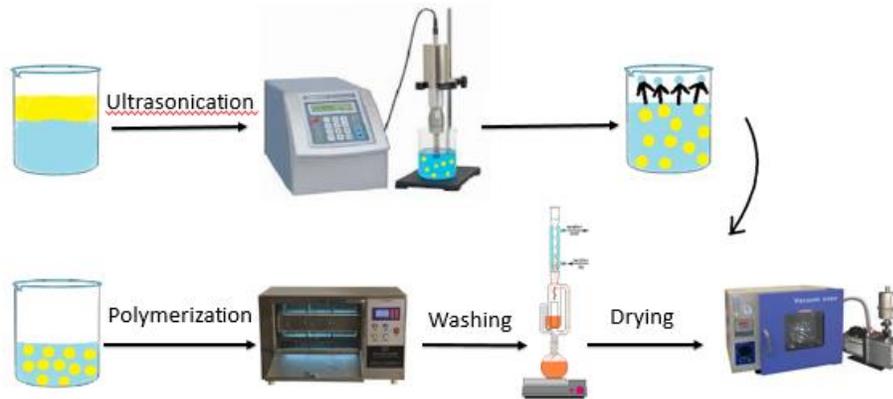
COLL 144

Structure-dependent properties of nanoporous hydrogels: Rheology and swelling

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Abstract

Porous materials with well-tuned structures are of great importance in various applications. There are a number of methods to produce materials with ordered porous structure in macro-scale and meso-scale ranges, but few works have been reported in the sub-micron range. In the present work, we investigate the synthesis of nanoporous hydrogels by emulsion templating approach and controlling the pore structure through the evaporation process. First, oil-in-water nanoemulsions are prepared with low dispersed phase volume fraction by using ultrasonication process. Then, the nanoemulsions are concentrated to high droplet phase volume fraction by evaporation of continuous phase with a controlled rate to approach the maximum achievable ordered pore structure. Photo-polymerization of nanoemulsions and removing the internal phase produce nanoporous hydrogels. Rheological properties of nanoemulsions exhibited higher shear modulus of the samples with higher degree of ordering. Furthermore, swelling kinetics and crosslink density measurement of resulting nanoporous hydrogels confirmed the higher modulus of those samples due to higher crosslink density.



COLL 145

Dynamics and mechanism of polyelectrolyte-neutral block copolymer micellization in aqueous solution by atomistic MD simulations

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The clustering mechanism, micellization kinetics, and various dynamical aspects and diffusional properties of asymmetric and symmetric poly(styrene)-*block*-poly(acrylic-acid) polyelectrolyte-neutral block copolymer chains in salt-free aqueous solution were investigated as a function of the copolymer composition (X_{PS}) for un-ionized (acidic, $f = 0$) and ionized (charged, $f = 1$) PAA block by molecular dynamics simulations. The mechanism of the formation of the micelle was tracked using the population of unimer and clusters across the simulation trajectory, which confirmed that the asymmetric copolymer micelle follows a combined approach of unimer insertion and cluster fusion mechanism, while the symmetric micelle follows unimer insertion method exclusively. Micelle formation takes a longer time for copolymers having charged (ionized) PAA block ($f > 0$) and relatively short PS block ($X_{PS} < 0.5$) due to the presence of a greater number of hydrophobic groups, in qualitative agreement with observations from DPD simulation study of model uncharged copolymer micelles in literature. Conformational dynamics studied using relaxation of backbone dihedral angle and radius-of-gyration, specifically for core and corona blocks, shows a slower relaxation of the hydrophobic insoluble PS blocks as compared to the soluble PAA blocks. The interaction dynamics of PS-*b*-PAA copolymer micelles studied via the relaxation times of PAA-PAA inter-chain hydrogen bonds ($T_{HB,PP}$) and PAA-water inter-molecular hydrogen bonds ($T_{HB,PW}$) show an increase of $T_{HB,PP}$ and a decrease of $T_{HB,PW}$, with increase in X_{PS} . The relaxation of PAA-water h-bonds is slower at $f = 1$ than at $f = 0$, due to the stronger

affinity of ionized PAA units to water molecules. The diffusivity of the micelle cluster decreases non-linearly (exponentially) with increase in X_{PS} in agreement with results available in literature from coarse-grained and DPD simulations of model star polymer and copolymer micelles, as well as PFG-NMR measurements of PEO-*b*-PCL and POE-*b*-PDMS micelles in water.

COLL 146

Multiresponsive microspheres crosslinked by rotaxane networks

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Multiresponsive microspheres that exhibit an extremely rapid change in size and physicochemical properties in response to environmental changes or external stimuli have needed to control their responsiveness to develop new applications. Our group has developed the rotaxane cross-linked (**RC**) hydrogel microspheres that show a decoupled thermo- and pH-responsive volume transition. The pH-induced changes of the aggregation/disaggregation states of cyclodextrin in the **RC** networks of the microspheres were used to control the swelling capacity of the entire the microspheres (**Figure**). Different from conventional thermo- and pH-responsive hydrogel microspheres, which are usually obtained by copolymerization involving charged monomers, the **RC** hydrogel microspheres respond to temperature as intended, even in the presence of charged functional molecules such as dyes in the microsphere dispersion. The results of this study should lead to new applications, such as drug delivery systems that require retention of their smart functions even in environments that may contain foreign ions. Additionally, the behaviors of elastomer microspheres crosslinked with **RC** will also be discussed. Partially reproduced with permission from

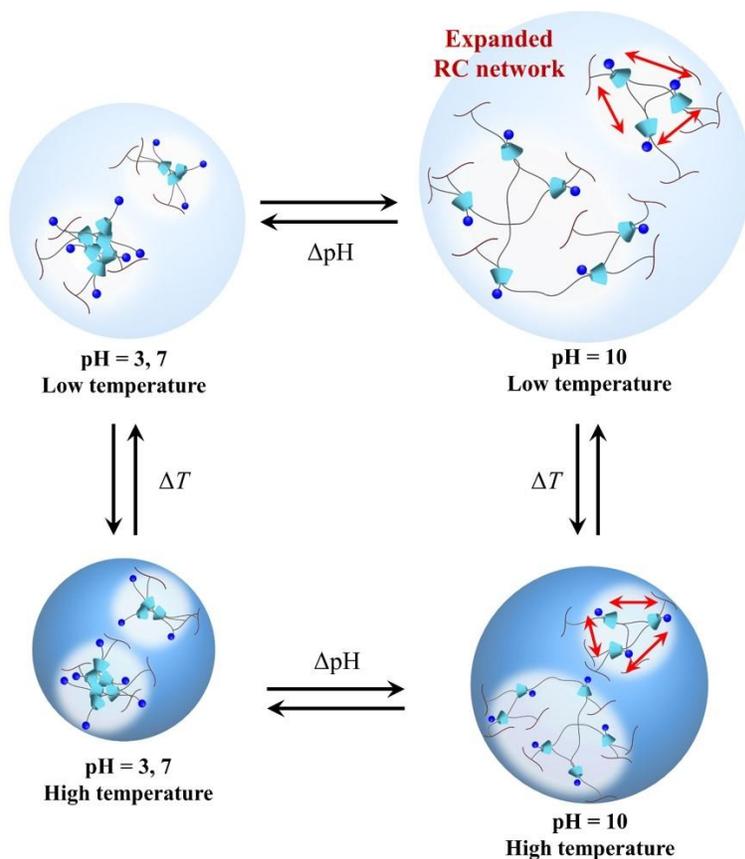


Figure Illustration of Rotaxane crosslinked hydrogel microspheres.

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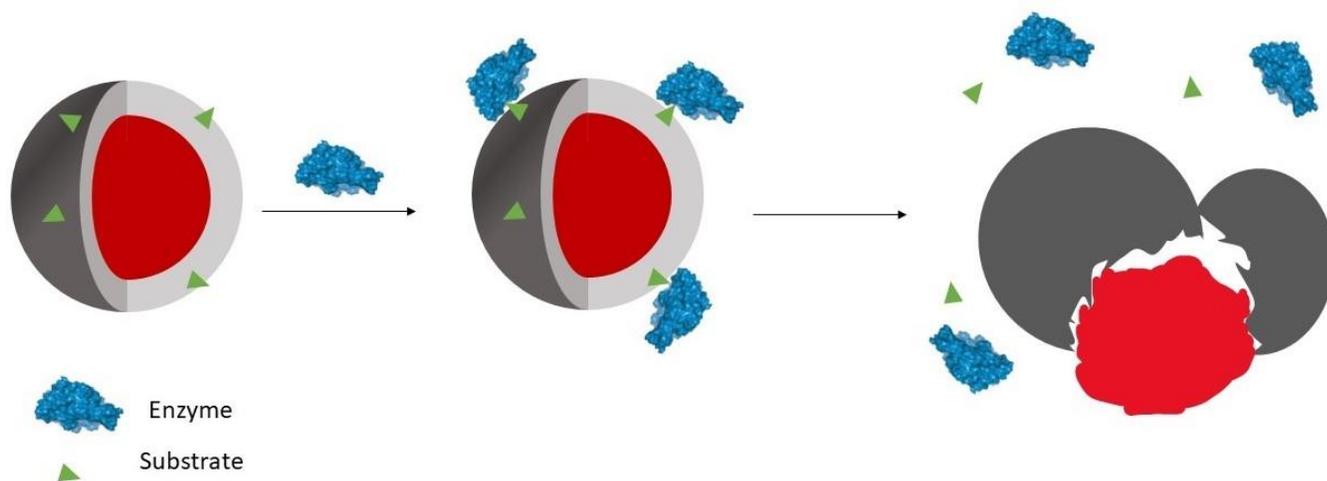
Thioether–polyglycidol as multivalent and multifunctional coating system for metal nanoparticles

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Thiofunctional polymers, especially thiol-terminated terminated poly(ethylene glycol) (PEG-SH) are the established standard for the coating and biofunctionalization of gold nanoparticles (AuNPs). However, the highly nucleophilic and oxidative character of thiols limits the possibilities introducing functional groups and provokes polymeric crosslinking.

We have thus examined whether thioether may be used as alternative to thiols for stabilizing gold colloids. Here we present a systematic comparison of PEG-SH and PEG thioether (PEG-SR) with multifunctional analogs, linear polyglycidol (PG) with multiple

responsive nanoassemblies made up of amphiphilic building blocks such as block copolymers or dendrimers, one of the major drawbacks with these systems is that they show a very slow response. The reason for such slow response is due to the fact that the enzymatic substrate present in such assemblies are buried in their hydrophobic core which provides a poor accessibility to enzymes. To solve this problem, we used a self-immolative polymer capped with a phosphate group which is a good substrate for enzyme alkaline phosphatase and is hydrophilic in nature. When the polymer was treated with alkaline phosphatase, it degraded from head to tail through a domino effect mechanism. A hydrophobic modification of the polymer was used to make the polymer soluble in organic solvent. Furthermore, we used an oil in water emulsion methodology to formulate surfactant stabilized core shell particles with phosphate groups exposed on their surface. In the formulation process, Dichloromethane soluble polymer was used as the dispersed phase while water was used as a dispersion medium in presence of tween 80 as an emulsifier. The assemblies were characterized using dynamic light scattering (DLS), transmission electron microscopy (TEM) and NMR experiments. These assemblies could encapsulate hydrophobic dyes as model guest molecules. Upon treatment with enzymes, these core shell particles disassemble and release the encapsulated guest molecules at a rapid rate which was studied using UV-Vis and TEM experiments. The strategy mentioned in this study can have significant implications in the development of imaging and rapid drug delivery carriers for certain cancer cells where alkaline phosphatase is overexpressed.



COLL 149

Hydrothermal synthesis of monodisperse tin oxide nanoparticles and doped tin oxide nanoparticles

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Tin oxide is a wide band gap semiconductor for which the band gap can be tuned upon doping. The synthesis and ready availability of monodisperse uniformly shaped tin oxide nanoparticles is needed for applications requiring stable dielectric materials either in solution, in bulk, or deposited as films on substrates. To this end, this presentation describes simple and reproducible procedures for the hydrothermal synthesis of uniform monodisperse tin oxide nanoparticles and doped tin oxide nanoparticles. The tin oxide nanoparticles were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-Ray photoelectron spectroscopy (XPS). In addition, their optical properties were evaluated by UV-vis spectroscopy and diffuse reflectance spectroscopy (DRS). The band gap of the tin oxide nanoparticles was successfully tuned upon doping, which led to enhanced absorption/extinction in the visible region. A complete summary of the physical properties and potential applications will be described.

COLL 150

Interfacial rheology with sub-phase exchange used to investigate dynamics of cyclopentane hydrate film formation and dissociation

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At low temperatures and high pressures gas molecules can become trapped in a crystalline cage of water molecules. This process is an interfacial phenomena in that it occurs at the interface of a liquid organic phase and an aqueous phase. The resulting ice-like solid is a gas hydrate, and their frequent formation during oil and gas recovery can cause significant problems by blocking flow lines. Extensive resources have been devoted to understanding the connection between hydrate film growth at oil-water interfaces and bulk hydrate formations from emulsions, but that connection is still unclear in part because of the challenge of characterizing film mechanics during nucleation, growth, and dissociation. Interfacial rheological methods are sensitive to changes in film mechanics, and have been used to study cyclopentane gas hydrate films, which conveniently form at atmospheric pressure. We are using interfacial rheology to further establish connections between interfacial dynamics in hydrate systems, and bulk rheological properties. We have modified our interfacial rheology setup to include the ability to exchange the sub-phase fluid with minimal disruption to the interface. With this setup we are able to measure film mechanical properties after the introduction of hydrate inhibitors, and during film dissociation. This poster will include discussion our experimental setup, the data obtained on the formation and dissolution of cyclopentane hydrate films, and results from ongoing, complementary bulk hydrate rheological testing.

COLL 151

Olefin-linked dithiol adsorbates for the generation of self-assembled monolayers on gold

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A series of custom-designed olefin-bridged bidentate adsorbates of the form $[\text{CH}_3(\text{CH}_2)_n]_2\text{CC}[\text{CH}_2\text{SH}]_2$, where $n = 12-15$, were synthesized and used to generate self-assembled monolayers (SAMs) on gold. To elucidate the effect of the bridging olefin moiety on film thickness, surface coverage, and wettability, SAMs generated from the analogous n -alkanethiols, $\text{H}(\text{CH}_2)_n\text{SH}$, where $n = 15-18$, were included in the study for comparison. The structural and interfacial properties of all of the SAMs were investigated using ellipsometry, X-ray photoelectron spectroscopy (XPS), polarization-modulation infrared reflection-adsorption spectroscopy (PM-IRRAS), and contact angle goniometry. The results from these studies and the potential uses of these new adsorbates will be discussed.

COLL 152

Seedless, one-pot synthesis and simulations of infrared-absorbing silver nanoparticles

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Many literature reports describe methods of producing silver nanoparticles of controllable size and shape, which leads to UV-Visible absorption peaks that are tunable throughout the visible region; however, there are only a few that report maxima above 800 nm, and these generally use a seeded synthetic approach. Moreover, large, often polymeric, ligands are used as capping agents to sterically stabilize the IR-absorbing nanoparticles. In this study, we further develop the method of producing silver nanoparticles via the reduction of silver ions by sodium borohydride in the presence of sodium citrate and hydrogen peroxide. Through careful variation of reactant concentrations, mixing rates, and other reaction conditions, the UV-Visible absorption peaks can be tuned well into the near-infrared region. This approach is one-pot, seedless, and yields nanoparticles that not only possess reproducible optical properties but also are stabilized for at least one month at room temperature by the small, easily-displaced citrate anion. This latter property makes the nanoparticles very suitable for binding to substrates. Additional characterization of the nanoparticles was done by dynamic light scattering, transmission electron microscopy, and Raman spectroscopy.

Extinction spectra simulated via the Discrete Dipole Approximation (DDA) for nanoparticle sizes and shapes observed in the transmission electron micrographs agree relatively well with the experimental spectra. The DDA simulations were done using conditions that resemble those of the experiments (dielectric constants of the environment, rotational averaging, etc.).

COLL 153

Bidentate phosphonic acid-based self-assembled monolayers on silver oxide

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Self-assembled monolayers (SAMs) on silver oxide surfaces were prepared from a perfluoro-terminated aromatic bidentate phosphonic acid having the formula ((5-9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16-heptadecafluorohexadecyl)oxy)-1,3-phenylene)bis(methylene))bis(phosphonic acid) (**F8H8BPA**). SAMs generated from this new bidentate adsorbate, were compared to SAMs generated from the analogous monodentate phosphonic acid (**F8H8PA**), serving as a reference system. The synthesized adsorbate was characterized using ³¹P, ¹H, and ¹³C nuclear magnetic resonance (NMR) spectroscopy prior to SAM formation. The monolayers were analyzed with X-ray photoelectron spectroscopy (XPS) to determine the elemental composition of the SAMs as well as their packing densities. The resulting SAMs were also examined by polarization modulation infrared reflection-absorption spectroscopy (PM-IRRAS) to determine the conformational order of the films, and contact angle goniometry to determine their hydrophobicity. The enhanced stability anticipated for this bidentate adsorbate is expected to protect oxide surfaces during selective etching techniques used in various fields, such as the fabrication of patterned superconducting tapes for reduced AC loss.

COLL 154

New water-free method for the synthesis of chiral QDs and fine tuning of their optical activity

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We have reported that functionalization of achiral colloidal quantum dots (QDs) with chiral organic capping ligands by phase transfer ligand exchange as a simple yet powerful method for the induction of chirality in QDs. Yet, the presence of chiral capping

ligands on the surface of CdSe QDs was necessary but not sufficient condition for the induction of optical activity in QDs, and several chiral ligand failed to induce chirality in QDs. We will present a newly developed water-free and purification-free ligand exchange protocol for the synthesis of chiral QDs as well as the optical and chiroptical properties of the newly acquired chiral QDs. Relationship between chemical structure of the amino acid capping ligands and the induced circular dichroic properties of QDs will be elucidated.

COLL 155

Monitoring the temperature-responsive behavior of cholesteric liquid crystal films and emulsions using QCM-D

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This work addresses the objective of understanding molecular events involved in cholesteric liquid crystal (LC) phase changes over a temperature range. The temperature-responsive behavior of formulations containing cholesteryl oleyl carbonate, cholesteryl pelargonate and cholesteryl benzoate were characterized using quartz crystal microbalance with dissipation monitoring (QCM-D). As temperature was varied, changes in molecular orientation within LC films were observed in relation to the transition temperatures of the formulations. The molecular behavior of liquid crystal domains encapsulated within polymer-LC emulsions was also explored. This knowledge will inform the development of smart materials for use in textiles and provide a novel characterization technique for materials that undergo phase changes.

COLL 156

Synthetic methods for preparing partially fluorinated and selectively deuterated adsorbates for self-assembled monolayers

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Self-assembled monolayer-based films (SAMs) enjoy a wide range of uses and applications throughout various technological fields. Of particular interest in SAM-based research is the design of adsorbate molecules that can impart specific properties to the resulting films. Among the many adsorbates studied, fluorinated adsorbates have been shown to alter the physical properties of the resulting films, such as friction, wettability, work function, and capacitance. Likewise, SAMs generated from deuterated-molecules

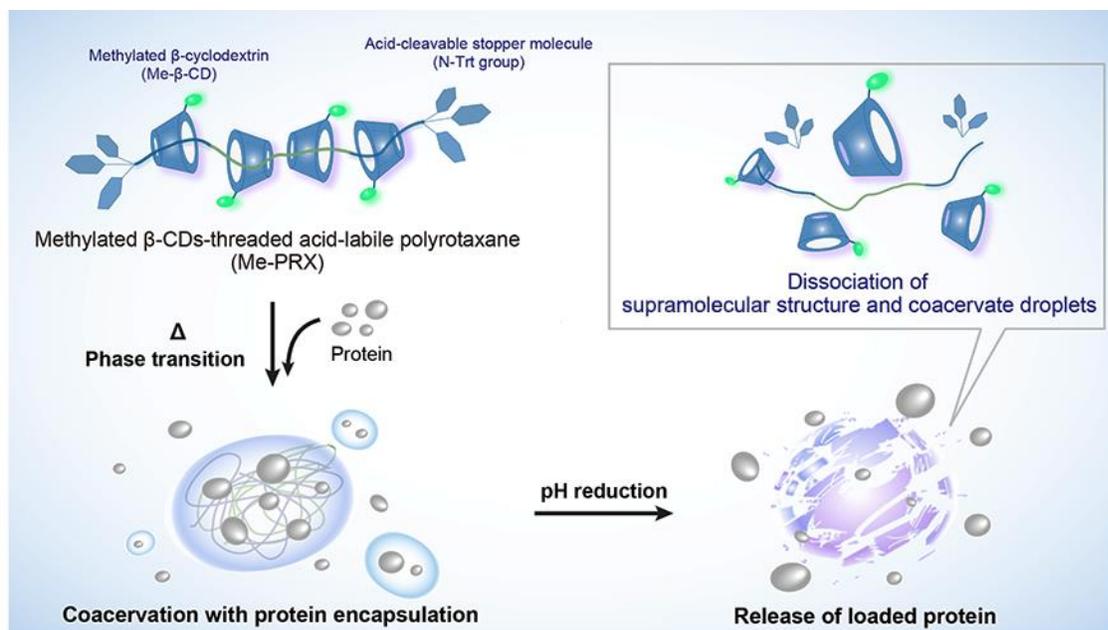
have been used to probe specific interactions between surfaces and other small molecules, such the reorientation of acetonitrile in response to surface dipoles. This presentation summaries various synthetic strategies used for the synthesis of partially fluorinated and selectively deuterated adsorbates that can be used in the preparation of self-assembled monolayers (SAMs). Moreover, the effectiveness, advantages, and/or limitations of these methods will be compared and highlighted.

COLL 157

Coacervate droplets formation of methylated β -cyclodextrin-threaded polyrotaxanes in aqueous media and their applications as an injectable protein carrier

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Polyrotaxanes (PRXs) composed of threading methylated cyclodextrins exhibit a temperature-dependent reversible phase transition across the lower critical solution temperature (LCST) in water. In this study, a variety of methylated β -cyclodextrin (β -CD)-threaded PRXs (Me-PRXs) with different number of methyl groups modified on the β -CD and with compositions of axle polymers (PEG-*b*-PPG-*b*-PEG) were synthesized, and the relationship between the LCST value and structural parameters was investigated. The LCST values of the Me-PRXs decreased with an increasing the methylation degree of the threading β -CD. Interestingly, the Me-PRXs formed coacervate droplets above their LCST. Additionally, the encapsulation of proteins in coacervate droplets and the pH-responsive release of proteins, through the acid-induced dissociation of the Me-PRX, were demonstrated. The coacervate droplets encapsulate various proteins, such as bovine serum albumin (BSA), lysozyme, and β -galactosidase, at pH 7.4, into their hydrophobic inner phase. Accompanied with the pH-dependent dissociation of the Me-PRXs, the coacervates degraded below pH 6.5 and released encapsulated proteins. Additionally, the subcutaneous injection of coacervate droplets encapsulating BSA in mice revealed that the retention time of the BSA at the injection site was prolonged compared to that of free BSA. Altogether, the coacervate droplets of the Me-PRX would be utilized as a new class of pH-responsive and injectable carrier for the controlled release of therapeutic proteins.



COLL 158

Palladium nanoparticles as ROS scavengers

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Introduction

Palladium nanostructures have gained great interest in the recent years, due to their catalytic properties such as hydrogenation, C-C bond formation and oxidation, prodrug activation, etc.¹. Catalytic nanomaterials show enormous potentiality in nanomedicine as radical scavengers, due to their antioxidant properties². In this work, we explored the use of Pd nanoparticles (PdNPs) in nanomedicine as antioxidant nanozymes, taking advantage of the cellular model of an oxidative stress-related disease, namely cerebral cavernous malformation (CCM).

Methods

Pure, monodisperse citrate-capped PdNPs of 8 nm diameter were synthesized and thoroughly characterized. A systematic characterization of their superoxide dismutase (SOD)-, catalase (CAT)- and peroxidase (HRP)- like activities in cell-free environment were performed. A systematic toxicity assessment was performed. Finally, to test the hypothesis that citrate-capped PdNPs can act as a scavenging material in biological systems, PdNPs were tested on the cellular model of a cerebrovascular disease, namely Cerebral Cavernous Malformation (CCM), characterized by an abnormal angiogenesis and associated with a significant increase in intracellular reactive oxygen

species (ROS) levels.

Results and Discussion

We demonstrate that Pd nanozymes are capable to restore physiological ROS homeostasis in the experimental model of CCM disease, founding that PdNPs can completely recover the cellular phenotype (Figure). This is possible because of the strong and broad antioxidant nanozyme activity of PdNPs, which are simultaneously endowed with strong CAT-, HRP-, and SOD-like activities, with similar performance levels of PtNPs which are known to have high ROS scavenging activity, as reported by Moglianetti *et al.*³. These findings are important and of broad interest, and open up novel perspectives in nanomedicine for the development of multifunctional active nanocarriers integrating the function of high-performance antioxidant drugs with strong potential for therapies of complex oxidative stress-related diseases.

COLL 159

Synergistic O₂ generation by manganese ferrite/ceria co-decorated nanoparticles induce M2 polarization of macrophages for rheumatoid arthritis treatment

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Synovial inflammation induced by poor O₂ supply in rheumatoid arthritis (RA) can be resolved by eliminating pro-inflammatory M1 macrophages and inducing anti-inflammatory M2 macrophages. Since hypoxia and ROS in the RA synovium play a key role in the induction of M1 macrophages and reduction of M2 macrophages, herein we develop manganese ferrite and ceria nanoparticle-anchored mesoporous silica nanoparticles (MFC-MSNs) that can synergistically scavenge ROS and produce O₂ for reducing M1 macrophage levels and inducing M2 macrophages for RA treatment. MFC-MSNs exhibit a synergistic effect on O₂ generation and ROS scavenging, which is attributed to the complementary reaction of ceria nanoparticles (NPs) that can scavenge intermediate hydroxyl radicals generated by manganese ferrite NPs in the process of O₂ generation during the Fenton reaction, leading to efficient polarization of M1 to M2 macrophages both in vitro and in vivo. Intra-articular administration of MFC-MSNs to rat RA models alleviated hypoxia, inflammation, and pathological features in the joint. Moreover, MSNs were used as a drug-delivery vehicle, releasing the anti-rheumatic drug methotrexate in a sustained manner to augment the therapeutic effect of MFC-MSNs. This study highlights the therapeutic potential of MFC-MSNs that simultaneously generate O₂ and scavenge ROS, subsequently driving inflammatory macrophages to the anti-inflammatory subtype for RA treatment.

COLL 160

Application of hemoglobin-capped fluorescent gold nanoclusters for cancer cell targeting and inhibition of cancer cell proliferation

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Cancer has always been one of the targets of clinical medical research, with tens of thousands of people dying every year all over the world. Gold nanoclusters (AuNCs) have been widely used in biosensing and bioimaging due to their excellent biocompatibility, stable chemical structure and easy surface modification. Because the iron ion held in the heme is an essential nutrient source for cell proliferation, we applied hemoglobin-capped AuNCs (Hb-AuNCs) as nutrient sources for human breast cancer cells (MDA-MB-231 and MDA-MB-468) in this study. After cultured together, breast cancer cells metabolized Hb-AuNCs in order to maintain their growth. Hence, Hb-AuNCs can be a fluorescence probe for breast cancer cells. After breast cancer cells metabolized hemoglobin on the surface of Hb-AuNCs, cancer progression was evaluated by fluorescence intensity changes of Hb-AuNCs and also the proliferation of breast cancer cells were inhibited.

COLL 161

Evaluation of cancer progression and inhibition of cancer cell proliferation by using target-specific 2A3 antibody-conjugated gold nanoclusters

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Fluorescent gold nanoclusters conjugated with 2A3 antibody (2A3-AuNCs) were developed for evaluation of cancer progression and inhibition of cancer cell proliferation. The 2A3 antibody can specifically bind onto carcinoembryonic antigen-related cell adhesion molecule 6 (CEACAM6) on the cancer cell surface to decrease cancer cell proliferation, metastasis and angiogenesis. In this study, we can target CEACAM6 overexpressed breast cancer cells by applying target-specific 2A3-AuNCs as fluorescent probes. After binding with CEACAM6, the fluorescence changes of 2A3-AuNCs were measured and calculated to simulate their kinetics for assessment of breast cancer progression. Moreover, the fluorescence imaging and fluorescence change of 2A3-AuNCs were applied to investigate their inhibition of breast cancer cell proliferation. Overall, the target-specific 2A3-AuNCs were demonstrated as a promising fluorescent probe for evaluation of cancer progression and inhibition of cancer cell proliferation.

COLL 162

Metabolic mechanism of cysteine conjugated fluorescent gold nanoclusters in *Escherichia coli*

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Fluorescent gold nanoclusters (AuNCs) have been widely applied in the applications for biosensing and bioimaging because of their high biocompatibility, facile surface modification and unique optical properties. In this work, the cysteine conjugated gold nanoclusters (Cys-AuNCs) were prepared by one-step hydrothermal approach with orange-red fluorescence, high water solubility and superior biocompatibility. After incubation with *Escherichia coli* (*E. coli*), Cys-AuNCs were metabolized by *E. coli* demonstrated through fluorescence intensity decrease, indicating the metabolism of cysteine on Cys-AuNCs, which was further confirmed via X-ray photoelectron spectroscopy to observe the size decrease of Cys-AuNCs post metabolism. By fitting the fluorescence change as a function of incubation time, zero-order kinetics was the most appropriate kinetics to reveal the metabolic kinetics of Cys-AuNCs in *E. coli*. Moreover, the death of *E. coli* was characterized via the increase of intracellular reactive oxygen species (ROS) through metabolism. Our work provides a potential method for bacteria detection and inhibition in a short period of time.

COLL 163

Synthesis of cysteine-conjugated silver-gold alloy nanoclusters and their application in antimicrobial

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Gold nanoclusters have been recently demonstrated as the antimicrobial reagents. In this work, a one-pot hydrothermal approach was applied to synthesize cysteine-conjugated silver-gold alloy nanoclusters (Cys-AgAuNCs) for the detection and inhibition of *Escherichia coli* (*E. coli*). The structural and optical properties of Cys-AgAuNCs were systematically characterized by transmission electron microscopy, UV-Vis spectroscopy, fluorescence spectroscopy, Fourier-transform infrared spectroscopy, and X-ray photoelectron spectroscopy. Cys-AgAuNCs revealed higher fluorescent intensity compared to that of gold nanoclusters. Cys-AgAuNCs were demonstrated as a fluorescent probe for the detection of *E. coli* because the fluorescence change was caused by the metabolism of Cys-AgAuNCs in *E. coli*. Furthermore, the death of *E. coli* was also demonstrated due to the increase of intracellular reactive oxygen species through the metabolism of Cys-AgAuNCs. Overall, our work provides a practical approach for bacteria detection and inhibition.

COLL 164

Cysteine conjugated silver nanoclusters for the detection and inhibition of *Escherichia coli*

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The detection and inhibition of *Escherichia coli* (*E. coli*) is an important task for water quality monitoring and food hygiene. Silver nanoclusters (AgNCs) have been known for the ability for sterilization while cysteine has also been known as the nutrient of *E. coli*. In this study, we developed a facile strategy for rapid detection and inhibition of *E. coli* with the uses of cysteine-conjugated gold nanoclusters (Cys-AgNCs). After incubation with *E. coli*, the Cys-AgNCs were metabolized by *E. coli* in order to maintain their growth. After the metabolism of Cys-AgNCs inside the *E. coli*, the fluorescence intensity of Cys-AgNCs was decreased and then the metabolic kinetics of Cys-AgNCs by *E. coli* was systematically simulated based on the change of fluorescence intensity of Cys-AgNCs. Moreover, after the metabolism of cysteine on Cys-AgNCs by *E. coli*, significant intracellular reactive oxygen species (ROS) generation was induced by AgNCs to kill *E. coli*. Our work provides a potential approach for bacteria detection and inhibition.

COLL 165

General model for the permeation of nanoparticles through cellular membranes

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A molecular understanding of the interactions between nanoparticles (NPs) and biological systems is crucial for the systematic advance of many high-impact fields, such as biomedicine and nanotechnology. A key aspect to understand and predict the biological effect of nanoparticles (e.g., cytotoxicity, bioavailability), is their interaction with cellular membranes, specifically the mechanisms that regulate passive transport. In this work, we present a new streamlined theoretical model that is able to predict the average permeation time of particles in biological membranes. By separating the contributions that depend only on NPs' characteristics (size, shape), membrane properties (density distribution of the membrane) and mixed factors (solubility), the model allows the combination of both experimental and computational data, as well as the rapid estimation of large numbers of nanoparticles/membranes combinations. We validated our model comparing the results with data obtained from molecular dynamics simulations of the permeation of three different carbonaceous NPs and with experimental measures of NP leakage from lipid vesicles.

COLL 166

Thermal responses of multi-L-arginyl-poly-L-aspartate conjugated with polyethylene glycol

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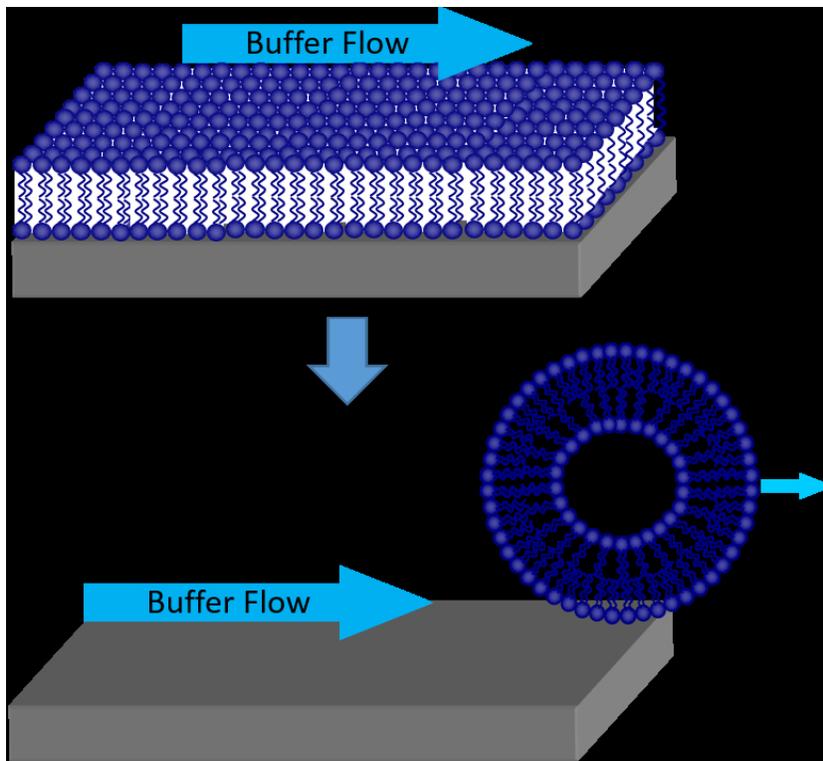
Multi-arginyl-poly-aspartate (MAPA), also known as cyanophycin, containing a backbone of poly-aspartate with arginine and lysine as side chains was prepared with recombinant *Escherichia coli*. The insoluble part (iMAPA) was conjugated with polyethylene glycol (PEG) of different molecular weights by a reductive reaction between the aldehyde group of PEG acetaldehyde and the amine group of lysine of iMAPA. In contrast to the unmodified iMAPA which has limited solubility in phosphate buffered saline (PBS), the conjugates exhibited UCST-type responses, and the cloud-point temperature of each conjugate also showed a positive correlation with concentration after PEG conjugation. Hysteresis was observed to follow approximate paths under the same condition during repeated heating and cooling. Reversible formation of vesicles with different morphologies appeared at room temperature, depending on the molecular weight of PEG. Some core-shell structures of size ranging from micron to submicron can be observed under TEM. These vesicles are expected to construct a drug delivery system with temperature regulation.

COLL 167

Supported lipid bilayer stripping by buffer flow

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Supported lipid bilayers are valuable tools for investigating membrane components. Several supported lipid bilayer techniques allow work with membrane components, such as membrane proteins, which is difficult to accomplish using vesicles. For example, several separation methods have been developed in supported lipid bilayers. Although supported lipid bilayers provide many techniques, the solid support may be problematic when measuring transport or transmembrane signaling. We have developed a method to convert supported lipid bilayers into vesicles using fast buffer flow. Using a microfluidic device, we stripped a fluorescently labelled supported lipid bilayer from its glass support. This stripping was observed directly on the glass slide using fluorescence microscopy, and the stripped lipids were fluorescently detected in solution.



Fast buffer flow converts supported lipid bilayers into vesicles.

COLL 168

Surface modification of nanofibrous mats with polymeric micelles for enhanced tissue regeneration

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Nanofibrous (NF) mats have shown great promise to facilitate wound healing. In this work, we aim to engineer a NF-based scaffold for hard-to-heal diabetic ulcers. Specifically, we explore the surface modification of polycaprolactone/collagen NFs with ultrathin coatings of polymeric micelles and natural antioxidant molecules as a means to modulate NF topography, tune antioxidant capabilities, and modulate cellular responses to aid wound healing. Multilayers of polymeric micelles, composed of poly(acrylamide-

co-acetonitrile) cores and polyvinylpyrrolidone coronae, were deposited onto fibers by assembly with tannic acid (TA), which possesses anti-inflammatory and pro-wound healing effects. Such micellar coatings display dense coverage of micelles on fiber surface, and show layer-dependent topography and radical-scavenging capability enabled by TA. Upon exposure to serum, micelles detached from the NF surface between 4 and 6 days of culturing *in vitro*. Free micelles in solution had negligible effects on macrophage viability but induced a transition in phenotype from M0 to M1 upon intracellular uptake. A similar modulation of macrophage phenotype was observed for macrophages cultured on micelle/TA-coated NFs, which exhibited more M1 phenotype (iNOS positive) compared to those on bare NF mats, which showed more M2 phenotype (CD206 positive). In addition, micellar coatings on NF are also attractive because of the availability of the functional upper critical solution temperature micellar cores, which allow the loading and controlled release of small bioactive molecules (such as pioglitazone hydrochloride) critical for tissue regeneration and wound healing.

COLL 169

Synthetic charge-invertible polymer for rapid and complete implantation of layer-by-layer microneedle drug films for enhanced transdermal vaccination

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The utility of layer-by-layer (LbL) coated microneedle (MN) skin patches for transdermal drug delivery has been proven a promising approach, with advantages over hypodermal injection due to painless and easy self-administration. However, the long epidermal application time required for drug implantation by existing LbL MN strategies (15 to 90 minutes) can lead to potential medication noncompliance. Here, we developed a MN platform to shorten the application time in MN therapies based on a synthetic pH-induced charge-invertible polymer poly(2-(diisopropylamino) ethyl methacrylate-*b*-methacrylic acid) (PDM), requiring only 1-minute skin insertion time to implant LbL films *in vivo*. Following MN-mediated delivery of 0.5 μg model antigen chicken ovalbumin (OVA) in the skin of mice, this system achieved sustained release over 3 days and led to an elevated immune response as demonstrated by significantly higher humoral immunity compared with OVA administration via conventional routes (subcutaneously and intramuscularly). Moreover, in an *ex vivo* experiment on human skin, we achieved efficient immune activation through MN-delivered LbL films, demonstrated by a rapid uptake of vaccine adjuvants by the antigen presenting cells. These features—rapid

administration and the ability to elicit a robust immune response—can potentially enable a broad application of microneedle-based vaccination technologies.

COLL 170

Size-matching hierarchical micropillar arrays for detecting circulating tumor cells

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Circulating tumor cells (CTCs) are important markers for cancer diagnosis and treatment, but it is still a challenge to recognize and isolate CTCs because they are very rare in blood. To selectively recognizing CTCs and improving capture efficiency, micro/nanostructured substrates have been fabricated for this application, however, the size of CTCs is often ignored in designing and engineering the micro/nanostructured substrate. Herein, a spiky polymer micropillar array is fabricated for capturing CTCs with high efficiency. The surface of micropillar is composed of nanospikes, as shown in Fig.1. This hierarchical polymer array is fabricated according to the size of CTCs, which allows for more interactions of the CTCs with the array by setting the size of gaps among the micropillars match with the CTCs. This polymer array is created by taking molding on an ordered silicon array, and then is coated with antiepithelial cell adhesion molecule antibody (anti-EpCAM). After co-culture with MCF-7 for 45 min, the capture efficiency of this array for CTCs is up to $91\% \pm 2\%$. Moreover, the anti-EpCAM modified polymer micropillar arrays present excellent capacity to isolate CTCs from the whole blood samples of breast cancer patients. This study may provide a new concept for capturing target cells by designing and engineering micro/nanostructured substrate according to the size of target cells.

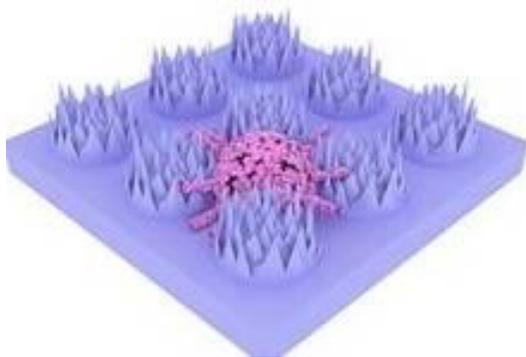


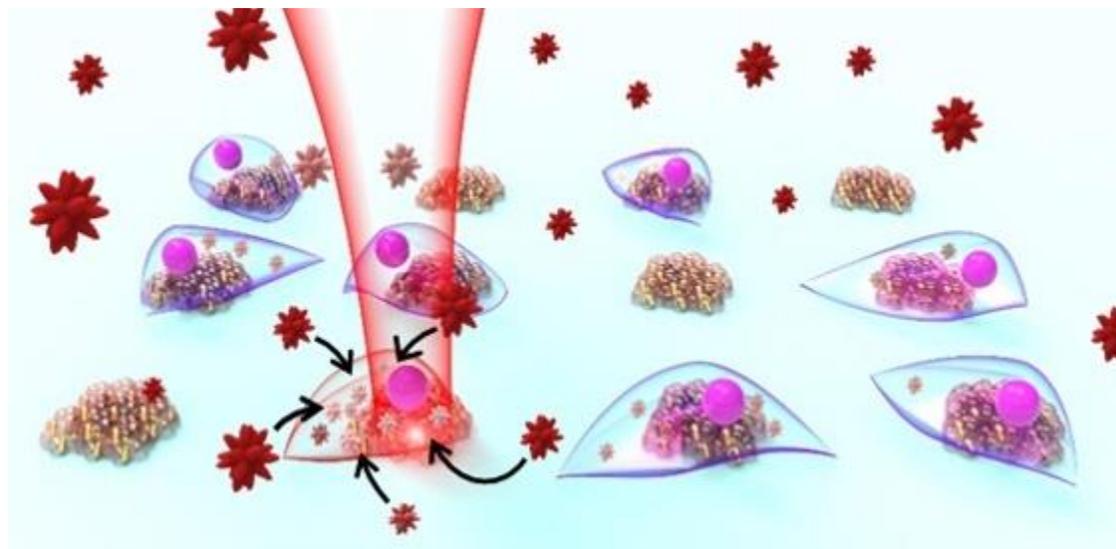
Fig. 1 Schematic diagram of size-matching hierarchical polymer micropillar array for capturing CTCs.

COLL 171

Directed cell positioning and photothermally enhanced drug delivery on patterned gold nanorods

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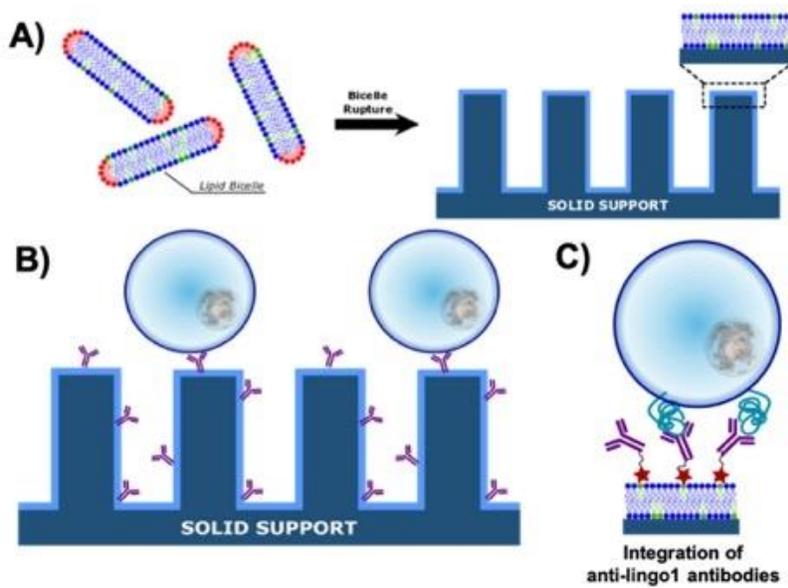
Photothermal conversion effect, that thermal energy is produced by photoexcitation of plasmonic nanoparticles which absorb light, is considered as a promising tool in cellular and molecular manipulations due to the controllability of local temperature. Therefore, it has been widely applied to biological studies such as controlling cellular behavior, biologics delivery, and biomolecular detection. In this presentation, we propose a novel method for directed cell positioning and photothermally-enhanced drug delivery to the cells by using patterned plasmonic substrates. We first fabricate plasmonic circle arrays composed of gold nanorods (GNRs) and poly-L-lysine by simple microcontact printing and optimize them for guided cell positioning on the circle patterns. Then, we further utilize the photothermal conversion effect from the patterned GNRs to facilitate the targeted temporal and spatial delivery of the drugs into the cells. When the resonant near infrared light is illuminated to the GNRs' pattern, drug uptake is dramatically enhanced compared with non-illumination condition. We expect that this study provides a new way to enhance molecular delivery into the target cell.



Supported lipid bilayer coated microfluidic device for capturing circulating tumor cells

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We report a new lipid bilayer-mediated strategy for the detection and enumeration of circulating tumor cells (CTCs) that are shed from a primary tumor site and enter into the bloodstream. Microfluidic devices that integrate nanostructured surfaces have been explored as a promising method for capturing CTCs efficiently. Existing approaches suffer from low capture purity due to clogging and nonspecific cell adhesion, impeding effective translation into routine patient care. To address this issue, we use supported lipid bilayers (SLBs) to prevent the adhesion of nonspecific cells and incorporate biotin-streptavidin conjugated antibodies for the specific detection of CTCs. We use Ewing sarcoma (EWS), an aggressive form of bone and soft tissue tumors with high metastatic potential, as an initial model to test this microfluidic platform. Altogether, this study represents a key step to designing diagnostic tools that incorporate nanostructured, cell-interactive interfaces, which enable high-throughput isolation of EWS-derived CTCs, paving the way for exciting new diagnostic methods that enable “liquid biopsies” for monitoring a patient’s disease status and which can be connected directly to precision medicine analyses to inform therapeutic decisions.



(A) Schematic illustrating the formation of supported lipid bilayers using bicelles. (B,C) Schematics showing the mechanism of capturing cells *via* biofunctionalized surfaces that incorporate cell-capture antibodies into the supported lipid bilayer *via* streptavidin-biotin complexes.

COLL 173

Using scanning force microscopy to unveil the main factors responsible for microorganism adhesion

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Scanning force microscopy (SFM) is a powerful tool which can be used to elucidate surface topography and provide force measurements at high resolution. Its ability to probe non-conductive samples in aqueous environments allows for the accurate investigation of bacterial surface properties in their native state, making it an excellent method of measuring cell-cell and cell-substrate adhesion.

The poster explores this interdisciplinary area of research concerning the adhesive properties of bacterial cells. Adhesive forces associated with bacterial attachment can be probed using various methods including the pulling of adhered cells with functionalised cantilevers, attachment of individual bacterial cells to cantilever apices, or coating colloidal probes with bacterial cells. Our research, however, concentrates on the growth of bacterial biofilms on tipless cantilevers, hence creating conditions resembling their natural environment. We will be discussing our data collected while investigating the interactions which occur between these bioprobes and various surfaces such as stainless steel and PVC. In particular, the use of SFM to determine the adhesive forces of *Pseudomonas Aeruginosa* and a *Micrococcus Luteus* biofilms will be explored. For instance, our research findings indicate that *P. Aeruginosa* biofilms attach to surfaces with an affinity of up to 4 times that of *M. luteus*. Additionally, possible future studies which can be carried out to obtain further insight into the mechanism of bacterial adhesion to surfaces will also be explored. For example, research into the change of these adhesion forces as a function of time is proposed.

The studied prokaryotic organisms pose a considerable problem in our society due to their role in widespread human disease as well as the increasingly pressing issue of antimicrobial resistance. Bacteria which live in the collaborative, multicellular communities known as biofilms benefit from the protection conferred by their extracellular polymeric matrix resulting in the enhancement of bacterial pathogenicity. Since the mechanism of bacterial surface attachment is known to play a crucial role in

biofilm formation, our research into the relationship between bacteria and their attachment to various substrates can potentially be applied in emerging research into novel antimicrobial agents.

COLL 174

Design of adaptive magnetic carbon nanotubes to mimic stimuli-responsive cell culture substrates

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Objective:

The extracellular matrix (ECM) regulates many aspects of cell behavior and is constantly remodeled as for instance in different types of disease. Although a variety of substrates have been engineered to investigate ECM-cell interactions they do not exhibit the topographical features of native healthy/diseased tissues nor possess dynamic properties responsiveness (including remodeling) within the physiological range. Hence, starting from the functionalization of oxidized multiwalled carbon nanotubes (O-MWCNTs) with superparamagnetic iron oxide nanoparticles (SPIONs), magnetically adaptive fiber-like substrates were designed by various deposition approaches with the aim to provide a stimuli-responsive ECM to influence cell morphology in situ.

Methods:

O-MWCNTs functionalization with SPIONs exhibiting a diameter of 9 ± 3 nm was carried out via N-(3-Dimethylaminopropyl)-N'-ethyl carbodiimide hydrochloride (EDC) N-Hydroxysuccinimide (NHS) coupling. The coated O-MWCNTs were characterized by Transmission Electron Microscopy (TEM). Surface charge was evaluated by Zeta-potential measurements. By applying static magnetic fields, functionalized O-MWCNTs patterns were assembled once deposited on coverslips with a layer by layer approach. Patterns were thoroughly investigated with Scanning Electron Microscopy (SEM). Mice fibroblasts (NIH-3T3 cell line) were used to address the biocompatibility of the substrate. Confocal microscopy was used to study the cell morphology and focal adhesions were visualized with F-Actin and Paxillin staining.

Results:

TEM images analysis showed an even distribution of SPIONs along the O-MWCNTs fibers with a total width of 34 ± 8 nm. Functionalized O-MWCNTs exhibited a Zeta-potential of -47 ± 2 mV. SEM analysis clearly demonstrate anisotropic orientation of O-MWCNTs into bundles of 805 ± 127 nm along the magnetic field lines when subjected to a static magnetic field overnight. Confocal pictures demonstrate fibroblast adhesion after 24 hours of incubation and an increased cell spreading upon introduction to a static magnetic field. Analysis for alternating magnetic fields are currently ongoing.

Conclusions:

A novel anisotropic, magnetically adaptive substrate was successfully designed as a

platform to study cell behavior on a stimuli-responsive substrate. We demonstrated alignment of functionalized O-MWCNTs under a magnetic field as well as cell cytoskeleton spreading when a static magnetic field is applied to the system.

COLL 175

Acoustofluidic gene delivery for cancer immunotherapies

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State-of-the-art cancer immunotherapies that utilize engineered T cells to attack cancer cells are rapidly evolving and providing new hope for patients with disease unresponsive to conventional treatments. The effective development and manufacturing of these cell-based immunotherapies requires reliable gene-modification that is not subject to the limitations associated with existing methods (e.g., electroporation, lipofection, viral vectors), which include unwanted toxicity, slow processing throughputs, and high costs. We report an acoustofluidic strategy for delivering biomolecular cargo to model and clinically-relevant cell types rapidly and safely by shearing cells against a glass microcapillary wall. Mechanistic investigations of cell membrane permeability post-acoustofluidic treatment revealed that the cell and nuclear membranes are disrupted in model cell types. We apply this acoustofluidic approach for manufacturing chimeric antigen receptor (CAR) T cells that are used to treat B cell malignancies. We characterize the intracellular delivery of a second-generation CD19-targeting CAR-expressing plasmid to primary human T cells and monitor expression of the CAR to establish a robust and sustainable processing method for generating cellular therapies.

COLL 176

NaCl induced changes in unilamellar DOPC liposomes

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We investigate the influence of sodium chloride on the structure and dynamics of DOPC unilamellar liposomes and the phospholipid bilayer. We expect that our study will assist current liposomal drug delivery formulations to look at ionic strength in the range of physiological limits in a new light and to broaden the fundamental understanding of the biological membrane structure and dynamics with the widely overlooked saline environment. Several techniques such as cryo-transmission electron microscopy (cryo-TEM), dynamic light scattering (DLS), small-angle X-ray scattering (SAXS) and small-

angle neutron scattering (SANS) reveal structural changes with increasing NaCl concentration. We observe a change of the membrane rigidity at the physiological ionic strength. We also notice the importance of investigating beyond the established traditional Zilman-Granek analysis with a more advanced model that includes the mobility of fatty acid tails to obtain accurate values for the bending elasticity.

COLL 177

Experimental study on the self-assembly of polyesters

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Degradable polyesters constitute one of the most popular choices for biomedical applications, as they degrade to components present in the human metabolome, and thus get eliminated via natural pathways. In addition, the use of FDA-approved materials to build nanoplateforms can make more feasible their clinical translation. In the case of amphiphilic block copolymers, minor tuning of the hydrophobic segment (i.e. altering the ratio of one polyester to the other) can allow accessing unique architectures, as well as defining the physicochemical properties of the nano-assembly (e.g. softness of the material). A change in the physicochemical profile (e.g. T_g) is directly reflected on the behaviour of the polymer in water. For instance, reaching the vesicular morphology can potentially occur through a different mechanism. Aside from the polymer nature, the process of self-assembly is strongly affected by several physicochemical parameters. Starting from the most simple way to assemble particles, namely the top-down film hydration, the thickness of the film, as well as the shearing stress during the hydration process are all parameters demonstrated to affect both the speed of formation and the quality of particles size distribution. The question of controlling self-assembly with bottom-up techniques like solvent displacement becomes far more complex. This is due to the contribution of the solvent where the polymer is dissolved. Additionally, parameters like temperature, and the rate of phase addition have been demonstrated to play a pivotal role in guiding the assembly. The self-assembly profile of a series of PEGylated polyesters is investigated here employing both bottom-up and top down approaches. We show how experimental processing (e.g. choice of solvent) can exert control over the nanoparticle morphology while we also follow how different polyesters reach the vesicular morphology under a distinct growth mechanism.

COLL 178

Characterization of the bioaccessibility of nanoparticles in consumer products advertised to contain colloidal silver

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Given the potential for human exposure to silver nanoparticles from spray disinfectants and dietary supplements, we characterized silver-containing nanoparticles in 22 commercial products that advertised the use of silver or colloidal silver as the active ingredient. Characterization parameters included: total silver, fractionated silver (particulate and dissolved), primary particle size distribution, hydrodynamic diameter, particle number, and plasmon resonance absorbance. A high degree of variability between claimed and measured values for total silver was observed with concentrations ranging from 0.54 mg/L to 960 mg/L. Although only 7 of the products showed total silver concentrations within 20% of their nominally reported values, silver containing nanoparticles were identified in all the product suspensions by transmission electron microscopy (TEM). Since many of these products are meant for ingestion, we simulated gastrointestinal exposure in selected products to determine bioaccessibility parameters such as particle aggregation, dissolution and chemical transformation. Incubation of products 4, 6, and 10 in apple juice, vinegar and synthetic stomach fluid (SSF) resulted in an increase in hydrodynamic diameter of silver nanoparticles (AgNPs) as measured by dynamic light scattering (DLS) and nanoparticle tracking analysis (NTA). Exposure of these products to SSF also resulted in the formation of AgCl determined by X-ray absorption spectroscopy (XAS) and TEM-energy dispersive X-ray spectroscopy (EDS). For the products tested in the simulated GI system, AgNP aggregation and formation of low solubility AgCl would suggest a decrease in bioaccessibility from the original formulations.

COLL 179

Low-field NMR relaxometry for characterizing wetted surface area in colloids and polymer particle dispersions

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For polymer particle dispersions, traditional gas adsorption techniques (e.g. BET surface area) are insufficient to elucidate the structure of a wetted material, which may collapse during sample preparation steps (vacuum). To address this limitation of conventional surface area measurements, we are developing low-field NMR methods to characterize materials under inherent conditions, e.g. as a wetted slurry. The physical basis for these methods and example data sets for colloidal silica and polystyrene will be discussed to underscore the value of low-field NMR for challenging characterization problems. In the case of silica colloids, a linear relationship exists between colloid concentration (weight percent) and the measured spin-spin relaxation rate ($1/T_2$) for a number of different commercially available colloids. For polystyrene the behavior is much different; essentially $1/T_2$ is invariant with concentration. The differences are consistent with the degree of hydrogen-bonding between the water and the surface. In line with others in the literature, we suggest that $1/T_2$ can be used to infer the wetted surface area of particle suspensions. The influence of surface chemistry upon this attribute will be described.

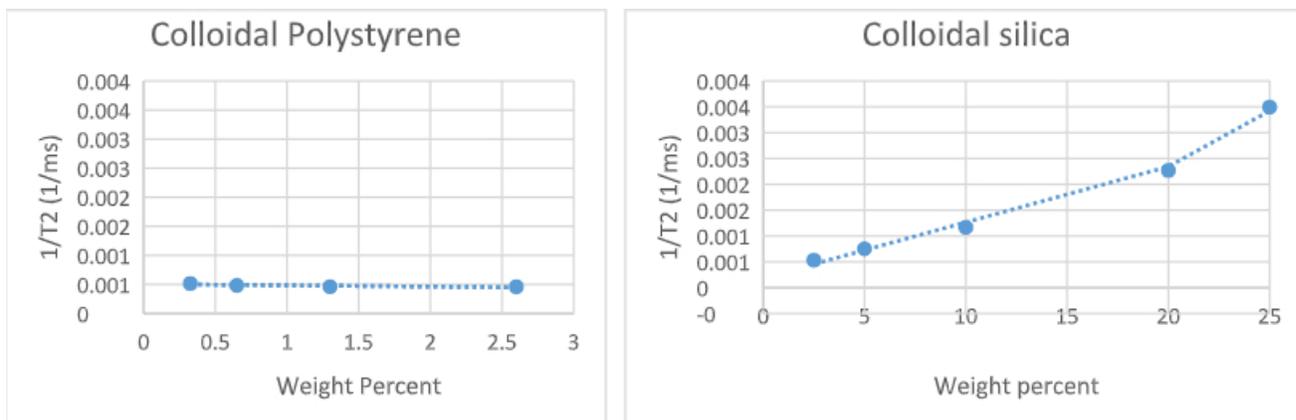


Figure 1. Linear response between colloid loading and low-field NMR transverse relaxation rates ($1/T_2$)

COLL 180

Building and testing a budget-friendly tensiometer

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In this build, a water tensiometer was assembled using various, inexpensive components. Using a Dremel tool press as a base, a 5-10 μL pipette was fitted so that it can perform a Drop-Shape Analysis. From there, a Raspberry Pi camera along with the computer was introduced and the whole assembly encased in a felt-lined cabinet to prevent any light pollution. Then, using the Circle Fit MATLAB program by Izhak Bucher, and another program written by the research group, the contact angle of the surface was computed. The goal of this device is to measure the polarity of a substrate, such as in this case with nano-composite materials. From here, the plan is to use the control data and compare it to commercial water tensiometers to see if the device is in an acceptable range of accuracy and precision.

COLL 181

Biopolymer functionalized liposomes for enhanced dispersion stability of nano vesicles

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Liposomal nanoparticles are essential in the delivery of chemotherapeutic drugs in the treatment of multiple myeloma cancer. The development of an ideal liposomal nanoparticle drug delivery system is of increasing interest to ensure that the conjugated drug carrier complex arrives and acts preferentially at the tumor site with high efficacy and lower toxicity. The focus of this work lies in the synthesis of biopolymer functionalized multilamellar (MLV) vesicles to enhance the stability and bio adhesivity of the liposomal nanoparticle system. Characterization of the liposome vehicles were studied using Fourier Transform Infrared Spectroscopy (FTIR), zeta potential analysis, particle size analysis (PSA), and scanning electron microscopy (SEM). Preliminary findings in the characterization of the synthesized liposomes using FTIR showed characteristic symmetric and antisymmetric CH_2 (at $2,800\text{--}3,000\text{ cm}^{-1}$) bands and the C=O (at $1,740\text{ cm}^{-1}$) stretching bands attributed to the presence of chitosan on the liposome surface. Structural characteristics of the synthesized liposomes were also studied by dynamic light scattering. The liposome suspensions presented exhibited mean diameters between 150 nm and 250 nm, polydispersity indexes (PDI) around 0.4, zeta potential values between -40 mV and -30 mV, indicating complex formation between the anionic liposomes and cationic chitosan molecules. The surface morphology of the scaffolds were studied using scanning electron microscopy (SEM) and it was observed that the liposomes are uniform in diameter ($\sim 190\text{nm}$) with multilamellar structures. XRD analysis exhibited diffraction peaks corresponding to chitosan functionalization occurring at 20° . Stability studies of the functionalized CS-liposomes showed increased stability to aggregation than pristine liposomes when stored at ambient temperatures. The development of chitosan functionalized liposomal nanoparticle drug delivery systems (DDS) shows great promise in the delivery of anticancer drugs, through the reduction/elimination of toxic and adverse effects resulting from their administration.

COLL 182

Effects of humidity on the formation of indoor organic thin films

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People spend 90% of their lives indoors, yet the majority of research on air quality relates to outdoor spaces. Indoor chemistry is fundamentally important to understand since indoor air quality impacts human health. The indoor environment presents challenges because of the increased concentrations of pollutants and larger surface to volume ratio. Many indoor surfaces, like titanium dioxide, have unique catalytic properties with common organic emissions. There exists a very limited understanding of the basic physical and chemical interactions that occur between surfaces and various indoor emissions. A recent study conducted during the House Observations of Microbial and Environmental Chemistry (HOMEChem) experiment observed organic aerosols, formed from human activities, deposited onto window glass. Past studies have shown

that the oxidation of organic aerosols, like oleic acid, results in morphological deformations, which could be an important contributor to the formation of an organic thin film. An experiment was conducted in a Teflon chamber to reproduce surfaces observed in HOMEChem. Window glass was fixed vertically and exposed to oleic acid particles and ozone at different relative humidity levels. Analysis of thin organic films via atomic force microscopy-infrared spectroscopy (AFM-IR) suggests that the presence of water vapor is important for the formation of organic depositions which resemble surfaces placed in more realistic home environments both morphologically and chemically. Reproducing the surfaces seen in these indoor field studies using a controlled environment will lead to an improved model for the formation of organic films in the indoor environment.

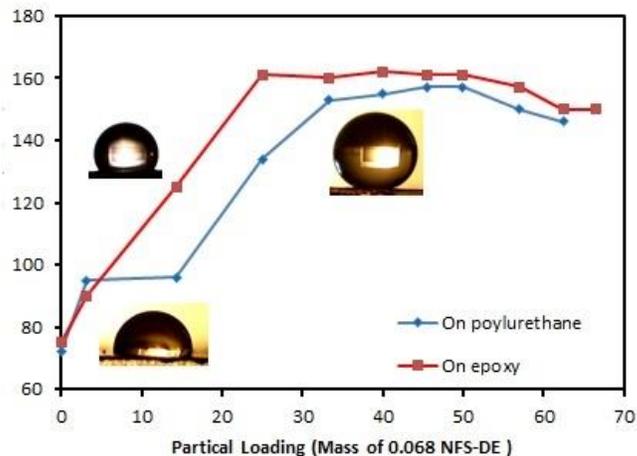
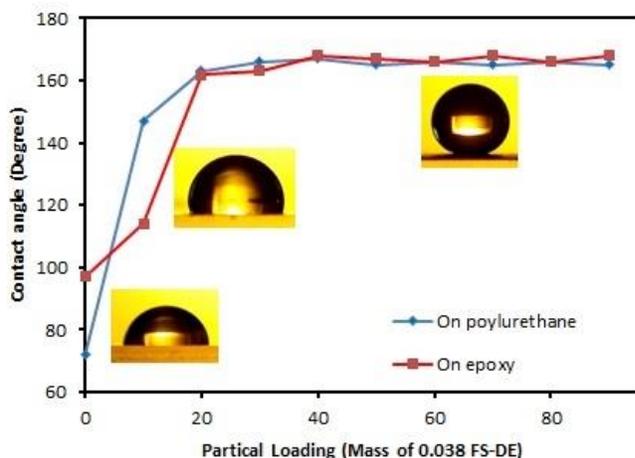
COLL 183

Treated diatomaceous earth particles on polymers

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Diatomaceous earth (DE) is a sedimentary rock that found in natural. DE mainly composed of siliceous skeletons of aquatic plant diatoms. Siliceous skeletons are composed of micro and nano pore structure and species characterized unique patterns such as pores, channels, ridges, spikes, and spines. Which makes DE particles ideal on for forming hydrophobic and superhydrophobic surfaces. Surfaces with water contact angles greater than 90° are considered hydrophobic, and surfaces with very high water contact angles (particularly larger than 150°) and sliding angle typically less than 5-10° are usually considered superhydrophobic. Superhydrophobicity is result of combination of micro-nano roughness with low surface energy material.

Superhydrophobic/hydrophobic surfaces were made using low surface energy fluorinated (FS) and non-fluorinated (NFS) silane treated DE with different polymeric resins/binders. These surfaces and treated DE particles are been characterized with contact angle measurements, scanning electron microscopy and thermogravimetric analysis. Contact angles greater than 150° were attainable if the particles were sufficiently treated with fluorinated and non-fluorinated silane coupling agents and also if there were enough particles in the surfaces. The critical particle loadings depended on the resin/binder system used. The behavior of these surfaces mimics that from, for example, the lotus and rice leaves as they had low surface energies and also appropriate nano-micro structures.



COLL 184

Impact of gold nanostar morphology on bioassay sensitivity

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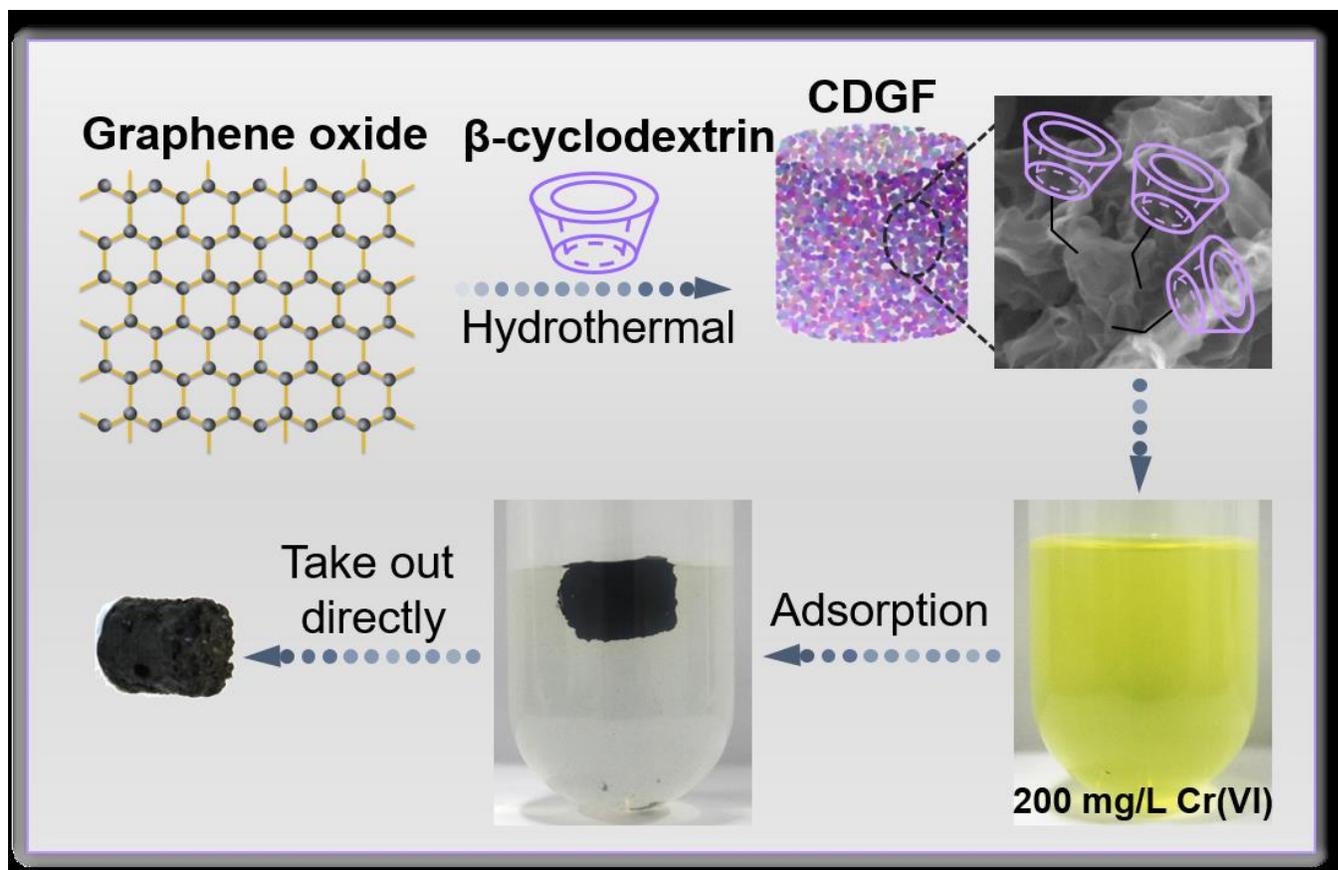
This presentation details the use of gold nanostars (GNSs) in lateral flow assay (LFA) applications and the influence of the morphology of the stars on the sensitivity and detection limit of the LFA toward human chorionic gonadotropin (hCG) hormone. The gold nanostars used in this study were synthesized through a seed-growth method and functionalized with a self-assembled monolayer (SAM) generated from a custom-designed bidentate carboxylate-terminated dithiol, 16-(3,5-bis(mercaptomethyl)phenoxy)hexadecaonic acid (BMPHA). Functionalization of the surface of the stars with the SAM enables bioconjugation (e.g., with antibodies) and utilization in various biological applications, such as nanosensors, biological assays, and drug delivery. The functionalized GNSs were characterized with UV-Vis spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray spectroscopy (EDS), and Fourier-transform infrared (FTIR) spectroscopy. The engineering and evaluation of hCG-targeted bio-sensing nano-platforms using these colloiddally stable GNSs will be described.

COLL 185

Cyclodextrin functionalized 3D-graphene for the removal of Cr(VI) with the easy and rapid separation strategy

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As a useful heavy metal ion, chromium has seen its applications in various fields. While it is also a toxic contaminant in water and may cause serious threats to the environment and human health. To develop a novel material with high adsorption capacity and easy solid-liquid separation strategy was necessary and significant. In this paper, the β -cyclodextrin (β -CD) functionalized three-dimensional structured graphene foam (CDGF) was successfully synthesized with the facile and one-step hydrothermal method. The SEM, BET, XRD, FT-IR and XPS analysis were carried out and the results confirmed the successfully grafting of β -CD onto GF. The batch adsorption tests of Cr(VI) also taken out and the adsorption capacity could reach to 145 mg/g at pH=3. The adsorption capacity reduced gradually as the pH of the Cr(VI) solution grew higher, which could ascribe to the anionic species of Cr(VI) in water. The easy separation strategy of the CDGF was also demonstrated and the CDGF could be taken out easily with a tweezer after the adsorption of Cr(VI), which significantly simplified the separation procedure and reduced time. By comparing the FT-IR and XPD analysis results, the adsorption mechanism was explored and the C-O bond on CDGF played the main role in the adsorption process. This work brings a novel material for the adsorption of Cr(VI) from water and provides an innovative direction for the easy and fast solid-liquid separation strategy in the adsorption and other application fields.



COLL 186

Effects of alloying on exciton recombination in InP-ZnSe quantum dots

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Fluorescent nanocrystal quantum dots (QDs) offer a wide range of fluorescing capabilities as emitters in molecular probes, biolabels, solid-state lighting, and quantum informatics. Currently, the best studied and highest performing QD systems are cadmium based. Yet because of cadmium's inherent toxicity, they cannot be used in many biological and industrial applications. Indium, with its low toxicity, offers an alternative QD system that also exhibits size-tunable fluorescent emission throughout the visible and lower IR spectrum. Despite substantial synthetic efforts, indium-based QDs still exhibit significantly lower photostability and size tunability when compared to

their higher-toxicity counterparts. Growing thick shells of a wider-band gap material, such as ZnSe or ZnS, over InP QDs has been shown to passivate surface trap sites and increase their photostability. Here for the first time we show control over indium doping into the ZnSe shell and provide an unprecedented view into the effects of interface doping on the photophysical properties of individual nanocrystals.

COLL 187

Second harmonic generation in mesoscale semiconductor helices

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Chirality in semiconductor particles has emerged as prolific topic for designing systems with applications in photocatalysis, biomedical or telecommunication areas. The design of superstructures obtained from chiral nanoparticles still remains challenging but offers great perspectives in terms of modulation of chiroptical activity.

Here, we show that mesoscale helical structures formed by self-assembly of chiral cadmium telluride (CdTe) nanoparticles can be imaged by second-harmonic generation (SHG) microscopy. While the self-assembly process also produces random aggregates resulting in a poor yield of helical superstructures, SHG from those aggregates is not visible as compared to helices, and a contrast between helices and those aggregates can be enhanced. Our results pave the way to more applications of chiral superstructures in the field of nonlinear optics.

COLL 188

CdHgSe/HgS/CdZnS colloidal quantum wells: Bright short-wave infrared nanoemitter

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Bright short-wave infrared or second near-infrared (SWIR or NIR-II; wavelength = 1000–1700 nm) light emitters provide unique opportunities for deep tissue biological imaging, telecommunications, and night-time surveillance. Researchers have introduced various SWIR emitters including carbon nanotubes, molecular dyes, rare earth-doped nanoparticles, and semiconductor quantum dots. However, wavelength-tunable SWIR emitters with high quantum yield (QY) in the entire SWIR region has not been realized. In this work, we present the fabrication of a new bright SWIR light emitter by synthesizing CdHgSe/HgS/CdZnS colloidal quantum well (QW) structure. CdHgSe cores with NIR absorption ($\lambda_{\text{abs}} \sim 750$ nm) were prepared via Cd-to-Hg cation exchange

on zinc-blende CdSe QDs. Then HgS emitting layer with controlled thickness (0.8-2.4 monolayers, MLs) was grown over the CdHgSe core to tune the emission wavelength in SWIR region. Finally, CdZnS protecting layer (typically CdZnS ~4ML) was overcoated to boost QY, increase photostability, and improve their resistance to surface modification necessary for water solubilization. Photoluminescence (PL) spectra showed that our SWIR QWs show narrow-band emission (FWHM <0.2 eV) which can be tuned in the entire SWIR region (1050-1550 nm). More importantly, absolute PL QYs of SWIR QWs can be maintained high at 50-90% in the most of SWIR region in 1000-1350 nm and reduced to 20-40% in 1350-1550 nm. Furthermore, SWIR QWs show bright emission in water (QY >40%) after applying with amphiphilic polymer coatings. In addition, we could fabricate high-intensity AC-driven LED devices with our SWIR QWs to produce electroluminescence covering the whole SWIR spectrum.

COLL 189

Doping metal ions into CsPbCl₃ perovskite nanocrystals with improved optical properties for potential optoelectronic applications

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Doping metal ions into lead halide perovskite nanocrystals (NCs) has attracted significant attention over the past few years due to the emergence of novel optical properties. Previous successful dopants include transition metal ions like Mn²⁺, Cu²⁺, Zn²⁺ and rare earth metal ions such as Yb³⁺, Ce³⁺, Er³⁺, etc. Here, we report a synthesis of Cd²⁺-doped CsPbCl₃ NCs by a hot injection method. The resulting NCs show a dual-wavelength emission profile with the preservation of cubic morphology and crystal structures. The emission profile can also be tuned by controlling different dopant precursor amounts. The secondary emission is proposed to be induced by an energy transfer process from host NCs to the dopants after photo-excitation, together with a subsequent electronic transition from excited state (3E_g) to ground state (1A_{1g}) of [CdCl₆]⁴⁻ units, which matches well with a first-principles density functional theory calculation. Further, the resulting doped NCs can undergo fast anion exchange reactions by post-synthetic treatment. Our studies present a new model system for future doping chemistry studies and the potential of doped perovskite nanocrystals for various optoelectronic applications.

COLL 190

Investigation of the effects of quantum confinement and grain size on the photoconductivity of CdSe nanocrystal thin films

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Size-tunable band gap materials offer an advantageous method for developing high efficiency solution processed nanocrystal optoelectronic devices. The effect grain size on charge transfer across thin films was investigated by varying the CdSe nanocrystal size via control of the nanocrystal synthesis. Additionally, growing CdS/CdSe core/shell materials with various shell thicknesses allowed for the investigation of the effects of quantum confinement, due to the confinement of photogenerated holes and electrons to the CdSe shell layer. Comparing the photoconductivity of confined (2.6 nm diameter) and non-confined (13 nm diameter) CdSe has shown a 15-fold greater conductivity for large CdSe. Grain size has shown to be more significant factor than quantum confinement for thin film conductivity. However, the role of quantum confinement was investigated independent of grain size via CdS/CdSe nanoshells. The CdS core dimensions are allowed to exceed the exciton Bohr radius, which leads to nanostructures approaching 30 nm in total diameter while exhibiting CdSe shell quantum confinement. By adjusting the dimensions of CdS/CdSe materials even greater thin film photoconductivity than CdSe (of the same size) is achieved by taking advantage of both grain size and quantum confinement effects on photo-induced charge transfer.

COLL 191

Role of spacers towards directing the interactions in silicon quantum dots: Fluorescein dyads

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The unique properties of silicon quantum dots (SQDs), such as their unique optical properties, low toxicity, and ease of surface functionalization have made them great candidates for various biological and optoelectronic applications. Unfortunately, the low quantum yield, unstable photoluminescence, and poor colloidal stability of SQDs hindered their wide applicability. Herein, we report the synthesis of four assemblies of SQDs (1.6 – 1.8 nm average diameter) functionalized with fluorescein dye through isothiocyanate (-NCS) and carboxylate (COO) spacers to produce the dyads Am-SQD-FI, DiAm-SQD-FI, Urea-SQD-FI, and SiF. The photophysical results showed that the interaction between SQDs and Fluorescein chromophores in the dyads Am-SQD-FI, DiAm-SQD-FI, and SiF is mainly proceeding through photoinduced electron transfer at different rates, while energy transfer was confirmed to be the predominant process in the dyad Urea-SQD-FI. Furthermore, the utilization of the isothiocyanate spacer in the dyads led to a significant improvement in the quantum efficiency of SQDs (up to 65%) and extended their photostability for a year. The nature of the spacer played a vital role

toward directing and controlling the optical properties of SQDs. To demonstrate the suitability of the functionalized SQDs for bioimaging, the four dyads were examined for fluorescent imaging of human bone cancerous U2OS cells.

COLL 192

Synthesis and photocatalytic performance of recyclable core-shell mesoporous $\text{Fe}_3\text{O}_4@ \text{Bi}_2\text{WO}_6$ nanoparticles

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Composite photocatalysts composed of semiconductor and magnetic matters are of great concern due to their excellent catalytic and recyclable performances. In this work, Fe_3O_4 nanoparticles (~300 nm) are modified by a fibrous mesoporous silica layer (F-SiO₂), on which a mesoporous Bi_2WO_6 shell is grown in situ through hydrothermal reaction. Along with the formation of Bi_2WO_6 shell, the F-SiO₂ layer fades away by the acid etching. As a result, novel spherical core-shell mesoporous $\text{Fe}_3\text{O}_4@ \text{Bi}_2\text{WO}_6$ nanoparticles with a high BET surface area of 127.3 m²/g are fabricated, as shown in Fig.1. The HRTEM image of the prepared $\text{Fe}_3\text{O}_4@ \text{Bi}_2\text{WO}_6$ nanoparticle shows the mesoporous shell consists of Bi_2WO_6 nanoparticles with a size of 5-15 nm. The mesoporous $\text{Fe}_3\text{O}_4@ \text{Bi}_2\text{WO}_6$ nanoparticles can strongly absorb the visible light with a wavelength as long as 750 nm, and have a band gaps (E_g) of 1.7 eV. The photocatalytic decomposition of methylene blue (MB) under visible light irradiation reveals that the mesoporous $\text{Fe}_3\text{O}_4@ \text{Bi}_2\text{WO}_6$ nanoparticles show excellent physisorption and photocatalytic performances. The total removal ratio of MB can be achieved as high as 98%. Furthermore, the mesoporous $\text{Fe}_3\text{O}_4@ \text{Bi}_2\text{WO}_6$ nanoparticles can be easily separated from aqueous solution in dozens of seconds using a magnet, and maintain high photocatalytic activity after five cycles. This work provides a new way to construct recyclable mesoporous Bi_2WO_6 -based nanomaterials with high performance to remove organic pollutants.

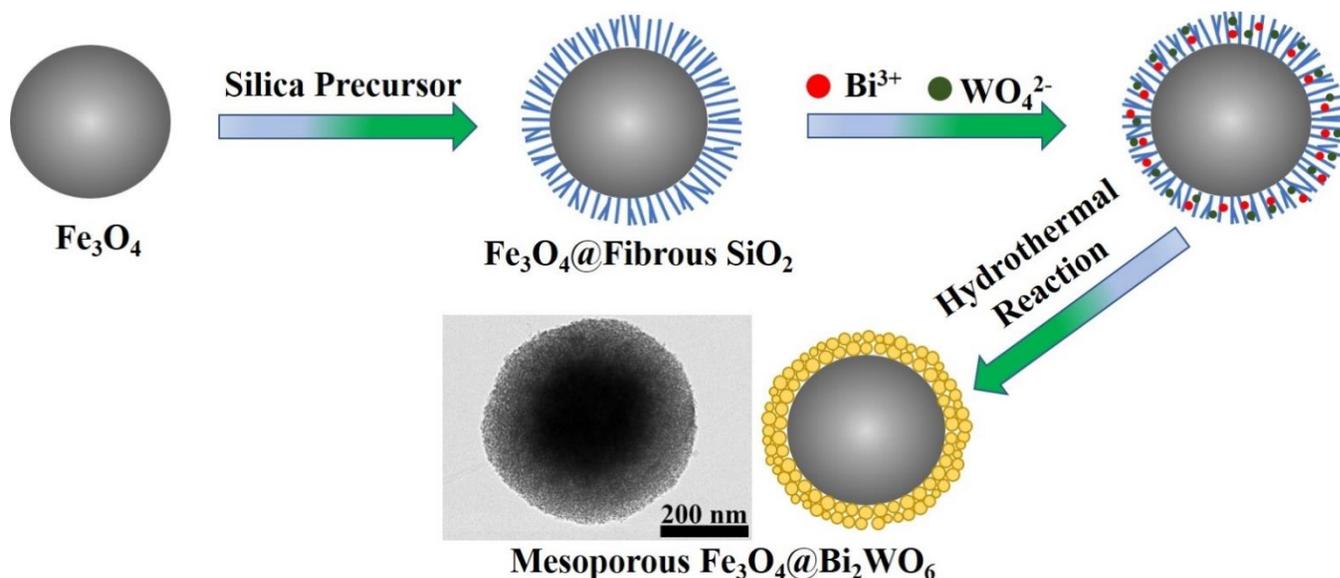


Fig.1 Preparation process and HRTEM image of core-shell mesoporous $\text{Fe}_3\text{O}_4@ \text{Bi}_2\text{WO}_6$ nanoparticles

COLL 193

Fibrous N-doped hierarchical porous carbon microspheres: Synthesis and adsorption performance

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The creation of high surface area and effective active sites is the key problem for the synthesis of high-performance porous carbon materials. In this work, polyacrylonitrile-coated fibrous silica ($\text{F-SiO}_2@ \text{PAN}$) microspheres were prepared by in situ polymerization of acrylonitrile on fibrous mesoporous silica microspheres induced by γ -ray radiation. After $\text{F-SiO}_2@ \text{PAN}$ microspheres were carbonized and etched with hydrofluoric acid, uniform fibrous N-doped porous carbon (FNC) microspheres with an average size of 286 nm and a molar ratio of C/N of 5.2 were successfully prepared, as shown in Fig.1. As revealed by TEM, SEM, and N_2 adsorption-desorption isotherms analysis, FNC microspheres have a hierarchical micro-macroporous structure with a particular high surface area of $554.5 \text{ m}^2/\text{g}$. The FNC microspheres also exhibit a good water dispersibility and an excellent adsorption ability to rhodamine B in water. The equilibrium adsorption capacity of FNC microspheres could reach 95.4 mg/g , which is 1.6 times as that of the primary silica template microspheres. The adsorption kinetics and thermodynamics of FNC microspheres are in accord with the pseudo-second-order kinetic equation and Freundlich isotherm model, respectively. This work provides a

facile synthesis method for novel N-doped hierarchical micro-macroporous carbon microspheres as a potential high-performance adsorbent material.

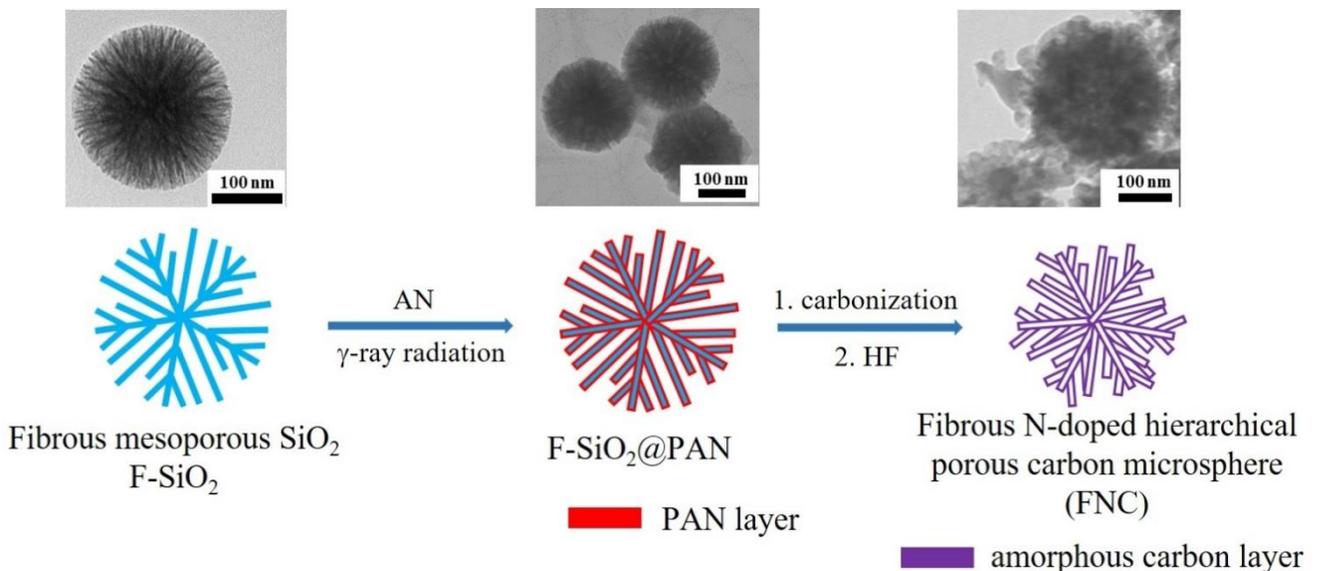


Fig.1 Synthesis and TEM image of fibrous N-doped porous carbon (FNC) microspheres from fibrous mesoporous silica template microspheres (F- SiO_2)

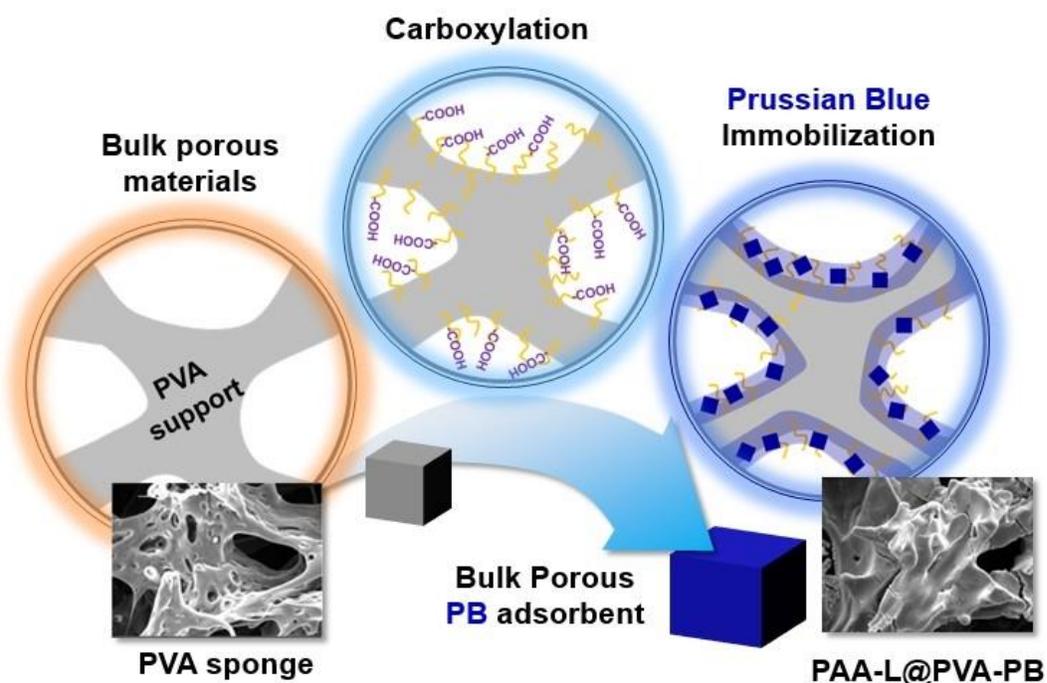
COLL 194

Prussian blue immobilized filter materials for the selective removal of aqueous cesium

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Cesium is a typical radioisotope that has a long half-life and can be emitted in the event of a nuclear accident. Prussian blue (PB) is known to be an effective cesium adsorbent, but the direct application of PB is limited by the difficulty of its recovery from solution. In this study, a simple and versatile approach to immobilize Prussian blue in the supporting matrix via surface functionalization was investigated. The commercially available poly vinyl alcohol (PVA) sponge and cellulose filter (CF) was functionalized by acrylic acid (AA) to enhance the PB immobilization, which increased both PB loading and binding strength. The amount of AA added was optimized by evaluating the weight change rate and iron (III) ion adsorption test. The AA functionalization changed the

major functional groups from hydroxyl to carboxylic, as confirmed by Fourier-transform infrared spectroscopy. PB was further synthesized in the AA modified PVA (PAA-PVA) and the AA modified CF (PAA-CF) using layer-by-layer (LBL) assembly, which contributed to more stable PB formation, and reduced detachment of PB during washing. The prepared adsorbents (PAA-L@PVA-PB, PAA-L@CF-PB) were tested for its cesium adsorption capability. Cesium adsorption was equilibrated within three hours, and the maximum cesium adsorption capacities of AA treated adsorbents were much higher than pristine PVA and CF. The observed decrease in the solution pH during cesium adsorption inhibited the overall cesium uptake; however, this was minimized by buffering. The prepared PAA-L@PVA-PB, PAA-L@CF-PB were used as a filter material and its potential use as a countermeasure for removing radioactive cesium from a contaminated water stream was demonstrated.



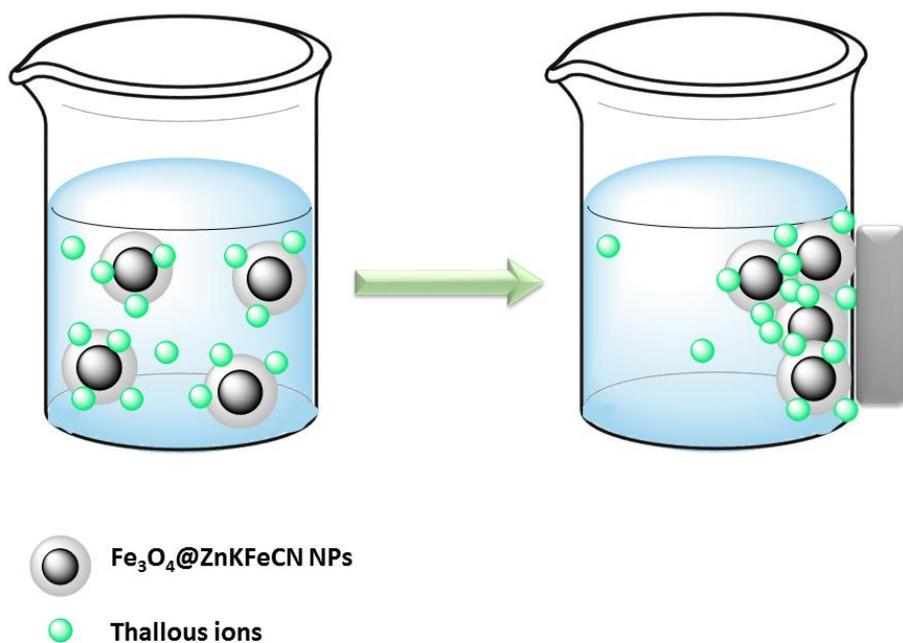
COLL 195

Functionalized magnetite nanoparticles for thallium(I) removal in an aqueous environment

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Thallium(I) is known to be one of the most toxic metals to human health given it substitutes potassium in biological reactions and shows high affinity toward sulphhydryl groups. In the past few years, there has been an increase in the environmental Tl concentration, above the permitted limits according to guidelines of USEPA (drinking water ($2 \mu\text{g L}^{-1}$) and wastewaters ($140 \mu\text{g L}^{-1}$). Despite its toxicity, Tl removal studies have received little attention, compared to other heavy metals.

Contaminants removal using magnetic sorbents has gained a privileged position among water treatment techniques due to its relatively low cost and toxicity as well as high removal efficiency. Herein a new strategy based on functionalized magnetite nanoparticles (Fe_3O_4 NPs) is presented for thallium(I) removal. $\text{Zn}_3\text{K}_2[\text{Fe}(\text{CN})_6] \cdot x\text{H}_2\text{O}$ was employed as an agent for the surface functionalization of the Fe_3O_4 NPs. The obtained magnetic composites were characterized and their Tl removal from water capacity was tested. Kinetics and interferences studies related to the removal procedure were carried out. An efficiency ranging from 95 to 98 % for thallium removal was obtained using an easy to prepare, low-cost and eco-friendly sorbent.



Magnetic removal of thallos ions from water

COLL 196

Synthesis of hollow structured CuO-rutile phase TiO_2 hybrid nanoparticles and applications for water purification under visible light condition

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Hollow materials have many kinds of advantages, such as larger specific surface area, short diffusion distance of reactant molecules to active sites on the shell and favorable dispersion in liquid media. In this point of view, hollow structured materials can be a good candidate as an effective solid catalyst for water treatment. TiO_2 is one of the well-known photocatalysts, for its non-toxic, high stability toward photo- and chemical corrosion and abundant amount on the earth. It is well known that two representative crystalline phases of TiO_2 , which are phototactically active, are anatase and rutile ones. Anatase phase has good electron lifetime resulting in superior performance under UV light irradiation. But limited use of UV in solar spectrum are hampering practical use of TiO_2 . In order to overcome the limitation, photocatalysis should have narrow band gap energy resulting increasing utilization of solar spectrum. In this work, we synthesize CuO-rutile TiO_2 hybrid hollow nanoparticles via template assisted sol-gel method. Both CuO and rutile TiO_2 which have narrower band gap energy (2.58 eV, and 3.0 eV) than anatase one (3.2 eV) should absorb visible light and show superior activity. The synthesized CuO-rutile TiO_2 hybrid hollow nanoparticles characterized by SEM, TEM, XRD and BET. When used as photocatalysts in phenol (10 ppm) photodegradation, hollow CuO- TiO_2 hybrid samples showed improved photocatalytic activities compared to hollow anatase TiO_2 counterpart under visible light irradiation conditions. In this presentation, we will discuss details of the synthesis and characteristics of hollow CuO- TiO_2 hybrid and photocatalytic activity on phenol photodegradation.

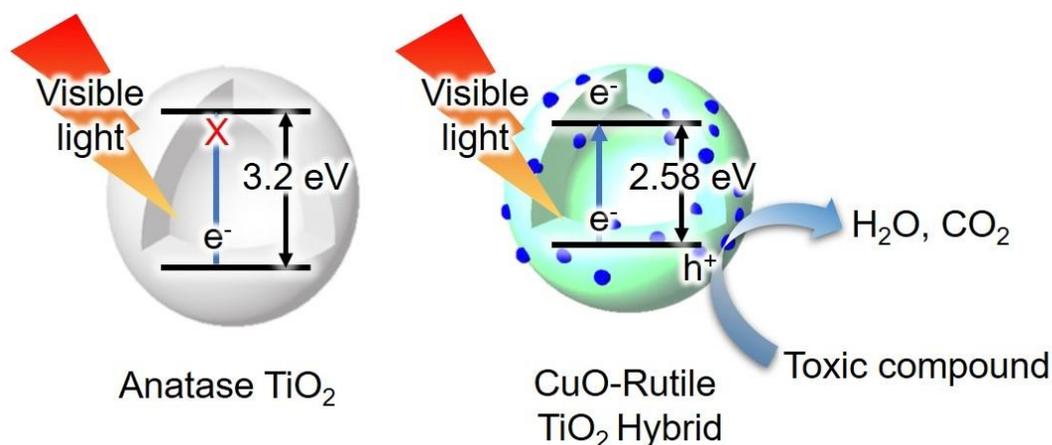


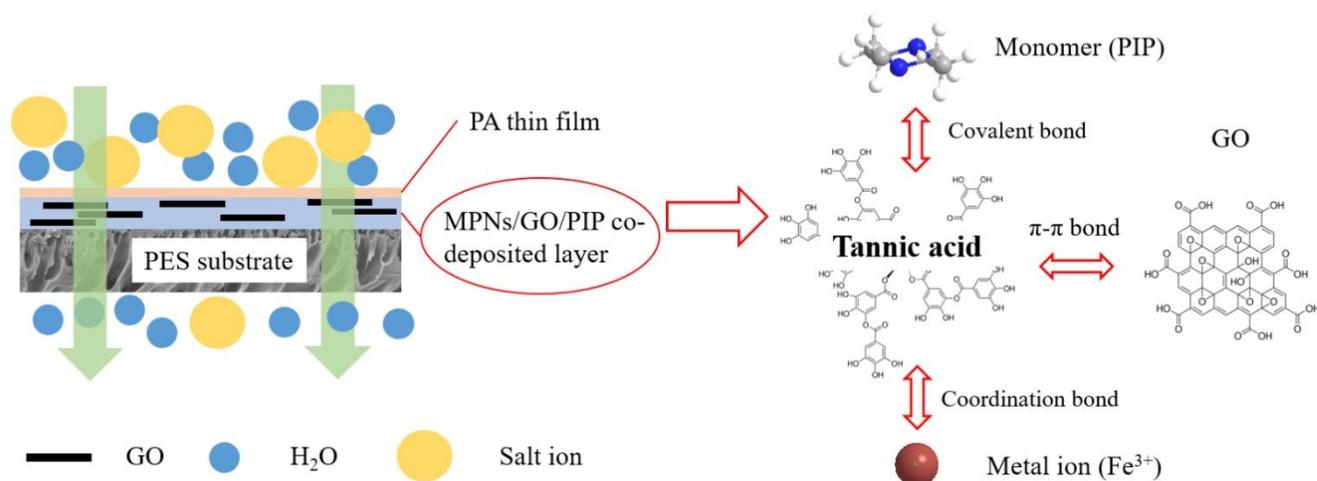
Illustration of hollow nanoparticle having lower bandgap energy

COLL 197

Novel graphene oxide based thin film composite nanofiltration membranes assisted by rapid codeposition of metal-phenolic network/piperzaine

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Developing methods for surface engineering on various platform with well controlled morphology and structure have attracted tremendous research interest due to their great application potential. In this study, we present, for the first time, a one-step surface modification strategy via metal-phenolic networks (MPNs) to tether graphene oxide (GO) nanosheets and monomers on membrane surface for state-of-art thin film composite (TFC) membrane fabrication. The method initially involved the surface modification of graphene oxide (GO) nanosheets into dual-functionalized TA-GO-PIP through a π - π interaction with tannic acid (TA) and further Michael addition reaction to anchor piperazine (PIP). The resultant then was employed into membrane surface coating procedure to form Fe^{3+} /TA-GO-PIP complex, which served as an ideal platform for final polyamide (PA) selective layer formation via interfacial polymerization (IP) reaction. Impact of TA and GO nanosheets concentration on 'sandwich' structure membrane morphology, hydrophilicity, charge profiles and separation performance was investigated. The synthesized membrane with TA-GO-PIP incorporation achieved a water permeance at 21.66 LMH/bar, along with a well maintained MgSO_4 rejection at 91.25 % and $\text{NaCl}/\text{MgSO}_4$ selective (α) at 10.02 under 2 bar operation pressure. This facile and rapid methodology via polyphenol as molecular glue to connect nanomaterials and functional monomers could provide better opportunities for various nanomaterials attachment on versatile surface on large scale.



Illustrative structure of metal-phenolic networks (MPNs) deposited thin film composite NF membrane

COLL 198

Gold-decorated barium titanate nanoparticles for enhanced photocatalysis

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This presentation details the synthesis and characterization of gold-decorated alkaline earth barium titanate (BTO) nanoparticles. BTO nanoparticles were synthesized using a low-temperature sol-gel method. X-ray diffraction (XRD) patterns confirmed the cubic structure of the BTO nanoparticles. Furthermore, gold nanoseeds were decorated on the surface of the BTO nanoparticles, and partial gold shells were grown using a simple seeded-growth method. Extinction spectra showed broadening of the extinction band in the visible region due to the localized surface plasmon resonance (LSPR) of the gold nanoparticles. Additionally, photoluminescence spectra indicated a decrease in electron-hole recombination of the BTO nanoparticles in the presence of gold on the surface. Studies of the use of these nanoparticles in visible light-driven water-splitting photocatalytic reactions will be described.

COLL 199

Which aminosilane molecules are the most suitable for surface functionalization of GO toward hexavalent chromium adsorption?

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Chromium compounds are commonly used in a variety of industries, including paint processing, leather tanning, metallurgy and wood preservation. However, Hexavalent chromium is most toxic and carcinogenic to human body among all the valence states of chromium. Moreover, it exists as chromate (CrO_4^{2-}) at normal pH. So it is stable in water and pollutes soil and groundwater. For this reason, many researches has been done to effectively eliminate them. Among others, adsorption is one of promising methods due to high efficiency and operational simplicity. Adsorption, especially using amines, effectively removes hexavalent chromium through electrostatic attraction between the positive amines and the CrO_4^{2-} .

This study investigated the mechanisms of hexavalent chromium removal by synthesized various amino silanes-graphene oxide composites to elucidate the effects

of primary and secondary amines. Through various analyses such as hexavalent chromium removal experiment, TGA, and XPS, it was confirmed that amino silanes are uniformly grafted on GO surface and hexavalent chromium removal efficiency of primary and secondary amines was calculated. In conclusion, we achieved a relatively high hexavalent chromium removal capacity of 260.74 mg/g. In addition, we found primary amines are more effective for hexavalent chromium adsorption. But the hexavalent chromium adsorption capacity order is 1N-GO < 2N-GO < 3N-GO, which is that total number of amines, the sum of primary and secondary amines was more important.

COLL 200

Effect of dielectric saturation on the ion activities in membranes

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Polymeric membranes are widely used in separation processes. The distribution and transport of ionic species through these membranes controls the performance of these membranes and depends on factors like surface charge density, pore morphology, chemical structure and ionic species present in the fluid. Manning's counter-ion condensation model is one of the simplest and most widely used activity coefficient models used to estimate the ion activity coefficients. However, it has been shown to work only for a limited range of ion concentrations. At low ion concentrations the model vastly over-predicts the ion activity coefficients. In the current work we show that this discrepancy is resolved if the variation in dielectric permittivity of the fluid medium with electric field strength is taken into account. A semi-analytical model is presented that accounts for the variation in the dielectric permittivity of water in the confined pore space of a charged polymer membrane. It is shown that such a model accurately predicts the ion activity in the membrane over a wide range of ion concentrations.

COLL 201

PLGA fiber containing AuNRs for on-off controlled anticancer drug release system

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Near-infrared (NIR) light-induced photothermal therapy (PTT) has attracted much attention as an alternative to traditional cancer therapy due to its minimal invasiveness and selective localized treatment. It can lead to the killing of cancer cells using PTT agents that can absorb and convert NIR light to heat in the tumor cells.

Herein, we report the fabrication of a fiber system for chemo-photothermal therapy composed of poly (D,L-lactic-co-glycolic acid) (PLGA) hollow fiber. An anticancer drug is encapsulated into core of the fiber. The shell containing gold nanorods (AuNRs) not only prevents unexpected release of the drug but also serves as a NIR light-absorbing PTT agent to construct NIR light-triggered on-demand drug release. Under NIR irradiation, AuNRs embedded in the shell produces heat to make the local temperature of the fibers higher. When NIR irradiation is switched off, the inactivity of the PTT agent will pause the segmental movement of the chains, which stops the release of the drug. This segmental switching of the polymer chains in response to the on-off operation of NIR light enables a repeated and precise release of the drug in an on-demand manner, causing the considerable improvement of antitumor activity in combination with the hyperthermia effect endowed by the PTT agent.

COLL 202

Delivery of the SN50 peptide via PLGA particles for increased immunological control and delayed boosting

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Effective vaccine adjuvants and formulations often fail to achieve FDA approval due to their adverse immunostimulation. In particular, over activation of the NF- κ B pathway via pattern recognition receptors results in inflammation. Here we present a new approach where we aim to add a selective inhibitor of NF- κ B alongside an agonist in a vaccination to stimulate the targeted immune response while reducing inflammation. The peptide selected for this study, SN50, has a sequence that matches the nuclear localization sequence of NF- κ B. As a result, when the cells' receptors are stimulated by an agonist (e.g. LPS), NF- κ B is partially impaired from being translocated into the nucleus due to competition from SN50 binding to the Nuclear Pore Complex. Previous work in the lab has shown that the SN50 peptide coupled with a TLR9 agonist, CpG, successfully increased antibody response while reducing inflammation. Furthermore, it has been reported that particle vaccinations that discharge agonist and antigen encapsulants in a controlled release produce a higher and longer antibody titer than its unencapsulated counterpart. In this study, poly(D,L-lactic-co-glycolic) particles containing SN50, OVA, and CpG are formulated, tested, and compared to unencapsulated versions. In addition, to further control the release mechanism and timing of the payload to the immune system, we plan to coat the PLGA microparticles with a secondary polymer. Depending on the thickness and polymer used as the secondary coating, the outer polymer will eventually degrade, revealing the agonist and antigen, PLGA core, allowing the encapsulants to remain dormant inside the body. Thus, a mixture of different sized particle coatings can be used to create dosages of drug to be released at different time points. We believe that by using the proper polymer coating, we may generate a single dose vaccine to improve vaccine use and efficiency via biodegradable microparticles.

COLL 203

Piezoelectrically-mediated mechanochemical reactions for adaptive materials

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Biological materials display great adaptability to their environment, as is the case of bones, muscles and skin which can adapt in response to mechanical stimuli by changing their composition and structure through a process called mechanotransduction. These cellular systems efficiently convert mechanical stimuli into chemical signals that can drive reactions leading to structural changes, deposition and removal of material. These adaptive properties give them great advantage in terms of efficiency and durability. Currently, synthetic polymeric materials mostly lack similar adaptability, resulting in mismatches in their physical properties and the need to replace them repeatedly. Recently, we and others have started investigating methods to use mechanical energy, in the form of ultrasound, to conduct controlled chain-growth, step-growth and crosslinking polymerization reactions. Our approach relies on activating piezoelectric nanoparticles with ultrasound to initiate or promote polymerization reactions. Previously, we used ultrasonic agitation of piezoelectric BaTiO₃ nanoparticles to mechanically generate a Cu^IL_n catalyst that then promoted atom transfer radical polymerization (ATRP) of acrylate monomers. We have since demonstrated mechanically activated step-growth polymerization and crosslinking reactions mediated by the copper-catalyzed azide-alkyne cycloaddition (CuAAC), commonly known as copper 'Click' reaction. These results showed great promise in using piezochemically-mediated polymerization strategies to develop adaptive synthetic polymeric materials that strengthen themselves with mechanical force. Our current goals include demonstrating that the above mentioned mechano-activated chemistries can indeed reinforce a gel/solid polymeric composite, thus conferring adaptability to a synthetic polymeric material; and exploring alternative piezo-polymerization reactions to expand the repertoire of materials that can be reinforced.

COLL 204

Piezocatalytic activity of piezoelectric nanoparticles induced by audible frequency vibrations

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Piezocatalysis, which is driven by mechano-induced electricity of piezo-material, has been proven to be a powerful tool for energy transformation and material science. However, current research has not explored audible frequency vibrations as mechanical sources for triggering piezocatalysis as most of them are conducted in high-frequency ultrasonic agitation. In this study, we designed a simple and robust system which can go down to audible frequency range and explore whether the high frequency (> 20 kHz) is necessary to drive piezocatalysis effect. Piezoelectric nanoparticles such as lead zirconate titanate, zinc oxide, and barium titanate are utilized as transducers to evaluate

the piezocatalytic activity of dye degradation and radical polymerization using audible frequency vibration source. The results demonstrate that the nanoparticles can harness the low-frequency mechanical force and convert it to piezochemical energy to drive organic dye degradation and radical polymerization. Furthermore, we explored the impact of energy conversion efficiency on piezocatalytic activity by controlling the output frequency and displacement. Compared with piezocatalysis driven by ultrasonic agitation, our work can calculate the exact amount of vibration energy scavenged by tuning output signals to save more dissipated energy and provides insights on piezocatalysis efficiency using frequency response function analysis.

COLL 205

Pd nanoparticle-quantum dot nanodisc hybrids for photo-enhanced colloidal catalysis

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Our group has employed the thiosulfate protocol, using sodium S-alkylthiosulfates instead of alkanethiols, to generate catalytically active Pd nanoparticles (PdNP) capped with the lower density of alkanethiolate ligands. The controlled alkanethiolate capping has provided nanoparticles the partial poisoning necessary for selective hydrogenation and/or isomerization of olefins. To further increase the utility of Pd nanoparticle catalysts, the colloidal hybrids of PdNP with graphene quantum dots (GQD) and bismuth selenide (Bi_2Se_3) nanodiscs (BSD) were prepared. It has been found that significant enhancement of photocatalytic efficiency is achieved by the deposition of noble metal nanoparticles on the semiconductor particle surfaces, since metal acts as a reservoir for photogenerated electrons or holes and promotes interfacial charge separation processes.

Our research hypothesizes that the transferred electrons or holes created by the semiconductor supports might have strong effects on the catalytic activity and selectivity of colloidal PdNP. GQD was found to be an excellent UV-active semiconductor, with its optical and electronic properties induced by the quantum confinement effect. The strong near-infrared (NIR) absorption of Bi_2Se_3 nanodiscs also allowed to utilize a solar spectrum to generate electrons and holes. Photo-enhanced catalysis of PdNP-GQD and PdNP-BSD hybrids was investigated for understanding the effect of photo-generated electrons or holes in the activity of PdNP using the model alkene hydrogenation reaction. The ligand-capped PdNP, PdNP/GQD, and PdNP/BSD were characterized using UV-vis spectroscopy, fluorescence spectroscopy, Raman spectroscopy, and transmission electron microscopy (TEM). The catalytic alkene hydrogenation was monitored using gas chromatography-mass spectrometry (GC-MS) and nuclear magnetic resonance (NMR).

COLL 206

Liposome-embedded hydrophobic palladium nanoparticles for biphasic catalysis in water

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Despite the availability of many water-soluble organometallic and nanoparticulate catalysts, the direct application of water-soluble catalysts for the reaction of immiscible and hydrophobic substrates has been hindered by the low solubility of nonpolar reactants in water. Our research group has shown that alkanethiolate-capped palladium nanoparticles (PdNP) exhibit excellent catalytic activity and selectivity for hydrogenation of unsaturated compounds in organic solvents. This PdNP was synthesized using the thiosulfate protocol using sodium S-dodecylthiosulfate as ligand precursor. The purpose of this study is to examine the catalytic activity of PdNP embedded in the bilayers of 1,2-distearoyl-sn-glycero-3-phosphocholine (DSPC) lipids in water. After the liposome film assembly of PdNP with PC in chloroform, the solvent was removed under vacuum and the hybrid was hydrated with phosphate buffered saline (PBS) solution. The resulting liposome-PdNP hybrids dissolved in water were characterized using UV-vis spectroscopy, inductively coupled plasma atomic emission spectroscopy (ICP-AES), dynamic light scattering (DLS), and transmission electron microscopy (TEM). During the catalysis reaction, the bilayer characteristics of liposome-PdNP hybrid would allow the hydrophobic substrate such as 1-octene and its isomers to momentarily enter the hydrophobic region of the catalysts with adequate stirring force. After the reaction, the resulting products from bi-phasic system were subsequently extracted with organic solvents and analyzed using ^1H NMR spectroscopy and gas chromatography. The results suggested that the transformation of 1-octene to *trans*-2-octene and *cis*-2-octene initially occur after 1 h of reaction time. Hydrogenation of *trans*-2-octene and *cis*-2-octene to octane takes place as the reaction proceeds. Final results suggest complete transformation of 1-octene to octane within 24 h of catalysis reaction under atmospheric pressure and at room temperature. In comparison, the catalytic reaction of 1-octene with the same PdNP in chloroform produces mostly the isomerization product, 2-octene. The increase in hydrogenation activity of PdNP in water after liposome encapsulation indicates that the surrounding environment of PdNP further controls its catalytic activity and selectivity.

COLL 207

Pressure induced transformation of formamidinium lead halide perovskite and quantum dot gold heterostructural nanocrystals

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Semiconductor and semiconductor-metal heterostructural nanocrystals (HNC) have drawn an increased amount of attention owing to their superior optoelectronic properties and potential applications. Herein we report a study of pressure- induced structural and optical evolution of FAPbI₃ hybrid organic–inorganic perovskite nanocrystals and pressure-driven processing of HNC superlattices self-assembled from quantum-dot-Au (QD-Au) satellite-type HNCs into monodispersive hetero-dimers and hetero-rods. Using a synchrotron-based X-ray scattering technique coupled to *in situ* absorption and photoluminescence spectroscopies, the structural and optical evolution were successfully monitored during the whole pressure cycle. Our results show that FAPbI₃ NCs exhibit a wide range of band-gap tunability (1.44 to 2.17 eV) as a function of pressure and QD-Au HNC-SLs underwent a permanent structural transformation at both the atomic- and the meso-scales during the pressure processing. The intra particle coalescence of Au satellites at QD surfaces transforms individual QD-Au satellite HNCs into hetero-dimers, whereas the interparticle fusion drives assembled HNCs into ordered hetero-rods arrays. The pressure synthesis of the unique nanostructures suggests the use of high-pressure-processing as a clean and fast means to controllably engineer the nanocrystals both in morphology and properties.

COLL 208

Using spin coating to fabricate polydopamine thin films

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Spin coating is one of the most common methods for thin film fabrication. Here, it is evaluated as a tool both for studying dopamine (DA) oxidative polymerization in solution, and preparing polydopamine thin films on native and functionalized silicon wafers. Sodium periodate was chosen as the oxidant because it is strong and exhibits fast reaction kinetics. All the DA solutions were prepared in acidic acetate buffers to avoid interference from oxidation by oxygen. The main feature investigated was DA reaction time prior to coating. This uniquely permitted taking snapshots of PDA particle size and surface adhesiveness as a function of reaction time. Other variables studied were surface chemistry, solution pH, DA concentration, and solution contact time prior to spin. Results indicated that controlling reaction kinetics, mostly in terms of solution pH and DA concentration, is most critical in order to produce thick and homogeneous PDA films. Surface chemistry also has a significant effect on film growth kinetics and morphology as well as PDA film stability in aqueous and organic media.

COLL 209

Photophysics of fluorescent probe molecules in confined environments

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The photo physical properties of Cyanine-5 (Cy5) in aqueous and confined reverse-micellar environments were investigated by using steady-state UV-Vis absorption and emission and time-resolved fluorescence spectroscopic techniques. For these studies, the fluorescent dye molecules were encapsulated in both anionic sodium-di-2ethylhexyl sulfosuccinate (AOT) reverse micelles and cationic cetyltrimethyl bromide (CTAB) reverse micelles of various sizes. The photo physical properties of the dyes in water as well as in reverse micelles of various sizes were examined by analyzing various photo physical parameters such as quantum yields, band shifts and fluorescence life time etc. Our observation provides us the future protocols to use reverse micelles as simple model systems, which can mimic the complex biological systems and will help us to understand the dynamic properties of biomolecules.

COLL 210

Interactions of nanomaterials with model lipid bilayer

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We investigate nonspecific interactions between model membranes and nanomaterials. Nanomaterials have found broad applications in fields, including for environmental sensing, drug delivery, and cell imaging. The ecotoxicology and environmental impact of nanomaterials depend on interactions with the membrane of living cells. In order to foster applications on the cellular biochemical level, it is essential to commence systematic investigation of nanomaterials and their membrane interactions. In light of the complexity of cell membranes, a simplified model system, so called Droplet Interface Bilayer (DIB), is used. A DIB is a model lipid bilayer existing between two aqueous droplets, submerged in an oil phase, each of which is stabilized by a lipid monolayer. Our present studies build on this platform to use the water permeability coefficient as an assay from which to deduce the structural modulation of a lipid bilayer induced by interaction with nanomaterials. Variations in the compositional library of the lipid bilayer permit us to determine whether these nanomaterials preferentially interact with specific lipids or lipid mixtures. This study will contribute to an increased understanding of how subtle compositional variations in the environment surrounding the liquid-liquid interface can have significant relevance for biological membranes and their physicochemical properties

COLL 211

Anti-inflammatory drugs and the lipid bilayer

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Many drugs can bind to the lipid membranes and potentially modulate its physical properties. Nonsteroidal anti-inflammatory drugs (NSAIDs) are among the most widely used medications for their capability in reducing pain, fever, and inflammation. A deeper understanding of the effect of commonly consumed NSAIDs on biophysical properties of lipid membranes extends our knowledge of molecular interactions of these drugs with biological systems. In this study, we investigated how various NSAIDs interacts with bilayers made of various lipid compositions, including the presence of varying concentrations of cholesterol, at physiological temperature. The methods employed in this study include water permeability determination across a droplet interface bilayer, a model cell membrane, as well confocal Raman spectroscopic studies to monitor changes in relative Raman scattering peak intensities. Our results suggest that specific NSAIDs influences the water permeability and structural integrity of the lipid bilayer in a unique way, and the nature and extent of modification depend on the concentration of NSAIDs, and lipid composition. Our findings provide evidence for direct interactions of NSAIDs with the model cell membrane and its structure, which potentially affect the function of proteins embedded in it.

COLL 212

The interactions of PAMAM dendrimers with lipid bilayers

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There has been growing biological applications of dendrimer-based nanomaterials in recent years, such as the use as drug or gene delivery vehicles. However, one of the major challenges is related to the dendrimer uptake into the cell and resulting the disruption of lipid bilayers and the cytotoxicity. Therefore, it is important to understand how these dendrimer-based nanomaterials interact with biological membranes for the successful development of pharmaceutical agent and wider biomedical application based on these materials. Polyamidoamine (PAMAM) dendrimers are highly branched synthetic macromolecules with various level of branching described by the generation G_n . In this study, we investigated the water permeability of the simple models of biological membrane, lipid bilayers, made by Droplet Interface Bilayer method. In addition, we also investigated the thermal properties of lipid membranes using liposome as model system. As cell membranes, we used both saturated and unsaturated lipid molecules to form a lipid bilayer and their interactions with various generations of PAMAM dendrimers. Our findings will provide an insight into the nature of interaction between dendrimers with a lipid interface.

COLL 213

Confocal Raman microspectroscopy for biomembrane characterization

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Phospholipids are a major component of cellular membranes and therefore the understanding and characterization of lipids is a critical to understanding biological systems. The characterization of lipids in phospholipid bilayers has significant implications in the fields of drug delivery and development, as well as aids in the understanding of trans-membrane diffusion. Raman spectroscopy provides an effective method for characterizing lipids found in biological membranes. Relative features of Raman spectra of lipids can be monitored in order to determine intramolecular and intermolecular order, as the spectral frequency, intensity, and line-width of vibrational bands are extremely sensitive to structural alterations. In this study, antisymmetric PC lipids, SOPC and SDPC, were utilized to examine the effect of cis double bonds in the acyl chain on membrane order. SDPC contains 6 cis double bonds, while SOPC contains one double bond. Additionally, the effect of concentration of caffeine on membrane order was evaluated utilizing DOPC liposomes. Our findings will add greater knowledge to the role of polyunsaturation and small molecule interactions in membranes, and their ability to modulate the membrane order at the molecular level, as probed by a sensitive Raman spectroscopic technique.

COLL 214

Insights into biomembrane structure by water permeability and raman spectroscopy

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The fundamental scaffold of all biological membranes is lipid bilayers that form a barrier between the cell interior and the surrounding environment. These membranes are essential to both the structure and function of mammalian cells and consist of compositionally diverse lipids arranged in a dynamic structure. In this study, we examine how changes in acyl chain structure alter bilayer properties and structural modulation, as probed by water permeability and Raman microspectroscopy. The water permeability has been shown to have strong dependency on the characteristic lipid bilayer structure. The water permeability was measured using a Droplet Interface Bilayer (DIB) as a model of cell membranes. Raman spectroscopy is a vibrational spectroscopy based on inelastic scattering of light. The energy changes detected from the process of inelastic scattering of light are those required to cause molecular vibration. Raman spectra exhibit well-resolved bands of fundamental vibrational transitions, characteristic of each unique bond, thus providing a high content of molecular structure information. We discuss the molecular insights obtained from osmotic water permeability and Raman structural studies of various types of prototypical

membranes formed by single hydrocarbon chain (monoglycerides) and double hydrocarbon chain (phospholcholine) lipids.

COLL 215

Computational studies of the effect of caffeine on water permeability in DOPC/cholesterol model membrane

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There has been great deal of interests in studying the effect of drugs on the structure and function of cell membranes, as drug-membrane interaction is an important part of the overall effectiveness of a drug. Many experimental and theoretical approaches have been conducted to understand the detailed mechanism of how drug would perturb membrane in such a way to modify its physical property, such as water permeability. The water permeability is known to be sensitive to the composition and surrounding of the membrane. Drugs such as caffeine can modify membrane structure to result in change of water permeability. To examine the effects that caffeine may have on water permeability, a DOPC (1,2-dioleoyl-sn-glycero-3-phosphocholine) (1,2-dioleoyl-sn-glycero-3-phosphocholine) with and without Cholesterol membrane was simulated with addition of varying concentration of caffeine solution. These results will provide useful comparison to the experimental water permeability measured using the Droplet interface Bilayer method.

COLL 216

Role of cis and trans double bond on water permeability of model membrane in the presence and absence of cholesterol: Computational studies

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Biological membranes consist of lipids having a large fraction of hydrocarbon chains with at least one unsaturation, which can have cis- and/or trans-isomers in their hydrocarbon chain. The double bond arrangement, either cis or trans, in the hydrocarbon chain of the lipid can have profound effects on the membrane properties, such as water permeability. In this study, we report our computational study on the effect of acyl chain double bonds between cis and trans-forms on the energetics of water permeability. Model membrane investigated include monoolein and DOPC (1,2-dioleoyl-sn-glycero-3-phosphocholine) in the presence and absence of cholesterol. Cholesterol is one of the most important lipids distributed among cellular membranes, playing an important role in the metabolism and in the regulation of the different physicochemical properties of these cellular bilayers. Using molecular dynamic simulations and free energy calculations, our study will provide a valuable insight to the

current understanding of the unique membrane properties (e.g. water permeability) caused by either cis or trans forms of unsaturated hydrocarbon chain of lipid and its interactions of cholesterol.

COLL 217

Computational studies on water permeability across a DOPC biological membrane: Effect of cation

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The plasma membrane, an essential component of the cell involved in cellular structure, protection, and transport, is surrounded by various ions. Cation binding to cellular membranes is biologically significant due to their involvement in membrane fusion, signal transduction, and protein regulation. Cation binding to artificial cellular membranes has been shown to increase the order of the lipid bilayer in terms of acyl chain ordering, headgroup tilt angle, and bilayer swelling. In this study, DOPC (1,2-dioleoyl-sn-glycero-3-phosphocholine) model membrane has been established with various cations (Na⁺, K⁺, Mg²⁺, and Ca²⁺) at two different concentrations (0.1 M and 0.5 M), to investigate the effect of cations in varying nature and concentration. Using molecular dynamic simulations and the adaptive biasing force method, the energy that is required to force a water molecule through the different model membrane systems in the presence of various cations will be calculated. Our findings will provide insights into the nature and strength of ion-membrane interactions and resulting changes in physical properties of membrane, such as water permeability.

COLL 218

Ultrasound-stimulated cargo release at low temperature for spatiotemporally and quantitatively controllable contrast enhancement by magnetic resonance guided high intensity focused ultrasound

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We developed a new technique for externally controlled on-command magnetic resonance (MR) imaging contrast enhancement using an MR-guided high intensity focused ultrasound (MRgHIFU)-stimulated cargo delivery strategy with minimal bulk heating. The Gd-based MR contrast agent Gd(DTPA)²⁻ was used as the cargo in polymer-coated mesoporous silica nanoparticles (MSNs) nanocarriers. The polyethylene glycol-based polymer served as an ultrasound-sensitive cap that regulated the controlled release of Gd(DTPA)²⁻ from MSNs when triggered by ultrasound. Gel

phantom experiments and an *ex-vivo* study in chicken breasts were performed to demonstrate the controlled MR image contrast enhancement with less than 10 °C of bulk heating. This approach is advantageous in several aspects. First, the polymer is biocompatible and effectively stabilizes the particles' dispersion in physiological environment. Second, the release of Gd(DTPA)²⁻ was spatiotemporally and quantitatively controlled by HIFU and monitored by MRI. Third, the polymer is mainly responsive to mechanical forces, so that Gd(DTPA)²⁻ could be efficiently released from MSNs at low temperature (temperature rise no more than 4 °C) during ultrasound stimulation. Finally, the amount of Gd(DTPA)²⁻ released from MSNs was regulated by the ultrasound stimulation power level, duration per cycle, and number of cycles. The amount of released Gd(DTPA)²⁻ was characterized by measuring changes in T₁-weighted image intensity and T₁ relaxation time before and after ultrasound stimulation. This ultrasound controlled on-command cargo delivery strategy was applied to deliver an anticancer drug to ovarian cancer cells and greatly enhanced the cell killing efficiency compared with that of the free drug itself. This new technique showing on-command MR imaging contrast enhancement and drug delivery opens up an opportunity for future image-guided theranostic applications.

COLL 219

Amoebae assemble synthetic spherical particles to form reproducible constructs

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Diffugia are testate Amoebae that use particulate inorganic matter to build a protective shell (generally called a test or theca). *Diffugia globulosa* were grown both in culture containing only naturally occurring theca building materials and under conditions where synthetic particles were present as well. The presence of particles, monodisperse Stöber silica microspheres of 1, 3 and 6 µm diameter or 4 µm polystyrene spheres, dramatically increased the rate of *Diffugia* growth, and foreign microspheres became the overwhelmingly dominant construction material. Optical and electron microscopy of the 6 µm particle studies revealed that *Diffugia* construct spherical vase-shaped thecae with strikingly reproducible composition, morphology and size. Time-lapse photography revealed construction techniques and masonry skills as *Diffugia* herded particles together, trapped them using phagocytosis, and applied the particles with bio-cement from inside the developing theca. The reported observations identify taxonomy complications, biomicrofabrication possibilities, and a discrete environmental impact of synthetic particle pollutants. The initial objective of this research was to produce monodisperse diatoms from which monodisperse silica microparticles (frustules) with complex and multiple-length-scale morphology could be prepared. Stöber particles were added as a diatom nutrient (silicic acid source). Our interest turned from monodisperse diatom preparation to the *Diffugia* after thecae became obvious and abundant in samples within two days of when the cultures were prepared with Stöber particles.

COLL 220

Enzyme immobilization in mesoporous silica shells of magnetic nanoparticle cluster supports: Does pore size matter?

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In our preceding work we reported magnetically recoverable biocatalysts based on magnetic nanoparticle clusters (NPCs) coated with a solid silica shell. The catalysts were designed for enzymatic oxidation of D-glucose to D-gluconic acid with high product yields using a glucose oxidase (GOx) covalent attachment via the glutaraldehyde linker. However, low surface areas of these NPCs led to a low loading density of GOx. To overcome this shortcoming, we developed NPCs with mesoporous shells. We studied the GOx loading capacity of these catalysts as well as their catalytic properties in D-glucose oxidation depending on pores sizes. The high stability of these GOx based biocatalysts in several consecutive reactions as well as facile magnetic recovery combined with excellent catalytic activity in “tolerant” pH range make this biocatalyst design promising for other types of enzymatic catalysts.

COLL 221

Magnetically recoverable Pd and Ru nanoparticulate catalysts based on polyethyleneimine or chitosan: Major factors in nitroarene reduction

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Here, we will discuss the development of robust Pd- and Ru-containing magnetically recoverable catalysts using commercially available, branched polyethyleneimine (PEI) or semi-natural chitosan as a green alternative to PEI. Both polymers stabilize magnetite nanoparticles (NPs) and then serve as capping and reducing agent for the formation of ~3 nm Pd or Ru NPs in the polymer shell. The catalyst properties were studied in a model reaction of 4-nitrophenol hydrogenation to 4-aminophenol with NaBH₄. A similar catalytic NP size allowed us to decouple the NP size impact on the catalytic behavior from other parameters and to follow the influence of the catalytic

metal type and amount as well as the polymer type and amount on the catalytic activity. The best catalytic performance, the 1.2 min^{-1} rate constant and the 433.2 min^{-1} TOF, were obtained for the Ru-containing catalyst based on PEI. High catalytic activity as well as the high stability of the catalyst performance in five consecutive catalytic cycles after magnetic separation makes this catalyst promising for nitroarene hydrogenation reactions.

COLL 222

Evaluation of stability of concentrated hydrosol with the droplets of unsaturated lipid

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Recent years have seen the problematic global trend countries of an increasing aging society. Chewing ability and intake functionality decrease with increase in age, and this can induce aspiration pneumonia. Thus, appropriate food texture, such as viscosity, is needed for easy swallowing by the elderly to prevent aspiration. Use of unsaturated lipid in food for the elderly is limited due to its high lipophilicity and low oxidative stability. A hydrosol, where liposoluble components are dispersed in the water phase, is useful as a utility form of lipid for the elderly food. However, the hydrosol with the droplets of lipid is a thermodynamically metastable dispersed system, and it leads to phase separation after flocculation, coalescence, and creaming due to high interfacial tension between the aqueous and oil phases. Therefore, stably concentrated hydrosol is required for the production of food with functional lipid for the elderly. In this study, the effect of the viscosity on the oxidative and the dispersion stabilities of concentrated hydrosol with the droplets of unsaturated lipid was examined, and a comprehensive stability including lipid oxidation and collapse was evaluated based on the viscosity.

First, a 90-mL aqueous solution containing pectin (6%–8%, w/v) and decaglycerol monolaurate (1%, w/v) was prepared and was added to 10 mL of soybean, olive, or fish oil. Then, the mixture was emulsified using a rotor/stator homogenizer for 15 min at 15,000 rpm in a tube immersed in ice water. The prepared hydrosol was stored at 37°C in a dark container. The viscosity of the hydrosol was measured at $20 \pm 2^\circ\text{C}$ using a rotating cylinder viscometer. Moreover, the particle size distribution of oil droplets in the hydrosol and the peroxide values of the hydrosol was periodically measured.

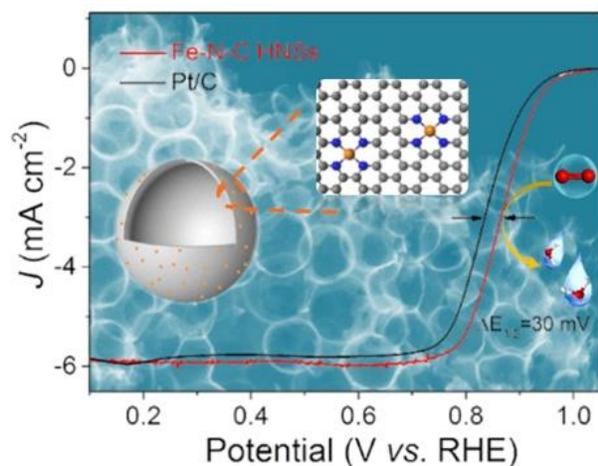
The rate constant for the oxidation of the hydrosol decreased with increasing the initial median diameter of oil droplets. The particle sizes for all the tested hydrosol were almost constant for storage period. The tendency that the floating velocity of oil droplets in the hydrosol decreased with increasing the rate constant for the oxidation was observed. The index, whose low value showed comprehensively high stability of the hydrosol, was estimated from rate constant for the oxidation and the floating velocity of oil droplets. Its dependency on the viscosity of the hydrosol was downwardly convex. This indicates that the viscosity strongly contributes to the stability the hydrosol.

COLL 223

High-efficiency electrocatalyst for the oxygen reduction reaction: Atomic Fe-dispersed on N-doped carbon hollow nanospheres

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Exploration of high-efficiency, economical and ultrastable electrocatalysts for the oxygen reduction reaction (ORR) to substitute precious Pt is of great significance in electrochemical energy conversion devices. Single atom catalysts (SACs) have sparked tremendous interests for their maximum atom-utilization efficiency and fascinating properties. Therefore, the development of effective synthetic methodologies toward SACs becomes highly imperative, yet still remains challenging. This presentation will show a reliable SiO₂-templated strategy to synthesize atomically dispersed Fe atoms anchoring on N-doped carbon nanospheres (denoted as Fe-N-C HNSs) using a cheap and sustainable biomaterial of histidine (His) as the N and C precursor. By virtue of numerous atomically dispersed Fe-N₄ moieties and a unique spherical hollow architecture, the as-fabricated Fe-N-C HNSs exhibited excellent ORR performance in alkaline medium with outstanding activity, high long-term stability and superior tolerance to methanol crossover, exceeding a commercial Pt/C catalyst and many previously reported non-precious metal catalysts. This synthetic strategy will provide inspiration to the fabrication of new high-efficiency single atom catalysts for diverse applications.



COLL 224

Self-assemblies of truncated tetrahedral quantum dots with anisotropic patchiness

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Packing problems of tetrahedra is a long-standing research subject in math. In contrast its simplest shape, superstructures made from tetrahedra are complicated and intriguing. Self-assembly of tetrahedral nanocrystal building blocks into well ordered superstructures is a fundamental strategy for chemistry, however, it has not been well explored because of the difficulty in synthesizing a high-quality nanocrystals and the structural characterization.

Here we report the packing of truncated tetrahedral quantum dots into four distinct superstructures—one-dimensional chiral tetrahelices, two-dimensional quasicrystal-approximant superlattices and three-dimensional cluster-based body-centred-cubic single supercrystals, and 10-fold quasicrystal superlattices—by controlling the assembly conditions. Characterization of the superstructures were conducted using techniques in real and reciprocal spaces, e.g. Synchrotron-based rotational X-ray scattering. We identified the structures from their nanocrystal translational orderings down to the atomic-orientation alignments of individual quantum dots. The selective facet-to-facet contact induced by the anisotropic patchiness of the tetrahedra were commonly found in the four superstructures, which is the key to facilitate such unusual self-assembling processes. This study provides information about the packing of non-spherical nanocrystals into complex superstructures, and may enhance the potential of self-assembled nanocrystal metamaterials in practical applications.

COLL 225

Amplifying hot electrons with Schottky barrier lowering by application of an external bias on a metal–semiconductor nanodiode

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We report the observation of increased hot electron flux generated by both incident light energy and the heat of the catalytic reaction by controlling the Schottky barrier height. This phenomenon was monitored using a Schottky nanodiode composed of a metal–semiconductor. The formation of a Schottky barrier at nanometer scale inevitably accompanies an intrinsic image force between the metal–semiconductor junction, which lowers the effective Schottky barrier height. When a reverse bias is applied to the nanodiode, an additional image force participates in a secondary barrier lowering, thus

giving rise to a highly increased hot electron flow detected as negative current. This enhanced hot electron flux induced by the chemical reaction followed the Arrhenius' equation and each activation energy taken throughout the whole bias range is comparable, which shows that additional bias-generated catalytic reactions or pathways do not exist. Theory also supports the phenomenon of increased hot electron flux when the effective Schottky barrier decreases. All other possible candidates contributing to the electron flow, such as bias- or thermally-induced electrons, were excluded by in-depth analytic experiments. This study can shed light on our quantitative understanding of hot electron behavior and the result can be used to obtain the energy distribution of hot electrons.

COLL 226

Generation of hot electrons at metal-oxide interfaces during the decomposition of hydrogen peroxide on Pt nanowire/Si nanodiodes

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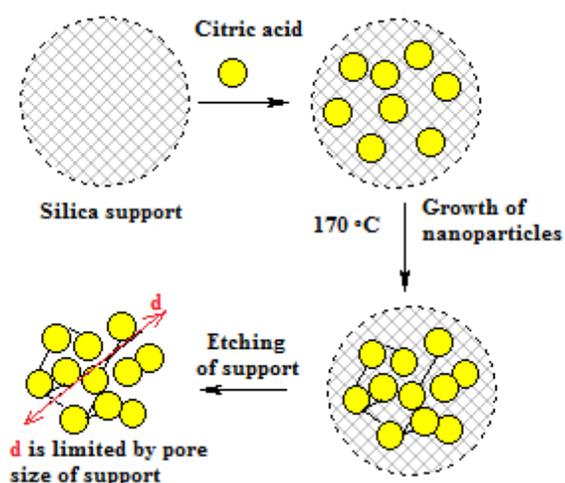
The detection of hot electrons in catalytic exothermic reactions occurring on the surface of metal catalysts is crucial for explaining the mechanism of the catalytic reaction. To measure hot electrons generated through non-thermal dissipation of energy from exothermic chemical reactions, researchers have been trying to fabricate a metal-semiconductor Schottky nanodiode. Meanwhile, research into various metal-semiconductor nano-catalysts has continued to figure out the effect of the metal-semiconductor interface in heterogeneous catalysis. Therefore in this study, we prepared a Pt nanowire (NW)/n-Si nanodiode and a Pt film/n-Si nanodiode to detect hot electrons during the decomposition of hydrogen peroxide, which is a promising oxidizing agent in industry. Hot electrons were measured as a chemicurrent and the catalytic activity of the Pt was determined by measuring the oxygen evolution rate. The Pt NW/n-Si nanodiode (nanowires stacked with a width of 25 nm and a period of 50 nm) had a chemicurrent density of 0.58 $\mu\text{A}/\text{cm}^2$, and the Pt film/n-Si had a chemicurrent density of 0.22 $\mu\text{A}/\text{cm}^2$. The oxygen evolution rate was 1.27 $\mu\text{mol}/\text{L sec cm}^2$ for the Pt NW/n-Si and 0.90 $\mu\text{mol}/\text{L sec cm}^2$ for the Pt film/n-Si. The chemicurrent yield, which is the number of hot electrons per O₂ molecule, was 2.37x10⁻⁵ for the Pt NW/n-Si and 1.29x10⁻⁵ for the Pt film/n-Si. From the experimental results, we conclude that the electric field was enhanced at the interface of the Pt-Si because of the narrower barrier, which resulted in the increased charge transport. This study might help to better understand the effect of the metal-semiconductor interface in heterogeneous catalysis.

COLL 227

Effect of functionalization of porous silica as nanoreactor for preparation of fluorescent carbon dots

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Fluorescence (FL) detection has excellent sensitivity, short response time but requires compounds either to have native fluorescence or to be chemically modified to induce fluorescence. Carbon dots (CDs) are new one kind of carbon materials that exhibit high fluorescence. These small particles have non-toxic carbon structure and can be modified with different functional groups. Crucial step of fabrication these fluorescent nanomaterials is synthesis approach. Composition, structure and final properties of CDs depend on the initial materials used as sources of carbon and the conditions of production (temperature, pressure, solvent) employed. CDs represent a mixture of particles with different sizes. Complex separation methods are used to obtain unimodal distribution of particle size. Controlling the morphology and size distribution of CDs during synthesis is a problem, therefore a new and simple method is required. The new approach was proposed to overcome those difficulties by using an external support capable of restricting the size and shape of the nanostructures generated. Porous silica material can be used as nanoreactor of the CDs formation. During thermal decomposition of citric acid at high temperature in the absence of oxygen, particles that emit blue light are formed. It was found that silica gel modified with amine groups promotes retention of high fluorescent nanoparticles in dispersion after etching of support. Emission spectra did not change the band position ($\lambda_{em} = 445 \text{ nm}$) after excitation at different wavelengths, which attest to narrow size distribution of prepared particle.



Preparation of CDs

COLL 228

Study of collective magnetic behavior of iron oxide at nanoscale interparticle distances through DNA-assisted self-assembly

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Magnetic nanoparticles (MNPs) attract much attention due to their unique magnetic properties and have a wide range of applications; from data storage media to cancer treatment hyperthermia. Iron oxide magnetite (Fe_3O_4) is a group of MNPs that exhibits high magnetic anisotropy and magnetization as well as biocompatibility making them a great tool to study magnetic properties at the nanoscale. When the length scale is reduced to a few nanometers, remarkable phenomena such as Superparamagnetism, Exchange Bias and Giant

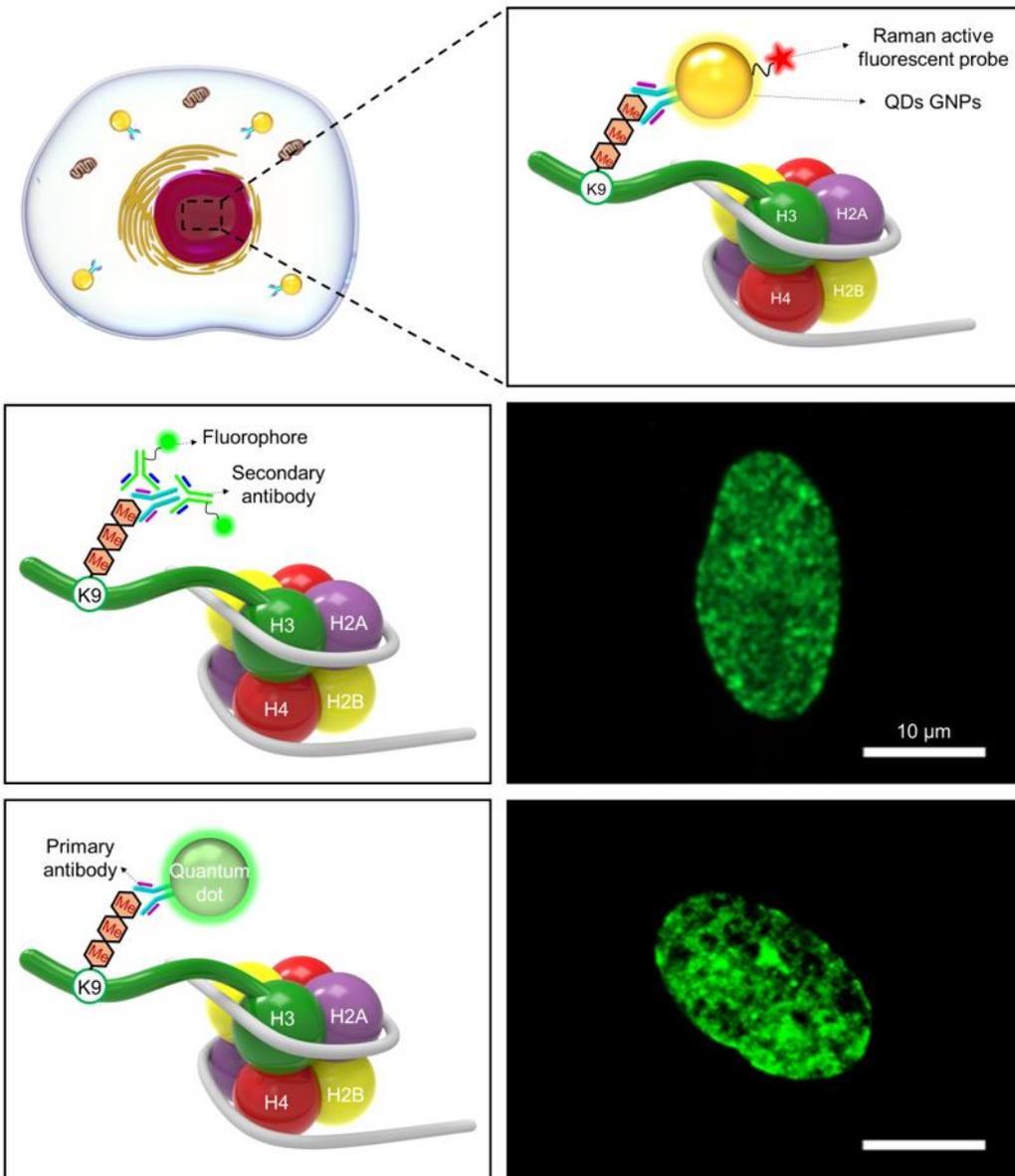
Magnetoresistance occur. The magnetic properties of individual particles depend on their size, shape, and their intrinsic magnetic characteristics. However, as the concentration of the particles increases, the magnetic properties of the particles become dependent on the interparticle interactions and collective magnetic behaviors are observed. The strength of the interaction depends on the length of the distance between adjacent particles and their environment. Modulating these interparticle interactions leads to different collective behaviors such as; superparamagnetism (SPM), superspin glass (SSG) and superferromagnetism (SFM). The current self-assembly methods used to make ordered structures of MNPs are limited to closed packed morphologies that are not capable of modulating the regularity and the interparticle spacing. Therefore, fail to efficiently tune MNP's collective properties. We introduce a DNA-Assisted self-assembly technique which allows controlling the regularity and the distance between the nanoparticles with precision. First, Monodispersed MNPs are synthesized by thermal decomposition and then coated with gold followed by functionalization with thiol-modified oligonucleotides. DNA Functionalized MNPs are then pinned on the DNA origami surface, used as the building block to assemble MNPs, by hybridization of the complementary strands on the particles and the origami.

COLL 229

High-spatial single cell histone mapping using optically tunable nanoparticles

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Histones, well known as packing components of DNA, have been extensively studied because their modifications are closely related to epigenetic processes. Thus, it is very important to map the position and distribution of the histone modifications for elucidating the underlying mechanism behind. However, conventional histone imaging methods are performed by using organic fluorescent dyes combined with secondary antibodies, has limitations in multiplexed and high-spatial imaging. To overcome these, optically tunable nanoparticles, such as gold nanoparticles (GNPs) and quantum dots (QDs) have recently drawn attentions as excellent imaging probes owing to their high-spatial resolution and multiplexing modalities. In this study, we develop novel imaging probes using GNPs and QDs conjugated with primary antibodies of histone proteins to visualize the distribution of the modified histone in a single nucleus. As conceptual demonstration, different trimethylation level and distribution of histone 3 lysine 9 (H3K9) in normal and senescence induced cells is clearly visualized by using GNPs and QDs. Furthermore, we demonstrate multi-functional imaging probes consist of both GNPs and Raman active fluorescent probes, which make it possible to apply to multiple imaging apparatus including dark-field microscopy, fluorescence microscopy, and Raman microscopy for histone mapping. The proposed imaging probes provide a powerful way to study not only histone codes, also other cellular targets such as organelles and biomolecules.



COLL 230

Novel nanohybrids of chemically active boron based nanosheets with gold nanoparticles and graphene: Assembling mixed dimensional heterostructures in solution

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The discovery of graphene inspired ground-breaking research in the field of two-dimensional materials. The current decade, however, has seen the 2D materials landscape evolving beyond graphene. Boron, carbon's neighbor in the periodic table, has been seeking significant attention regarding its existence in planar forms analogous to graphene. 2D Boron has been in the limelight since 2015 when the first reports on the bottom-up synthesis of 'borophene' nanosheets were published. Although several theoretical studies predict quasi-planar forms of boron, their experimental realization remains challenging. The apparent absence of a suitable layered 3D precursor has precluded the top-down synthesis of boron sheets by exfoliation. We present a fundamentally new perspective to this growing science of 2D Boron by proposing to use layered metal borides towards the exfoliative synthesis of boron-based nanosheets. Metal borides are layered compounds constituted of (graphene-like) honeycomb planes of boron sandwiched between hexagonal layers of metal atoms. We recently developed a chemical exfoliation strategy in which organic chelators selectively extract metal ions from layered borides in an aqueous medium. This causes delamination of boride crystals into few-layer-thick boron-based nanosheets. Detailed chemical characterization indicated that the nanosheets possessed hydride, hydroxy and oxy based functional groups. The presence of borohydride groups confers a unique chemically active character to the nanosheets to reduce several organic and inorganic molecules. Mixing these nanosheets with gold salt results in a spontaneous formation of ultra-small gold nanoparticles that subsequently anchor onto the nanosheets and form mixed-dimensional (0D-2D) heterostructures in solution. This process neither requires any reducing-stabilizing chemical nor an external inducing aide like sonication, electrochemical or thermal treatment. These nanosheets can also reduce graphene oxide to reduced graphene oxide subsequently forming quasi-2D boron-carbon nanohybrids. We present for the first time the possibility of using a boron-rich 2D material as a nanoscale reducing agent. The concurrence of reducing nature and planarity makes these nanosheets intriguing alternatives over conventional reductants. A wide range of possibilities can be realized by employing these as nanoscale reagents, and as building blocks towards assembling heterostructures with other low-dimensional systems.

COLL 231

Cu-catalyzed synthesis of CdZnSe-CdZnS alloy quantum dots with highly tunable emission

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Semiconductor quantum dots (QDs) exhibit unique properties including high absorbance cross section, broad excitation spectrum, tunable emission profile, high photoluminescence quantum yields (PL QYs) and superior photo-chemical/physical stabilities. Fabrication of quantum dots (QDs) with narrow emission covering a wide spectral region has been persistently intriguing due to their potentials in a range of practical applications such as biological labelling and imaging, solar cells, light-emitting diodes (LEDs) and next generation displays. We report a synthesis of CdZnSe-CdZnS core-shell alloy QDs through a Cu-catalyzed solid solution alloying strategy starting from CdSe-CdS core-shell QDs. The resulting CdZnSe-CdZnS alloy QDs exhibit emission profiles covering a wide wavelength range of 470-650 nm while maintaining high PLQYs. In addition, high morphological uniformity of the starting CdSe-CdS QDs can be largely retained in the final alloy QDs. The alloying process is attributed to the high mobility nature of Cu cation in Cd-chalcogenide crystals at elevated reaction temperature, which allows Cu cation act as a transporting agent to transfer Zn component into CdSe-CdS QDs while maintaining the particle integrity. This unique alloying strategy is independent of the shape of starting QDs and can be also applied to the synthesis of CdZnSe-CdZnS nanorods. We anticipate our study will instigate synthesis of various high-quality alloy QDs and other alloy nanocrystals beyond what currently can be achieved.

COLL 232

Quantum-well CdS/CdSe/CdS nanoshells exhibiting long-lived biexciton populations

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Multiple excitons play an important role in the photoinduced dynamics of semiconductor nanocrystals. The utilization of multiexciton effects in photovoltaic and photoelectrochemical devices has long been considered for converting the energy of a single high-energy photon into multiple carriers as a mechanism for mitigating thermal energy losses. Unfortunately, non-radiative Auger decay of multiple excitations greatly diminishes the multiple exciton feasibility in nanocrystal-based devices. Here we report on the synthesis of semiconductor quantum-well nanoshells exhibiting long-lived biexciton populations. The demonstrated nanoparticle architecture utilizes a CdS_{bulk}/CdSe/CdS_{shell} core/shell/shell morphology, which effectively reduces the rate of Auger recombination in the quantum-confined layer of CdSe. This leads to increased biexciton lifetimes, as was demonstrated in this work through methods of ultrafast

spectroscopy. In particular, we show that the biexciton lifetime of CdS_{bulk}/CdSe/CdS_{shell} nanostructures featuring an 8-nm-diameter CdSe shell ($\tau_2 \approx 1.24$ ns) was more than thirty times longer compared to that of zero-dimensional CdSe nanocrystals. The slower biexciton decay in quantum-well nanoshells was attributed to a large confinement volume, which compared favorably to other existing multiple exciton architectures.

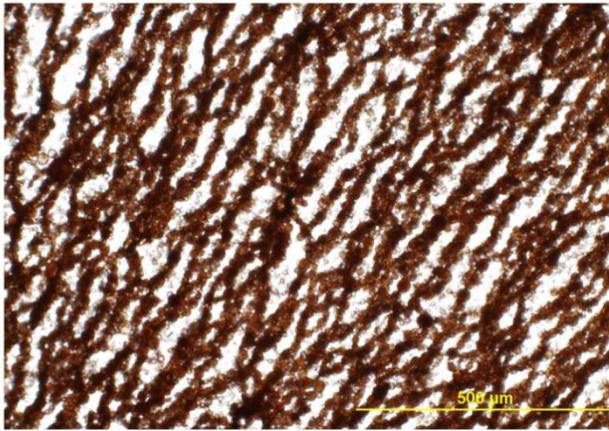
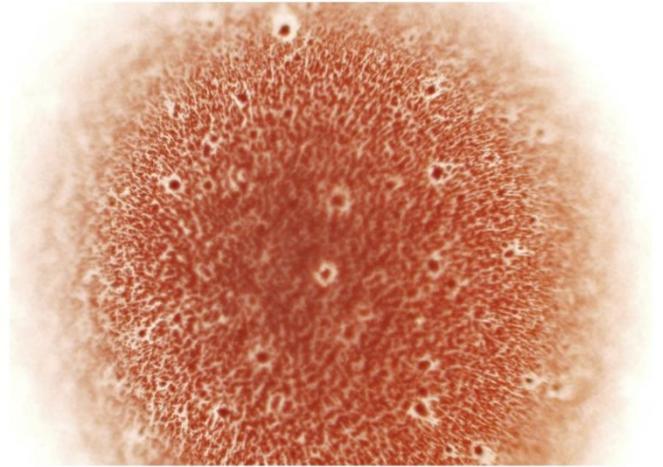
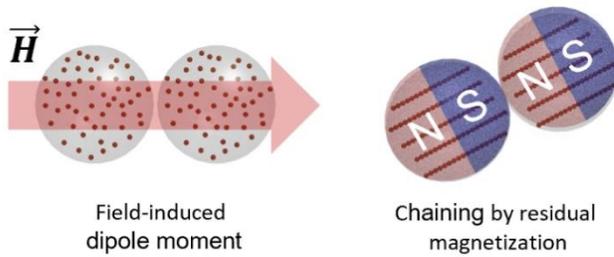
COLL 233

Magnetic chaining of PDMS beads in new gels and anchor sites for the improvement of wall slip conditions

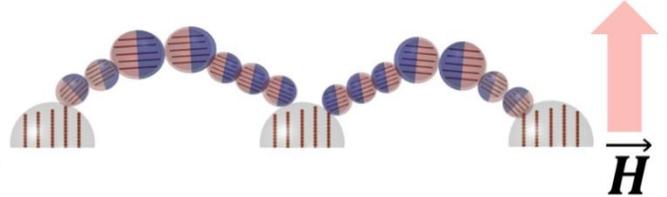
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We are conducting research involving magnetic interaction templating to study and manipulate magnetic response. We have demonstrated the formation of soft micromagnets composed of polydimethylsiloxane (PDMS) beads with internally embedded chained magnetic nanoparticles (MNPs). We present here the design, synthesis, and early characterization of such beads. These chain-containing microspheres could have a permanently embedded dipole moment and hence, residual polar magnetization. Once magnetized, their response results in the formation of branched structures or percolation networks. We have compared these chained beads with the PDMS beads with randomly dispersed MNPs from our previous work. Upon introducing an external magnetic field and disturbing the system, the PDMS beads with randomly dispersed MNPs demonstrated no residual polarization and thus the formed networks were destroyed. We proved the tunability of this new chained bead system by conducting magnetization, demagnetization, and re-magnetization experiments that were evidence of the successful reformation of percolating networks. Nature's example of such directional linear chaining can be found in magnetotactic bacteria. These bacteria synthesize iron oxide-based MNPs in their cells to create a permanent magnetic dipole moment that aligns and enables the bacteria to sense a magnetic field and coordinate their movement accordingly. An interesting finding of this chained bead system is that the beads mimic magnetotactic bacteria through the formation of self-aligning linear structures in the direction of Earth's magnetic field. Lastly, we recently began to study these beads as potential magnetic anchor sites for no-slip conditions of magnetic gel characterization. Our end goal would be to be able to use these anchor sites in order to have more well-distributed rheology sample loading and thus more accurate rheological characterization. Overall, we have constructed and are developing further a rich structural and interaction toolbox of novel magneto-networks.

Magnetic force induced gelation



Magnetic anchoring



COLL 234

Formation of 2D liquid crystal phases by *de novo* designed proteins at crystal-solution interfaces

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Living systems utilize macromolecular-inorganic hybrid structures to create biomaterials with outstanding properties. Precise programming of the protein-inorganic interface is crucial to the development of such materials. Hence, understanding the mechanism by which the protein matrix assembles and using that understanding to mimic the structure of protein matrices at the crystal-solvent interface would enable the creation of materials

with precise control over the morphology and spatial arrangement of the subunits. In this work, protein nanorods exhibiting an arrangement of amino acid sidechains lattice-matched to the cation sublattice on muscovite mica (001) were designed using Rosetta, and their self-assembly was studied by high speed in situ AFM for a range of electrolyte types and concentrations. Our results show that the proteins formed 2D liquid crystal (LC) phases. Moreover, for KCl concentrations above 1 M, a 2D smectic phase with long-range order was achieved. The results also show that protein mobility increases dramatically with KCL concentration, thus promoting the formation of ordered LC phases. The known effects of high salt concentration on both charge screening and the structure of the interfacial hydration layers likely play decisive roles in achieving order. When muscovite, which possesses buried hydroxyl groups that break the 3-fold symmetry, was replaced with phlogopite, which has an identical cation sublattice but exhibits true 3-fold symmetry, the smectic phase was lost and the protein rods assembled into an isotropic phase with domains equally aligned along the three equivalent directions. By comparing our experimental results with Monte Carlo simulations, we find that assembly is primarily driven by entropic effects, while orientation selection is controlled by the arrangement of the cation sub-lattice, biased by the alignment of the hydroxyl groups.

COLL 235

Development of virus-like hierarchical silica nanoparticles using an engineered capsid protein for biomedical applications

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Silica nanoparticles have attracted great attention for biomedical applications, because of the merits of nano-sized form, biocompatibility, easy surface functionalization. Nanoparticles with hierarchical surface have advantages in biomedical applications, including a large surface area, a long circulation time in blood, and a high binding efficiency to cancer cell, compared to flat ones for biomedical applications. However, previous methods have some difficulties in synthesis due to a use of multi-step synthetic process and harsh reaction condition for generation of hierarchical structure with porosity and encapsulation of bioactive molecules as well as low biodegradability of sole inorganic particles. In this study, we have developed silica nanoparticles with hierarchical surface through two bioinspired strategies from controlled silica mineralization of diatom and hierarchical structure of human papillomavirus (HPV) 16. A new fused protein, HPV16 L1-R5, was designed and produced in *Escherichia coli* by genetically fusing HPV 16 L1 protein with silica-forming R5 peptide. HPV16 L1-R5 proteins self-assembled into virus-like particles (VLPs) identical with native HPV 16. Hierarchical silica nanoparticles with controllable size were developed through controlled silica mineralization process of diatom on HPV16 L1-R5 VLPs. We anticipate that our novel silica nanoparticles could be used as effective nanocarrier for successful biomedical applications.

COLL 236

Interlayer structure control and self-assembly of two-dimensional MXene thin films for gas sensors

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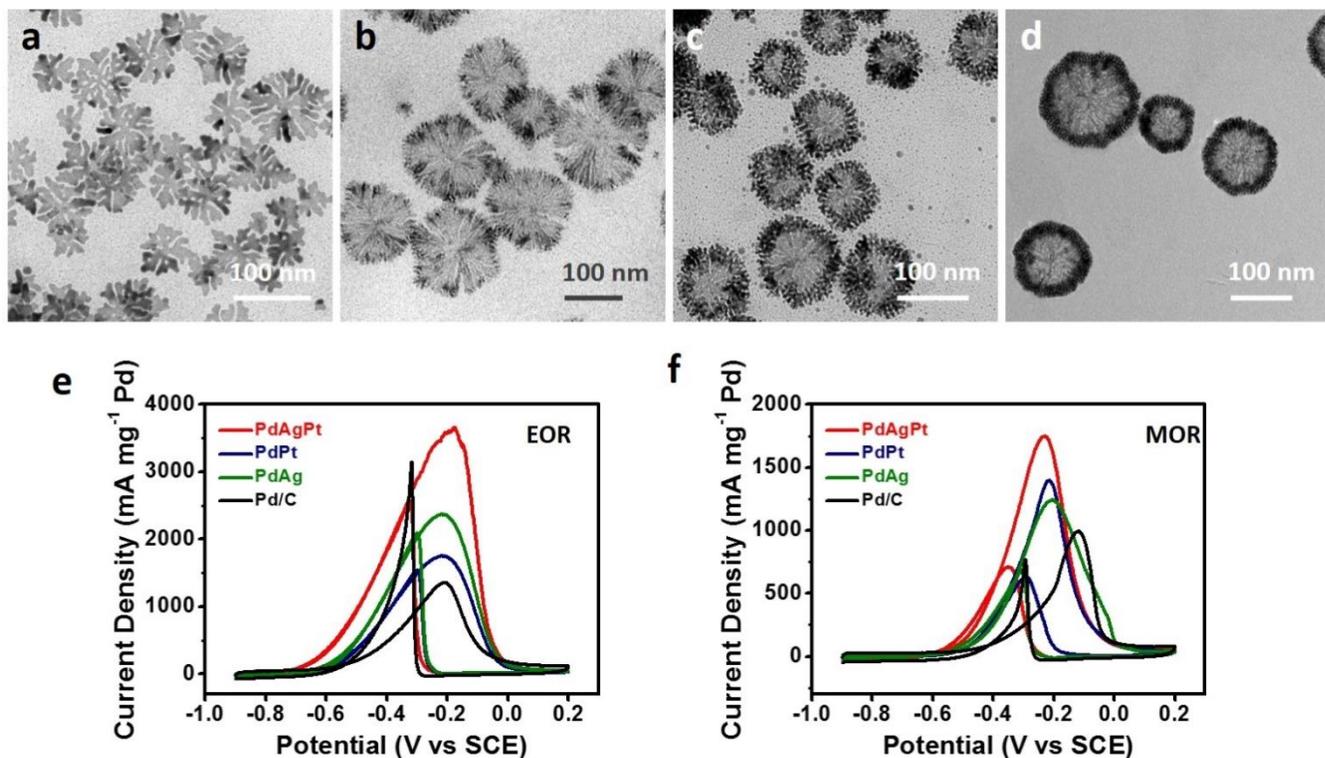
MXenes are a rapidly emerging class of two-dimensional transitional metal carbides/nitrides with very high electrical conductivity, high density of surface functionalities, and excellent solution processability. Also, their easiness to be coated on a wide variety of surfaces render MXenes excellent candidates for functional films and composites toward numerous applications. In this presentation, the utilization of MXenes thin films for highly sensitive gas sensors will be discussed. In detail, methods to control the stacking and interlayer structure of MXene thin films and their application as gas sensors will be presented. Assembled MXene films were able to detect ppb-level volatile organic compound (VOC) gases at room temperature, being more sensitive than any other reported material, which is critically important for therapeutic applications. Furthermore, the controlled intercalation of metal ions into the interlayers of MXene films dramatically increased the selectivity of MXene gas sensors toward VOCs.

COLL 237

2D Pd-based multimetallic nanosheets

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Two-dimensional (2D) metallic nanosheets with nanodendrites are a rare class of materials with high structural anisotropy. They have enlarged surface areas and abundant under-coordinated sites and may hold unexpected promise for catalytic applications. Their formation condition is very stringent and usually requires the help of structure directing agents, such as CO and PVP. However, the catalytical active sites of the nanosheets would be blocked more or less by the toxic CO and polymeric capping agent. In this work, we report the facile solution synthesis of two-dimensional Pd-based nanodendrites (PdAg and PdAgPt) without CO and PVP as high-performance electrocatalysts for ethanol and methanol electrooxidation.



TEM images of PdAg and PdAgPt nanosheets and their EOR and MOR activities.

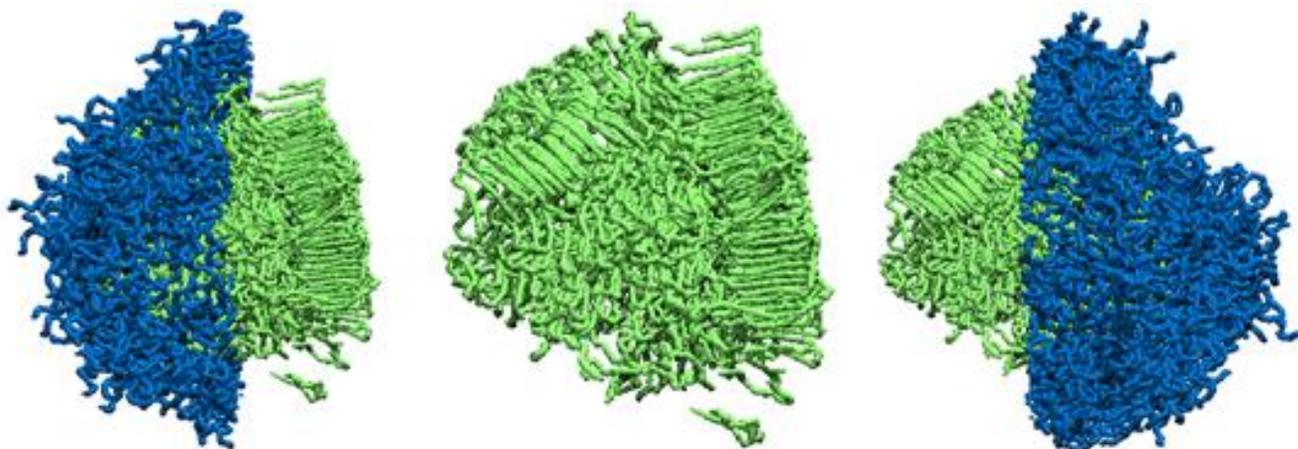
COLL 238

On solid lipid nanoparticles

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Solid lipid nanoparticles (SLNs) have a crystalline lipid core which is stabilised in solution by interfacial surfactants. They are considered favourable candidates for future drug delivery vehicles as they are capable of storing and release bioactive molecules. However, when stored over time it is thought that the lipids undergo polymorphic transitions which result in the premature expulsion of the drug molecules. To date, significant experimental studies have been conducted with the aim of investigating the physico-chemical properties of SLNs, including their long-term stability, but as-of-yet, no molecular scale investigations have been reported on the behaviours that drive SLN formation and their subsequent polymorphic transitions. Using a combination of small angle neutron scattering (SANS) and all-atom molecular dynamics simulations (MD) we have generated a detailed, atomistic description of the internal structure of an SLN formed from the triglyceride, tripalmitin, and the Brij O10 surfactant. We also reveal the

molecular scale mechanisms by which the surfactants stabilise the crystalline structure of the SLN lipid core. By comparing these results to simulated liquid and solid aggregates formed from the tripalmitin lipids, we demonstrate how lipid morphology varies between the nanoparticles, providing further insight into the key molecular mechanisms that control drug encapsulation and release from SLNs.



COLL 239

Creation of gyroid nanostructured polymer films having 3D continuous aqua-sheet for fast proton conduction

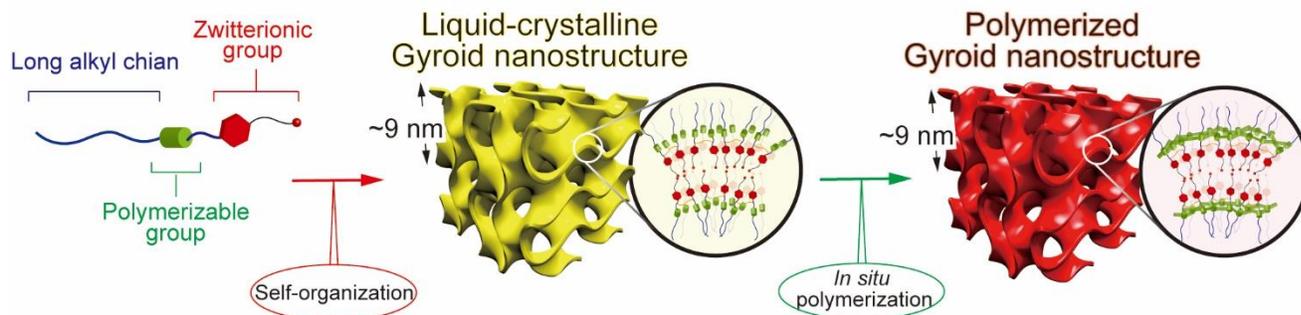
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Bicontinuous cubic (Cub_{bi}) liquid crystals are representative materials that form gyroid-nanostructures with 3D interconnected nanochannels and a 3D continuous surface. Owing to its inherent structural characteristics, they have attracted growing attentions for the development of functional materials including electrolytes, separation membranes, and so on.

We have reported molecular technology for inducing Cub_{bi} liquid crystals, which is to use zwitterionic amphiphiles and suitably designed acids. In this system, one end of amphiphile, sulfonic acid group, forms a 3D continuing gyroid surface, resulting in the induction of 3D proton conduction. To enable efficient proton conduction in the order of 10⁻¹S cm⁻¹, it is essential to incorporate a sufficient amount of water molecules onto the gyroid surface in order to form successive hydrogen bonding networks (approximately 10 wt%). We expect the fixation of liquid-crystalline (LC) nanostructures is a promising approach for achieving the construction of such water networks with keeping the gyroid

structure.

We designed and synthesized a polymerizable zwitterionic amphiphile to fix gyroid nanostructures. By performing *in situ* polymerization in the Cub_{bi} assembled state, we successfully obtained self-standing polymer films having gyroid nanostructures. The polymer film has an ability to absorb water without losing the molecular assembled nanostructures even in the attached condition with water. We performed alternating current impedance measurements for the water incorporated films. It showed high ionic conductivity in the order of $10^{-1} S cm^{-1}$.



Schematic image of this study.

COLL 240

Formation of double gyroid nanostructures by self-organization of atropisomeric ionic amphiphiles

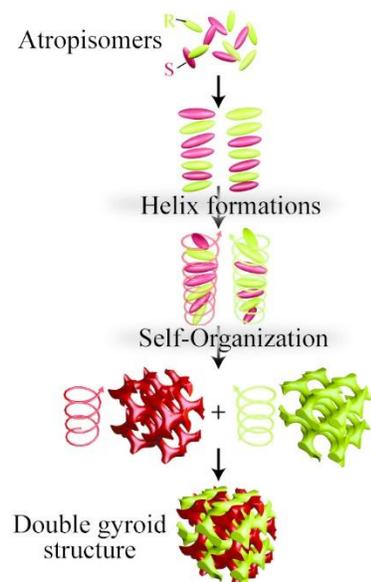
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Double gyroid structures are a class of 3D periodic structures that are composed of two interwoven networks of 3D branched channels. Owing to the unique structural characteristics, they have been applied for creating a variety of functional nanostructured materials. In particular, self-organized double gyroid nanostructures formed by bicontinuous cubic (Cub_{bi}) liquid crystals have been studied for size-selective separation membranes and mass transport materials. However, it is still not easy to intentionally design liquid-crystalline molecules exhibiting Cub_{bi} phases.

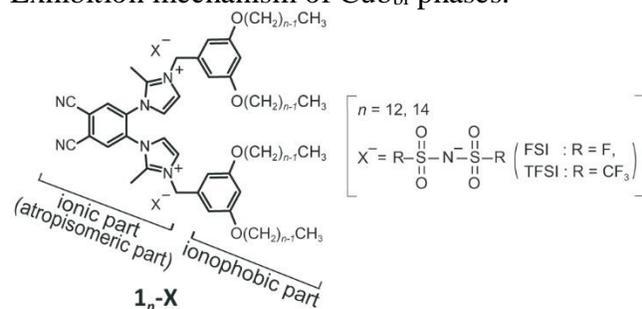
An explanation on the exhibition mechanisms of Cub_{bi} phases is shown in Figure 1. When liquid-crystalline molecules produce local right- or left-handed helix assemblies, these opposite-handed assemblies organize into two channel networks of double gyroid

structures. This mechanism leads us to envision that the use of chiral building block is an effective approach. In the present study, we have focused on molecular building blocks forming atropisomers as a chiral source.

We designed ionic amphiphiles 1_n-X (Fig. 2). We found that 1_n-X organizes into Cub_{bi} phases forming double gyroid structures. In the poster, the relationships between atropisomerization and self-organization behavior will be discussed.



Exhibition mechanism of Cub_{bi} phases.



Molecular structure of the ionic amphiphiles 1_n-X .

COLL 241

Polymerization of vinylimidazolium-based amino acid ionic liquids in bicontinuous cubic liquid-crystalline assemblies

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Lyotropic liquid crystals form various nano-segregated structures such as 1D channel, 2D layer, and 3D network structures. By introducing polymerizable groups into amphiphile design and then performing in-situ polymerization in lyotropic liquid-crystalline (LC) states, it is possible to convert LC fluidic materials to polymer films with preserving the nanostructures. To date, many researches on in-situ polymerization of LC assemblies have been reported using polymerizable amphiphiles. We have developed lyotropic LC systems containing amino acid ionic liquids as self-organization solvent. Owing to high designability of ionic liquids, we expect it is possible to introduce polymerizable groups into these ionic liquids. In this study, we designed amino acid ionic liquids having vinylimidazolium cations to perform in-situ polymerization of ionic liquids in LC states, especially in bicontinuous cubic states having 3D network structure. By mixing several types of amphiphiles with the polymerizable ionic liquids, we obtained lyotropic LC samples forming normal- and inverse-type bicontinuous cubic phases (Figure 1). It is assumed that ionic liquids in these mesophases are aligned on 3D networked channel structure (Figure 1, blue) or 3D networked layer structure (Figure 1, red). We will present the polymerization behavior of ionic liquids in the two types of bicontinuous cubic LC phases and physicochemical properties and functions of the obtained nanostructured ionic polymers.

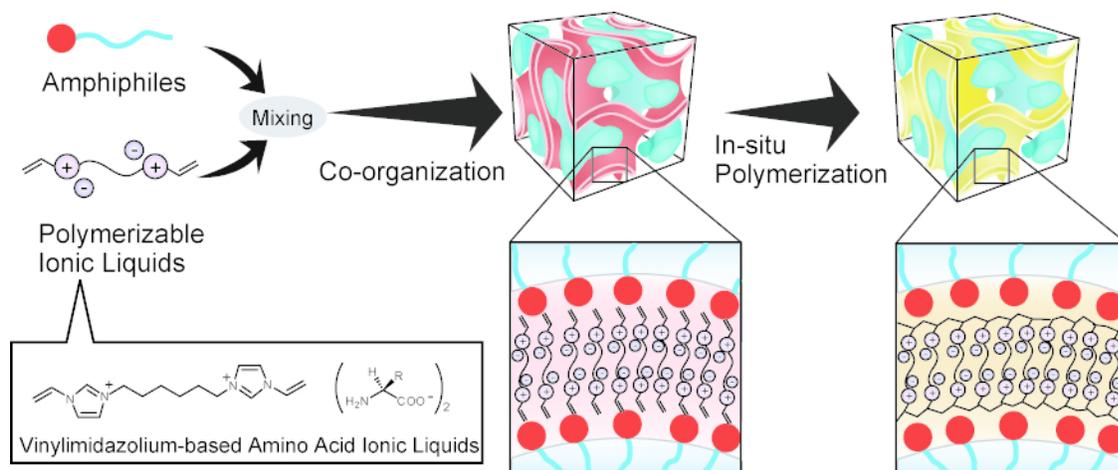


Figure 1. Our strategy for polymerizing ionic liquids in 3D bicontinuous cubic assemblies.

COLL 242

Assembly of anisotropic nanomaterials for flexible resistive switching device

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Self-assembly is Self-organization of system components into a small building structure. The driving forces of the assembly are capillary force, convection of solvents, inter-molecular force and Electrostatic force. Various methods have been explored to produce hexagonally closely-packed (2D, 3D) array for biosensors, inverse opals, chemical sensors and photonic crystals. Some of the simple processes involve centrifugation procedures and sedimentation, which take a long time and cause macroscopic defects in the ordered crystalline. As an alternative method, to increase to enhance the colloidal ordering and speed of crystal formation rate to a controlled thickness of the assembly. Vertical deposition, capillary deposition, convective assembly, electrophoretic assembly, convective assembly and spin-coating are included in this category. However, these processes often consumes long deposition time or complex configurations.

In the present study, we demonstrate a flexible resistive switching device based on Au nanosheet (NS) and ultrathin Ag_2Te nanowire (NW) film electrode by employing assembled monolayer on the water surface for macroscale two-dimensional structures. Firstly, ultrathin TeNWs (diameter: ≈ 10 nm) are, rapidly, assembled on the water surface as a form of monolayer and transferred to fabricate TeNW film on various substrates with any available size. An assembled TeNW film was used as a template to produce Ag_2TeNW film through chemical transformation. A well-aligned Ag_2TeNW film device showed reversible resistive switching properties when the Ag composition of silver telluride NW becomes the stoichiometric Ag_2Te . Additionally, non-stoichiometric $\text{Ag}_{2+\delta}\text{TeNW}$ film shows increased On/Off ratio. In the case of the flexible memory devices, ultrathin AuNS (thickness: ≤ 20 nm) was adopted as working electrodes, since thermally-deposited gold electrodes tend to go through cracks under strain, which can fail to maintain the electrical properties. The Flexibility of AuNS, like paper, has proven its capability as optimal electrodes of ultrathin Ag_2TeNW film-based resistive memory devices.

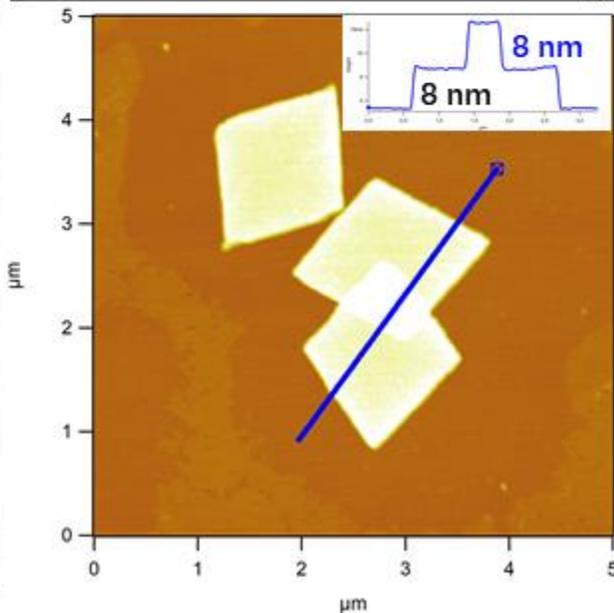
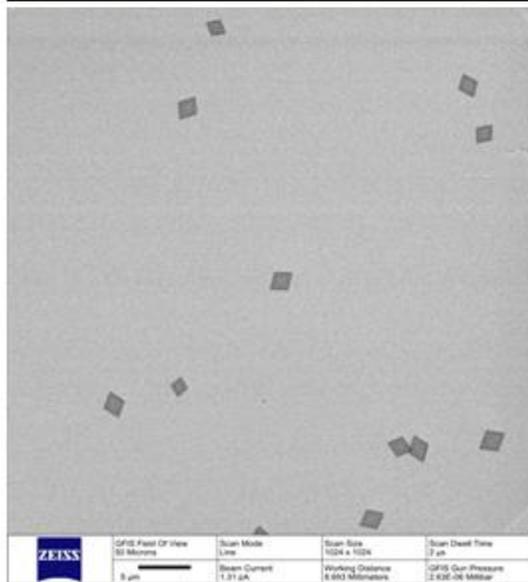
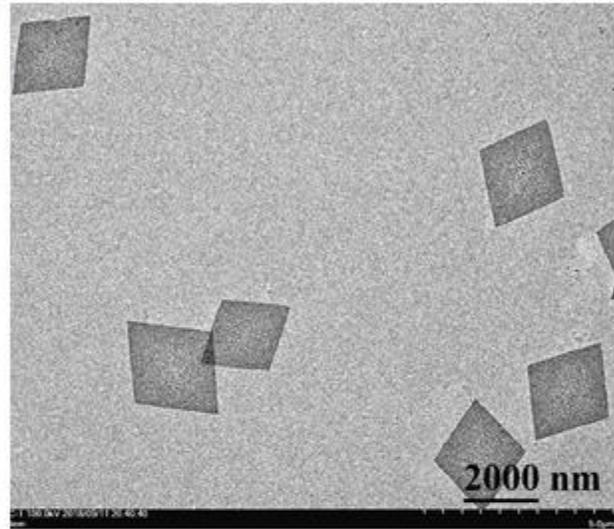
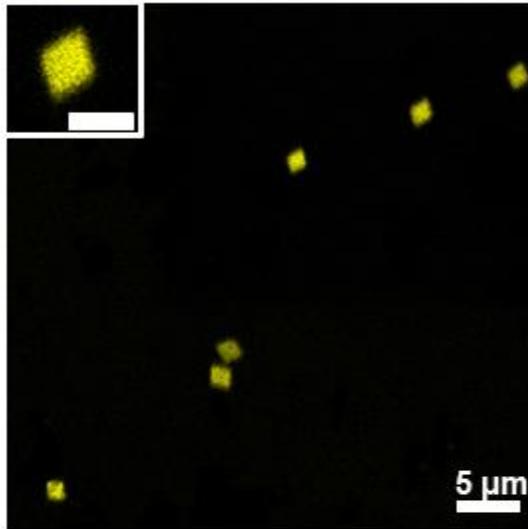
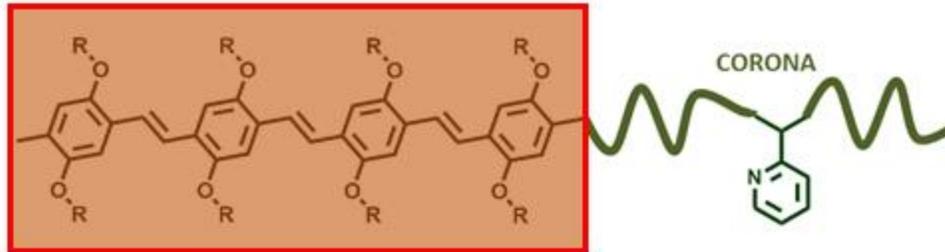
COLL 243

Growth and control of 2D rhombus supramolecular structures of fluorescent block copolymers

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Block copolymers can be easily controlled to fabricate 1/2D nano-/micro-supramolecular morphology as building blocks, and the formed nano-/micro-architectures are readily to functionalized by introducing functional blocks. We combine conjugated fluorescent block poly (phenylene vinylene) (PPV) and poly (2-vinyl pyridine) (P2VP) to build diblock copolymers PPV7-b-P2VPn with strong fluorescence and self-assembly properties. Regular and homogeneous supramolecular 2-D fluorescent rhombus micelles were obtained by dissolving-cooling-aging process. The scales of the achieved 2-D rhombus micelles were significantly dependent on the concentrations of the growing solutions and the block ratios of the copolymers. Furthermore, it was found that the assembling process of two-dimensional micelles in solution was closely related

to the temperature and aging time. Different from the CDSA approaches, the forming rhombus 2-D assembly structures showed extremely low crystalline properties. And indicated by GIWAXS measurement, the formation of rhombus micelles had an important bearing on the intermolecular π - π interaction and the packing angle with each other.

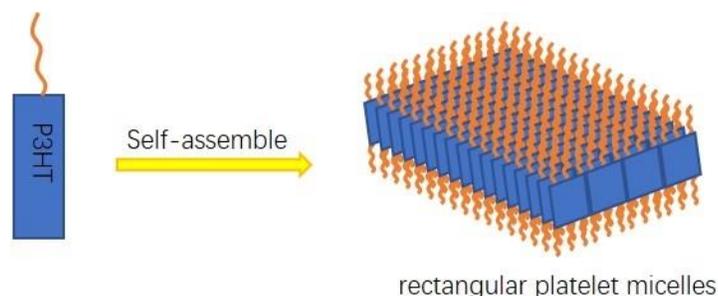


COLL 244

Well-controlled rectangular and square platelet micelles self-assembled by poly(3-hexylthiophene)-b-polyethylene glycol

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Two-dimensional nanomaterials attract many interests in the self-assembly for their potential applications, such as templates, supports for catalysis, chemical inductive devices and medicines, etc. However, it is still challenging to control the morphologies and sizes of the two-dimensional nanomaterials. Here we developed a series of 2D nanomaterials by the self-assembly of the amphiphilic diblock copolymers based on poly(3-hexylthiophene) (P3HT) and methoxypolyethylene glycols (MPEG) in isopropanol. The shapes of the 2D nanomaterials varied from rectangular platelet micelles to square platelet micelles with the increase of the length of P3HT. Meanwhile, the sizes of these 2D platelet micelles could be controlled by the length of the MPEG and the concentration of the diblock copolymers. We also obtained single platelet micelles and hierarchical 2D platelet micelles composed of several single platelet micelles by varying the concentrations. This project would probably offer a new idea for the preparation of the 2D nanomaterials with well-controlled shapes and sizes.



Well-controlled rectangular and square platelet micelles self-assembled by poly(3-hexylthiophene)-b-Polyethylene glycol were developed. The shapes and sizes of the 2D nanomaterials could be controlled by tailoring the length of chain segments.

COLL 245

Self-assembled nano-chamber arrays for liquid cell transmission electron microscopy

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Liquid cell transmission electron microscopy attracts much attention in biological and chemical research area as a high-resolution characterization method for dynamic processes in liquid media. Typical liquid cells mainly fabricated with silicon nitride membrane or graphene as a window material are widely used, however, both of them have technical limitations. In the former case, the thickness of the window is not thin enough to achieve sub-nm spatial resolution. The latter ensures high spatial resolution with remarkable mechanical, chemical, and physical properties suitable for facile liquid phase TEM, but it has the disadvantage that liquid pockets are formed with heterogeneous size and distribution. Herein, we propose a new design of liquid cell based on highly-ordered nanoscale chambers composed of self-assembled anodic aluminum oxide (AAO) membrane, sandwiched on both sides with graphene windows. The new liquid cell design allows high-resolution with simplicity TEM imaging process and statistical analysis of obtained in situ datasets. By using this, we monitor the dynamic motion and interaction between metal nanoparticles, especially focusing on the dependency of coalescence behavior on surface capping agents.

COLL 246

Colloidal gold nanostars as a SERS substrate for the detection of methimazole in urine using a handheld Raman spectrometer

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Portable, handheld instrumentation is driving the development of applications of Raman spectroscopy in a variety of industries. Analytical applications of Raman requiring lower detection limits typically rely on surface enhanced Raman scattering (SERS). Thus, the combination of handheld instrumentation and SERS can be valuable for on-site sensing and monitoring. It follows that the development of field deployable SERS substrates will be crucial to these types of applications.

Our primary focus is to develop water dispersible SERS substrates for simple and rapid on-site analyses of water soluble analytes. In-solution SERS analysis is not as common as that performed on planar substrates, but has been reported using aggregated spherical particles or anisotropic shaped particles. In this work we investigated the SERS capability of gold nanostars as a dispersible SERS substrate using a handheld Raman spectrometer. The nanostars were synthesized using Good's buffers and were optimized based on buffer choice, buffer to gold ratio, and with and without salt aggregation. Our analyses demonstrated reproducible detection of ciprofloxacin, thiabendazole and malachite green in under 5 minutes. Moreover, we developed a SERS assay to quantify methimazole, an anti-thyroid drug, in urine as a potential clinical application.

Our substrate demonstrates good long term storage and is easily deployed as a sensitive SERS substrate for rapid analyses. The merging of a handheld Raman spectrometer with gold nanostars provides a feasible field deployable SERS analysis platform.

COLL 247

Seed-mediated co-reduction as a route to shape-controlled PdCu-PtCu core-shell nanoparticles

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Smart design of Pt-based nanomaterials is of interest due to their potential as electrocatalysts for the oxygen reduction reaction (ORR). Specially, electrocatalytic activity can be optimized through engineering strain of multimetallic surfaces. Particularly, core-shell nanoparticles (NPs) present a unique architecture to induce surface strain and achieve efficient catalysis. Previous work has shown that intermetallic cores stabilize multimetallic surfaces to create more durable catalysts. Additionally, shape-controlled catalysts provide higher activity and selectivity. Thus, there is a need to develop strategies to synthesize Pt-based core-shell NPs with a high degree of shape control to correlate structural properties of NPs with their catalytic performance. Here, seed-mediated co-reduction (SMCR) is shown to be a versatile route to shape-controlled multimetallic nanostructures with strained surfaces. Specifically, studies were undertaken to achieve core-shell PdCu-PtCu NPs with a cubic shape, where Pt and Cu precursors were simultaneously reduced to deposit alloy shells on intermetallic PdCu seeds. The quality of the synthesized cubes relies on the selection of stabilizing and capping agent as well as the complexing agent. Efforts are now directed toward the evaluation of catalytic performance of the synthesized NPs for use as electrocatalysts in ORR and manipulating the synthetic conditions to express different facets for catalysis.

COLL 248

***In situ* monitoring of the heterogeneous nucleation of a second metal on silver nanocubes using an isocyanide molecular probe**

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We demonstrate the use of 2,6-dimethylphenyl isocyanide (2,6-DMPI) to monitor the heterogeneous nucleation of Pt or Pd on Ag nanocube seeds *in situ* by surface-enhanced Raman scattering (SERS). This endeavor is made possible based on the differences in the frequency of the NC stretching mode (ν_{NC}) as the 2,6-DMPI binds to different metal atoms. 2,6-DMPI binds to Ag atoms through σ -donation, which involves the transfer of electrons from the antibonding σ^* orbital of the molecule to the Ag d-band and strengthens the NC bond to blue-shift the ν_{NC} frequency. Conversely, 2,6-DMPI

binds to Pd or Pt atoms through π -back-donation, which involves the transfer of electrons from the metal d-band to the antibonding π^* orbital of the NC group, weakening the NC bond to red-shift the ν NC frequency. Because the SERS hot spots located at the edges of Ag nanocubes coincide with where the Pd or Pt atoms are first deposited, we could monitor the initial stages of their heterogeneous nucleation on Ag. In the case of Pt, we demonstrated that we could resolve down to 27 Pt atoms nucleated on the edges of Ag nanocubes. In the case of Pd, we found that the 2,6-DMPI could bind to one, two, or three Pd atoms through different configurations, each resulting in distinct ν NC frequencies. This allowed us to study the atomic arrangement of Pd adatoms on the Ag nanocube surface at different reaction times and temperatures simply by monitoring the ν NC band. Moving forward, it is hoped that this *in situ* SERS method could be utilized to elucidate the mechanistic details of the heterogeneous nucleation of several other metals (such as Ir, Rh, or Ru) onto Ag seeds and contribute to the development of a rational design for the synthesis of functional bimetallic and multimetallic nanocrystals.

COLL 249

Glycation of human serum albumin alters nanoparticle-protein interactions

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Applications of nanotechnology as drugs or in diagnostics developments can be complicated by biomolecular interactions and physiological conditions that vary across individuals. Among the biomolecules that mediate nanoparticle transformations and fate are a population of proteins that adsorb to the nanoparticle surface, known as the protein corona. Variations in the protein corona depend on the biophysical features of the solution and nanoparticles, as well as the population of proteins. Recent results have even demonstrated that the protein corona varies with a patient's disease states. In addition to alterations in the protein population, disease states alter protein post-translational modifications (PTMs). Despite a decade of research in the protein corona, the role of PTMs in mediating protein interactions with nanomaterials remain poorly understood. Here we present data on how a common PTM, glycation, alters nanoparticle interactions of the most abundant blood protein, human serum albumin (HSA). The effects of glycation on HSA interactions with silver nanoparticles have been evaluated with fluorescence quenching experiments to gain insight into changes in binding affinity. In addition, we evaluated changes to the protein and particle upon interactions. Protein structural changes were monitored using circular dichroism spectroscopy, while nanoparticle transformations were monitored to assess particle agglomeration, surface charge, and dissolution. The results provide insight into how protein glycation alters protein corona formation. This dataset serves as the first step to interrogating the role of PTMs in altering protein corona formation.

COLL 250

Tuneable emission in mercury chalcogenide nanoplatelets

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Mercury telluride (HgTe) is commonly used with cadmium telluride (CdTe) as an alloy semiconductor (HgCdTe) for infrared photodetectors because of the narrow band-gap that is tuneable across the infrared. A major challenge is that processing of these alloys requires high

temperature synthesis which can be problematic given the toxicity of mercury and cadmium. Quantum dots of HgTe have emerged as a possible solution for IR devices due to a high degree of control over the band-gap, but they often still require high temperature methods. A simpler route to synthesizing HgTe nanoplatelets (NPL) has been found through a room temperature cation exchange by introducing mercury salts to CdTe NPL. This results in stable and highly emissive HgTe NPL (~900 nm) with thickness of only a few atoms and large lateral surface areas. Current results show that the surface chemistry of these nanoplatelets can have significant effects on the wavelength of emission. The type of surface capping ligands and their relative amount of coverage can be used to introduce emission further into the short wave infrared (SWIR) as well as tune it from 1000-1500 nm with high photoluminescence quantum yields. Herein we aim to understand the role of surface ligands on the NPL in order to gain insight on the mechanisms of this emission and develop synthetic methods for controlling it.

COLL 251

Aqueous stability and SERS activity of polydopamine functionalized aluminum nanocrystals

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Nanoparticles based on Au and Ag have established a fruitful history of nanophotonic applications including photothermal therapy, chemical sensing, and photocatalysis. The utility of these nanoparticles arises from their collective electron resonances, known as localized surface plasmons, which result in strong optical responses at frequencies in the visible and near infrared (NIR). Aluminum (Al) has recently emerged as a far more earth abundant and inexpensive plasmonic material, capable of supporting surface plasmons across the NIR, visible, and UV region. However, Al suffers from poor aqueous stability, rendering it ineffective for many plasmonics applications. Here, we functionalize colloidal Al nanocrystals with the bioinspired polymer, polydopamine (PDA), to vastly improve their aqueous stability and impart versatile surface chemistry. We leverage the plasmonic properties of the Al core, capable of enhancing Raman

scattering, and the hydrophobic domains in PDA, capable of capturing pollutants, into an inexpensive surface-enhanced Raman scattering assay capable of sub-ppb detection of carcinogenic polycyclic aromatic hydrocarbons. We also investigate the oxidation products of Al nanocrystals and observe a 700% increase in surface area upon mild aqueous treatment, resulting in highly stratified AlOOH nanoparticles which may find use as catalyst support material or water treatment media.

COLL 252

Aluminum nanocubes have sharp corners

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We demonstrate the colloidal synthesis of single-crystalline Al nanocubes by decomposing AlH₃ with Tebbe's reagent in tetrahydrofuran. The size and shape of the Al nanocubes is controlled by the reaction time and the ratio of AlH₃ to Tebbe's reagent, which together with reaction temperature, establish kinetic control over Al nanocube growth. Electron paramagnetic resonance spectroscopy indicates Tebbe's reagent is reduced by AlH₃, generating Ti³⁺Cp₂μ₂H₂AlH-THF, the active catalyst for the reduction of AlH₃ by hydride oxidation. We suspect formation of an Al-C bond between AlH₃ and the cyclopentadienyl ring of Ti³⁺Cp₂μ₂H₂AlH-THF is essential to the growth of Al nanocubes. The reaction proceeds through the formation of cubic superlattices composed of uniform Al clusters that grow into Al nanocubes provided a sufficient excess of AlH₃. Theoretical calculations reveal that Al nanocubes have extremely high localized electric fields at their corners and have an optical response that is incredibly sensitive to coupling with metallic substrates. Chemically synthesized Al nanocubes are cost-effective Earth-abundant alternatives to noble metal nanoparticles for plasmonics and nanophotonics.

COLL 253

Synthetic control of nanowire structure for high resolution electron microscopy

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The Boerdijk-Coxeter-Bernal (BCB) helical structure arises from the inability to pack tetrahedrons regularly, leading to an aperiodic helical wire. Numerous Au alloys,

including AuAg, AuCu, and AuPt, have been reported to take on this complex configuration. Since structure ultimately determines the properties of nanomaterials, it is of great interest to modify the synthesis of these nanowires for fine structural tuning. Predictably controlling the nanowire length, diameter, and defect concentration will lead to the careful control of unique optical and catalytic properties. Here, we investigate amendments in the colloidal synthesis of Au alloyed nanowires exhibiting the BCB helix to carefully control their features. Ultimately, a recipe for structural control of the BCB nanowires will be realized using High Resolution Scanning Transmission Electron Microscopy (HRSTEM) for detailed structural analysis in 2 dimensions. Future work will encompass a three-dimensional atomic resolution analysis of the BCB variants using Atomic Electron Tomography and a quantitative study linking the nanowire structure to their optical and catalytic properties. Together, these results will provide an outline on controlling the physical properties of complex nanostructures based on their atomic scale features.

COLL 254

Visible-transparent and UV-reflective supraballs of hollow silica nanospheres in solution

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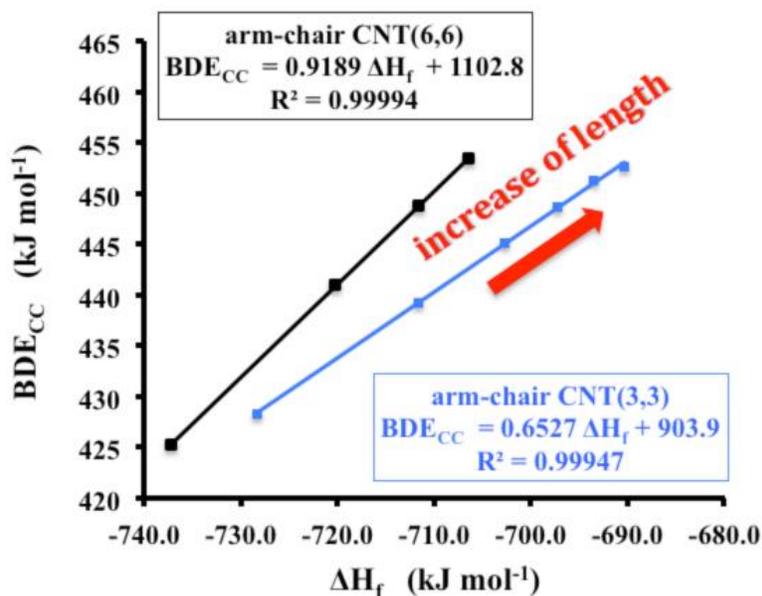
Micron-sized spherical aggregates or 'supraballs' of hollow silica nanospheres were prepared by emulsion-assisted evaporation-induced self-assembly of polystyrene-silica core-shell nanoparticles and thermal annealing at 600 °C for 3 hours. Hollow nanospheres are smaller than the wavelength of visible light and average interparticle distance between hollow silica is matched with interference resonance condition ($d \sim \lambda/2$) for UV. However, when supraballs are dispersed in solvent of refractive index is matched with silica shell, we found that samples are still white reflecting visible light which may be ascribed to strong multiple scattering from supraballs because effective index of refraction are not matched with solvent. Therefore, we have matched average refractive index of supraballs with that of medium by adjusting mixing ratio in water and ethylene glycol, which showed optically transparent photonic microspheres reflecting UV strongly and selectively.

COLL 255

Quantum-size effect of the bond dissociation enthalpies and formation enthalpies in single walled carbon nanotubes

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We have studied computationally the bond dissociation enthalpy (BDE), the formation enthalpy and the local electronic properties of Single-Walled Carbon Nanotubes (SWCNT). The arm-chair (i.e. CNT(n,n) where $n=3,4,5,6,7$) and zig-zag (i.e. CNT($m,0$) where $m=6,7,8,9,10$) chirality CNT, with various lengths (i.e. 9.0-36.2 Å) and diameters (i.e. 4.2-9.6 Å), were considered. The dangling bonds in these SWCNT were terminated with H-atoms. Our analysis shows that there is a strong quantum-size effect on the BDE and the formation enthalpy of these SWCNTs, which is inversely proportional to the curvature-squared ($1/r^2$) and inversely proportional of the SWCNT length ($1/l$). This suggests that SWCNT become less stable as their length increases due to the emergence of metallic properties and as their radius decreases, which is due to smaller overlap of the p orbitals. This clearly shows that there is a quantum-size effect of the thermodynamic properties of SWCNTs when their length and diameter is less than 4 nm.



COLL 256

Ultrathin hydroxide nanosheets for old paper deacidification

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Paper deacidification is very important for the protection of ancient Chinese civilization.

Nevertheless, the present method for paper deacidification is still limited by some disadvantages, such as the poor dispersity, the low alkali reserve and the nonuniform effect of deacidification, etc. The development of novel deacidification agent should be the most promising solution for this bottleneck. In this report, colloidal suspension for two-dimensional (2D) atomically thin inorganic hydroxide nanosheets have been synthesized to realize the function of both paper deacidification and flame retardancy. They show good performance in deacidification treatment of paper. During the heat aging test, the change of pH value, color difference, degree of polymerization and the corresponding mechanism will be discussed. It will provide scientific evidence of the synthesis of 2D hydroxide colloidal suspension, and also develop novel nanomaterials for paper conservation with long-time stability, excellent paper deacidification and flame retardancy effects.

COLL 257

Tuning the nitrogen species content in N-doped CNTs for catalytic applications

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Nitrogen doped carbonaceous materials have emerged as an outstanding alternative to metallic catalysts due to its catalytic properties. They have shown to be suitable for attractive reactions such as the Oxygen Reduction Reaction (ORR) either generating on-site H₂O₂ (via the 2 electrons pathway) for environmental remediation applications or generating water (via the 4 electrons pathway) for fuel cells.

Nitrogen doped carbon nanotubes (N-doped CNTs) correspond to an attractive building block for this type of applications. It is well known that the Nitrogen doping atoms can be incorporated in the sp² Carbon network in different type of configurations such as: pyridinic nitrogen, graphitic nitrogen, pyrrolic nitrogen or even as oxidized nitrogen species. These different type of nitrogen species have shown to play different roles for the catalytic reactions applications.

Here we obtained N-doped CNTs by the spray pyrolysis CVD technique. First we included N-containing precursors as additives to the precursor solution to be nebulized modifying the N-species proportions present in the N-doped CNTs. We explored the percentage of total nitrogen in the obtained nanotubes and the different Nitrogen species present in the samples.

The obtained samples were heat treated under inert atmosphere and the annealing effect on the N-doped CNTs modifying the proportion of nitrogen species were analyzed.

The samples were analyzed by Scanning Electron Microscopy (SEM), X-ray

Photoelectron Spectroscopy (XPS), Thermogravimetric analysis (TGA) and Transmission Electron Microscopy (TEM).

COLL 258

Inclusion of plasmonic nanoparticles into low density materials

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Molecules detection in gaseous solutions is of great importance for controlled substances monitoring, food safety control and detection of highly toxic molecules. As general rule fast and efficient detection is request it, therefore the highest possible sensitivity is required.

Raman signal is rich in information related with the structure and chemical composition but low in intensity. However, noble metal NPs are excellent candidates as plasmonic building blocks due to their ability of supporting localized surface plasmon resonances (LSPRs) when excited by visible light photons. To increase the Raman signal intensity, the interaction between the analyte and a metallic NP is exploited, where high intensity electric field regions are generated when their LSPR is excited by visible light. These regions amplify the Raman intensity generated and the resulting signal is called SERS (Surface Enhanced Raman Scattering). Moreover, if the metal nanoparticles (NPs) are very close to themselves, the electric field redistribution (LSPR coupling) yields local regions with intensity increments called hotspots which increase more the SERS signal intensity, lowering the detection limits.

The main challenge for detection of molecules in gaseous solutions is to promote the interactions between the analyte and the probe surface. Therefore, a material which allows an efficient and high flow of gaseous solution at the surroundings of the plasmonic NPs is required.

In this work, we proposed the inclusion of Au nanoparticles into low density materials as candidates to detect analytes from gaseous solutions. Three morphologies: spheres, rods and concave cubes are explored due to its different plasmonic response. The Au NPs concentration is also explored to modify their proximity with each other in the final material looking for the generation of hotspots.

COLL 259

Nanoscale interactions between liposomes and magnetic/plasmonic nanoparticles investigated by means of (surface - enhanced) Raman spectroscopy

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The synthesis of hybrid multifunctional nanosystems is in the limelight of modern nanotechnology research. Among the different classes of nanohybrids that have been proposed so far, magneto-liposomes are of particular interest. In a very recent paper [1], our group reported the successful synthesis of this new types of nanohybrids by synergistically taking advantage of two types of interactions: hydrophobic ones, acting between superparamagnetic iron oxide nanoparticles (SPIONs) and the inner bilayer of the liposomes, and electrostatic ones manifesting between cationic liposomes and anionic gold nanoparticles. In this research we present a detailed (Surface - Enhanced) Raman Spectroscopy analysis performed on different regions of the multifunctional nanohybrids. The successful incorporation of SPIONs nanoparticles together with the modifications they generate in the lipid bilayer are analysed for the first time by means of Raman spectroscopy performed on dry samples whereas the plasmonic properties of the hybrids (able to provide useful insights concerning the interaction of plasmonic nanoparticles with liposomal outer membrane) were evaluated in solutions. The spectroscopic results were validated by other techniques such as TEM, Hyperspectral Microscopy, DLS.

COLL 260

AgAu alloy nanoshell: Decorated BaTiO₃/TiO₂ and SrTiO₃/TiO₂ for photoelectrochemical catalysis

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In this work, we describe the deposition of BaTiO₃ or SrTiO₃ on the surface of TiO₂ followed by decoration with AgAu alloy nanoshell particles. Since the discovery of the photoactivity of TiO₂ by Fujishima and Honda, TiO₂-based photocatalysts have drawn the interest of researchers. However, their low charge-separation efficiency and their poor utilization of sunlight bar TiO₂-based photocatalysts from use in practical applications. Research has shown that the built-in electric field in BaTiO₃ and SrTiO₃ is

able to aid in charge separation when deposited on the surface of TiO₂. Furthermore, AgAu alloy nanoshell particles can be tuned to absorb/scatter in the near infrared region, abundant in sunlight. The novel nanostructure developed in this work can not only improve the charge-separation efficiency, but also take better advantage of sunlight, improving the overall efficiency of TiO₂-based photoelectrochemical systems.

COLL 261

Tunable 3D DNA origami-gold nanoparticle hybrid: Self-assembled ultrasensitive SERS substrate

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One of the critical challenges of surface enhanced Raman spectroscopy (SERS)-based detection is the precise alignment of metal nanoparticles. DNA origami has emerged as a promising candidate to organize metal nanoparticles due to its spatial accuracy and reproducibility. Here, we synthesized a three-dimensional (3D) hollow DNA origami cage as a template to assemble a gold nanoparticle (AuNP) trimeric substrate for advanced SERS-based detection. A 10-nm AuNP was encapsulated in the inner cavity, and two 30-nm AuNPs were positioned at the two opening ends of the DNA origami cage with 5-nm gap between the smaller and larger AuNPs. Thiol-modified DNA functionalized AuNPs were anchored to the complementary capture strands on the DNA origami cage through DNA base pairing. The accurate geometric control of AuNP trimer structures should provide over 10¹¹ SERS signal enhancement as predicted by Finite-Difference Time-Domain (FDTD) simulation. This approach allows us to control gap sizes and customize binding sites that enable specific binding of analytes into hotspots. In addition to ultrasensitive detection, these highly tunable complex and precise nanoparticle assemblies could also serve as a versatile test bed of plasmonic theories.

COLL 262

Computational study on the binding affinities of aliphatic α -amino acids with graphene

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Density functional theory (DFT) calculations were performed to understand the binding of naturally occurring aliphatic amino acids (glycine, alanine, valine, leucine, cysteine, methionine, aspartic acid, glutamic acid, lysine, arginine, serine, threonine, asparagine, and glutamine) individually with two finite size graphene sheets. After performing conformational analysis for these fifteen amino acids using Merck Molecular Force Field (MMFF) implemented in Spartan '18 software package, geometries of all conformers were optimized at the HF/6-31G(d) level and then up to 300 conformers were chosen to

be optimized at the M06-2X/6-31G(d) level. The most stable conformer obtained at the M06-2X/6-31G(d) level was used to build complexes with graphene by considering different possible binding modes. All complexes were fully optimized using M06-2X/6-31G(d) level. Binding energies with and without basis set superposition error (BSSE) correction were calculated and analyzed. Our study reveals that multiple C-H... π , N-H... π , and O-H... π interactions contribute for stabilization of the complexes. The data obtained from our computational study may be helpful for force field development and for future experiments on non-covalent interactions of amino acids with graphene. Our goal is to understand the relationship between the binding affinities of various complexes and structural features including the orientation of amino acid adsorbed on two different sizes of graphene sheets.

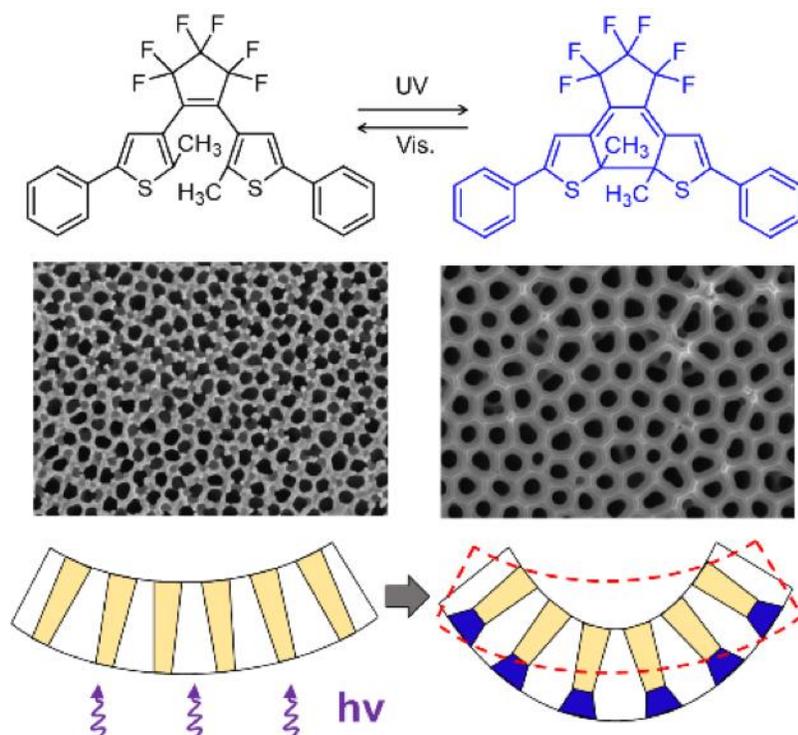
COLL 263

Effects of template and molecular nanostructure on the performance of organic-inorganic photomechanical actuator membranes based on aligned nanocrystals

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Photomechanical nanocrystals themselves are organized on macroscopic length scales using a porous inorganic template. The resulting organic-inorganic composite can function as a photomechanical bending actuator. This hybrid organic-inorganic photomechanical material acts as a bending actuator. Using ultraviolet and visible photons as power inputs, as little as 0.1 mg of reacted material generates enough force to tilt a 1.28 g mirror and steer a laser beam. The motion can be cycled multiple times in air and under water. Actuator figures-of-merit such as energy-to-work conversion efficiency and stiffness are probably limited by the high elastic modulus of the inorganic template, providing an obvious pathway for optimization.

In order to investigate how the nanostructural properties of both the organic and inorganic components affect the photomechanical response, the composite mechanical properties are characterized using a variety of methods. The templates with a lower average elastic modulus (16 GPa versus 68 GPa) generate almost an order of magnitude more photomechanical work. The dependence of the photomechanical response on the chemical structure of the photochrome is assessed by comparing the performance of a diarylethene that undergoes a crystal expansion to that of one that undergoes a contraction, which leads to a decrease in curvature. Both the inorganic template and the organic active component play important roles in the overall photomechanical response, with substantial room to improve the performance.



The actuators with a lower average elastic modulus (16 GPa versus 68 GPa) generate almost an order of magnitude more photomechanical work. Both the mechanical properties of porous inorganic templates and chemical characteristics of active organic components are important to the improvement of the composite's performance.

COLL 264

Relationship between surface topography and ice adhesion on superhydrophobic surfaces

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Ice accretion and accumulation leads to critical application failures in transportation, aircraft, electrical devices etc. due to significant weight balance shift, visibility interventions, and other potentially dangerous situations. When ice forms, reduced ice adhesion will be one of the most desired features from the surface. Superhydrophobic coatings stand out among other ice removal strategies due to their outstanding water repellent nature and the potential to provide a durable, economical and environment-friendly approach. Many groups evaluate the ice adhesion strength of a surface based on the wettability, closely related to the water receding angle value, since water rolling off behavior is considered comparable to ice removal procedure. While others indicate

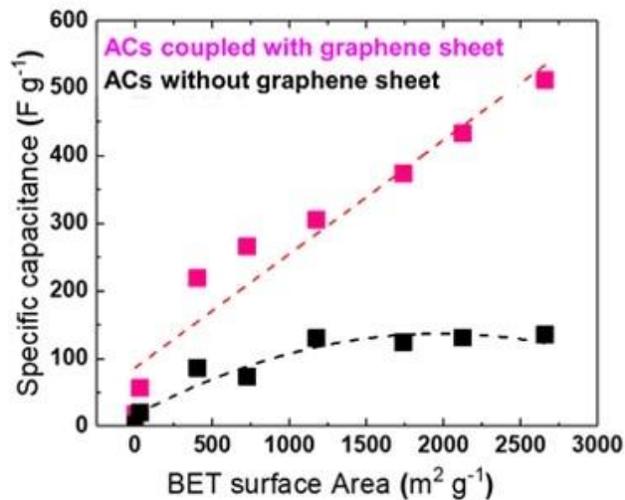
that ice process follows completely different mechanisms which indicate the fact that superhydrophobic coatings may not always support reducing ice adhesion. This study focused on the relationship between ice adhesion strength and the topography of superhydrophobic surfaces (SHS) coatings. Fluorescent microscopy is firstly used to characterize the real solid-ice contact area on spray-coated SHS with different roughness which explains how ice adhesion correlates to topography.

COLL 265

Porous carbons derived from renewable biomass as high-performance supercapacitor with high mass loading

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With increased interest in energy and environment issues, high-performance energy storage is needed for renewable energy. Supercapacitors (SCs), also called electrochemical electrical double-layer capacitors, have been of great attention as one of the most attractive energy storage devices for sustainable energy storage devices due to their high power capability, fast charge/discharge rates, ultra-long cycling life and low maintenance cost. The breakthroughs in the design of nanostructured carbon materials lies at the heart of developing advanced SCs. Naturally abundant biomass is a green, alternative carbon sources and they can be easily converted into porous carbons with many desired properties via simple, low cost and environmentally friendly methods. In this study, we have developed porous carbon based electrodes from waste coffee grounds for SCs. The resulting electrodes for SCs exhibited excellent electrochemical performances with a high mass loading of active materials. These properties are attributed to the synergistic combination of the high surface area of ACs and reduced graphene oxides that provide a multi-functional binder between ACs. This combination can also improve the wettability of electrode, which is beneficial for enhanced contact between the electrode material and electrolyte. Symmetric two electrode system exhibits outstanding charge storage capacity, reaching a high specific capacitance and excellent rate capability in both aqueous electrolyte and non-aqueous electrolyte.



COLL 266

Potential of click nucleic acids in widening nanoparticle functionality

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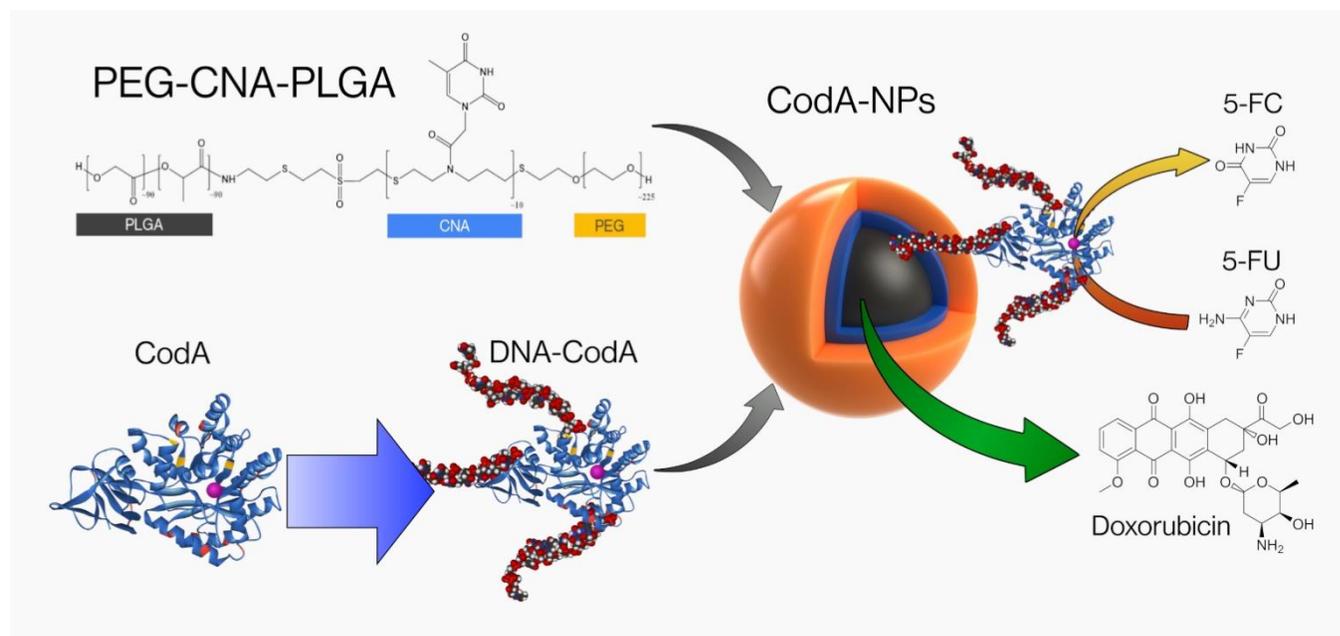
Co-Delivery of therapeutics is a promising technique for cancer treatment as it both limits drug resistance and makes use of synergetic effects, thereby a lower effective dose is necessary, with potentially lower side effects. However, it is sometimes of interest to co-deliver a hydrophobic agent together with a hydrophilic drug or bioagent in the same delivery agent.

In previous work we have shown the incorporation of novel artificial nucleic acids, Click Nucleic Acids (CNAs), into PEG-PLGA nanoparticles adds DNA encapsulation capability in a sequence specific manner to the particles without affecting its hydrophobic encapsulation functionality.

In our latest work we have further studied this capability by transitioning to a therapeutically relevant combination. For this we modified the protein cytosine deaminase with DNA of the complementary sequence as well as a fluorescent marker to track the fate of the protein. Cytosine deaminase catalyzes the conversion of the prodrug Flucytosine to the chemotherapy drug Fluorouracil, the activity after the modifications was assessed and potential therapeutic value of encapsulated protein estimated by a series of *in vitro* toxicity assays whilst simultaneously introducing Doxorubicin as a hydrophobic therapeutic.

This work shows potential for the inclusion of these novel synthetic nucleic acids to widen the capabilities of existing nano-delivery agents, so DNA functionalized

molecules or biomolecules as complex as the proteins shown in this study can be successfully delivered.



COLL 267

Functionalized nanodiamonds in the investigation of the aggregation phenomenon

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Nanodiamonds (NDs) have gained an increased interest in the field of biomedical applications due to their low cytotoxicity, intrinsic biomarker capability, and versatile surface chemistry. Unfortunately, NDs suffer from a severe aggregation phenomenon due to the myriad functionalities existing on the NDs surface. In this work, we focus on disaggregating NDs to increase the surface area by removing impurities of the surface of NDs using HNO₃ and H₂SO₄ eliminating any existing weak van der Waals interactions. Ideally, subsequent surface modification of the NDs is accomplished by covalent bonding between the biopolymer, chitosan (CS) and the carboxylate NDs (cNDs) surface of the NDs. Furthermore, in this work we will show possible surface repulsion enhanced with the use of the biopolymer CS. The surface coverage of the NDs surface by CS was studied by modifying the ratio between the cNDs and CS wt/wt%. Studies observed in this paper include FT-IR, ZPA, DLS and TEM.

COLL 268

Chemically modified titanium boride nanosheets: High yield synthesis and hierarchical assembly into paper-like macrostructures

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The ability to isolate graphene, a single atom thick layer present in graphite, forms an important milestone in the science of nanomaterials. It not only helped realize the first truly 2D nanomaterial, but also motivated the scientific community to explore if other layered materials can also be nanoscaled in a similar fashion. The last decade has been witness to a rapid growth in the research efforts towards achieving an entire spectrum of inorganic nanosheets analogous to graphene. It is expected that boron nanosheets can present excellent platforms to utilize the versatile science of boron. The experimental discovery of borophene in recent times has added momentum to the 2D boron research front. Metal borides represent a family of strongly bonded layered materials in which boron honeycomb planes are held together by hexagonal arrays of metal atoms. Their construct, which is isostructural to intercalated graphite, holds utmost promise especially in view of realizing quasi-2D forms of boron. So far, metal borides have been primarily employed for their superior physico-chemical properties; for example titanium boride is a super hard ceramic while magnesium diboride is a well-known superconductor. Scientists have recently reported the delamination of layered metal diborides like MgB_2 and AlB_2 , and have shown that nanosheets obtained from these metal borides are functionalized, but rich in boron. Here, we present the chemical synthesis of boron based nanosheets from another layered diboride, TiB_2 . The methodology utilizes an oxidative intercalation strategy to achieve the colloidal synthesis of chemically modified boron based nanosheets as aqueous dispersions in ultra-high yields of up to 10 mg/ml. The nanosheets are characterized by FESEM-EDX, UV-Vis, FTIR, and X-Ray Photoelectron spectroscopy. We also present evidence of the ability of these nanosheets to be easily assembled into paper-like macrostructures by vacuum assisted filtration. These free standing macrostructures have rich potential to be employed in fields as diverse as electrodes in energy applications to chemical filters. We show initial results of these nanomaterials' ability to act as efficient dye adsorbents for waste water remediation.

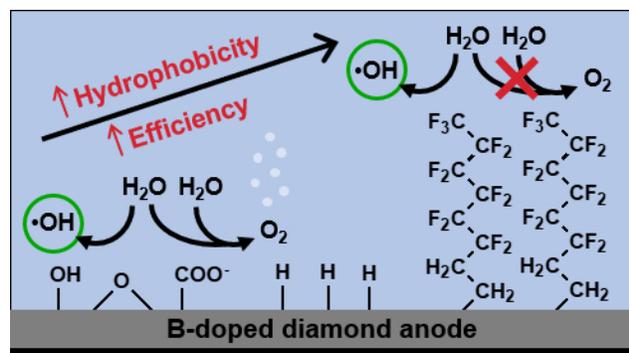
COLL 269

Enhancing electrochemical efficiency of hydroxyl radical formation on diamond electrodes by functionalization with hydrophobic monolayers

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Electrochemical formation of high-energy species such as hydroxyl radicals ($\cdot\text{OH}$) in aqueous media is inefficient because oxidation of H_2O to O_2 is a more thermodynamically favorable reaction. Boron-doped diamond (BDD) is widely used as an electrode material for generating $\cdot\text{OH}$, including in water purification applications, because it has a large kinetic overpotential for O_2 production, thus increasing electrochemical efficiency for $\cdot\text{OH}$ production. Yet, the underlying mechanisms of O_2 and $\cdot\text{OH}$ production at diamond electrodes are not well understood. We demonstrate that boron-doped diamond surfaces functionalized with hydrophobic, polyfluorinated molecular ligands (PF-BDD) have significantly higher electrochemical efficiency for $\cdot\text{OH}$ production compared with hydrogen-terminated (H-BDD), oxidized (O-BDD), or poly(ethylene ether)-functionalized (E-BDD) boron-doped diamond samples. Our measurements show that $\cdot\text{OH}$ production is nearly independent of surface functionalization and pH (pH = 7.4 vs 9.2), indicating that $\cdot\text{OH}$ is produced by oxidation of H_2O in an outer-sphere electron-transfer process. In contrast, the total electrochemical current, which primarily produces O_2 , differs strongly between samples with different surface functionalizations, indicating an inner-sphere electron-transfer process. X-ray photoelectron spectroscopy measurements show that although both H-BDD and PF-BDD electrodes are oxidized over time, PF-BDD showed longer stability (~ 24 h of use) than H-BDD. This work demonstrates that increasing surface hydrophobicity using perfluorinated ligands selectively inhibits inner-sphere oxidation to O_2 and therefore provides a pathway to increased efficiency for formation of $\cdot\text{OH}$ via an outer-sphere process. The use of hydrophobic electrodes may be a general approach to increasing selectivity toward outer-sphere electron-transfer processes in aqueous media.



COLL 270

Intramolecular insights into adsorbate-substrate interactions by tip-enhanced Raman spectroscopy at the angstrom-scale

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Tandem analytical techniques, such as scanning tunneling microscopy (STM) tip-enhanced Raman spectroscopy (TERS), offer the capability to combine spatial resolution with chemical information. These methods allow the interrogation of surface interactions with angstrom-scale resolution. Intermolecular and molecule-substrate interactions determine the self-assembly of organic molecules on a surface, and highly localized chemical effects can have profound consequences on the formation of nanoarchitectures. As a result, new techniques must be applied to these systems in order to more fully interrogate and understand the effects of these interactions. Through the combination of Ultrahigh Vacuum (UHV) STM-TERS with density functional theory (DFT) calculations we have studied and characterized the interactions of self-assembled organic molecules on metal surfaces. Porphyrin and phthalocyanine derivatives relevant to organic and printed electronics as well as photovoltaics were selected in this study, as their surface interactions are fundamental to the nature of their implementations in devices. STM-TERS and DFT calculations were used to reveal molecular fingerprints and intramolecular bond information spectroscopically with sub-nanoscale spatial resolution. Through this method the location of specific vibrational modes can be defined, and subtle differences visualized. Subsequently, this intramolecular resolution has been applied to investigate the highly localized effects of molecule-substrate and molecule-molecule interactions based on shifts in the energies and intensities of specific vibrational modes.

COLL 271

Evaluating the binding of ligands on silver nanocubes by *in situ* surface-enhanced Raman spectroscopy

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The adsorption of ligands on the surfaces of colloidal Ag nanocubes was studied using *in-situ* surface enhanced Raman spectroscopy (SERS). In a typical experiment, time-resolved solution-phase SERS data were collected from a sample of Ag nanocubes dispersed in an ethanol-based ligand solution at different concentrations, from which we could evaluate the binding of the ligand to the Ag nanocubes. We found that 4-nitrothiophenol (4-NTP) would rapidly bind to the Ag surface due to the favorable thiol-Ag interactions. The red-shift of SERS peaks at lower concentrations suggests a different molecular orientation, consistent to what is described in the self-assembled monolayer (SAM) theory. We also found that 4-aminothiophenol (4-ATP) would also rapidly bind to Ag, but with significantly weaker SERS intensity due to the electron-donating amine group of 4-ATP. In addition, we evaluated the binding of 1,4-phenylene

diisocyanide (1,4-PDI), which interacts with Ag weaker than thiols, and found that they would readily bind to the Ag nanocube surface. As the concentration of 1,4-PDI increased, we found that more molecules were oriented perpendicular to the surface. Finally, we evaluated the competitive adsorption of the thiol and isocyanide groups to Ag by introducing them simultaneously to Ag nanocubes. The signals for 1,4-PDI were not visible when the same amount of 4-NTP (4-ATP) as the 1,4-PDI was introduced simultaneously, and they were weakly visible only when their amount was increased relatively by 100 times. This suggests that thiols selectively bind to the Ag surface over isocyanides, inhibiting the adsorption of isocyanides to the Ag surface.

COLL 272

Breathable moisture responsive fibrous materials

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A stoma (plural stomata) is a pore or opening in the epidermis of plant leaves, through which carbon dioxide is received for photosynthesis and water vapor is transpired. A stoma consists of two guard cells, having thicker and inextensible inner walls and outer walls that are thinner and more extensible. The stomata open and close through the swelling and shrinking of the two guard cells in response to environmental stimuli, e.g. high light intensity and high humidity.

In this study, we are fabricating the pores in a breathable fabric to mimic the structure and function of leaf stomata via a surface chemistry approach. In the artificial stomata, a special polymer is coated around a slit ("pore") of the fabric to form "guard cells". The polymer will bend under higher humidity (wet), leading the "pore" to open, while it stays still under normal humidity (dry) which keeps the "pore" close. In both conditions, the fabric maintains a flat surface without buckling, which means little effect on the overall dimension of the fabric.

The process is simple and easy to scale up. The polymer can be coated via digital liquid dispensers, or various industrial printing techniques, like screen printing or 3D printing. The slit can be cut by laser etching technology, and the dimensions can vary from micro- to millimeters. The dimension change of the pore under "open" and "close" states can be easily measured by the length and width change, or observed under optical microscope. The fine structure and morphology can be examined under scanning electron microscope (SEM). The air penetration or vapor transmission through the pores under different states can be measured by air permeability tester (e.g. KES-AP) or moisture vapor transmission rate (MVTR) tester.

COLL 273

Identifying the barriers to sub-nanometer resolution non-contact atomic force microscopy of hydrophobic surfaces in liquid

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Noncontact amplitude modulated atomic force microscopy (NCAM-AFM) has successfully imaged, at the sub-nanometer scale, individual molecules of hydrophilic surfaces in aqueous solutions. It remains unclear why such resolution has not been reported for hydrophobic surfaces under water. Previously, using amplitude vs. distance AFM spectroscopy combined with molecular dynamics (MD) modeling, we showed that a ~5 Å void exists between a methyl terminated surface and the first hydration layer but is not observed over a comparable hydroxyl terminated surface. We hypothesized that the hydration layer formed over this gap creates a region of force noise between the AFM tip and surface preventing molecular imaging of hydrophobic surfaces in aqueous conditions. In this study we used nanografting to pattern separate regions of alkanethiols of similar lengths with differing terminal groups on an Au (111) surface. Although the lengths of the alkanethiols on the surface are nearly identical, our results show a difference in height between hydrophobic and hydrophilic groups. This suggests that the AFM is imaging the hydration structure over the void rather than interacting directly with the surface preventing resolution of the surface lattice. The knowledge of the contrast mechanisms at the sub-nanometer scale may inform the development of methods for reproducible sub-nanometer scale NCAM-AFM imaging of functionalized surfaces in liquid.

COLL 274

Domain structures in mechanically exfoliated single-layer MoS₂ on Au(111)

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Heterojunctions of semiconductors and metals are the fundamental building blocks of modern electronics. Coherent heterostructures between dissimilar materials can be achieved by composition, doping or heteroepitaxy of chemically different elements. Here we report, the formation of coherent single-layer MoS₂ heterostructures, which are chemically homogenous with matched lattices, but show electronically distinct semiconducting (1H phase) and metallic (1T phase) domains when deposited on Au(111) by mechanical exfoliation. The exfoliation technique we developed and employed in these studies, eliminates the tape residues usually found in other exfoliation methods, and also leads to single-layer MoS₂ with millimeter size. Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) have been collectively employed to elucidate the nature of the heterostructures of MoS₂/Au. Our work provides some

intriguing guides to the production of macroscale two-dimensional heterostructures, which represent unique candidates for future electronic devices and applications.

COLL 275

Surface immobilized thermos- and light-responsive hybrid microgels for modulation of surface properties

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The swelling/deswelling behavior of photo-themo-responsive microgels dispersed in aqueous media and immobilized on substrates were investigated and correlated to their chemical and physical properties. The hybrid microgels were prepared by in-situ reduction of gold salts in the presence of thermo-responsive microgels based on poly(N-isopropylacrylamide) (PNIPAM). Their behavior was compared with bare thermo-responsive microgels. It was shown that the temperature induced volume phase transition for bare PNIPAM microgels is maintained with the hybrid microgels. Moreover, while PNIPAM microgels do not respond to light, the hybrid microgels undergoes a volume change upon irradiation. The dependence of the crosslink density and gold content of the microgels on the responsive-behavior in aqueous media and on substrate will be discussed. The investigation was performed using DLS, AFM, TEM and SFA.

COLL 276

Antioxidant hydrogen-bonded coatings of linear synthetic polyphenol polymers

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Polyphenols are promising antioxidant molecules that can be used as hydrogen-bonded donors in layer-by-layer (LbL) assemblies. We report antioxidant LbL films of methacrylamide- and acrylamide-based synthetic polyphenols with PEO, and explore the effect of polyphenol functionality on antioxidant activity, substrate adhesion, and morphology of the constructed films. The antioxidant capability of the coatings was quantified by the reduction rate of 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) (ABTS) and 2,2-diphenyl-1-picrylhydrazyl (DPPH) radicals and film morphology was monitored by SEM and AFM. Importantly, linear polyphenols included within LbL films were capable of efficiently scavenging reactive oxygen species from solution and demonstrated prolonged antiradical activity. The duration of antiradical activity depended on the penetration rate of ABTS and DPPH radicals into the films and was controlled by film structure. Exposure of the films to radical species induced crosslinking as indicated by Fourier-transform infrared spectroscopy (FTIR), largely increasing stability of the films in organic solvents. Finally, antioxidant and adhesion properties of

films, containing either hydrophobic methacrylamide-based or newly synthesized hydrophilic poly(vinyl alcohol)-based polyphenols, is discussed.

COLL 277

Noncovalent microcontact printing for hierarchically patterned striped phases of polymerized lipids

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Advances in applications from electronic device manufacturing to the controlled display of complex biomolecules require interfaces with precisely constructed chemical environments at micrometer and nanometer scales. The challenges of precisely structuring interfaces include not only positioning functional groups on the surface, but also controlling their orientation and clustering. Microcontact printing (μ CP) enables geometrically patterned assembly over microscopic (or large nanoscopic) areas. However, traditional μ CP, such as alkanethiols on gold, creates interfacial lattices with molecular footprints ($\sim 0.25 \text{ nm}^2$) smaller than many biomolecules. Striped phase monolayers, in which noncovalently adsorbed alkyl chains extend across the substrate, have larger, more complex lattices (*i.e.* nm-wide stripes of headgroups with 0.5 or 1-nm lateral periodicity along the row, separated by wider ($\sim 5 \text{ nm}$) stripes of exposed alkyl chains). These anisotropic interfacial patterns provide a potential route to controlled clustering of complex functional groups. Here, we demonstrate that, with appropriate modifications, microcontact printing can be used to generate well-defined microscopic areas of noncovalently adsorbed striped phases of both single-chain amphiphiles (fatty acids) and dual-chain amphiphiles (phospholipids). This approach generates hierarchical molecular-scale and microscale interfacial clustering of functional ligands, prototyping a strategy of potential relevance for controlled clustering of complex functional groups.

COLL 278

Intermolecular π -interactions lead to homogeneously mixed phenyl-terminated self-assembled monolayers

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This presentation investigates homogeneously mixed self-assembled monolayers (SAMs) derived from the adsorption of phenyl- and perfluorophenyl-terminated

alkanethiols and the role of π -interactions in inhibiting phase separation. Two kinds of perfluorophenyl-terminated alkanethiols, $C_6F_5(CH_2)_nSH$ ($n = 12-15$) and $C_6F_5CF_2(CH_2)_nSH$ ($n = 11-14$), as well as their hydrocarbon analogs, $C_6H_5(CH_2)_nSH$ ($n = 12-15$) were synthesized. The phenyl-terminated alkanethiols were used to generate two series of mixed SAMs on gold surfaces. The SAMs were characterized using ellipsometry, X-ray photoelectron spectroscopy (XPS), polarization-modulation infrared reflection-absorption spectroscopy (PM-IRRAS), contact angle goniometry measurements, and atomic force microscopy (AFM). This presentation will offer insight into the π -interactions present in the monolayers and their role in influencing the interfacial structures and properties of the films.

COLL 279

Recovering rare earth elements (REEs) from coal fly ash and power plant wastewater sludge leachates with an engineered sorbent

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The global demand for rare earth elements (REE) has increased significantly in the past 20 years due to their extensive use in electronics and other applications. Although many recent studies related to quantifying rare earth elements in coal and coal combustion byproducts have been published, methods of extracting and concentrating rare earth elements are still not economical. The objective of our study is to investigate the potential extraction of the REEs from coal ash and from wastewater sludge collected from a power plant near Detroit, MI. The collected ash and sludge is subjected to a hydrothermal extraction process developed by Los Alamos National Laboratory to extract REEs from the sludge or coal ash, resulting in a liquid enriched in dissolved REEs. Batch experiments were conducted using an organosilica sorbent (Osorb®) and a commercially-available ligand [P-di(2-ethylhexyl) methanediphosphonic acid (DIPEX)] to adsorb neodymium from a synthetic hydrothermal extraction solution. DIPEX-associated Osorb media was produced by first dissolving DIPEX into a solvent (e.g., methanol). Different amounts of DIPEX-methanol solution were then added to 0.2 g of Osorb to determine the maximum capacity. The methanol was evaporated and, after a rinse step, the DIPEX-Osorb sorbents were used in sorption experiments. A 300 ppm neodymium (Nd) synthetic ash/sludge leachate was tested. Results show that DIPEX-Osorb ratios of 4.3, 1.1, 0.5, and 0.05 (g/g) sorbed 60, 51, 25, and 7 mg Nd per g media, respectively. Column experiments are currently being conducted to enable the quantification of various sorption parameters of the media (e.g., capacity, kinetic rate constants). We continue to investigate the reusability of the DIPEX-Osorb media by

measuring how many cycles the media can be regenerated by extracting Nd with acid and reusing the sorbent for additional cycles.

COLL 280

Reactivity of 4-NBD with single and multilayer layer MoS₂ on Au(111)

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The use of single layer MoS₂ (SLM) in nano-devices is of significant interest, and its optoelectronic properties have been shown to be able to be tuned by modifying its surface. To explore this, radical reactions of compounds such as 4-nitrobenzenediazonium tetrafluoroborate (4-NDB) with MoS₂ in aqueous solution have been previously investigated as a means for facile modification, but a detailed study has yet to have been carried out of the nature of its chemical reactivity with MoS₂ on Au(111) substrates with varying layer thicknesses. Here, the mechanical, optical and chemical properties of single and multilayer (bulk) MoS₂ on Au(111) substrates were investigated before and after being functionalized with 4-NDB in aqueous solution. By employing AFM to study the exfoliated MoS₂ sheets on Au substrates after 4-NDB modification, it was found that the nitrobenzene formed a multilayer molecular film on the MoS₂ surface. The extent of coverage of nitrobenzene on SLM was observed to be larger than on bulk MoS₂, mostly likely due to increased electronic coupling between monolayer MoS₂ and the gold substrate. Nitrobenzene films formed on SLM and bulk MoS₂ could be readily worn away by AFM under modestly applied loads of 10 nN and 3 nN, respectively, indicating that the binding of nitrobenzene on SLM is stronger than that on bulk MoS₂. The thickness of molecular films formed was observed to be ~1.5 nm regardless of the number of MoS₂ layers or, the solution reaction concentration.

COLL 281

Copper-based oligomerization/functionalization of patterned, ligand presenting, self-assembling monolayers (SAMs) at the liquid-HOPG interface

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Physiosorbed self-assembled monolayers (SAMs) that form meta-stable, multi-component patterns on graphite have garnished attention in recent years. Ligands extending from the SAM into solution have been chemically modified at the solution-SAM interface post assembly. Our current efforts seek to implement ligand reactions that (i) oligomerize multiple components to enhance monolayer / pattern robustness while maintaining pattern fidelity, (ii) utilize chemically orthogonal ligand reactions to

build monolayer patterns in the 3rd dimension. This contribution will report results from copper catalyzed alkyne couplings and azido-click reactions at the monolayer-solution interface.

COLL 282

Highly efficient, biofriendly exfoliation of α -zirconium phosphate nanosheets in water using proteins

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Traditionally, exfoliation of α - zirconium phosphate, $Zr(HPO_4)_2 \cdot H_2O$ (α -ZrP) has been carried out with tetra-n-butylammonium (TBA) hydroxide, surfactant modifications and ionic liquids. α -ZrP is a model system for most 2D layered materials and therefore, it is crucial to develop a method of exfoliation that is both scalable and biologically compatible. We have reported exfoliation of α -ZrP with bovine serum albumin (BSA) protein and shear force carried out in water. Various physiochemical conditions such as pH, temperature, surface charge and concentration of reactants, have been optimized to achieve 100% exfoliation efficiency, allowing for possible scale-up. Exfoliated α -ZrP prepared with this passivating BSA layer has showed enhanced binding to hemoglobin, with almost 80% bound to exfoliated α -ZrP opening the door to biological applications. In this context, we utilized surface plasmon resonance to further characterize the interaction of various proteins with exfoliated α -ZrP. The exfoliated α -ZrP sheets were also characterized using UV-Visible spectroscopy, Raman spectroscopy, X-ray Diffraction, scanning electron microscopy, and transmission electron microscopy.

COLL 283

Experimental and theoretical study of the optical properties of benzoic acid and benzoate, for understanding complex macromolecular photosensitizers

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Benzoic acid (BA) is a small unit of very complex macromolecules called cDOM (chromophoric dissolved organic matter) found in sea water, at the sea surface microlayer and recently in sea spray that are good photosensitizers. These are similar to humic substances, or humic like substances (HULIS) found in ground water and in other atmospheric aerosols besides sea spray. Therefore, the investigation of the UV-vis spectra of small molecules allowed us to understand is there the reflection of these

small molecules/units to the UV-vis region of more complex cDOM system. To contribute for the better understanding of optical properties of Benzoic Acid, the TDDFT calculations were combined with experimental measurements of UV-vis spectra in aqueous solution at different pH.

COLL 284

Using easy ambient sonic-spray ionization mass spectrometry (EASI-MS) for depth profiling organic particles

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Both atmospheric and laboratory-generated particles can be semisolid in phase under many conditions. The slow molecular diffusion that occurs within these highly viscous particles may lead to heterogeneous composition in which the particle core is different from its surface. We demonstrate that Easy Ambient Sonic-Spray Ionization - Mass Spectrometry (EASI-MS) can provide molecular level information on both the surface and the bulk of organic particles, depending on the experimental configuration. EASI-MS is a solvent-based spray ionization method that generates ions from the friction of a sheath gas against the solvent spray without the need for heat or voltage. Bulk composition of particles can be obtained by mixing the analyte particles with the μm -sized charged solvent droplets close to the nebulizer (the "droplet mode"). Alternatively, the surface of the particles is preferentially probed by allowing the solvent droplets to evaporate significantly before interacting with the particles (the "orthogonal mode"). We present the application of EASI-MS to detecting the bulk and surface composition of model core-shell organic particles using the droplet and orthogonal modes, respectively. The probe depth of EASI-MS in orthogonal mode is quantified by controlling the thickness of the particle coating. Ongoing studies include application of EASI-MS to understanding the bulk and surface composition of solid and liquid particles undergoing heterogeneous chemical reactions with gaseous oxidants. These measurements will provide insight into products under different conditions of viscosity and mixing, and how these might change under atmospheric conditions.

COLL 285

Stability of lipid monolayers at the air/sea water interface

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Lipid monolayers are known surfactants present at the air/sea water interface of the sea surface microlayer (SSML) and sea spray aerosol (SSA). However, little is known about the stability of these lipid monolayers at the air/water interface under different environmental conditions and in the presence of a chemically complex subphase that contains complex light absorbing species and/or biological components. In this

research, we have investigated lipid monolayers and their stability at the air/sea water interface. Specific studies include: (1) the stability of palmitic acid (PA) monolayer on salt water interfaces in the presence of simulated solar light with and without a photosensitizer and; (2) the dynamics and impact of lipase embedded within negatively charged, neutral or zwitterionic lipids. By using surface sensitive techniques such as a Langmuir trough for relaxation curves and Infrared Reflectance Absorbance Spectroscopy (IRRAS), we have elucidated that PA monolayers in salt solutions become less stable in the presence of light and a photosensitizer. Upon interaction with lipase, negatively charged, neutral and zwitterionic lipid monolayers became disordered as demonstrated by IRRAS measurements and all-atom molecular dynamic simulations. Furthermore, lipase is shown to interact differently depending on the charge of the lipid monolayer; while lipase is squeezed out of the negatively charged lipid monolayers, it remains stable in the zwitterionic lipid monolayers even at high surface pressures and large lipase concentrations. Overall, these studies provide insights into environmental factors such as sunlight and the presence of chemically complex subphases on lipid monolayers at the air/sea water interface that can have important atmospheric implications such as changing SSA reactivity, hygroscopicity and aerosol lifetimes. Furthermore, these detailed measurements coupled with simulations provides insights on the interactions, structure and dynamics of these important interfaces present in the environment.

COLL 286

Atmospheric organic aerosol acidity sensing via polymer degradation

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Atmospheric organic aerosols have complex effects on global climate and human health. Acidity of atmospheric organic aerosol is a critical factor that can affect the amount of secondary organic aerosol formation, as many of the key multiphase chemical reactions are pH-dependent. However, scientific understanding is limited by the lack of accurate methods to directly measure submicron atmospheric organic aerosol acidity. Specifically, there are no direct methods available to determine submicron atmospheric organic aerosol acidity using single particle methods and most methods rely on inferences or idealized modelling. Thus, a method is needed that can directly measure acidity for submicron atmospheric organic particles.

This study developed a novel pH measurement using polymer degradation to determine the pH of individual submicron particles. The acidic aerosol particles with known pH were deposited on the polymer, and the polymer film was incubated with acidic particles impacted upon them for up to 15 days in a humidity chamber. Acidic particles were rinsed and the degraded polymer film caused by acidic particles was characterized

using atomic force spectroscopy coupled with infrared spectroscopy (AFM-IR) and Raman micro-spectroscopy. Based on the relationship between pH and polymer degradation thickness, a pH measurement standard was determined and used to measure the acidity of laboratory generated secondary organic aerosol. It was found that decreasing acidity of aerosol increases polymer film degradation. The results from this study provide a new method to directly determine individual atmospheric organic aerosol acidity and improve current understanding of atmospheric organic aerosols.

COLL 287

Surface potential of aqueous fatty acid and alcohol surfaces: Understanding temperature effects and ice nucleation

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Heterogeneous ice nucleation (IN), prompted by organic material, is fundamental for understanding cloud formation and the global radiative budget. Numerous surfactant species at the sea surface microlayer (SSML) appear to contribute to IN. It has been shown that fatty alcohols are often effective ice nucleators whereas fatty acids appear to be weak ice nucleators. Here we investigate the molecular interactions and organization of stearic acid (C18 acid) and stearyl alcohol (C18 alcohol) films at varied temperatures through surface potential (related to the interfacial electric field) measurements upon film compression. Surface potential provides information regarding hydration effects and water dipole orientation induced by the surface-active substances. Results show that the surface potential increases as temperature decreases and that the maximum surface potential achieved is higher for the fatty alcohol than the fatty acid indicative of larger dipole contributions. Interestingly, at low surface coverage, the fatty acid has a higher surface potential than the fatty alcohol.

COLL 288

Synergistic performance of antimicrobial coatings deposited on air particulate filters

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The variation in responses of different microorganisms has limited the activity spectra of many biocides. Hence, some biocides are bactericidal and fungicidal but not sporicidal. This not only heightens cost and material use, but also increases chances of

antimicrobial resistance. By tailoring the properties of different antimicrobial systems, a synergistic performance can be achieved which not only saves cost and resources, but also delivers superior antimicrobial performance. In this work, a two-layer coating system was fabricated on a particulate filter substrate by the sequential deposition of colloidal solution of cationic polymers and iodine-based coatings. Surface topography of the coated filters was analyzed by scanning electron microscopy. The coated filters possessed both bactericidal, and sporicidal properties, and can rapidly inactivate the microorganisms on contact. Over 2 log ($\geq 99\%$) reduction in viable bacteria (*Escherichia coli*, *Staphylococcus aureus*, and *Pseudomonas aeruginosa*), 1 log ($\geq 90\%$) reduction in viable fungal spores (*A. niger* and *P. chrysogenum*) and bacterial endospore (*B. subtilis*) was achieved at a short contact time when compared with single layer coated filters.

COLL 289

Effects in cellular physicochemical properties by copper oxide nanoparticulate matter

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Abundant metallic and metal oxide particles such as Pb, Fe, Cu, ZnO, TiO and CuO are found in ambient particulate matter (PM) and their biomedical mechanisms involved in pathological and physiological processes have been well validated. Nevertheless, the roles of metallic or metal oxide PM in cell biophysical dynamics and biomechanical properties are still obscured. In this study, we utilized CuO nanoparticles (NPs) to imitate the PM-induced biomechanical impacts. Two human hepatoma cell lines of well-differentiated HepG2 cells and poorly differentiated SK-Hep-1 cells were selected to monitor the CuO NPs-induced the heterogeneity of cellular surface topography, stiffness, and adhesiveness using AFM analysis and immunofluorescence assay. Our results demonstrated that CuO NPs significantly increase cellular surface roughness, actin cytoskeleton reorganization and increased nuclear condensation in SK-Hep-1 cells. Moreover, AFM force-distance curve verified that CuO NPs effectively decrease Young's modulus and cellular adhesion forces in SK-Hep-1 cells rather than in HepG2 cells. In addition, CuO NPs-induced biomechanical properties in subcellular regions of both cell lines were further analyzed. As compared to HepG2 cells, our results further revealed that CuO NPs increase a significant Young's modulus elasticity of non-periphery regions and elicit an extremely attenuation of adhesion forces on both periphery and non-periphery subcellular regions in SK-Hep-1 cells. Therefore, this study demonstrated that CuO NPs perturb the biomechanical properties and induce the actin cytoskeleton reorganization, which was associated with ROS generation and accumulation, have played important roles in CuO NPs-mediated cytotoxicity. Altogether, our results show a comprehensive approach to monitor the cell mechanics in a well-differentiated vs poorly differentiated cells which are quite significant to understand the physical nature of cancer and exploring novel diagnosis methods. This

study is beneficial in the aspect of evaluating nanomechanics in the context of estimating cytotoxicity and oxidative stress mainly induced by chemical nanoparticles, especially the metal oxide nanomaterials.

COLL 290

Nanoscale morphology and spectroscopic analyses of glass surfaces in indoor environments

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Surfaces play a major role in the indoor environment, influencing the lifetimes and reactivity of indoor emissions. The physiochemical interactions between surfaces and deposited material impacts the lifetime of these compounds, potentially persisting on surfaces for months or years. Past studies have focused on characterizing the chemical composition and quantifying the amount of material deposited on indoor-relevant surfaces in both field and laboratory generated indoor environments. However, there have been a lack of studies directly probing the morphology and physical state these thin films or particle deposits. Furthermore, the underlying chemical and physical interactions involving these surface adsorbed compounds have not been thoroughly examined. Window glass, a ubiquitous indoor surface, was placed vertically in both in the field to single event indoor activities throughout the House Observations of Microbial and Environmental Chemistry (HOMEChem) campaign, and in the laboratory using a small Teflon environmental chamber to evaluate deposition both physically and spectroscopically. Atomic force microscopy-infrared (AFM-IR) spectromicroscopic analyses reveal that the deposition of submicron particulate matter is a significant contributor to modifying the chemical and physical state of glass surfaces due to cooking and cleaning events. Spectroscopic analyses of these particles reveal signatures of carboxylates bound to surfaces, suggesting the importance of chemisorption of these organic rich particles onto the glass surface. Reproducing these findings in the Teflon environmental chamber establishes the connection between the physical state of these surfaces and the chemical composition of the molecules binding to these surfaces. Thus integration of laboratory studies under more controlled conditions and field studies such as HOMEChem is crucial for understanding the implications of surfaces in indoor air quality.

COLL 291

Investigation of monoethanolamine adsorption on oxide surfaces

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The fate and transport of chemical contaminants in the environment is driven by complex molecular processes occurring at geochemical interfaces. One class of these contaminants are volatile chemical products (VCPs) which include cleaning agents, personal care products and pesticides, and represent half of all volatile organic compound emissions. Compounds in this class of products can partition into the water phase and adsorb onto geochemical surfaces in contact with groundwater, where their surface chemistry and fate are currently unknown. This work was conducted to determine how these compounds adsorb onto oxide surfaces. TiO₂ nanoparticles have found widespread use in consumer products but possess high toxicity potential to humans and the aquatic environment. TiO₂ is found naturally and can also get into the environment as it is in a number of consumer products, making it a suitable geochemical interface for further study. Monoethanolamine (MEA) is widely used in consumer cleaning products and in industrial CO₂ capture and storage from the combustion of flue gasses and can be readily found in the environment as a contaminant. Most importantly, MEA can form a wide range of degradation products including ammonia, aldehydes and ketones that can further react with surfaces, other contaminants and MEA itself. Some of these degradation products are associated with mutagenicity, genotoxicity, carcinogenicity and reproduction effects. In this study, attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy was used to determine the adsorption behavior and chemical transformations of MEA on TiO₂ as a function of concentration and pH. This study helps to better understand how MEA reacts in the environment and provides new insight into possible degradation products.

COLL 292

Impact of concentration and the presence of salt on the surface pKa of fatty acids at the air-water interface

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Organic coatings, such as fatty acid surfactants, on sea spray aerosol (SSA) can determine the lifetime, reactivity, and properties such as light scattering and ice nucleation of the aerosol in the atmosphere. Moreover, the protonation state of the surfactant can affect those properties. Studies have revealed that there is a difference between the surface and bulk pKa values for medium-and long-chain fatty acids. However, the effects of fatty acid concentration and salts on the surface pKa are not

well understood. Although the bulk pKa changes little with acid concentration, surface pKa values do depend on concentration due to the unique environment of the interface that can concentrate the fatty acid and can increase the intermolecular interaction. It is interesting to find that surface pKa decreases with decreasing concentration of the fatty acid. Furthermore, the change in surface pKa of various fatty acids at different concentrations of salt solutions has not been probed. These experiments with the addition of salts can mimic marine-relevant conditions. Overall, this study provides insights into the properties of sea spray aerosol while predicting its compositional and structural change due its environment.

COLL 293

AFM-IR and SFG analysis on various geochemical interfaces with adsorbed BSA

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Surface chemistry is important in many key molecular processes that drive the fate and transport of chemical contaminants as well as water quality treatment in the environment. There are three key important components of these environmentally-relevant water systems that are well-known to interact with geochemical interfaces: organic matter, oxyanions, and biological components. Due to their prevalence in the atmosphere, these components act as adsorbates that bind to various surfaces in the environment. Mineral surfaces in particular are extremely diverse in composition and structure; they can include iron oxides, clay minerals, carbonates and other metal oxides such as titanium dioxide, aluminum oxide, and silicon dioxide. The various combinations in which these compounds can adsorb onto these different geochemical interfaces present a complex array of systems wherein surface catalyzed reactions and potential byproducts are of great interest, as possible sources of chemical contaminants in the environment. By utilizing interfacial vibrational probes Atomic Force Microscopy-Infrared (AFM-IR) spectroscopy and Sum Frequency Generation (SFG), we can investigate the presence of chemical transformations in these multicomponent mixtures. In this work, for the first time, we present an investigation on the interaction between aqueous phase bovine serum albumin (BSA), a biological model for proteins in the environment, on titanium dioxide and iron oxides using complementary studies via AFM-IR spectroscopy and SFG. We show how morphological and chemical changes in these metal oxides as a result of protein-surface interactions can be monitored with nanoscale resolution using AFM-IR spectroscopy; these analyses are supplemented with SFG, a surface sensitive technique with ultrafast time resolution, providing information on the orientation and ordering of these adsorbates on geochemical interfaces. Together, these two methods of analysis allow for clear spatial and temporal resolution in efforts to understand both the physical and chemical transformations that are occurring during these adsorbate-surface interactions.

COLL 294

α -Amino acid adsorption onto metal oxide nanoparticles: A spectroscopic study to understand the effects of pH and particle type

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Rising use of nanoparticles (NPs) in many applications has brought concerns on the fate of these NPs in the environment and human body. In biological media, the composition of protein corona and its formation are directly related to the affinity between NP surfaces and amino acid sequences. This study will provide information to elucidate the potential impacts of manufactured and environmental metal oxide NPs in biological media. Effects of pH and NP type on adsorption of individual α -amino acids onto iron oxide (Fe_2O_3) and titanium dioxide (TiO_2) NPs are discussed. Biomolecular interactions were probed with an attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy. Moreover, dynamic light scattering (DLS) is used to observe the changes to NP surface charge in the presence or absence of α -amino acids. Results show that the adsorption of α -amino acids onto NPs strongly depends on solution pH and the NP type. NP surface charge, aggregation behavior, and α -amino acid surface coverage are affected by changing pH. Overall, the results of this study provide insights into different transformations of NPs in aqueous environments; the effects of transformations onto biomolecule adsorption mechanisms; and the importance of the NP surface chemistry for further nano-bio interactions. This comprehensive work helps to better understand the fundamentals of NP interactions in the environment and biological media in order to build up to more complex systems, such as multi-component systems.

COLL 295

DNA adsorption on iron (III) oxide: Effects of pH and ionic strength on surface interactions

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Molecular processes at geochemical interfaces impact many environmental processes that are critical to the fate and transport of biological components in water systems. This study will help delineate molecular steps and processes involved with surface adsorption/desorption and molecular transformations. Iron oxide surfaces are ubiquitous in nature and can provide a large interface for biological molecules to interact with. As iron oxide suspensions flow with ground water, biomolecular interactions could be affected by changing environmental conditions, such as pH and ionic strength.

Deoxyribonucleic acid (DNA) is a commonly found biomolecules in ground water introduced from multiple sources such as cellular lysis and active secretion. Additionally, persisting genetically modified DNA in soil can leach into ground water can present a danger to surrounding areas. The fate of DNA is heavily dependent on surface interactions that could potentially preserve or prevent DNA stability. To develop an understanding of the fate and repercussions of biomolecules in the environment, it is necessary to first gain a fundamental insight into interactions with oxide surfaces. Effects of pH and ionic strength on the adsorption of DNA on hematite was investigated with Attenuated total reflectance-Fourier transform spectroscopy. Two-dimensional correlation spectroscopy was used to analyze spectroscopic changes and to elucidate adsorption/desorption mechanisms. This study serves to gain a fundamental understanding of individual interactions with surfaces in order to build up to more complex studies that involve multi-component systems.

COLL 296

Design of multi-functionalized liposomes for adsorbing and neutralizing target molecules *in vivo*

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Objective: Liposomes are widely used as highly biocompatible DDS carriers. Liposomes encapsulating drugs have been used for deep mycosis, age-related macular degeneration and cancer therapies in clinical. On the other hand, strong protein-protein interactions such as an antigen-antibody association are arisen from multiple weak interactions, namely electrostatic and hydrophobic interactions, and hydrogen bonds. We hypothesized that, as well as the antibody, liposomes modified with functional groups (multi-functionalized liposome; MF-Lip) that generate multiple weak interactions might bind to target proteins and neutralize their functions in the bloodstream of living animals.

Method: Melittin, a hemolytic honey bee venom, was used as a target molecule. Three functional lipids were synthesized by the reaction of *N*-(succinimidyl-oxy-glutaryl)-L- α -phosphatidylethanolamine, dipalmitoyl (DPPE-NHS) with neutral, negatively charged or hydrophobic amino acid derivatives. MF-Lip composed of each functional lipid, dipalmitoylphosphatidylcholine, and cholesterol was prepared. The binding affinity of MF-Lip for melittin was measured using quartz crystal microbalance. Effects of MF-Lip on melittin-induced hemolysis and cytotoxicity were evaluated *in vitro* by hemolysis test using red blood cells and a WST-8 assay using mouse endothelial cells, respectively. Inhibitory effect of MF-Lip against melittin toxicity *in vivo* was examined by intravenous administration MF-Lip into mice preinjected with melittin.

Results / Discussion: Affinity of MF-Lip for melittin was significantly changed by changing the percentage of each functional lipid in the liposomes. It was revealed that

the hemolytic activity and cytotoxicity of melittin were significantly inhibited by MF-Lip. However, these inhibitory effects of MF-Lip did not correlate with the binding affinity of MF-Lip for melittin. Intravenous injection of MF-Lip significantly improved survival rate of melittin-treated mice, indicating that MF-Lip bound to and neutralized melittin in the bloodstream. From these results, the liposomes functionalized with multiple functional groups is expected to be a highly biocompatible toxin neutralization agent.

COLL 297

Golden age revisited: Developing a resource sparing gold nanoparticle platform to rapidly triage immune cell targeting ligands in discovery

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The incorporation of immune cell-targeting ligands into vaccine and oncology drugs and drug delivery systems (DDSs) is an area of high interest due to the potential to improve efficacy and safety profiles when compared to their untargeted counterparts. Typically, evaluation of novel targeting ligands involves direct conjugation and formulation into the DDS of interest (*i.e.* lipid nanoparticles) for initial Tier 1 *in vitro* targeting studies. Such studies can be resource- and time-consuming, thereby limiting the number of ligands and formulations that can be tested. To reduce resource spend and accelerate go/no-go decisions on pipeline candidates, we have developed a gold nanoparticle (AuNP) platform that allows for facile functionalization to a broad range of ligands while still maintaining important physical characteristics of the intended DDS. The platform exploits the covalent Au-S bond and requires only the incorporation of a free thiol, usually through a terminal cysteine residue, in the targeting ligand. The functionalized AuNPs are then directly dosed in *in vitro* splenocyte uptake studies, allowing for the identification of targeted immune cell populations. To demonstrate the platform's impact and utility, initial proof-of-concept studies have focused on the evaluation of a novel Clec9A-targeting peptide ligand. Previous reports have shown that targeting antigens to a subset of dendritic cells known to express the Clec9A receptor improves cytotoxic T cell activation and antibody titers, which are important responses for prophylactic and therapeutic vaccines in infectious diseases and oncology. Thus, it's envisioned that learnings from the AuNP platform will inform on the design of new targeted formulations during drug discovery and aid in improved immune cell drug delivery for future vaccine and oncology drug clinical candidates.

COLL 298

Facile preparation of Au/Silk nanoparticles as a multifunctional drug delivery system

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Drug delivery technologies have been quickly innovated in the last few decades, especially in aspect of combination with nanotechnology to advance into multifunctional drug carriers, which can accomplish targeting a tumor, delivering therapeutic molecules, imaging and monitoring drug response. Many models were built and tested; still the challenge is at the choice of the appropriate materials and the facilitation of carrier preparation to achieve both safety and efficacy.

This presentation focuses on our recent results in the establishment of multifunctional Au/silk nanoparticles (NPs) for delivery, imaging and targeting in cancer treatment, prepared by a facile co-precipitation method. The synthetic approach is mainly carried out in mild condition with minimizing residues in the final product. Co-precipitation method is proven to be one of the most straightforward methods to incorporate inorganic and organic materials into a hybrid system with controllability of the resulting structure and characteristics. The obtained Au/silk NPs are expected to advance the drug nanocarriers to a multifunctional system with tunable drug release and designable targeting. The research also provides a NP library with diverse structures and properties, which can be used to manipulate the drug delivery performance. The results are discussed in terms of UV-Vis, DLS, XRD, TEM, XPS, and CLSM.

COLL 299

Counterintuitive droplet motion mediated by printed charges

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The droplet manipulation is crucial for many applications from liquid transportation to the biologic device. The asymmetric applied force can surmount contact hysteresis and drive droplet motion, techniques including heat, electrowetting, light, magnetism, and mechanical vibration have been used to achieve this. However, they all require an external device to supply the driving energy. A substrate having a spatial gradient in its surface free energy was capable to transport liquid without additional energy, but the mechanism need sacrifice the liquid mass to gain the surface free energy of the substrate thus the transport distance is limited. Here we show that a droplet can transport to a long distance without mass loss and no need external energy input. We found on a superamphiphobic substrate the drop impacting induced surface charge can dominate the droplet wetting dynamics. Based on the fundamental understanding of the charge generation kinetics, we can locally control the charge distribution and intensity to form a charge gradient superamphiphobic surface by tuning the drop impacting dynamics. This surface can actuate droplet self-propulsion along the charge gradient with an ultra-high velocity (10 times higher than the literature reported) and theoretically unlimited distance without mass loss because of superwetting. This charge printing technic can programmable and rewritable the liquid transport trajectory in a facile way.

The droplet transportation can also achieve on a flexible substrate and climb vertically. We envision this novel liquid droplet manipulation strategy enables us to achieve a wide variety of autonomous fluidic devices applications; it also gives feasibility for novel physics and biomedical experiment.

COLL 300

Designing the armor for ultra-robust superhydrophobic surfaces

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Superhydrophobic surfaces with multiple functions such as self-cleaning, anti-biofouling and staying dry are promising for applications in biotechnology, medicine and heat transfer. Water droplets placed on superhydrophobic surfaces feature large apparent contact angle ($\theta^* > 150^\circ$) and low roll-off angle ($\theta_{\text{roll-off}} < 10^\circ$). To achieve superhydrophobicity, two conditions must be met: a low liquid-solid contact fraction created by micro- or nanoscale surface roughness, and low surface energy chemistry. However, one major problem is that surface roughness is fragile and highly susceptible to abrasion, especially for nanoscale surface textures as they bear high pressures under mechanical load. Mechanical force will flatten or remove the roughness and increase liquid-solid contact area. Additionally, abrasion exposes underlying materials and may change the local surface chemistry from hydrophobic to hydrophilic, leading to pinning of water droplets and loss of superhydrophobicity. Here we show a generic approach defying the common assumption that mechanical robustness and water repellency are mutually exclusive properties. By decoupling the design criteria for fracture mechanics and non-wetting, we propose an armor concept that enables unprecedented levels of abrasion resistance. The armor surfaces preserve water repellency after sharp steel blade and sandpaper abrasion, and 1000 cycles of linear abrasion. We demonstrate that the armor protection concept is also generic and can be applied on polymer and ceramic substrates for a myriad of self-cleaning applications where robustness is vital. We envision that this fundamental understanding and rational design strategy will be useful in self-cleaning, anti-fouling and heat transfer materials operating under harsh environments.

COLL 301

Identification of natural evaporation-induced ionovoltaic electrical energy conversion system

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Natural evaporation in water surface, ubiquitous phase transition in ambient condition, has been employed to various researches like an energy conversion device based on a solid-liquid interfacial phenomena. Remarkably, they showed off interesting characteristics such as spontaneous and continuous electricity generation. However, concrete origins and mechanisms of the device are still in obscurities because of limited approaches based on carbon materials and difficulties in a direct observation of the solid-liquid interface. In this study, the origin of the evaporation-induced electricity generation was identified in terms of an 'ionovoltaic' phenomenon^[1,2], which is natural evaporation-induced ionic motions and charge carrier flows in nanoscale capillary water, through a controllable metal oxide platform. The zinc oxide (ZnO) semiconductors-based device showed spontaneous electricity generation with constant electrical signals of ~0.4 V (open circuit voltage) and ~ 20 nA (short circuit current). This study improves a grasp of ionic behaviors and corresponding charge carrier motions by coulombic interaction in the natural evaporation-driven energy generation system. The investigation of the device mechanism provides an expandability to various materials and an applicability as an advanced energy conversion device.

COLL 302

Omni-liquid droplet manipulation platform

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Droplet manipulation is of importance in a wide range of applications in biomedicine, chemical analysis, and synthesis, among other fields. Over the past decade, extensive efforts have been made to develop different strategies of transporting droplets by using various external stimuli. However, these methods could fail to manipulate some complex liquids with a low surface tension, high viscosity, or corrosivity. Herein, we describe a magnetic digital microfluidics platform (MDMP) that is capable of manipulating almost all liquid droplets. The MDMP is designed by combining a magnet-controlled deformable substrate and a slippery liquid-infused surface. Such a structure allows creating a site-specific gravitational potential gradient to propel droplets under different conditions. We demonstrate that our MDMP can rapidly and reversibly transport various liquids for specimen sorting, chemical reactions, and accelerating mixing. We envision that this universal droplet manipulation device will lay the foundation to achieve a wide variety of autonomous open channel fluidic device applications.

COLL 303

Quantitatively revealing the distribution of water within hydrophobic polymers via differential scanning calorimetry and theoretical prediction of hydrated polymer thermal profiles

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Regardless of hydrophobicity, polymers have been found to imbibe and distribute water within in three states: non-freezable bound water (plasticizing water content), freezable bound water (so called second-layer water, and presumably water at an interface) and freezing free water (phase separated domains). The roles of each of these within these hydrophobic polymers continues to intrigue both industry and academia, as the associated water content can highly influence polymer properties such as transparency and the effective glass transition temperature. Indeed, it is this hydroplasticized glass transition, not only the polarity of the host polymer, that most strongly influences the water uptake dynamics. Permeability is a function of both solubility and diffusion, and even for more hydrophobic polymers if the system was below the effective glass transition significant phase separated water domains have still been observed. Few have attempted to quantitatively evaluate the dynamics and to correlate the associated water in these different states to the ultimate polymer properties. Here, a pseudo accelerated water-diffusion experiment for hydrophobic waterborne polymers was conducted and rigorously monitored by differential scanning calorimetry (DSC). Systematic variations in composition of hydrophobic polymers derived from emulsion polymerization were analyzed specifically for the dynamic evolution of their distribution of freezable free, freezable bound and non-freezable bound water content. This evaluation has successfully allowed us to not only quantify these distributions, but also to correlate them to specific variations in the host polymer properties. While we have previously reported quantitative analysis of the hydroplasticizing non-freezing bound water content by DSC, we emphasize here that the second-layer freezing free water content can also be quantitatively revealed by DSC. Careful consideration of sample preparation as well as the analytical method development is also highlighted. A second aspect of this work leverages the heat capacity and shape factors for the mixing of water with polymer specific to the glass transition. This has been observed as a result of our dynamic analysis contrasting cycles of the DSC profile as water diffuses into the polymer matrix. This data allows us to predict hydrated polymer DSC profiles for temperature regions that have been historically obscured by other transitions (for example, in the vicinity of 0 °C).

COLL 304

Ionovoltaic device for monitoring ion dynamics in aqueous-phase

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Researches of ion-surface interaction at liquid-solid interface have been actively studied with regard to electrical double layer (EDL) formation processes. Particularly, energy-

conversion devices driven by ion motion of droplet (called an ionovoltaic device) have attracted much attention due to a direct conversion of liquid-solid interfacial interaction into electrical signals without an external bias. However, a poor understanding of nanoscopic dynamics by ion diffusion in aqueous-phase poses challenges regarding monitoring technologies. Herein, we introduce an ionovoltaic device that works in the aqueous-soaked system to monitor various dynamic phenomena of ion diffusion and adsorption which cause the EDL formation. According to Fick's law, we investigated that a generated voltage from the ionovoltaic device has a correlation with the various critical factors such as concentration (ϕ), diffusion coefficient (D), viscosity (η), and temperature (T). Based on these characteristics, a mechanism of generating electrical signal for the aqueous-soaked ionovoltaic device was studied in detail. Our research provides a substantial potential to develop methods for monitoring ion dynamics at EDL by expanding understanding of ion behavior regarding the diffusion phenomena in the aqueous-phase. This study is another strong evidence that ionovoltaic phenomena occur by ion dynamics at liquid-solid interface.

COLL 305

Electrical energy generation from water droplets infiltration in porous copper oxide nanowires film

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Researches on electrical energy generation from natural water movement on solid surface have received great attention because of their potentials as eco-friendly and highly-efficient energy conversion methods. One of them, the electricity generation driven by solid/liquid interfacial interactions in a porous electrode is presented interesting characteristics such as spontaneous and continuous energy production. However, veiled characteristics of the systems pose difficulty in actual applications of these phenomena. Herein, we presented a natural water capillarity-induced energy-conversion device (V_{oc} of ~ 0.35 V, I_{sc} of ~ 60 nA) using a minute volume of a single droplet (5 μ L, 0.1 M NaCl solution) in a porous copper oxide nanowires (CuO NWs) film. Based on this, several important parameters influencing to the electricity generation (e.g. ion concentration, viscosity, and etc.) were investigated to study a working mechanism. We found that carrier movements in the CuO NWs film were induced by ionic dynamics at water capillarity and the CuO NWs interface. The experimental results demonstrate the applicability of the device as novel types of a natural water motion-induced energy generator and a liquid analytic sensor in the future.

COLL 306

Potential-induced nonlinear friction behavior between silica microsphere and gold surfaces in aqueous solution

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The investigation and regulation of interfacial mechanical of gold have a great theoretical and practice value in the field of biomedicine such as tiny biological devices , which involving many issues about interfacial tribology. In this work, the friction behavior between silica microsphere and gold-coated substrates was studied by the electrochemical atomic force microscopy (EC-AFM) under different applied potential. When the negative potential was applied to the gold surface, the friction force between silica microsphere and gold is increasingly linear with the loads. However, when the positive potential was applied, the increasing rate of friction forces is considerably increased and appears steeply rise with loads, which presents a strong nonlinear rather than linear with loads. We attribute the reason for such nonlinear behavior at a positive potential to the difference in interfacial affinity between silica microsphere and gold at different loads. At positive potentials, the confined ordered icelike water layer at Au/electrolyte interface is capable of hydrogen bonding with the silica microsphere. The pressed depth of microsphere into confined icelike water layer is small when the load is low resulting in a small number of hydrogen bonding, and when the load becomes high, the number of hydrogen bonding increases with the increases of pressed depth until it is saturated. Such interfacial force experiments in liquid provide new insight into understanding the structure and physical properties of water on the charged metal surface, which might inspire the development of biomedicine.

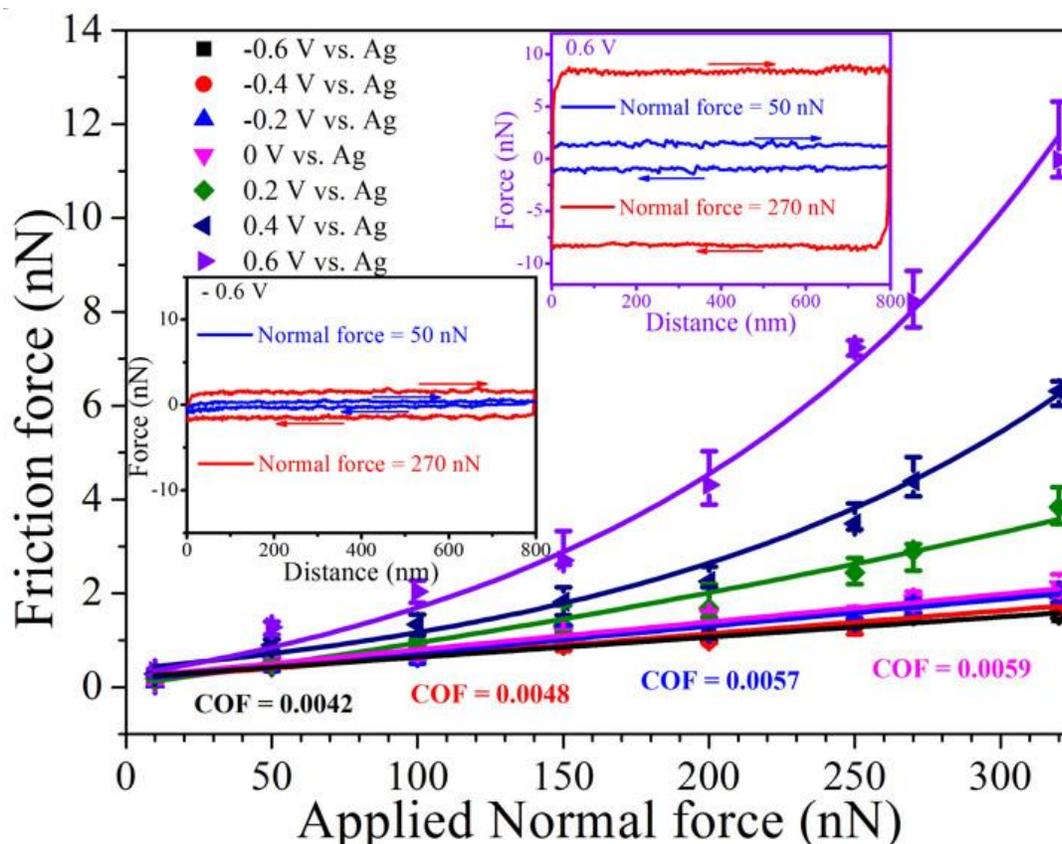


Figure 1. Normal force-dependent friction force between silica microspheres and Au surface at varies applied potential in 0.1 M aqueous NaCl. The solid lines are the linear (-0.6 V, -0.4 V, -0.2 V, 0 V) or nonlinear (0.2 V, 0.4 V, 0.6 V) fitting of experiment data. The slop of linear fitting lines are viewed as the COF at constant potential. The sliding velocity was set to 2 $\mu\text{m/s}$. The insets show the friction loop at the potentials of -0.6 V and 0.6 V. The friction forces were determined by the half of difference between upper line and nether line of a complete friction loop.

COLL 307

Intrinsically lubricating hydrogel coatings for HIV prevention

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Sexual health products (e.g. condoms) are important for reducing the risk of contracting HIV and sexually transmitted infections (STIs) during all forms of intercourse including receptive anal intercourse (RAI). Their prophylactic properties rely on the proper use of the condom as well as the inclusion of a lubricant, without which condom mechanical failure and risk of infection are dramatically increased. An intrinsically lubricious surface coating would overcome the limitations of external lubrication, and could further reduce risk if anti-HIV drugs can be incorporated in to the coating. Hydrogels are excellent candidates for this given their biocompatibility, highly tunable physical and chemical properties, ability to be grafted as thin coatings to traditional condom materials such as latex and silicone, and ability to be loaded with and elude drugs. Hydrogel coatings on latex have recently been shown to reduce the friction 20-fold relative to the native latex surface. However, an in-depth understanding of hydrogel lubricating mechanisms and performance limits at physiological conditions is lacking. To systematically study the tribological properties of hydrogels, bulk hydrogels and their thin-coating counterparts were synthesized at different monomer and crosslinker densities to control the mesh size, water content, Young's modulus, and frictional properties. Double network hydrogels were used due to their substantial mechanical durability. The frictional properties of the synthesized bulk hydrogels and hydrogel coatings were studied in aqueous environments at physiologically-relevant applied pressures, sliding speeds, and temperatures. A mini traction machine (MTM) was used for macroscale testing, providing additional insight into the mechanical durability of the hydrogels. Colloidal probe atomic force microscopy (AFM) was used to help further elucidate the underlying friction mechanisms. We observe low friction and wear, with a significant dependence of friction on sliding speed and hydrogel synthesis conditions. We will discuss how these characteristics impact the potential application use of hydrogels. Overall, the synthesis and characterization of the frictional properties of hydrogels aids the design of surface coatings with improved comfort and reliability, leading to a greater usage of sexual health products in HIV prevention.

COLL 308

Non destructive method to calibrate the torsional spring constant of atomic force microscope cantilevers in viscous environments

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Calibration of the torsional spring constant of atomic force microscopy cantilevers is fundamental to a range of applications, from nanoscale friction and lubrication measurements to the characterization of micro-electromechanical systems and the response of biomolecules to external stimuli. Existing calibration methods are either time consuming and destructive (*ex situ* static approaches), or rely on models using the frequency and quality factor (Q-factor) of the cantilever torsional resonance as input parameters (*in situ* dynamical approaches). While *in situ* approaches are usually preferred for their easy implementation and preservation of the cantilever, their

dependence on the torsional resonance Q-factor renders calibration in highly viscous environments challenging. This is problematic, for example, in many nanoscale tribological applications. Here, we propose a calibration method that does not depend on the cantilever torsional Q-factor, and show how the cantilever deflection can be converted into a lateral force. The method is tested with six cantilevers of different shapes and material composition, and in six fluid media. The derived spring constants are compared with predictions from existing methods, demonstrating a higher precision, in particular for highly viscous liquids.

COLL 309

Static friction phase diagram for hydrogel-like materials

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Unraveling the mechanisms of soft-matter lubrication is pivotal in understanding the functionalities and complexities of biological soft-matter and biolubrication. Biphasic materials, such as hydrogels, are key components in multiple natural tribosystems such as the articular and ocular lubrication systems. Yet, the origin of damage of such tribosystems still remains convoluted. While static friction and stick-slip have been proposed as precursors to damage and wear of soft interfaces, there is a lack of fundamental knowledge and framework. We investigate static friction and contact ageing of polyacrylamide hydrogels with three different microstructures using Atomic Force Microscopy (AFM). A conceptual phase diagram for hydrogels' static friction is developed where a subtle solid-like to liquid-like change of behavior is observed-->within the investigated range of temperatures. Furthermore, two characteristic peaks are mechanistically explained to result from two competitive mechanisms associated with the biphasic nature of hydrogels. We propose that depending on the hydrogel's microstructure, normal load, loading time and temperature, different behaviors can be probed on the static friction phase diagram. The knowledge emerging from this work will help inspire customized design of materials in a wide variety of fields having a core interest in tribology.

COLL 310

Understanding the IL-solid interface using water as molecular probes

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The properties of ionic liquids (ILs) near a charged solid-liquid interface are of great importance to applying ILs as electrolytes, lubricants, and solvents. Recent advances in the surface science community indicate gaps in the current understanding of the

interfacial structures in ILs and concentrated electrolytes. In the present study, we conduct direct force measurement on the IL-solid interface with a surface force apparatus (SFA) operated in two different modes. The ILs are either compressed in the direction normal to the confining mica surfaces or sheared laterally. By fitting the force-distance curves to a constitutive model, we deconvolute the contributions of various nano-scale interactions within ILs. Through rheology measurements, we investigate the presence of nanoscale assemblies. Coupling the normal-force measurements with the rheology measurements, we infer on the nano structures of ILs at the charged solid-liquid interface. In addition, water is introduced into the nano-confined ILs as a molecular probe to modify the interionic interactions. The findings will shed light on the paradox of electrical double layers of concentrated electrolytes, and provide practical hints for designing IL-based devices exposed to ambient humidity.

COLL 311

Investigating pressure-solution and frictional behavior of calcite with an extended surface forces apparatus

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The friction between two adjacent tectonic plates under shear loading may dictate seismic activities, while water has been recognized to alter the fault dynamics and earthquake nucleation. Our previous Atomic Force Microscopy (AFM) works investigating the frictional behavior of calcite in solution at the level of single asperity contact indicate that pressure solution can significantly reduce friction, and fluid chemistry plays a role. Recognizing the limitation of AFM that the pressure solution cannot be explicitly measured, in this work, we further scrutinize the effect of the fluid chemistry on the pressure solution and frictional characteristics of calcite in aqueous solution with an extended Surface Forces Apparatus (eSFA). The kinetics of pressure solution of calcite is unambiguously quantified by measuring the time-dependent deformation of the calcite substrates while friction is concurrently measured, as a function of the applied load and solution composition. The findings of this novel study advance the understanding of mechanisms underlying the frictional strength of carbonate rocks in presence of aqueous solutions. More broadly, the development of a new methodology for the investigation of interfacial reactions between surfaces of brittle minerals expands the range of applications of the SFA.

COLL 312

Interactions between arsenic and ferric iron during ferric coprecipitation treatment: Effect of arsenic on ferric oxides formation, and possible formation of ferric arsenate complexes

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Ferric iron plays a key role on the fate and transport of arsenic in water systems. Our recent works found that the arsenic had a significant effect on the ferric oxides formation when use iron chemicals (i.e. FeCl₃ and iron powders) for arsenic treatment. Specifically, the addition of FeCl₃ into arsenic solution (co-precipitation) had a much higher arsenic removal efficiency than adding arsenic in to a FeCl₃ solution (pre-aged). However, more arsenic released from the solids in the co-precipitation system. Multiple advanced characterizations revealed that the formed ferric oxides in solution were affected by the presence of arsenic, which consequently influenced the arsenic removal efficiency. The arsenic could be incorporated into ferric polymers, which therefore enhanced the arsenic removal efficiency. Nevertheless, theoretical calculation by density functional theory implied that the incorporated arsenic was less stable than the adsorbed arsenic thermodynamically, resulting in a release of arsenic from the solids. Moreover, our work indicated that the addition of arsenate resulted in a promotion of dissolution of ferric oxides. Spectroscopic measurements suggested that the dissolved ferric arsenate complexes were formed at both acidic and neutral pH. Possible molecular structures of the ferric arsenate complexes were proposed based on our density functional theory calculations, showing Fe:As mole ratio of 1:1 and 1:2 at acidic and neutral pH, respectively. The chloride ion was also complexed with ferric iron, which improved the stability of the ferric arsenate complexes. These findings are of vital importance to the fundamental understanding of the removal, mobility, and fate of arsenic in natural water systems, and valuable for the future study regarding the solubility of ferric arsenate precipitates.

COLL 313

Vibrationally energy-driven reactions of CO₂ on Cu surfaces

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We have long studied the formation of formate (HCOO_a) intermediates as an intermediates of methanol synthesis by hydrogenation of CO₂ on Cu surfaces [1-4]. It has been suggested based on the kinetic analysis for the high pressure bulb experiments that the formate formation proceeds via Eley-Rideal type mechanism, in which CO₂ directly reacts with adsorbed hydrogen atom on Cu. In order to clarify the mechanism and dynamics, we carried out CO₂ molecular beam studies with the translational energy of 1.12-1.97 eV and the nozzle temperature of 800-1100 K. It was found that hot CO₂ in the molecular beam reacts directly with pre-adsorbed hydrogen atoms on cold Cu(111) and Cu(100) surfaces at 120–220 K to form formate adspecies (CO₂ + H_a → HCOO_a). That is, even at the low surface temperatures, formate species is

formed rapidly when supplying energy only to CO₂. This indicates that the energy to overcome the reaction barrier comes from the hot CO₂ molecule itself instead of the Cu surface. The vibrational energy of CO₂ was much more effective for the reaction compared to the translational energy; and the reaction rate was independent of the surface temperature. The independence of surface temperature indicates the E-R type mechanism that the CO₂ molecule is not thermally equilibrated with the Cu surfaces but directly reacts with H_a. If the impinging CO₂ molecule chemisorbs on the Cu surfaces before reacting with H_a, the reaction rate should be dependent on the surface temperature, rather than the kinetic and the internal energies of CO₂. We evaluated the barrier distribution factors (W) of so-called Luntz equation by analysis of the reaction probability curves, which shows significant efficacy of the vibrational energy on the reaction of CO₂, which has not been observed before. DFT calculations are consistent with the experimental observations [5]. The direct reaction of CO₂ with adsorbed hydrogen atom can be regarded as the first example of vibration-driven bond formation reactions on surfaces.

COLL 314

Oxygen reduction reaction on Pt electrodes: From kinetics and spectroscopy to new materials

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The oxygen reduction reaction (ORR) is the major source of overpotential loss in low-temperature fuel cells. Pt-based materials have been found to be the most effective electrocatalysts, but exploration of alternatives has been hampered by stability constraints at the typical operating conditions of low pH and high potential.

I will discuss our studies of elementary mechanism of ORR on various metal electrodes using kinetic and micro-kinetic analysis of reaction pathways and quantum chemical calculations as well as surface enhanced Raman spectroscopic (SERS). These studies allowed us to identify the elementary steps and molecular descriptors that govern the rate of ORR. Using these performance descriptors we have been able to identify families of Pt and Ag-based alloys that exhibit superior ORR performance in acid and base respectively.

We have synthesized these alloys to demonstrate the superior ORR activity with rotating disk electrode experiments. We have also performed thorough structural characterization of the bulk and surface properties with a combination of cyclic voltammetry, x-ray diffraction, and electron microscopy with spatially resolved energy-dispersive x-ray spectroscopy and electron energy loss spectroscopy.

COLL 315

Kinetics of 1,4-bis (phenylethynyl) benzene (DEB) in Pd/C catalyzed hydrogenation

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Hydrogen “getters” compounded with a solid phase dispersed catalyst are used for scavenging of excess hydrogen in sealed systems to prevent corrosion of nuclear materials, electronic components, and explosion hazards. 1,4-bis (phenylethynyl) benzene (DEB) getters are commonly used as hydrogen scavengers due to their excellent hydrogen uptake capability. These compounds chemically bind H₂ gas through hydrogenation reactions as opposed to physical surface adsorption. Typically, the DEB getters are mixed with activated carbon and Pd nanoparticles, where activated carbon provides surface area to spread getters and Pd acts as a catalyst for hydrogen dissociation (see Figure 1). If in the process of hydrogenation, partially hydrogenated DEB molecules become volatile, then migration of partially hydrogenated DEB away from Pd sites would result in loss of capacity for the DEB/activated carbon/Pd system. In this work, the equilibrium vapor pressures, melting points, and structures of DEB from virgin state through fully hydrogenated state are probed by the Knudsen cell effusion technique, also known as effusion thermogravimetry and differential scanning calorimetry (DSC) experiments. Furthermore, hydrogenation kinetics are estimated from experiments conducted in isothermal and isobaric reactor conditions. Such kinetic parameters are used for the prediction of DEB getter performance under dynamic hydrogen pressure conditions.

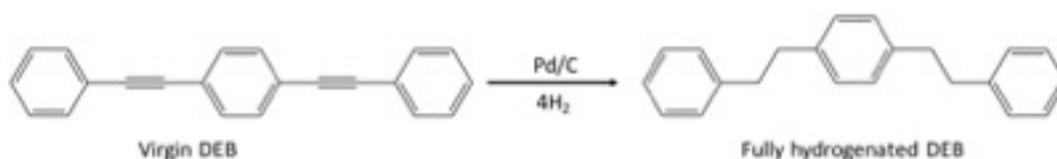


Figure 1: A schematic of the overall reaction showing complete hydrogenation of a virgin DEB molecule.

COLL 316

Mechanistic studies for the water-gas shift reaction on Cu-ceria catalysts

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The mechanisms of the water-gas shift reaction ($\text{CO} + \text{H}_2\text{O} = \text{H}_2 + \text{CO}_2$) has been investigated on model and powder CuO-CeO₂ catalysts, where ceria is present as a CeO₂(111) single-crystal, nanospheres, nanorods and nanocubes, using a combination of *in-situ* techniques: X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS),

infrared spectroscopy (IR), and ambient-pressure X-ray photoelectron spectroscopy (AP-XPS). Under reaction conditions, the CuO-CeO₂ catalysts undergo chemical transformations that drastically modify their composition with respect to that obtained during the preparation process. The active phase in the catalysts combines Cu and partially reduced ceria. The oxide support is not a simple spectator during reaction, facilitating the dissociation of water and in some cases modifying the chemical properties of the supported metal. Data of AP-XPS and IR spectroscopy indicate that formate species are not necessarily involved in the main reaction path for the water-gas shift. Thus, a pure redox mechanism or associative mechanisms that involve either carbonate-like (CO₃, HCO₃) or carboxyl (HOCO) species should be considered.

COLL 317

Recent advances in methods for finding the mechanism and rate of surface processes

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While a great deal of effort in surface science has been devoted to molecular beam measurements of dissociative adsorption of molecules on surfaces, the energy of the molecules in such experiments is typically so high that the dynamics governed by regions of the energy surface that are not so relevant for catalysis under typical conditions. In an alternative approach, Campbell et al. developed a method for determining the sticking probability of thermally equilibrated gas molecules and applied it to H₂ dissociative adsorption on Cu(110) [1]. This gives information more directly related to catalytic processes. On the theoretical side, these experiments stimulated the development of methods for calculating the rate of surface processes, such as the nudged elastic band method for finding minimum energy paths of transitions and generalized reversible work formulation of transition state theory as well as its extension to quantum mechanical systems where the possibility of particle tunneling is taken into account [2,3]. Recent developments of the methodology for finding the mechanism and rate of surface processes will be presented, with H₂/Cu(110) taken as one of the example applications. This includes the use of Gaussian process regression for acceleration of minimum energy path [4] and tunneling path [5] calculations. While the early applications of these theoretical methods relied on the availability of potential energy functions, the improved methods make it possible to evaluate rates directly from electronic structure calculations.

COLL 318

Ion imaging measurements of velocity resolved reaction rates: New insights into CO oxidation on Pt

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Ion imaging techniques are widely used in the measurement of chemical reaction dynamics in the gas phase. They allow rapid data acquisition because they enable simultaneous measurements of speed and angular distributions. The application of ion imaging to surface scattering experiments has so far been limited, but recent experiments have made great strides in measuring velocity and state resolved inelastic scattering and measurements of chemical reaction rates. Notably, we can now make measurements of reaction rates that are velocity resolved, making it possible for the first time to measure the reaction flux as a function of speed and angle. Measurements of this type on CO oxidation on Pt, $\text{CO}_a + \text{O}_a \Rightarrow \text{CO}_{2,g}$ on Pt surfaces provide new insights into this prototypical surface reactions. We demonstrate the measurement of CO oxidation rates at step edges and terraces on Pt(111) and Pt(332) surfaces. Reactions at terraces produce CO_2 with hyperthermal speeds in narrow angular distributions, while reactions at steps produce CO with thermal speeds in broad angular distributions. This settles the long standing “two channel question” in this important reaction and reveals that all previous reports of rate parameters attributed to terrace reactions actually were dominated by reactions at steps.

COLL 319

Kinetics studies of the direct conversion of methane to methanol by Cu/mordenite zeolites: What can they tell us about fundamental and process related aspects of the “Holy Grail” of catalysis?

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We have studied the direct and stepwise selective oxidation of methane to methanol over copper-mordenite, (Cu/MOR) under conditions of plug flow using is combined and quantitative time resolved Cu K-edge XANES and online mass spectrometry (MS). We delineate the kinetics and speciation involved in methane activation in Cu/MOR and then go on to understand aspects the character of product release through steaming in the temperature range 403 to 493 K. Time resolved Cu K-edge XAS, allied to Principal component analysis (PCA), reveals that two spectroscopically discrete Cu(I) species arise from the activation of methane. Moreover, we show that two distinct regimes for methane activation exist as function of methane exposure. We conclude that copper (I) hydroxyls, rather than being active species, are a direct product in both mechanisms. We show that the steaming of products (dimethyl ether, methanol, carbon dioxide, and carbon dioxide) is a process comprising three distinct phases: zeolite hydration; product release, and formation of further copper (I) hydroxyls; and finally slow re-oxidation of Cu (I) to Cu (II). We further show that product release can be achieved on much shorter

timescales than previously realized, and that different products are evolved on different timescales leading to temporal dependence in reaction selectivity within the stepwise process. Quantitative cross correlation of Cu K-edge XANES with mass spectrometry in a plug flow environment is shown to be extremely informative regarding fundamental copper speciation and reactive kinetics, but also aspects of process chemistry that are of significant import in respect of designing a viable application of this challenging but highly sought after chemistry.

COLL 320

Surface chemistry of transition metal doped MgO nanoparticles and their reaction products *in situ*

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Reacting low solubility magnesium mineral sources of high natural abundance with N and P from anthropogenic wastewater offers new, yet little explored, opportunities for nutrient recovery and sustainable fertilizer production. The fundamental aspects of a diverse set of low solubility, magnesium mineral surface conversions into complex salts, such as mineral struvite, in the presence of aqueous solutions of ammonium and phosphate ions, are presented under environmentally relevant conditions. First, nanoparticulate transition metal doped MgO nanoparticles are synthesized and their surface chemistry is probed using temperature programmed Diffuse Reflectance Infrared Spectroscopy. Second, magnesium mineral nature (oxide, carbonate, oxyhydroxide), composition (Mg, Mg and Ca, Mg and Fe), and ion transport (diffusion limited macrocrystal vs interface reaction limited nanoparticle) effect on their propensity to form struvite in simulated wastewater under varying N:P concentrations, dissolved organic matter and pH is investigated by means of *in situ* Raman confocal spectroscopy, Scanning Transmission Electron Microscopy and X-ray Photoelectron Spectroscopy. The proposed work suggests the abundant, magnesium-containing, natural minerals as proxies for struvite formation and measures the corresponding growth kinetics and the resulting reactive intermediate and product speciation.

COLL 321

Metal nodes in metal-organic frameworks as active sites for gas-phase catalytic hydrogenation

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The ability to tailor the geometry and ensemble size of the metal nodes in MOFs allows for unprecedented control of the active sites and could lead to significant advances in rational catalyst design. $(\text{Cu}_x\text{Rh}_{1-x})_3(\text{BTC})_2$ (abbreviated CuRhBTC, where BTC^{3-} = benzenetricarboxylate) is prepared from Rh^{3+} and CuBTC (HKUST) by post-synthetic ion-exchange. Using a combination of X-ray photoelectron spectroscopy (XPS) and X-ray absorption near edge structure (XANES) techniques, the oxidation state of Rh in CuRhBTC is identified as $2+$. These Rh^{2+} sites are active for the catalytic hydrogenation of propylene to propane at room temperature, and catalytic activity is stable over a 24 hour reaction period. In situ and post-reaction XPS studies show that the Rh^{2+} is stable under reaction conditions and over extended reaction times. Density functional theory (DFT) calculations suggest a mechanism in which hydrogen dissociation at the Rh^{2+} sites is facilitated by Rh-O bond scission. The experimental apparent activation energy (6.3 kcal/mol) is in general agreement with the barrier height predicted by DFT for the rate-limiting step.

COLL 322

Nanostructured adsorbents and catalysts for environmental applications

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In environmental applications, dispersion & Stabilization of active sites, facile mass transportation, and efficient mixing of the reactants are three key aspects of catalysis and adsorption. Hydrophilicity may also be one important issue as such process is usually occurred in aqueous solutions. With well controlled nanostructures, these three goals can be met. During recent years, we developed in situ deduction methods to ensure high dispersion of noble metal nanoparticles on various supports, and used an embedment method to physically stabilize the metal nanoparticles. With core/shell structure, in which the shell is nanoporous while the core are loaded with active nanoparticles as well as void spaces, diffusion of reaction species can be controlled, so that the activity and the selectivity of the catalysts are enhanced. One particular advantage of such core/shell structures is confinement effect inside the void space of the core shell structure for catalysis, including Fenton catalysis. Another advantage is high active carbocatalysts with suited heteroatom doping.



COLL 323

Kinetics study of heterogeneous reactions of n-butylamine with succinic acid using an ATR-IR flow reactor

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Kinetics of heterogeneous reaction of n-butylamine (BA) with succinic acid (SA) were studied via a flow system combined with attenuated total reflection infrared Fourier-transformed spectroscopy (ATR-FTIR) over wide ranges of BA concentrations (0.145-32.5 ppm), thin film thicknesses (0.05-0.15 mm), temperatures (263-295 K), and relative humidities (0-75% RH) under atmospheric pressure condition for the first time. Pseudo-first-order rate constants k_{app} and overall reactive uptake coefficients γ values were derived according to the changes in absorbance from peak located near 1634 cm^{-1} , which can be assigned to -COO^- antisymmetric stretch ($\nu_{as}(\text{-COO}^-)$). The results show that the heterogeneous reaction of SA with BA follows Langmuir-Hinshelwood mechanism and k_{app} is largely dominated by surface reaction over bulk phase reaction. The studies of the influence of temperature and RH on the reaction of SA with BA show that both the k_{app} and γ values display very strong temperature and RH dependence. Low temperature promotes the reaction mainly due to the physisorption of BA

predominated in the whole reaction. With an increasing RH, both the k_{app} and g values increase indicating that the water vapor enhances the reaction. In addition, the water uptake results indicate that the hygroscopic behavior of the thin film is enhanced after BA exposure.

COLL 324

Coupling molecular catalysts with light-harvesting surfaces for solar CO₂ reduction

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There is a critical need for robust photosynthetic systems that can achieve efficient solar fuel production by CO₂ reduction or water splitting. We combine highly efficient molecular catalysts with light-harvesting surfaces for use in solar CO₂ reduction. In particular, coordination complexes of rhenium and cobalt have been coupled with mesoporous SiO₂, TiO₂, C₃N₄, and Si nanostructures. A variety of techniques, including infrared and X-ray absorption spectroscopies, were utilized to investigate CO₂-reduction catalysis in these hybrid systems. Appropriate covalent linkages and catalyst/surface interactions were found to be important in promoting selective CO₂ reduction.

COLL 325

SFG spectro-microscopy for self-assembled materials

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By developing a new, spatially resolved infrared (IR) pump vibrational sum frequency generation (VSFG) probe microscope, we report mesoscopic ordering in self-assembled material, composed by beta-cyclodextrin (β -CD) and sodium dodecyl sulfate (SDS). Furthermore, we found mesoscopically homogeneous but macroscopically heterogeneous water dynamics in self-assembled materials. The strong hydrogen-bond interactions between host molecules and nearby water not only template nearby water networks to adopt the chirality of self-assembled materials, but also induce resonant energy transfer from β -CD to nearby water, which is heterogeneous among domains, but uniform within domains. We will also discuss water structure and dynamics in other self-assembly materials, such as metal-organic-frameworks (MOFs)

COLL 326

Heterogeneous molecular interactions at the silica/water interface

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We present a joint computational and experimental study on the adsorption of pyruvic acid on hydroxylated silica particles. Under dry conditions (<1% relative humidity, RH), transmission Fourier transform infrared (FTIR) spectroscopy reveals the presence of both the trans–cis (Tc) and trans–trans (Tt) pyruvic acid conformers as well as the (hydrogen bonded) pyruvic acid dimers. Under higher relative humidity conditions (above 10% RH), adsorbed water competes for surface adsorption sites, changing the relative populations of the different adsorbed pyruvic acid configurations. The detailed surface interactions are further discussed with the help of *ab initio* molecular dynamics simulations. Our results highlight the importance of the environment (relative humidity and co-adsorbed water) in the adsorption, partitioning, and configurations of pyruvic acid at the surface.

Using a free energy perturbation approach in combination with *ab initio* molecular dynamics simulations, we also show how the acidity of pyruvic acid at the quartz/water interface is increased by almost two units. Such increased acidity is the result of the specific microsolvation at the interface and, in particular, of the stabilization of the deprotonated form by the silanols on the quartz surface and the special interfacial water layer. This result shows that, at difference with the water/vapor interface where molecular acidity is generally reduced, at a hydrophilic solid/liquid interface the acidity can indeed also increase.

COLL 327

From calcite to nanospheres: Closing the surface gap between cloud condensation nuclei activity and water adsorption

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Insoluble atmospheric aerosol, such as mineral dust, has been identified as an important contributor to the cloud droplet number concentration and indirect climate effect. However, experimentally-determined Frenkel-Halsey-Hill (FHH) water adsorption parameters remain the largest source of uncertainty in assessing the effect of insoluble aerosol on climate. Recent studies have suggested that surface structure and porosity may be the cause of current disagreements in the literature between FHH parameters measured from water adsorption measurements below 100% RH and experimental cloud condensation nuclei (CCN) activation measurements under supersaturated conditions. Based on work begun as a post-doctoral fellow in Dr. Grassian's research group, results probing the effect of surface structure of insoluble particles on the application of FHH activation theory (FHH-AT) will be reported. Specifically, model

insoluble systems are studied with respect to water adsorption and CCN activation in an effort to improve experimental agreement and accuracy of FHH parameters used to model the indirect effect of insoluble atmospheric aerosols.

COLL 328

Surface chemistry of airborne mineral dust aerosols: Environmental and health implications

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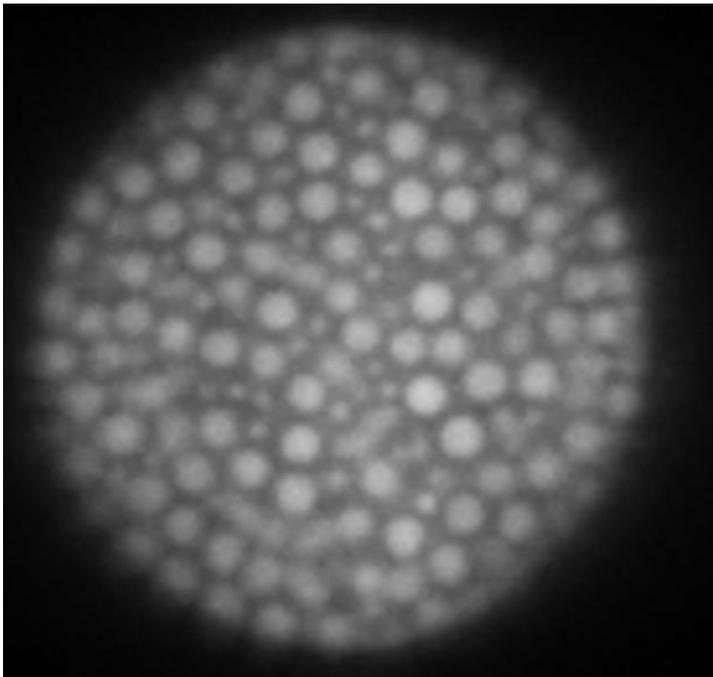
Atmospheric mineral dust continue to serve as an important component in climate, ecological balance, and human health. In addition to their environmental relevance, mineral dust also serve as inspiration for the understanding of heterogeneous processes, owing to their complex and chemically rich molecular frameworks. Some of the surface chemistry and photochemistry of airborne mineral dust are currently under investigation in our laboratory to better understand oceanic iron fertilization, and health implications of inhaled uranium dust. Atmospherically processed mineral dust aerosols has been identified as a major contributor to the bioavailable Fe in the ocean. While numerous studies have focused on single component Fe bearing minerals such as hematite, goethite or clay minerals, the impact of non-Fe bearing minerals on Fe dissolution is largely remain unknown. Our studies disclose surface reaction mechanisms that governs the atmospheric processing of Fe-containing mineral dust in the presence of a common semi-conductor oxide, titania (TiO₂) – “Fe-Ti hypothesis”. This work further reveals vital mechanistic insights on mineralogical controls in dust iron dissolution by molecular oxygen, acid anions, and solar flux to understand global iron mobilization. On the other hand, airborne mineral dust containing heavy metals can impact on human health. However, the surface chemistry of metal-containing-dust dissolution in lung fluids and the role of mineralogy are poorly understood. More recently, we focused on the dissolution of respirable-sized uranium-containing-dust in simulated lung fluids. We observe that the inhalable dust includes uranium minerals that yield the uranyl cation, UO₂²⁺, as the primary dissolved species. Further, the extent of uranium dissolution is greatly influenced by mineralogy; the types of uranium minerals as well as non-uranium-minerals in the inhaled dust. Thus, our findings emphasize the importance of site-specific toxicological assessments across mining districts with a specific focus on their mineralogical differences. Given that airborne mineral dust are capable of further transformation and interaction with atmospheric trace gases, our work also highlights the importance of detailed studies on the surface chemistry of these systems.

COLL 329

Colloidal glass transition in confined spaces

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Our lab studies how confinement modifies the structure and dynamics of densely packed colloidal suspensions. Colloidal suspensions are composed of micron-sized particles in a liquid, and the particles diffuse due to Brownian motion. The diffusion constant decreases rapidly as the volume fraction ϕ is increased toward $\phi = 0.58$, which has been identified as the colloidal glass transition point. When a colloidal suspension is confined to a small region we find the sample behaves glassier: diffusion is slower for a given ϕ than in an unconfined sample. We observe this motion using confocal microscopy in samples confined in one, two, or three directions. We find that the properties of the confining boundary influence how dramatic the confinement effects are. We also study glassy samples that are aging, near rough or smooth boundaries. These observations show that wall-induced layer structures strongly influence aging.



Emulsion droplet filled with a bidisperse colloidal suspension, viewed with confocal microscopy. The droplet diameter is 14 microns.

COLL 330

Appearance of a slow mode of polymer surface diffusion on polymer brush-patterned surfaces in aqueous solution

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Surface diffusion of poly(ethylene glycol) (PEG) as a function of increasing confinement is described. PEG is allowed to diffusion on a model surface bounded by poly[oligo(ethylene glycol)methyl ether methacrylate] (POEGMA) "walls". As the size of these "corrals" decrease, i.e. increasing confinement, a new mode of PEG surface diffusion is observed. The design of this compartmentalized model system for the investigation of diffusional transport in nanosystems is described. The arrays of corrals confined by POEGMA "walls" were fabricated using double-exposure interferometric lithography to deprotect aminosilane films protected by a nitrophenyl group. In exposed regions, removal of the nitrophenyl group enabled attachment of an initiator for the atom-transfer radical polymerization of end-grafted POEGMA (brushes). Diffusion coefficients of PEG of different molar mass in these corrals were obtained by fluorescence correlation spectroscopy. Two modes of surface diffusion were observed: one which is similar to diffusion on the unpatterned surface and a very slow mode of surface diffusion that becomes increasingly important as confinement increases. Diffusion within the POEGMA brushes does not significantly contribute to the results.

COLL 331

Advancements in fluorescence correlation spectroscopy super resolution optical fluctuation imaging (fcsSOFI) to quantify anomalous diffusion in crowded environments

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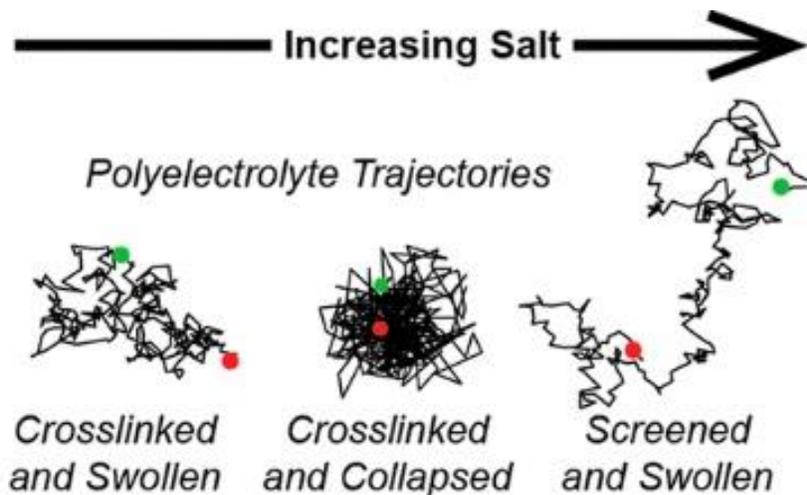
Fluorescence correlation spectroscopy super-resolution optical fluctuation imaging or "fcsSOFI" is a super-resolution optical imaging technique that simultaneously characterizes the nanometer dimensions of and diffusion dynamics within porous structures. By utilizing pixel-by-pixel second-order autocorrelation, maps of diffusion coefficients at subdiffraction-limited levels are achieved. fcsSOFI has previously imaged and quantified one- and two-dimensional Brownian diffusion within liquid crystals and porous hydrogels.¹ Application of fcsSOFI beyond Brownian diffusion and in non-porous, crowded environments will be presented. We have expanded the fcsSOFI algorithm to quantify multicomponent and anomalous diffusion. The computational analysis speed has been improved with GPU-based curve fitting.² The success of the algorithm is demonstrated with simulated data. Experimentally, fcsSOFI is applied to the diffusion of rheological sensors within crowded (bio)polymer condensates formed by liquid-liquid phase separation.³ fcsSOFI quantifies anomalous diffusion components that were challenging to observe by conventional single particle tracking techniques due to low signal-to-background ratios. fcsSOFI is therefore a viable imaging analysis technique to understand dynamics within porous or crowded environments.

COLL 332

Complex salt dependence of polymer diffusion in polyelectrolyte multilayers

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Polyelectrolyte multilayers (PEMs) have significant potential in many technologies, yet the dynamics of the constituent polymer chains remains poorly understood. We used total internal reflection fluorescence microscopy to observe microscopic single-molecule transport of fluorescently labeled poly-L-lysine (PLL) diffusing within the bulk of a PEM composed of PLL and poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS) when exposed to NaCl solutions ranging in concentration from 0 to 2 M. Statistical analysis of PLL trajectories revealed motion that was nonergodic, subdiffusive, and temporally anticorrelated under all conditions. In contrast with previous macroscopic measurements of polymer diffusion within PEMs, the microscopic diffusion was 2–3 orders of magnitude faster and varied nonmonotonically with salt concentration in a way that was similar to trends previously associated with PEM swelling and viscoelastic properties. This trend in the anomalous diffusion was attributed to complex salt-dependent changes in the viscoelastic properties of the film that balanced intermolecular binding and molecular conformation.



COLL 333

Modeling the Brownian hydrodynamics of intracellular motion

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Many mathematical representations of cellular behavior rely on abstractions that do not account for how macromolecules are organized and move within the crowded, watery cell milieu. For example, linear algebra- and differential equation-based models typically do not represent biomolecules or their spatial positioning and motion. For many questions in biology and medicine these simpler models have been sufficient. However, fundamental gaps in understanding of many cell functions persist; physics may provide a bridge to close such gaps. I will discuss our progress in developing computational and theoretical tools to model spherically confined colloidal suspensions, as a simple model cell, so that biomolecules and their interactions can be physically represented, individually and explicitly. By developing a more robust and fundamentally well-grounded physics model for how macromolecules interact within cells we can contribute to a more physically complete representation of living matter. A primary challenge in models of confined colloidal suspensions is the accurate and efficient representation of many-body hydrodynamic interactions, Brownian motion, and the enclosure itself. To this end, we developed a new “Cellular Stokesian dynamics” framework that accounts for spherically confined many-body hydrodynamic and lubrication interactions, Brownian motion, and active transport. Utilizing this model, we studied diffusion, cooperative motion, and self-organization with confinement and crowding levels representative of a cell interior. I will discuss the qualitative influence of hydrodynamics, confinement and crowding on transport behavior, as well as the consequences of neglecting such influences. Connections to underlying structure are made, and implications for cellular function are discussed.

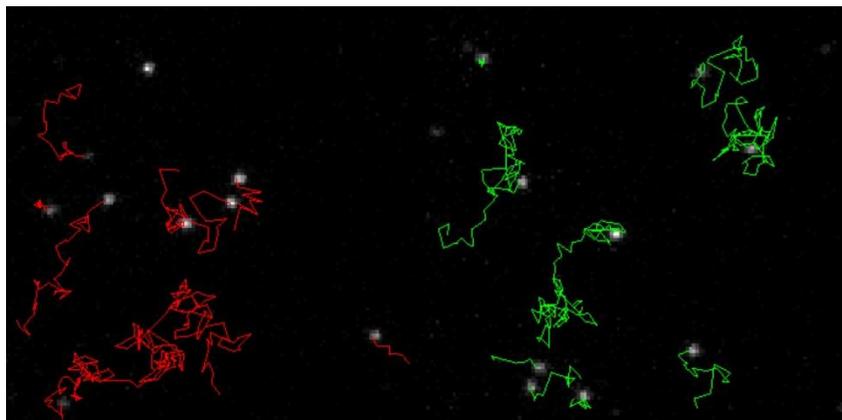
COLL 334

Brownian motion within lipid bilayers is correlated over large distances

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From a hydrodynamic perspective, a lipid membrane is considered to be a quasi-2D viscous liquid, with molecular motion confined to 2D, while momentum is also exchanged with the 3D surrounding solvent. The hydrodynamic picture, classically analyzed by Saffman and Delbrück, was recently proposed to lead to correlated motion of membrane-embedded biomolecules separated by distances much larger than their size. Here, we present the first experimental measurements of correlated Brownian motion in lipid bilayers. We study pairs of lipid tracers using dual-color single particle tracking techniques. Employing a novel laser modulation scheme that allows us to obtain sub-millisecond temporal resolution, we measure coupling diffusion coefficients (correlation functions) and find them to decay over a distance as large as ~100 nm. To

interpret the experimental results, we apply the “regularized Stokeslets” method, generalized to a two leaflet membrane. The correlated diffusion measured here provides a powerful means to probe membrane hydrodynamics. It has the potential to expose important differences between the dynamics of freely floating membranes and of supported bilayers, such as those attached to the cytoskeleton in cells or placed on a solid surface.



Dual-color single particle tracking to measure correlated motion of fluorescently labeled lipid probes in a lipid bilayer.

COLL 335

Controlling the location of membrane components in planar supported bilayers

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Supported lipid bilayers can be fabricated on planar silica supports via the vesicle fusion method. When this is done, it is often assumed that the individual lipid components that constitute the bilayer are uniformly distributed between the two leaflets. This, however, is not always the case. For example, negatively charged lipids are usually enriched in the upper leaflet of the membrane. This type of partitioning can occur on two separate grounds. First, there can be electrostatic repulsion between negatively charged lipid headgroups and the underlying glass substrate, that typically also bears a negative charge. Second, there is very limited interstitial space between the lower bilayer leaflet and the planar support. As such, membrane components can be expelled from this confined region or sometimes immobilized there on steric grounds. In this talk, we will consider methods of regulating this behavior based on pH, temperature, and buffer

conditions. Also, it will be shown that proteins can be exploited to sterically confine lipids with larger headgroups that protrude from the membrane.

COLL 336

Career using colloidal and surface science in government, academia, and industry

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This talk will highlight the commonalities and differences throughout one career using colloidal and surface science as a common theme in sectors from government to academia to industry, including on startup teams and rapidly growing teams. Whether publishing peer-reviewed papers working in national laboratories, developing curriculum on and teaching colloidal science at the undergraduate level, or working with companies to grow their revenue and increase their customer base in ways ranging from new product development to technical marketing, colloidal science careers can take on a variety of faces, both behind the bench and beyond.

COLL 337

R&D careers at the Clorox Company: Making a difference every day

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The Clorox Company is an exciting place to start your industrial career, where you can make everyday lives better every day. Our smart, values-driven people take pride in their work and their company. Our Research and Development (R&D) organization takes new generations of consumer products from concept to reality. With such diverse roles as scientists, engineers, mechanical designers and packaging experts, R&D is a community of technical leaders and managers actively involved in virtually every step in the lifecycle of our products, from initial concept to raw materials to final goods on store shelves. R&D is committed to leveraging the latest technology to bring consumers the high-quality, innovative products they expect and deserve. One of our R&D scientists will talk about the journey from grad school to a successful industrial career at Clorox and be happy to answer your questions. Clorox interviews at the ACS Fall National Meeting each year; if you are graduating or ending a postdoctoral fellowship in the 2019-2020 school year, we hope you'll consider interviewing with us at the San Diego National Meeting in addition to meeting us at the Symposium.

COLL 338

My experience from grad school to an industrial career at P&G

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P&G was founded over 180 years ago as a simple soap and candle company. Today, we're the world's largest consumer goods company and home to iconic, trusted brands that make life a little bit easier in small but meaningful ways. Our Research and Development (R&D) organization takes new generations of consumer products from concept to reality. With such diverse roles as engineers, scientists and packaging experts, R&D is a community of technical leaders and managers actively involved in every step in the lifecycle of our products, from initial concept to raw materials to final goods on store shelves. One of our R&D scientists at P&G will talk about the journey from grad school to an industrial career at P&G and will provide some examples from Hair care relevant to Colloids, Chemistry and Chemical Engineering.

COLL 339

Careers at the industry-academia interface: Insights from sustainable nanotechnology and entrepreneurship

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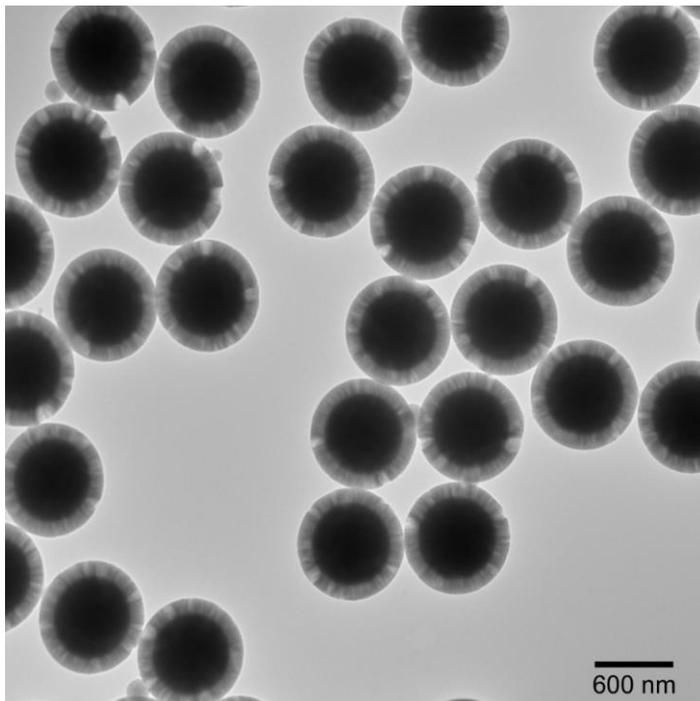
Interfaces are where the action happens. From developing nano-enabled catalysts to designing biochemical sensors, interfacial chemistry determines success. Interfaces are also profoundly important to shaping one's career, be it in industry, academia, government, a non-profit, or somewhere in between. The industry-academia interface can be particularly appealing for graduate students and post-doctoral scholars. Industry brings unique real-world challenges to academia, and academic research leads to new discoveries on which future industries are based. Although industrial and academic pursuits are highly complementary, they can differ from one another in fundamental ways. Understanding these differences and their underlying motivations are essential to building a successful career at the industry-academia interface. Example careers include performing industry-sponsored research, managing industrial affiliates programs (IAPs), protecting intellectual property (IP), facilitating technology transfer, perfecting legacy products or even launching new ones through a start-up venture. Establishing a career at this interface requires the development of skills that are not readily acquired through coursework and research. Rather, they require hands-on industry experience, mentorship, openness to new ideas, willingness to take risks and fail forward, patience, and grit. From founding NanoSafe, Inc., a startup dedicated to the safe and responsible use of nanotechnology, to nurturing an "innovation ecosystem" within Virginia Tech's NSF-funded NanoEarth user facility – the speaker will discuss the growing importance of careers at the industry-academia interface as well as the opportunities and challenges such careers present to recent graduates, post-docs, and faculty.

COLL 340

Not what I had thought: Surprising commercial applications of colloidal nanoparticles

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Over the last 20 years, a vast array of precisely engineered nanoparticles with various sizes, shapes, and surfaces have been produced. However, the path to widespread commercialization of these novel materials has not been straightforward. In order to disrupt existing technology, the nano-enabled idea must typically provide an order of magnitude increase in performance or create a completely new product class that did not previously exist. An additional criteria important for commercial success is the ability to cost effectively scale-up production. Many types of nanoparticles are made at dilute concentration and significant volumes are required for the fabrication of necessary quantities. Within these constraints, there are increasing examples of nanoparticles that have been successfully commercialized. Start-ups are developing high impact products in areas that range from photothermal topical therapeutics to ultra-sensitive biodiagnostics to one-way illumination. The necessary educational skills and background required to help these early stage companies succeed will be discussed.



Mesoporous silica shells on gold



cGMP nanoparticle fabrication

COLL 341

Contact lenses, insulation, memory foam, and composite lumber: Surface science is in everything!

Steve Diamanti, *steve.diamanti@yahoo.com*. Marketing, CooperVision, Guerneville, California, United States

This talk will highlight how surface science and chemistry principles are critical to a wide variety of fields from medical devices to everyday consumer products and beyond. The author will share his personal experiences in these fields and offer some examples of how polymer chemistry and surface science are critical in solving some of the key challenges faced in industry today. The talk will also discuss some of the key differences and commonalities between careers in industry, government and academia, and some important skills to develop to be successful in industry. Finally the author will discuss his unique career path that's taken him from the lab into marketing for a large multinational medical device company and around the world in the process.

COLL 342

One research chemist's career path in the public sector

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This talk will explore some of the experiences throughout the presenter's career in scientific research and metrology at NIST. The author will discuss his past 10 years of experiences as an early to mid-career research chemist focused on surface chemical analysis as well as nanomaterials characterization and transformations. Some key aspects of this discussion will include: transitioning from PHD program to a postdoctoral program, establishment and demonstration one's capabilities as an independent researcher, collaboration/networking and recognizing opportunities, and preparing/executing the next steps after the postdoctoral fellowship.

COLL 343

Assembly of anisotropic quantum dots from periodic superlattices to aperiodic quasicrystals

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Nanocrystal quantum dots have been widely studied for decades. Continuous optimizations in synthesis have allowed production of high-quality quantum dots with exquisitely controlled size, shape and compositions. These high-quality quantum dots can be used as building 'bricks' for constructing higher-order architectures. While building assemblies from isotropic particles has been well studied and documented, creating novel superstructures from complicated and anisotropic building blocks still lags significantly behind. In this talk, I will discuss about a new synthesis of pyramidal shaped quantum dots which can be used for generating a range of superstructures with and even without periodicities. Detailed analysis from translational alignment to orientational ordering provides understandings of the major driving force of assembly processes. Unlike conventional entropy-driven self-assembly processes, these highly faceted pyramids tend to have selective facet-to-facet attachment through directional inter-particle interaction. This anisotropic interaction offers enthalpy factors which are responsible for the obtained novel structures. Our findings show that high-complexity superstructural materials can be obtained from nanocrystals when anisotropic kinetic factors are fueled, providing a new avenue towards future explorations of processing and structure-related functionalities of nanomaterials.

COLL 344

Growth mechanism of five-fold twinned nanowires from multi-scale theory and simulations

***Kristen A. Fichthorn**, fichthorn@psu.edu. Pennsylvania State Univ, University Park, Pennsylvania, United States*

Five-fold twinned metal nanowires can be synthesized with high aspect ratios via solution-phase methods. The origins of their anisotropic growth, however, are poorly understood. We combine atomic-scale, meso-scale, and continuum theoretical methods

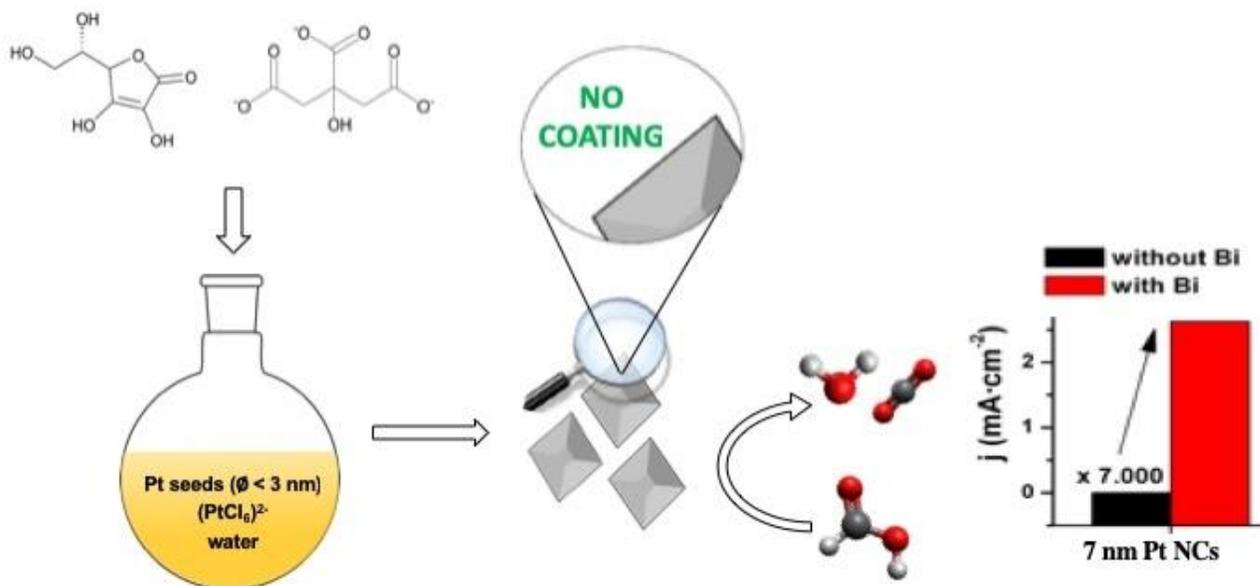
to predict growth morphologies of Ag nanowires from seeds and to demonstrate that high aspect-ratio nanowires can originate from anisotropic surface diffusion induced by the strained nanowire structure. Nanowire seeds are similar to Marks decahedra, with {111} "notches" that accelerate diffusion along the nanowire axis to facilitate one-dimensional growth. The strain distribution on the {111} facets induces heterogeneous atom aggregation and leads to atom trapping at the nanowire ends. We predict that decahedral Ag seeds can grow to become nanowires with aspect ratios in the experimental range. Our studies show that there is a complex interplay between atom deposition, diffusion, seed architecture, and nanowire aspect ratio that could be manipulated experimentally to achieve controlled nanowire syntheses.

COLL 345

Citrate-coated, size-tunable octahedral platinum nanocrystals: Novel route for advanced electrocatalysts

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New methods for green and scalable syntheses of size- and shape-controlled metal nanocrystals are of high interest in the areas of catalysis, electrocatalysis, nanomedicine, and electronics. We present a new synthetic approach based on the synergistic action of physical parameters and reagents to obtain size-tunable octahedral Pt nanocrystals, without the use of catalyst-poisoning reagents and/or difficult-to-remove coatings. We only use sodium citrate, ascorbic acid, and fine control of the reduction rate in aqueous environment. Pt octahedral nanocrystals with particle size as low as 7 nm and highly developed {111} facets have been obtained, as proven by transmission electron microscopy, X-ray diffraction, and electrochemical methods. The absence of sticky molecules together with the high quality of the surface renders these nanocrystals ideal candidates in electrocatalysis. Remarkably, 7 nm bismuth-decorated octahedral nanocrystals exhibit superior performance for the electro-oxidation of formic acid in terms of both specific and mass activities.



COLL 346

Maneuvering the surface chemistry of plasmonic Mg nanoparticles

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Light is powerful: photons carry energy at high speed, stimulate chemical reactions, and can be converted to electricity. However, light-to-chemical energy conversion is challenging, as light interacts only weakly with most molecules. Plasmonic nanoparticles of gold (Au) and silver (Ag) have found a myriad of applications as light harvesters, spanning the engineering, science, and bioscience fields. Meanwhile, several of the few metals with predicted plasmonic properties are amongst the most abundant elements on earth; for example, magnesium (Mg) has exciting optical properties across the UV, visible and IR range and better resource sustainability than Ag and Au to support mainstream applications.

We recently demonstrated the colloidal synthesis of hexagonal Mg nanoplates which support multiple plasmonic modes by reducing di-*n*-butylmagnesium with lithium naphthalenide in THF. This opened the way to a series of synthetic and numerical studies toward gaining an understanding of growth, functionalization, and optical properties. In this work, we analyzed the plasmon-induced far-field (photon scattering and absorption) and near-field (local enhancement of the electric field) behaviour of new Mg-based heterostructures. These include multi-metallic nanoparticles, where a Mg

core is decorated by small metal clusters; in the case of plasmonic metals (Ag, Au), we observed plasmonic coupling between the core and decorating structures. Furthermore, we developed approaches to coat and stabilize Mg particles for potential applications in aqueous environments. Together, these results expand the field of functional, earth-abundant plasmonics.

COLL 347

Integration of sequential reactions in a continuous flow droplet reactor: Route to architecturally defined bimetallic nanostructures

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Microreactors for nanoparticle (NP) synthesis offer advantages over batch reactions in terms of scale-up and integration with online analyses due to their ability to maintain thermal and compositional equilibrium. However, these droplet microreactors are usually limited to one synthesis inline. Herein, two microreactors (i.e., a duo-microreactor) are integrated to achieve sequential reactions for the synthesis of multimetallic NPs with architectural control. The generality of the duo-microreactor is shown with the synthesis of branched Pd-Pt NPs and core@shell Pd@Au NPs, both achieved by synthesizing Pd nanocubes in the first part of the microreactor and then using those nanocubes downstream as seeds for Pt or Au deposition. Control of the dimensions of these NPs was further demonstrated and achieved by tailoring metal precursor concentrations inline. This microreactor methodology is anticipated to be applicable to other multimetallic NP systems.

COLL 348

General synthetic strategy toward metal stannides, materials for next generation batteries

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On the way toward the synthesis of novel magnetic alloys with late 6p elements (Bi, Pb) and 3d transition metals, we studied a general approach to obtain intermetallic formulations of their analogues with Sn and Sb. Additional motivation came from the need for new Sn-based battery electrode materials, which withstand charge/discharge volume changes, as tin enables new generation high-energy lithium and sodium batteries. A variety of nanoscale transition metal stannides $M\text{Sn}_x$ where $M = \text{Cr-Cu}$ and Ge , including unreported compositions, has been synthesized using the general approach via the optimized reaction of metal alkylamidinate complexes, $M(\text{R}'\text{-C}(\text{NHR})_2)_z$, with $\text{Sn}(\text{II})$ precursors. The general trends of metal reactivity with tin have

been established and led to formation of size-controlled nanoparticles of these alloys with size variation below 10%. The nanocrystals are synthesized in a one-pot reaction via the *in-situ* nucleation of a beta-Sn “template” seeds, followed by the reduction of M^{2+} cation and the diffusion of M^0 into the liquid Sn lattice, as demonstrated by time-resolved XRD and TEM. Preliminary results on the use of the developed approach for the formation of 3d-6p alloys together with their magnetic properties will also be presented.

COLL 349

Liquid cell electron microscopy reveals origin of heterogeneity of individual nanocrystals and their 3D atomic structures

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Individual colloidal nanocrystals in a same synthesis batch follow different growth trajectories, resulting in heterogeneity of nanocrystal ensemble. Because of the strong structure-property relationship of nano-sized materials, investigation of growth trajectories for achieving the final size distribution and determination of 3D atomic structures of single nanocrystals is highly required for predicting actual physical properties of the nanocrystals. Here we will present i) ensemble analysis of individual nanocrystal growth mechanism and ii) 3D atomic structure analysis of individual nanocrystals using liquid phase transmission electron microscopy (TEM). First, we achieved comprehensive and quantitative analysis of nanocrystal growth using liquid phase TEM. The statistical analysis from more than 1000 nanocrystals shows interesting growth mechanisms that have not been explored by conventional ensemble characterization or previous liquid phase TEM studies that relied on only limited numbers of events. The growth mechanism study of ensemble trajectories deconvolutes roles of different types of pathways and uncovers how they contribute in change of size distributions. Second, we obtained atomic-resolution 3D structures of the resulting heterogeneous Pt nanocrystals using liquid-cell electron microscopy. The atomic maps reveal critical differences of the ligand passivated nanocrystals in solution such as atomic deviation on surface, distortions, and dislocations. The atomic disorder induces high strains on the grain boundaries and surfaces. Calculation of free energies of nanocrystals from their atomic coordinates can discover the origin of catalytic performance in a single particle level.

COLL 350

Tuning long-acting HIV drug release from a nanogel-based *in situ* forming implant

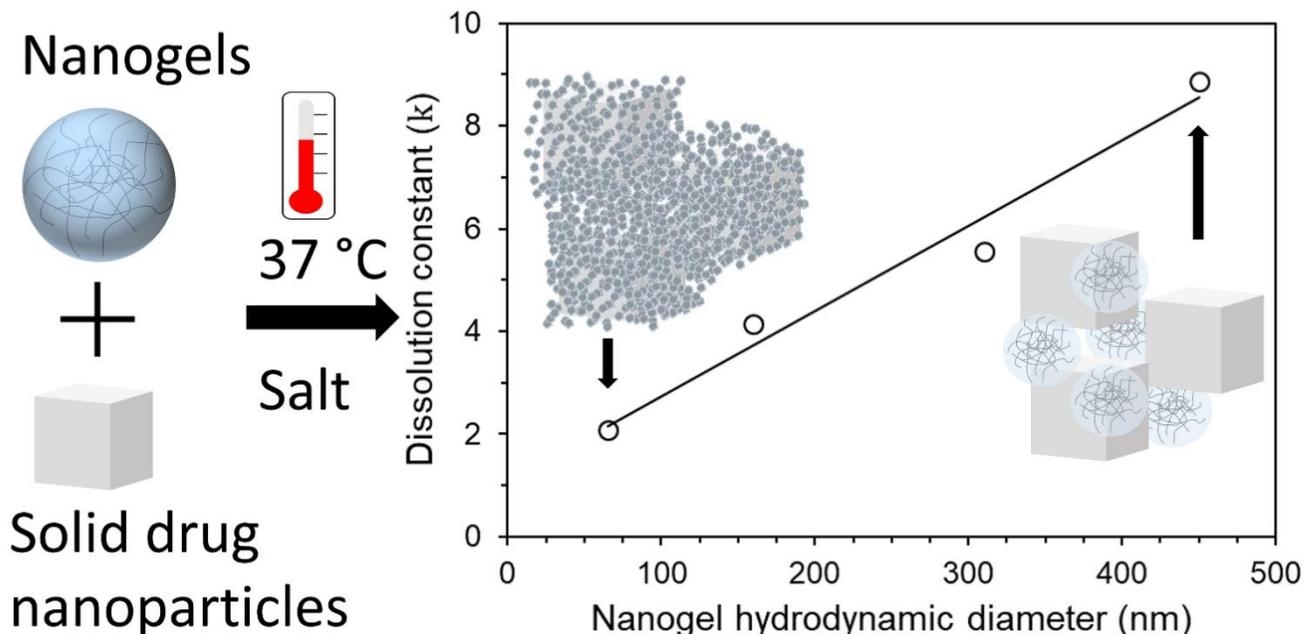
Adam R. Town¹, Jessica Taylor¹, Karl Dawson², Edyta Niezabitowska¹, Nancy Elbaz¹, Andrew Corker², Esther Garcia-Tuñón², **Tom O. McDonald**¹, *tomm@liv.ac.uk*. (1)

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HIV is a global public health threat and requires life-long, daily oral dosing to effectively treat. This pill burden often results in poor adherence to the medications. An injectable in situ forming implant (ISFI) with tuneable drug release kinetics would allow patients to replace some of their daily pills with a single injection. We have recently shown promising proof of concept data for a novel ISFI based on a colloidal assembly of two types of nanoparticles. In this system, poly(N-isopropyl acrylamide) (polyNIPAm) nanogels show a synergistic dual-stimuli responsive behaviour which require the simultaneous stimuli of body temperature and physiological ionic strength to cause aggregation of the nanogel particles into a solid implant. The reservoir of drug was provided by solid drug nanoparticles (SDNs) which are nanoparticles composed entirely of solid drug, stabilised by amphiphilic molecules. In our new work, we show how drug release behaviour can be tuned by changing the size of the nanogels.

Four polyNIPAm nanogels were synthesised by dispersion polymerisation with mean diameters of 65-450 nm. SDNs of the HIV drug lopinavir were prepared with a mean diameter of 330 nm. The exposure of a mixed dispersion of the nanogels and SDNs resulted in the formation of a solid nanocomposite implant. The drug release behaviour and stability of these nanocomposite implants displayed a single phase of drug release indicated Fickian diffusion. Nanocomposites with the lowest loading of SDNs (33%) showed a linear relationship between nanogel diameter and the dissolution constant (see figure). We hypothesise that the larger nanogels result in more porous nanocomposites which leads to faster drug release.

These results show an attractive method for tuning the release of lopinavir from in situ loading implants with high loadings of solid drug nanoparticles (up to 66%) that provide long acting drug release behaviour.



Nanocomposites of nanogels and SDNs are formed upon exposure to physiological temperature and ionic strength. The drug release showed a linear relationship between nanogel diameter and the dissolution constant.

COLL 351

Fabricating Janus particles using seeded emulsion polymerization: Loading and simultaneous release of two drugs

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Janus Particles are asymmetric colloidal structures where two or more different chemical natures are distributed in bulk or surface. This unique asymmetric structure is the source of many interesting properties and applications. In fact, the ability to assemble several different and sometimes contradictory natures on a single particle makes these particles attractive for researchers. Seeded emulsion polymerization is one of the most efficient methods based on phase separation of two different substances due to a powerful driving force. On the other hand, importance of co-delivery and simultaneous detect and treat of cells attracted more attentions towards Janus particles.

In this regard, we tried to produce biocompatible pH-sensitive Janus particles via seeded emulsion polymerization based on acrylate monomers and use them in simultaneous loading and release of two drugs. At first cross-linked poly(2-hydroxyethyl methacrylate) (PHEMA) and poly(methacrylic acid) (PMAA) cores as hydrophilic seed particles were synthesized via distillation precipitation polymerization (DPP) and then, MAA, HEMA and 2-dimethylaminoethyl methacrylate (DMAEMA) were used as second hydrophilic monomers to produce Janus particles with different morphologies such as dumbbell-like, snowman-like and cauliflower-like. The morphology, size and size distribution of resultant particles was investigated by field emission scanning electron microscope (FE-SEM), transmission electron microscopy (TEM) and dynamic light scattering (DLS). In some cases, the formation of core-shell structures was also observed. The effects of different parameters such as feeding approach and composition, polymerization medium, pH-sensitivity of secondary monomer and variation of used surfactant on morphology were investigated. Drug release studies showed that Janus particles can be used in loading and release of two drugs simultaneously. Release behaviors of DOX and ibuprofen were pH dependent and significantly affected by the structure of composite particles.

COLL 352

Solubilization of binary mixture of hydrophobic solutes in multicompartement polymer nanoparticle

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Incorporation of therapeutic, diagnostic, nutrient, reactive or catalytic molecules within a polymer nanoparticle is being widely investigated for various applications. The ability to incorporate two molecules differing significantly in their interactional characteristics, within a single polymer nanoparticle is of particular interest. Previous work on solubilizing a binary mixture of aliphatic and aromatic hydrocarbon solutes inside a block copolymer micelle showed that depending on the interactions of the molecule with the polymer block constituting the micelle core, one of the molecules may be very selectively incorporated in the polymer nanoparticle compared to the other. One way to incorporate both of the dissimilar molecules within the same nanoparticle is to create multiple, segregated compartments within the nanoparticle. An approach to accomplish this, using commercially available polymer molecules, is to self-assemble a binary mixture of block copolymers AB and AC, where A and C are hydrophobic blocks and B is a hydrophilic block. The binary mixture of block copolymers could either form multicompartement nanoparticles or undergo macroscopic phase separation. Through thermodynamic modeling, we investigate the influence of the polymer block molecular weights, block compositions, block A-block C incompatibility, and relative proportion of AB and AC block copolymers on the formation of thermodynamically stable multicompartement micellar nanoparticle. We also model the solubilization of a binary solute mixture in these nanoparticles and predict the extent of uptake of the two dissimilar solutes as a function of the various molecular parameters defining the block

copolymers. The results establish the molecular parametric domain over which one could create multicompartment nanoparticles incorporating dissimilar hydrophobic solutes.

COLL 353

Designed FN3 domains for extrahepatic delivery of oligonucleotides

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Unlocking the full potential of oligonucleotide therapeutics to address unmet medical needs requires development of strategies for efficient and functional delivery of oligonucleotides to target cells outside of the liver. We established a collaboration to explore extrahepatic delivery of chemically stabilized siRNAs as direct conjugates with Centyrins, a novel class of highly stable FN3 domain alternative scaffold proteins. This presentation will discuss preparation, characterization, in vitro and in vivo gene silencing properties of Centyrin – siRNA conjugates. Centyrins have been selected for conjugation on the basis of highly efficient internalization in target cells through receptor mediated endocytosis. Chemical and chemoenzymatic coupling of siRNA to Centyrins has yielded stable, well-behaved, fully homogeneous conjugates with good plasma stability. In vitro, these conjugates have demonstrated ability to knock down expression of mRNA and protein in cells expressing receptor target of the corresponding Centyrin, in the absence of transfection reagent. In vivo, Centyrin-siRNA conjugates induced robust gene silencing in mouse tumor xenograft model with RNAi mechanism confirmation obtained through 5' RACE assay on tumor samples.

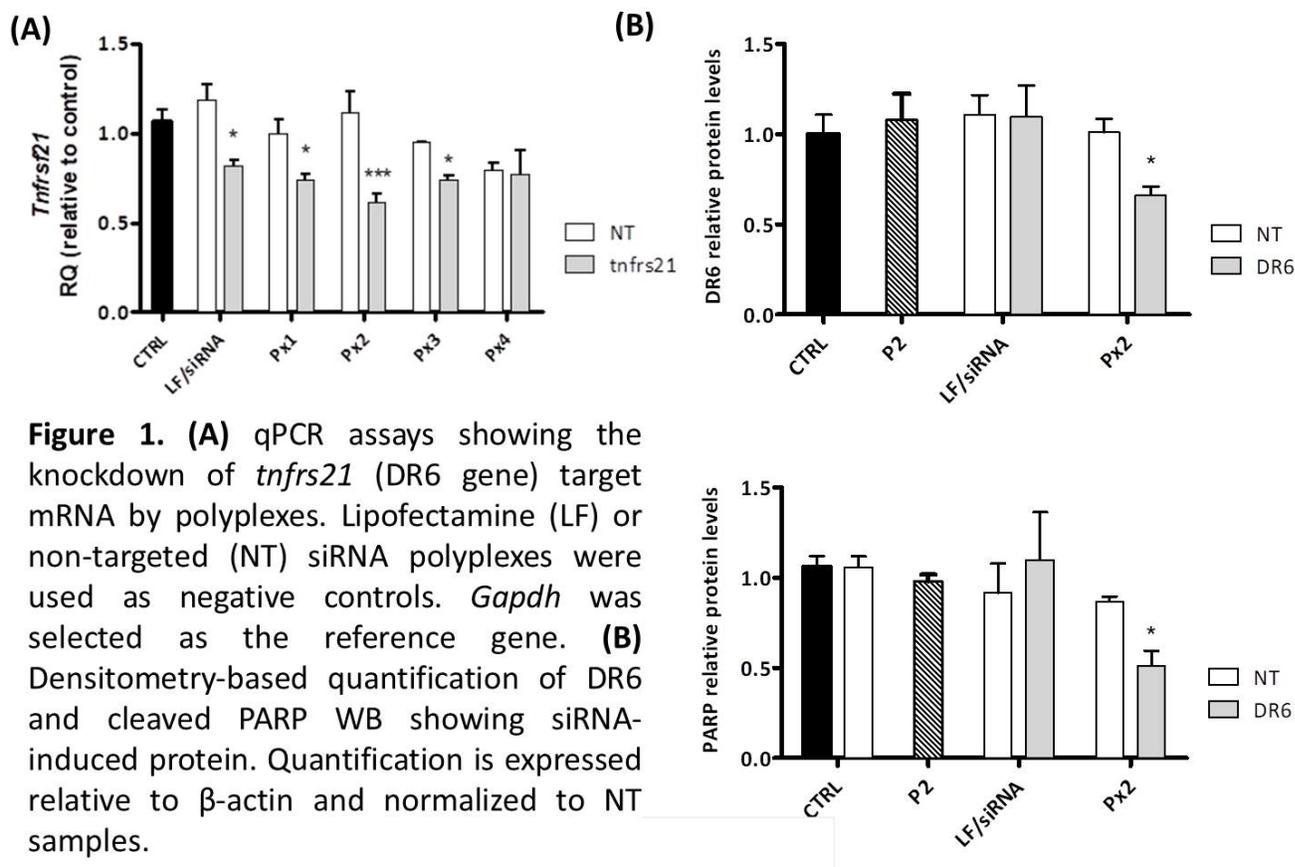
COLL 354

Polypeptide-based polyplexes to boost effective gene silencing in CNS disorders

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Gene silencing therapies have shown success in suppressing the translation of pathogenic target proteins and, hence, this strategy holds great promise for the treatment of numerous central nervous system (CNS) disorders. Endeavours arising

from our current knowledge of multimolecular delivery vehicles focus on overcoming the difficult delivery of siRNA to target tissues due to issues relating to anatomical accessibility, slow diffusion, poor safety, and the requirement for precise cell uptake within the unique CNS environment. To address this challenge, the present work proposes the use of novel poly-L-ornithine (PLO) derivatives to construct polyplexes as non-viral vectors. As a proof-of-concept therapeutic approach, a putative regenerative therapy for multiple sclerosis was pursued. Death receptor 6 (DR6) is described as a negative regulator of oligodendrocyte precursor cell (OPC) survival, maturation and myelination, and its attenuation has been shown to boost remyelination in vivo. We obtained well-defined PLO through a robust and scalable polymerization procedure. We found that PEG derivatization failed to alter the second structure of the main chain and observed derivative degradation by proteases. All derivatives generated formed complexes with siRNA(30-60nm) and slightly positive Z-potential, with said polyplexes displaying stability under in vitro/in vivo scenarios. The physicochemical and biological properties of our novel nanocarriers are exhaustively characterized, highlighting their unique biodegradability and biocompatibility properties and effective gene silencing in primary OPCs. Our polyplexes efficiently silenced DR6 at the gene and protein level (Fig. 1), with an associated downregulation in cell death. However, protein and immunocytochemistry analysis showed that this intervention did not translate into OPC maturation. The Px2 (PLO-PEG3000) polyplex exhibited the highest efficiency, leading to a reduction in DR6 and PARP protein expression.



COLL 355

Single-site catalysts on nanostructured semiconductor surfaces for solar CO₂ reduction

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Semiconductor-based photocatalysts have been extensively studied in solar fuel generation. The solar conversion efficiency of semiconductors could be significantly improved by grafting single-site catalysts on their surfaces. We have prepared single Cu⁺ and Co²⁺ sites on TiO₂ and C₃N₄ surfaces for use in solar CO₂ reduction. Active sites on the photocatalysts were investigated with infrared and X-ray absorption spectroscopies. Such surface chemistry studies could provide important insights regarding the design of highly efficient photosynthetic systems.

COLL 356

Single surface charges on aliovalently doped semiconductor nanocrystals determine their photoluminescence properties

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For decades, semiconductor nanocrystals (NCs) have been studied for their interesting electronic and optical properties, which also make them potentially suitable for a number of applications, including solar energy conversion, displays and biomedical imaging. Cation exchange, a chemical transformation used to modify a crystal whereby a cation from solution is replaces a host cation, has recently become a highly effective tool for enabling the synthesis of nanoparticles with novel chemical compositions. In particular, aliovalent doping of CdSe nanocrystals (NCs) via cation exchange of cadmium ions for silver ions has become quite popular for manipulating the optical and electronic properties of the doped NCs, such as for producing n- or p-type NCs. However, despite over a decade of study, the relationship between optical properties of the NC and the aliovalent dopants has largely gone unexplained, partially due to sample under characterization. We will discuss how electrostatic force microscopy (EFM) with single electron sensitivity can be used to determine the charges of individual, cation-doped CdSe NCs in order to investigate their net charge as a function of added cations. While there was no direct trend relating the NC charge to the relative amount of cation per NC, there was a remarkable and unexpected correlation between the average NC charge and ensemble exciton photoluminescence (PL) intensity, for all dopant cations introduced. We use an effective mass theoretical model to conclude that the changes in PL intensity, as tracked also by changes in NC charge, are likely a consequence of changes in the NC radiative rate caused by symmetry breaking of the electronic states of the nominally spherical NC due to the Columbic potential introduced by ionized cations. Further, we show through energy loss spectroscopy on individual NCs that the cation exchange process is highly heterogeneous, which has profound implications for possible future applications of doped NCs.

COLL 357

Selective photochemistry with quantum dots

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The ability of quantum dot (QD) surfaces to template the assembly of small clusters of molecules leads to addition reactions with high stereochemical selectivity. Here we explore the possibilities for regio-, diastereo-, and enantioselective photocatalysis of cycloadditions using visible light-absorbing QD and QD-molecule triplet energy sensitizers.

COLL 358

Hot carriers in action: Plasmon-driven photocatalysis and photocorrosion

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The energetic hot carriers, i.e. electrons and holes, generated during plasmon decay can be harnessed to drive or enhance a series of interesting photophysical and photochemical processes occurring on plasmonic nanoparticle surfaces. Here I will share with the audience several case studies, through which we have been able to gain important mechanistic insights regarding the detailed roles of plasmonic hot electrons and hot holes in driving the photocatalytic molecular transformations and photo-induced corrosion of anisotropic nanostructures. I will talk about how the plasmonic properties of deliberately designed nanostructures can be fine-tuned to optimize interfacial photochemical processes by focusing on three examples: (1) multimodal photocatalytic mineralization of organic dye molecules on Au@SnO₂ core-shell nanoparticles; (2) plasmon-enhanced enzyme-mimicking activity of Au surface-roughed nanoparticles; (3) plasmon-driven photo-corrosion of quasi-one-dimensional Au and Ag nanostructures.

COLL 359

Plasmon-mediated charge transfer and energy transfer in photocatalysis

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This talk discusses the charge transfer and energy transfer from a metal to a semiconductor in photocatalysis, including light scattering/trapping, hot carrier injection and plasmon-enhanced resonance energy transfer (PIRET). The talk also shows the energetics of plasmonic hot electrons after they are injected to the semiconductor. The presentation demonstrates how to use the plasmonic energy transfer theories to design the metal-semiconductor photocatalysts for solar water splitting and organic compound transformation.

COLL 360

Photoinduced hot charge transfer at aluminum nanohole array/C₆₀ interfaces

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The efficiency of photoinduced charge transfer at organic semiconductor/metal interfaces is crucial to photovoltaic and photocatalytic applications. Despite tremendous efforts in recent years, fundamental understandings of the interfacial charge transfer have not yet been fully understood. Here we examine interfacial hot charge dynamics between photoinduced aluminum nanohole arrays and C₆₀ thin films with transient reflection broadband spectroscopy. The photoinduced plasmons of aluminum nanohole array is injected into the lowest unoccupied molecular orbital for C₆₀ through a Schottky barrier. As the cavity thickness of the nanohole arrays increases, the surface plasmon moves to longer wavelength and exhibits a lower efficiency of charge injection. Our studies point to the significant potential of designing new plasmonic nanostructures to achieve more efficient interfacial charge transfer in the aspect of surface photochemistry, photocatalysis, and solar energy conversion.

COLL 361

Potential dependent plasmonic catalyzed cleavage of the C-Br bond of 8-bromoadenine on silver electrodes of nanostructures

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Localized surface plasmon resonance (LSPR) effect of plasmonic metal nanostructures has offered a unique way to trigger photo-catalyzed chemical reactions on nanoscale. 8-Bromoadenine is one of the halogenated nucleobases applied in the tumor tissue upon irradiation as a potential DNA radio-sensitizer. To utilize the high spatial sensitivity of noble metal nano-structures and improve the selectivity of plasmon catalytic reactions, we investigated the C-Br bond cleavage of 8-bromoadenine at electrochemical interface.

Surface-enhanced Raman spectroscopy (SERS) provides an excellent opportunity to probe photochemical reactions in-situ and in real time. The Fermi level of the metal electrode was modulated by applied potentials, which could be used in controlling the energy of LSPR absorption to facilitate the charge transfer reaction. Plasmon catalyzed reaction kinetics at different potentials were studied by analyzing the intensity change of the characteristic peak of the product adenine at 731 cm⁻¹ in electrochemical SERS spectra. With continuous illumination, the disappearance of the typical ring breathing mode of 8-bromoadenine at 763 cm⁻¹ suggested the plasmon driven electron transfer to break the C-Br bond. The SERS peak at 731 cm⁻¹ in Fig 1(d) shows the product

adenine appears at -0.2 V, a more positive potential than that at the dark condition ($E_p = -1$ V).

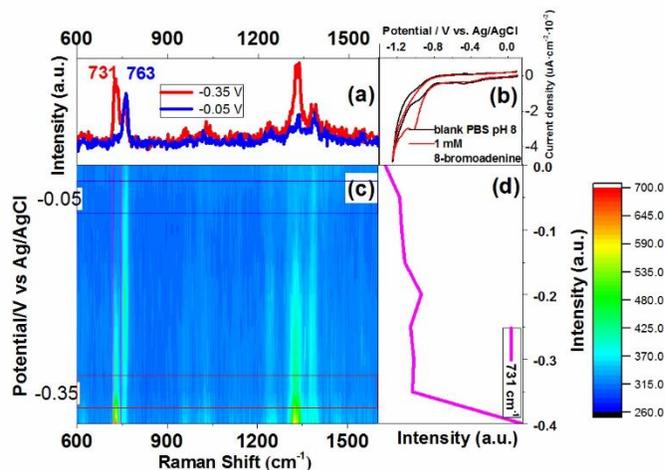


Figure 1 (a) EC-SERS spectra and (b) Cyclic voltammetry (CV) of 8-bromoadenine at a Ag electrode in PBS solution (pH=8). Ring breathing modes of 763 cm^{-1} for 8-bromoadenine at -0.05 V (blue) and 731 cm^{-1} of adenine at -0.35 V (red) are measured. (c) Contour map of potential dependent Raman spectra. The spectra were excited at a 532 nm laser with a power density of 3.2×10^6 mW/cm^2 . (d) The intensity change of the ring breathing mode of adenine at 731 cm^{-1} . The reference electrode is Ag/AgCl.

COLL 362

Stimuli-responsive and nanostructured polymer films for modulating adhesion and friction between surfaces: Fabrications, applications and limitations

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A number of experimental studies have shown that supported thin polymer films can be efficiently used to modulate surface properties including adhesion and friction. Such polymer coatings have properties and responsiveness that are contingent on the chemical composition, size and shape of structure, elasticity. However, they are generally suffering from major shortcomings such as lack of responsiveness selectivity and reversibility, poor environmental stability and limited understanding of the structure–function relationship, which are all critical to design reliable rules for building responsive surfaces in a selective way. Experimental surface forces studies of different classes of

solvated polymer-bearing surfaces carried out using the surface forces apparatus and similar molecular techniques will be presented in order to elucidate the responsiveness mechanism and the structure–property relationship between polymer-coated surfaces in aqueous media. Even though conclusive understanding is still hampered by the difficulty of systematically controlling the polymer grafting density and conformation under shear and compression, the studies suggest that the effective adhesion and lubrication mechanisms involve the facility with which macromolecules under compression remain hydrated and hold a significant amount of water at the surfaces to be lubricated. This could be optimized by immobilizing different microgels on substrates for which the friction coefficient decreased exponentially with an increasing the swelling ratio regardless of the size, surface coverage, and degree of ionization of the particles. In addition, the robustly attached microgel particles were able to sustain high pressure (up to 200 atm) without significant surface damage.

COLL 363

Lubrication and wear protection of soft materials using bioinspired polymers

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The coming end of earth's fossil energy is pressing humanity to develop more efficient and environmentally friendly technologies. Control of wear and fatigue of machine parts has become one of the most important field of research to meet the outstanding energy crisis the world is currently facing. The design of lubricating fluids able to protect fragile surfaces against wear and high friction has been one the several tools used by engineers to improve machines' life time. Inspired by many different biological systems that can resist fatigue wear for decades such as our synovial joints, different coating/lubricating technologies involving polymer brushes either in their molecular form or grafted on the surface have emerged.

We will describe our efforts in the design of lubricating systems designed to protect efficiently fragile materials such as hydrogels. Such systems use synergistic mixtures of bottle brushes (BB) and linear polymer solutions that mimic human synovial fluid and microstructured surfaces that control the lubricating fluid flow during shear. We will show that mixtures of a bottle brush and a linear polymer in pure water or in saline allows to drastically increase wear protection of structured and unstructured hydrogels under a wide range of shearing conditions. We demonstrate that this synergy between the BB and linear polymer emerges from a strong, yet transient, cohesion between the two components forming the boundary film due to entanglements between both polymers. Hydrogels with a two-layers structure mimicking articular cartilage exhibit stronger wear resistance compared to unstructured hydrogels. We show that the

presence of a dense hydrogel layer on top of the shearing surfaces provides enhanced fluid pressurization and excellent wear protection but poor lubrication (high friction coefficient). On the other hand, hydrogels with microchannels pointing towards the surface exhibit excellent lubrication (low friction coefficient) but very poor wear protection. Combination of structure and bioinspired lubricating fluid allows to mitigate these effect of hydrogel structure and to finally obtain superlubricating and superresistant hydrogel surfaces. Different applications of these materials will be described in the biomedical field.

COLL 364

Interaction forces and nanotribology of surfaces modified with bioinspired polymer coatings

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Structuring in polymer and polyelectrolyte films can be induced and controlled by modifying solution conditions or annealing procedures. These phenomena are of interest for controlling adhesion, friction, and lubrication of surfaces in biomedical applications. For example, changes in the solvent quality and the presence of multivalent ions in polyelectrolyte systems cause aggregation and strongly influence the normal and frictional forces between interacting layers. Some of these changes can be reversible upon changing the solution conditions and enable evaluation of the contributions to aggregation from solvent quality and electrostatic bridging of polyelectrolytes. To illustrate these phenomena, examples will be shown of structure formation observed with AFM and its effects on normal and friction forces as studied with the SFA.

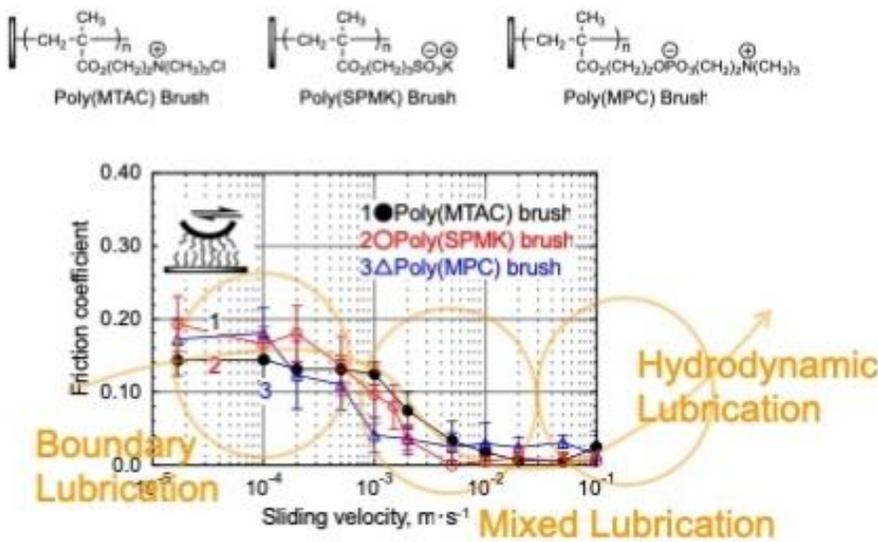
COLL 365

Tribological properties of polyelectrolyte brushes in water

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Surface-initiated controlled radical copolymerizations of 2-dimethylaminoethyl methacrylate (DMAEMA), 2-(methacryloyloxy)ethyl phosphorylcholine (MPC), 2-(methacryloyloxy)ethyltrimethylammonium chloride) (MTAC), and 3-sulfopropyl methacrylate potassium salt (SPMK) were carried out on a silicon wafer and glass ball to prepare polyelectrolyte brushes with excellent water wettability. The frictional coefficient of the polymer brushes was recorded on a ball-on-plate type tribometer by linear reciprocating motion of the brush specimen at a selected velocity of $1.5 \times 10^{-3} \text{ m s}^{-1}$ under normal load of 0.49 N applied to the stationary glass ball ($d = 10 \text{ mm}$) at 298 K. Poly(DMAEMA-*co*-MPC) brush partially cross-linked by bis(2-iodoethoxy)ethane maintained relatively low friction coefficients around 0.13 under humid air (RH>75%)

even after 200 friction cycles. The poly(SPMK) brush revealed a significantly low friction coefficient around 0.01 even after 450 friction cycles. We supposed that the abrasion of the brush was prevented owing to a good affinity of poly(SPMK) brush against water forming a water lubrication layer, and electrostatic repulsive interaction among the brushes bearing sulfonic acid groups. Furthermore, poly(SPMK-co-MTAC) brush with chemically cross-linked structure showed stable low friction coefficient in water even after 1400 friction cycles under the normal load of 139 MPa, indicating that the cross-linking structure improved the wear resistance of brush layer.



Sliding velocity dependence of friction coefficient of polymer brushes in water

COLL 366

Multi-responsive hierarchical coatings: Synthesis and characterization

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Stimuli-responsive polymer coatings enable surface properties to be tuned by external stimuli (i.e. variations of environmental conditions) via changes in their physical conformation, surface chemistry, or both. This capacity enables their use as functional elements in nanotechnologies such as valves in microfluidic devices, as membranes in biomedical engineering or as substrates for culture of biological tissues. However, such coatings usually suffer from major shortcomings such as lack of selectivity and

response rapidity or poor environmental stability. The present work aims to overcome some of these limitations by investigating a new generation of responsive hierarchical coatings whose physical properties and surface chemistry can be tuned independently and reversibly using different external stimuli such as temperature, pH, ionic strength or light. The hierarchical coatings consist of two-dimensional poly(N-isopropylacrylamide) microgel arrays surface-functionalized with polymers whose characteristic dimensions and surface properties can be independently controlled by different stimuli (pH, ionic strength of temperature) according to the desired surface properties.

COLL 367

Soft and slippery: Microgel-coated surfaces under shear

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Polymer layers immobilized at the interface affect the stability and rheology of colloidal dispersions, the lubrication properties and the biocompatibility of artificial surfaces, and static and dynamic forces between coated surfaces. In this work we have investigated the behavior of surfaces coated with dense layers of thermoresponsive pNIPAM-based microgels under compression and shear produced by self-assembly and chemical grafting. We describe how the presence of a long-range repulsive interaction can modify the geometry of approaching surfaces, with significant consequences on the experimental determination of normal and friction forces. Local surface deformations as small as few nanometers must be considered for a complete description of the behavior of surfaces under compression and shear, in particular when the range of action of normal and friction forces are significantly different, as is often the case for macromolecular lubrication. In dynamic conditions we observed the presence of shear-induced lift forces, which are evidenced by a variable gap between the surfaces under shear. The origin and consequences of this force will be discussed in detail. All these findings suggest simple mechanisms for robust control of lubrication by properly tuning stiffness and geometry of the interacting bodies.

COLL 368

Low-pressure contact experiments reveal multiple modes of relaxation in polyacrylamide hydrogels

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The standard for indentation and contact measurements is to perform them at moderate indentation rates to avoid long-term creep but account for quick relaxations that occur

due to fluid effects. However, low-pressure interfaces of interest such as those in the body are not contacted at moderate timescales, but rather held in contact, such as in the knee joint or the eyelid resting on the cornea when the eye is not blinking. Thus we investigate whether contact models like the Hertz model or Winkler model describe the behavior of long-duration soft, hydrated contacts, and whether all creep relaxation be attributed to poroelastic diffusion, as is reported widely in literature.

In this study we perform creep relaxation experiments in three contacting configurations: hard probe-soft substrate, the inverse, and self-mated soft surfaces. Soft probes and flat substrates were molded either in combination delrin/polyolefin molds or between polystyrene plates. The composition was a chemically-crosslinked polyacrylamide of 7.5% w/w acrylamide and 0.3% w/w bisacrylamide crosslinker. The hard probe was a steel sphere of 1.5 mm diameter. A custom microindenter was used in force-control mode to apply and hold a load of 0.50 to 1.00 mN. Simultaneously, either particle-exclusion or particle-inclusion microscopy was used to view the contact area and record its changes in time up to 10 minutes. All experiments are submerged in water at 25°C. All configurations exhibited creep relaxation, or increasing contact area under a constant-load contact experiment. The self-mated contact between the hydrogel probe and hydrogel slab increased in contact area ~ 20%. The soft probe-hard substrate area increased by only 10%. Each experiment was repeated at least 3X. The soft substrate configuration had the greatest extent of contact area growth, the self-mated contact a moderate extent, and the soft-probe the least extent.

These results add a new dimension to contact mechanics of soft materials, moving from quasi-static results to time-dependent results that evolve under constant load. The contact pressure evolution indicated that the Hertz model is only valid over short durations of contact, and that self-mated contact approaches a constant-pressure contact model. Additionally, pressure-driven diffusion of water away from contact is confirmed only briefly, and does not fully explain creep relaxation of polyacrylamide under low applied pressures.

COLL 369

Water content and lubricity in aqueous gels

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Aqueous gels are often selected as model materials for fundamental biotribological studies owing to their high water content, ease of synthesis, and optical transparency. Synthetic hydrogels are highly tunable and can be designed to emulate the mechanical and transport properties of common biological components (biopolymer gels, cells, and tissues) by controlling the water content. Increasing the water content increases the characteristic mesh size, the average spacing between neighboring polymer chains in a three-dimensional hydrogel network. In 1989, Canal and Peppas showed an empirical relationship between water content and mesh size (measured by wide-angle X-ray scattering) for charge-neutral, covalently cross-linked hydrogels. In 2015, Urueña et al. systematically varied the water content of polyacrylamide hydrogels by increasing the

polymer concentration and used small-angle X-ray scattering to measure the mesh size, which ranged from about 1 to 10 nm. Urueña et al. then performed a suite of self-mated or “Gemini” experiments using a custom-built microtribometer and found an inverse relationship between friction coefficient and mesh size, and thus water content. Here, we explore the scaling models that reveal high water content gels are optimized for lubricity as well as contact pressure, shear stress, and resistance to draining.

COLL 370

Water content and adhesion in aqueous gels

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Mucoadhesion occurs when two surfaces, one of which is a mucous membrane, adhere to one another, and is a concept relevant to pharmaceutical and biomedical fields. Despite the importance of mucoadhesion, there are relatively few models for contact mechanics involving mucous layers. Modeling soft, thin (< 100 μm) layers as a Winkler Foundation or a “bed of springs” can provide closed-form solutions for adhesive contact problems, as demonstrated by Hill and Sawyer in 2010, but more experimental contact mechanics studies are needed. Synthetic aqueous gels are useful model materials for understanding the contact mechanics and adhesion relevant to interactions between biological systems and industrial products, from oral dosage forms to contact lenses. Hydrogels are inexpensive, easy to synthesize, and can be used to systematically study relationships between structure and material properties for high water content gels, including permeability and osmotic pressure, both of which are known to strongly depend on the polymer mesh size. The mesh size—the characteristic length scale describing the average distance between polymer chains in the gel matrix—is influenced by the water content of the gel. Here, we report the impact of water content on the adhesion of soft, thin, layers of aqueous gel. We demonstrate that the adhesion between two aqueous gels submerged in a good solvent (water) increases with increasing difference between the equilibrated and non-equilibrated osmotic pressures (swollen vs. non-swollen conditions). Depending on the differences in osmotic pressure, closed-form solutions estimate the maximum force of adhesion to be 5-500 μN , which agrees with experimental findings. The findings of this work are relevant to understanding adhesion of natural (mucosal) and synthetic (hydrogel) systems.

COLL 371

Humidity-dependent and aqueous-immersion AFM: Nanotribological analysis of biomedical coatings

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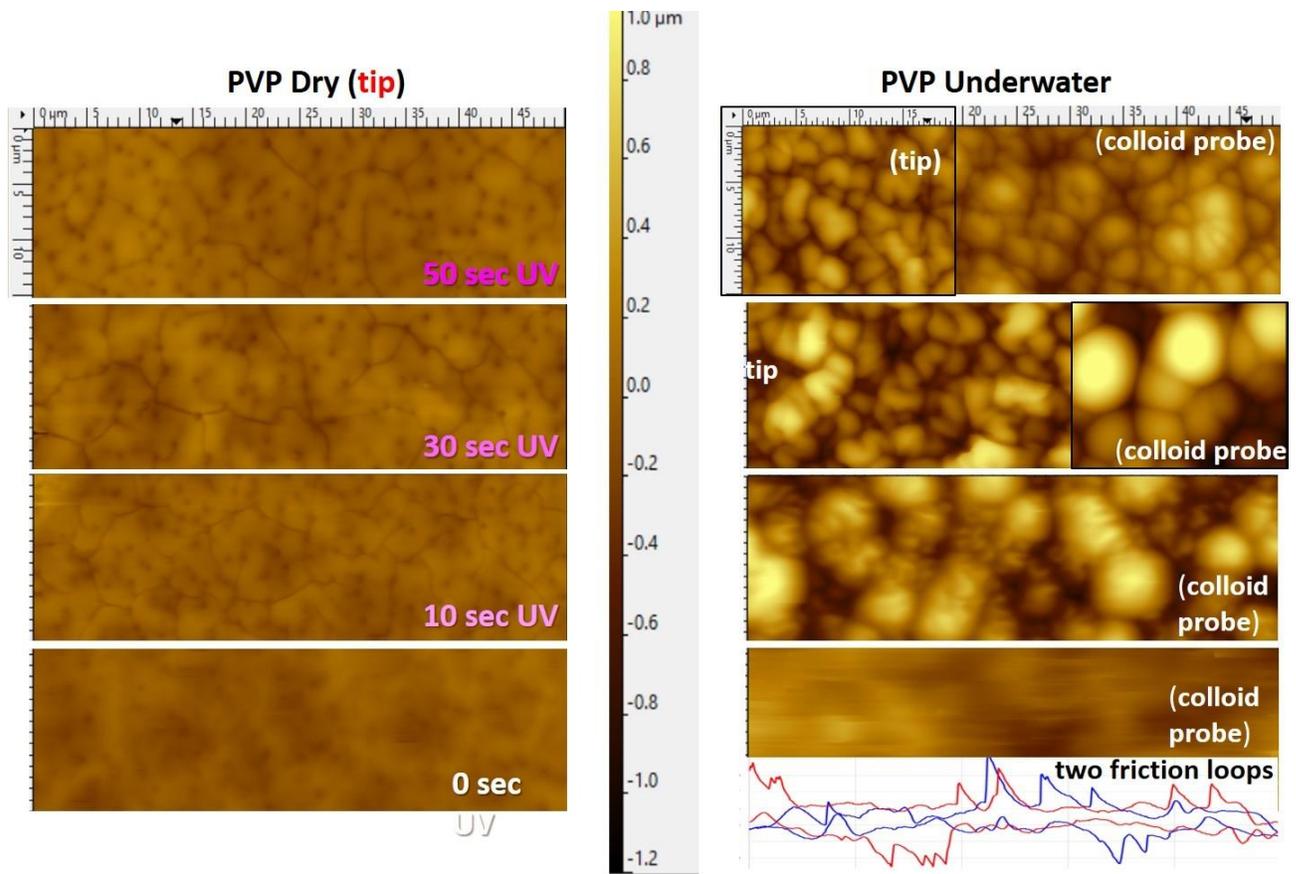
States (2) Sartorius, Göttingen, France (3) Boston Scientific, Inc., Maple Grove, Minnesota, United States

The nanoscale role of water at tribological interfaces on lubricious biomedical coatings is explored in AFM measurements. Our purview includes both normal and shear force methods, versus humidity and under full aqueous immersion.

On polyacrylamide coatings (PAm) we analyze dramatic changes in the shape of force-distance curves as a function of relative humidity (RH). Among other metrics, we find a maximum (rather than monotonically increasing) pull-off force from PAm versus relative humidity, in the mid-80 to low-90 RH percentage range, assigned to a glass-rubber transition and akin to loss modulus as a function of temperature. We further explore this transition as a function of coating thickness (confinement). In sliding contact we correspondingly record a maximum in both friction force and the propensity for shear-induced plastic deformation (“rippling”).

On polyvinyl pyrrolidone (PVP) coatings we similarly explore the humidity dependence of the glass-rubber transition but for different degrees of UV-activated crosslinking (cure). We find a 2-3% variation in the critical RH for a glass-rubber transition over a range of UV cure times, equivalent to a ~10 C shift in T_g . Normal force measurements on gel-state PVP under aqueous immersion reveal a <1 kPa to >100 kPa variation in elastic modulus versus crosslinking from 0-50 seconds UV cure, and corresponding differences in coating swelling. Friction force imaging with a colloid probe (to avoid tearing) further explores this curing dependence, revealing single macromolecular (Langevin) shear-extension forces for 0-5 second UV cure that are absent at higher levels of cure.

We relatedly discuss our developments in data analysis algorithms to enable the measurement science.



COLL 372

Nanostructured protein capsules

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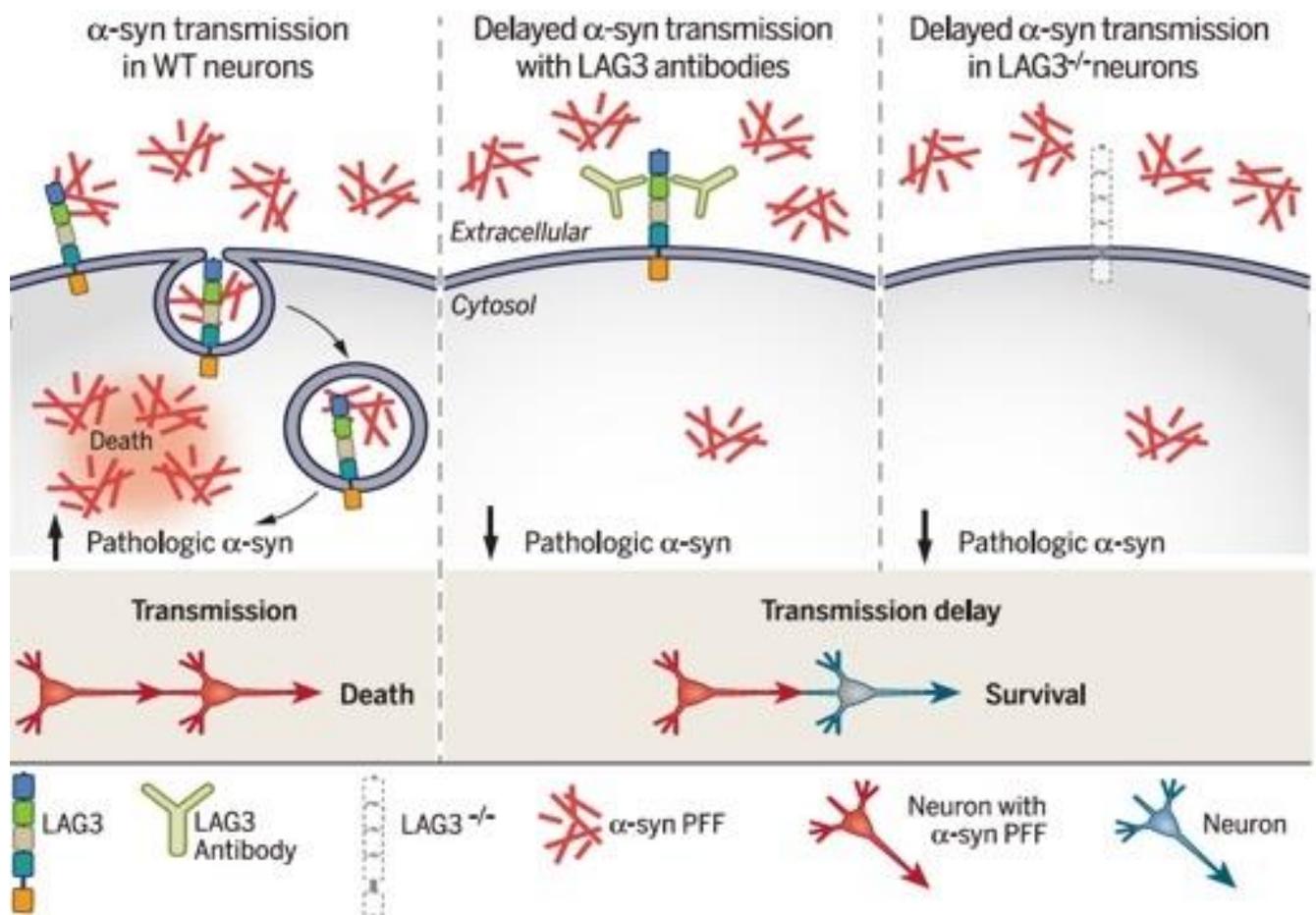
This talk outlines our efforts to explore the use of natural peptides and proteins as building blocks for the synthesis of microcapsules. We use the self-assembly of polypeptide chains into nanofibrils to define the structure of these materials on the nanoscale, and exploit microfluidics to determine their micron scale morphology. Such capsules can be used for the stabilisation, storage and release of sensitive materials, in particular aggregation prone antibodies. Moreover, we explore the use of peptide self-assembly within microdroplets as the basis of active materials and demonstrate chemo-mechanical actuation in such systems.

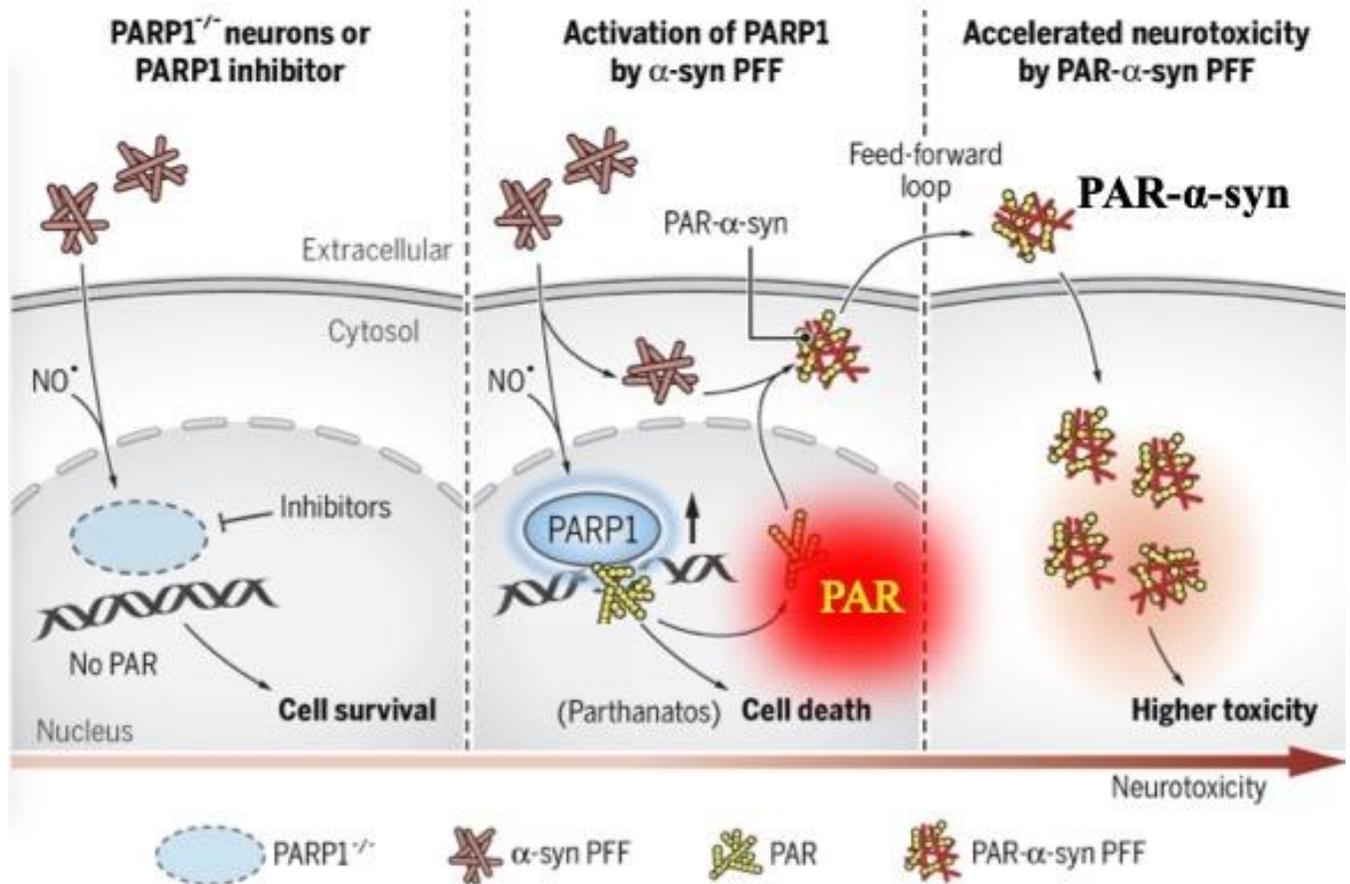
COLL 373

Transmission mechanism of pathological alpha-synuclein

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Emerging evidence suggests that prion-like α -synuclein (α -syn) cell-to-cell transmission is an important driver in the pathogenesis of Parkinson's disease (PD). Recently, we discovered LAG3 as the receptor of pathological α -syn transmission (1). Furthermore, internalized pathological α -syn caused PARP-1 activation and PAR accumulation, which converted α -syn into a more toxic strain and accelerated neurotoxicity (2). Depletion/inhibition of LAG3 or PARP-1 can substantially inhibit α -syn-induced neurodegeneration.





COLL 374

Phosphorylated amyloid protein forms different stains leading to neurodegenerative diseases

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Multiple lines of evidence indicate that cerebral amyloid protein plays a key role in pathogenesis of neurodegenerative disease, such as Alzheimer's disease, Parkinson's disease, Huntington's disease, and etc¹. Studies have shown that misfolding and local concentration of amyloid lead to formation of amyloid aggregates directly related to neurodegenerative diseases. Abnormal assembly of amyloid leads to the formation of senile plaques and is an important pathological hallmarks of severe neurodegenerative diseases².

Recently, research indicates that self-assembly of amyloid monomers forms oligomeric

species and amyloid fibrils in vitro, and they are toxic to cells. However, the cause of the presence of amyloid as a toxic molecular species of seeds remains unknown. In vitro, different strains can be produced by varying salt concentration, temperature and pH, and these strains can form different phenotypes when injected into mouse brains³. In vivo, a large number of phosphorylated proteins are present in the senile plaques of patient samples. Therefore, studies have suggested that phosphorylated modified amyloid may cause it to form different strains and is the key to disease progression⁴. In order to study the important role of phosphorylation on the structure and function of amyloid protein, Alzheimer's disease related protein β -amyloid with phosphorylated at Ser8 (pS8A β) and Parkinson's disease related protein α -Synuclein with phosphorylated at Ser129 (pS129 α -Syn) were synthesized. The results indicate that phosphorylation results in the formation of different strains of amyloid, respectively. We have also demonstrated that strains formed from phosphorylated monomers are more cytotoxic than non-phosphorylated monomers.

COLL 375

Peptide networking of beta 2 microglobulin over nano-gold colloidal particles' surfaces

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The aggregations of beta 2 microglobulin (β 2m) coated gold nano-colloid particles were investigated for nano-gold colloidal particles ranging from d (diameter) = 10 nm and 100 nm. Based on the analysis of the images taken by TEM (Transmission Electron Microscopy), the average spacing between adjacent gold nano-particles in an aggregate was extracted to be approximately 2 nm. Considering that the dimension of β 2m to be approximately 5 nm \times 9 nm prolate, the binding of peptides at the interface must be in an "entangled" conformation causing the inter-surface distance to be 2 nm. Based on the available hydrophobic sequences for adsorbing over gold colloidal particle's surface, aromatic-rich region in residues 62-70 implying ⁶³R: Arginine, ⁶⁶K, or ⁶⁹K: Lysine to be a plausible binding sites to the nano-surface. Thus, β 2m must be exhibiting δ^- dominated region (e.g., ⁹²E: Glutamic Acid, ⁹⁴D: Aspartic Acid, or ⁹⁵E) to the outward and those sequences are expected to be networking with δ^+ sequences, such as ⁹³K, ⁹⁹R, ¹⁰²H: Histidine, ¹⁰⁹K, ¹¹²K, and ¹¹⁵R.

COLL 376

Peptide assembly nanostructures: Structure, modulation and clinical applications

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Peptides and proteins are known to form a variety of ordered structures via assembling processes. The insight of the assemble peptide and protein structures could provide

basis for developing diagnosis and therapeutics for significant diseases, including neurodegenerative diseases and tumors. In this work, the peptide assembly nanostructures are applied in the Liquid biopsy nanotechnology, including detection of circulating tumor cells (CTC) and extracellular vesicles (EVs), which are crucial for the prognosis and diagnosis of cancer. We designed peptides binding to the target proteins with high affinity and selectivity. The peptide assembly nanostructures are conjugated with magnetic nanoparticles for fabrication of peptide-nanoparticles. Efficient and detection of circulating tumor cells are achieved by using the peptide-modified magnetic nanoparticles. The clinical application of this technology in breast cancer, lung cancer and other cancers proved the high sensitivity of this technology, which is also confirmed by the detection of CTC of the patients with stage Ia lung cancer. The molecular phenotyping of cancers by immunostaining of single CTC cells are facilitated for prognosis and prediction of immunotherapy efficacy of cancers. EVs carry molecular information from the cells of origin and are biomarkers of cancer. However, detection and molecular analysis of EVs has been challenging due to their nano-scaled size. Here, an assessment for the detection and molecular phenotyping of serum EVs based on microbead-assisted flow cytometry is established. The clinical utility of this method is validated in the diagnosis and HER2 phenotyping of breast cancer. EV-based HER2 phenotyping is consistent with tissue-based HER2 phenotyping by immunohistochemistry (IHC) and can be used as a surrogate for the invasive tissue assessments. The detection of CTCs and EVs enables rapid, non-invasive, and semi-quantitative detection and molecular phenotyping of cancer, and would help to personalized treatment and cancer survival. This technology is also applied in the evaluation of invasiveness and progression of lung cancer, pituitary adenoma and glioma.

COLL 377

Determination of polypeptides conformation in water with infrared nano-spectroscopy

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The folding and acquisition of native structure of proteins is critical to life-enabling biological processes. However, protein misfolding can lead to toxic amyloid aggregates, linked to the onset of neurodegenerative disorders such as Alzheimer's disease. To shed light on the molecular basis of protein function and malfunction, it is crucial to access structural information of single protein assemblies and aggregates under native conditions. Conformation-sensitive spectroscopic methods lack the spatial resolution and sensitivity necessary for characterizing heterogeneous protein aggregates in water. Photothermal induced resonance (PTIR) is an emergent AFM technique that provides IR spectra and maps with nanoscale resolution, thus opening a nanoscale observation window on the conformation of peptides and proteins, but its implementation in water has been challenging.

After a brief PTIR introduction to PTIR I will show that such limitations can be overcome

and that, for the first time, PTIR can be leveraged to acquire conformationally-sensitive nanoscale infrared spectra in water with high signal to noise ratio (SNR > 70). Using conventional AFM probes, we study supramolecular aggregates of diphenylalanine (FF), the core recognition module of the Alzheimer's disease β -amyloid peptide, and its derivative boc-diphenylalanine (Boc-FF). We demonstrate that nanoscale resolved IR spectra and maps in air, and water can be obtained with comparable SNR and lateral resolution, enabling accurate identification of the chemical and structural state of the aggregates at the single aggregate level. Our data confirm that the FF and Boc-FF fibrils differ structurally at the individual fibril level due to the additional presence of α -helical conformation in the Boc-FF with respect to the pure β -sheet conformation of FF. In the final part of my talk, I will introduce a novel nano-sized AFM probe that leverages integrated cavity opto-mechanics to improve, in air, the PTIR sensitivity (50x), time resolution (1500x) and throughput (>2500x) concurrently. I will highlight the potential of these novel nanoscale probes to also dramatically improve the PTIR performance in liquid thanks to a greatly reduced cantilever drag.

COLL 378

Characterizing the microscopic dynamics of biological macromolecules during folding reactions via direct observation of transition paths

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Transition paths represent the brief moments in a reaction when the energy barrier separating reactants from products is crossed. They contain crucial information about the mechanism of the reaction. In the context of biomolecular folding reactions, where the mechanisms are very complex, they hold the promise of providing previously unavailable information about the transition states that dominate the reaction kinetics. We recently demonstrated the first direct measurements of transition paths in the folding of single biological molecules. Here we will describe how using transition-path measurements on DNA hairpins as a model system to quantify the diffusion coefficient that characterises internal friction, via the transition path times and velocities. The transition path velocities will also be used to estimate the importance of diffusive barrier-recrossing events by determining the transmission factor from classic transition-state theory. Lastly, the shapes of the transition paths will be compared to theoretical estimates, and the variance in the path shapes will be used to show sequence-dependent diversity in the transition paths.

COLL 379

Bioinspired siRNA delivery system based on higher order architecture of designer peptides

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The therapeutic potential of small interfering RNA (siRNA) has long been recognized, but effective delivery remains challenging. The higher-order architecture observed in biological systems, like viruses, is effective in nucleic acid transport, but immune response of the host prohibits their broad applications. Here we describe a peptide/siRNA quaternary complex that functions as an siRNA delivery system. The rational design of a peptide assembly, inspired by viral capsids, is based on sequences that are characteristic of two functional peptide families: collagen and the cell penetrating peptide (CPP). The collagen domain provides structural stability and the folding framework while the CPP domain allows for effective penetration of biological barriers. The complex forms stoichiometric, 10nm nanoparticles, that show fast cellular uptake (<30 min), effective siRNA release, and gene silencing. The complex provides capsid-like protection for siRNA against nucleases without being immunostimulatory, or cytotoxic. Our data suggests that delivery vehicles based on synthetic quaternary structures that exhibit higher-order architecture may be effective in improving delivery and release of nucleic acid cargo.

COLL 380

NMR characterization of spider silk protein nanoparticle pre-assemblies

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In the field of biomimetics, spider silk is a very attractive material for medical, textile, defense and construction applications due to a host of impressive mechanical properties rivaling (and in some cases exceeding) man-made materials as well as the potential for greener polymer chemistry. Presently, however, synthetic spider silk fibers derived from recombinant proteins have disappointing mechanical properties, far inferior to their native counterparts. Much of the problem lies in the poorly understood molecular and nanoscale fiber assembly mechanisms for the large (>300 kDa) spider silk protein components and their conversion into fibers. We have applied a multi-technique approach to probe the nascent stages of spider silk assembly to better understand the biochemical mechanisms and triggers responsible for spider silk formation. Combining results from solution NMR (nuclear magnetic resonance), DLS (dynamic light scattering), cryo-TEM (cryogenic transmission electron microscopy) tomography, and coarse grain molecular dynamics simulations, we have produced a model for the early folding and organization of spider silk proteins. Spider silk protein fibroins (spidroin) assemble into hierarchical structures on the order of 200-300 nm comprised of approximately 300 silk protein monomers. These discreet micelle-like nanoparticle structures are an assembly of highly disordered (random coil) silk proteins until the application of shear force to the solution, upon which distinct fiber-like substructures appear within the larger parent nanoparticles. We believe that these micelle-like

structures are one key to understanding the formation of spider silk and are critical in order to obtain the necessary mechanical properties in the final fibers. Our research team is now exploring the conditions which stabilize these particles with the goal of spinning fibers from native dope solutions. In this presentation we will report on recent protein solution NMR studies to determine the intermolecular interactions and dynamic processes responsible for silk protein nanoparticle formation, stabilization and further processing into fibers.

COLL 381

Interaction of atomic oxygen with the Ag(111) surface

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Silver surfaces act as important industrial catalysts for the partial oxidation of ethylene to ethylene oxide and methane to methanol. While significant strides have been taken towards understanding the mechanism of heterogeneous catalytic oxidation by silver, the role of subsurface oxygen in such catalysis has yet to be elucidated. Subsurface oxygen is adsorbed just beneath the surface of the metal and is believed to play an important role in surface reconstruction and oxidation catalysis. In the present study, density functional theory (DFT) was used to study the interactions of atomic oxygen with the surface and subsurface of the Ag(111) surface. The goal was to investigate the adsorption of atomic oxygen at different coverages and examine its effects on the structural and catalytic properties of silver. Our study showed that adsorption of atomic oxygen was strong at low coverage but became weaker with an increase in coverage, much more so for surface oxygen than for subsurface oxygen. Therefore, at higher and industrially relevant oxygen coverages, oxygen preferred to bind to the subsurface than to the surface. Based on the results from DFT, we constructed an analytic model that explains the difference in coverage dependence of surface adsorption versus subsurface adsorption and consequently why surface and subsurface oxygen might have qualitatively different effects on the electronic, geometric, and catalytic properties of silver.

COLL 382

Oxygen dissociation on the Ag/Cu(111) near surface alloy

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Experiment and theory have both demonstrated the ability of near surface alloys (NSAs) to improve the reactivity of catalytic surfaces. The electronic and catalytic properties of NSAs are altered by the presence of a solute metal confined to the first few atomic

layers of a host metal. The AgCu NSA investigated herein forms a well-characterized reconstruction as a strain relieving mechanism due to the lattice mismatch between Ag and Cu. Though the structural and electronic properties of this system are well characterized, the catalytic properties remain to be investigated. Our interest in AgCu stems from the use of Ag-based catalysts in many industrial oxidation reactions, such as the partial oxidation of ethylene to ethylene oxide. Industrial catalysts for this reaction typically operate at non-optimal conditions to control oxidation products and avoid total oxidation to CO₂. We investigated the ability of AgCu to dissociate oxygen as this is the rate limiting step for most oxidation reactions.

A combination of density functional theory (DFT), temperature programmed desorption (TPD) and scanning tunneling microscopy (STM) techniques were used to elucidate the nature of oxygen dissociation on AgCu and how it compares to oxygen dissociation on pure Ag. We report enhanced oxygen dissociation on extended Ag ensembles on Cu(111). In a series of STM investigations, atomic oxygen coverage on Ag was observed to scale with increasing oxygen exposure. Through time-lapse STM images, atomic oxygen was found to diffuse locally to specific sites on the Ag ensembles. DFT and TPD were used to probe the dynamic nature of this system as well as its activity in partial oxidation reactions. The results of these studies highlight the potential for this NSA to perform partial oxidation reactions with enhanced selectivity and activity.

COLL 383

On-surface topochemistry of helicenes

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Surfaces functionalized with helicenes are of interest for chiroptical electronic devices or for electron-spin filtering. While self-assembled layers facilitate studying interesting phenomena, covalently linked chiral modified materials would be much more robust and therefore better suited for applications.

We report the stereoselective chemistry of different helicene species on noble metal surfaces. The stereochemical analysis of diastereoisomers formed on the surface is performed by scanning tunneling microscopy (STM). The Ullmann coupling reaction of 9-bromo[7]helicene proceeds with a high probability for heterochiral product, while homochiral products are favoured in C-C coupling dimerization and trimerization of 2-bromo[4]helicene and 2,3-dibromo-[4]helicene (Fig. 1). The diastereoselective chemistry is explained by topochemical effects due to the surface alignment of the helicenes during reaction.

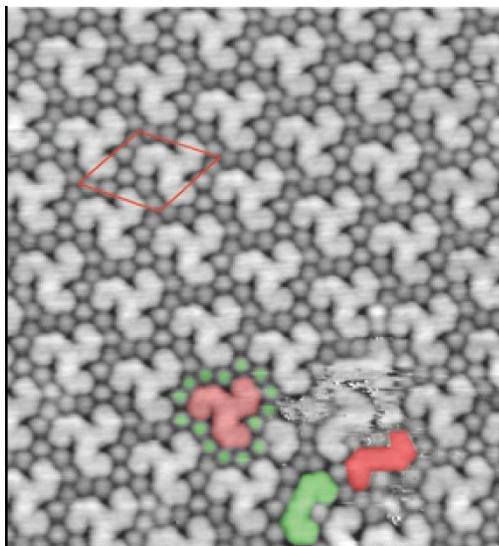


Fig. 1. STM image of homochiral tris[4]helicene (trisphenanthro[3,4; 3',4'; 3'',4''-b,h,n]triphenylene) after Ullmann coupling of dibromo[4]helicene. Each molecule is surrounded by bromine atoms (green dots) that were released in the C-C coupling reaction.

COLL 384

Lithium-doped TiO₂(110): Electronic structure and reactivity

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Tuning the electronic properties of semiconducting surfaces is important for a variety of applications that include catalysis, photovoltaics, sensors and light-emitting devices. In the present work, the room temperature deposition of lithium in ultrahigh vacuum (UHV) on sputter cleaned TiO₂(110) has been investigated using X-ray photoelectron spectroscopy (XPS), and the effects of lithium doping on the electronic structure of the surface have been studied with ultraviolet photoelectron (UPS) and inverse photoelectron spectroscopies (IPES). Changes in the valence and conduction band as a function of lithium dosing have been measured, and gap states, consistent with Ti (3d) character, have been observed. As expected, lithium lowers the work function of the surface by as more than 2.5 eV. Penetration of lithium into the bulk also occurs, as confirmed by XPS, and this is correlated with changes in the conductivity of the single crystal samples. The effects of electron donation on the reactivity of the surface have also been studied using thiophene as a model adsorbate by dosing it in UHV. The experimental studies are accompanied by density functional theory (DFT) calculations.

COLL 385

Synthetic surface chemistry: Versatile route to low-dimensional nanostructures

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Understanding the catalytic conversion of small molecules was a major driving force behind the development of surface science. The knowledge and the techniques of this field, however, can also be used for the synthesis and characterization of new functional materials. In this lecture, principles of the on-surface synthesis of low-dimensional nanostructures will be discussed using selected examples, including novel conjugated hydrocarbon and nitrogen-doped materials, organometallic compounds, and metal complexes with cyclic and open-chain topology. A wide range of surface-science techniques is applied to reach a comprehensive understanding of the zero-, one- and two-dimensional products. The competition between ring and chain formation can be steered by kinetic and thermodynamic reaction control [1] and on-surface template effects, which were used for the synthesis of lanthanide superphthalocyanines and their open-chain polycyanine counterparts. The electronic properties of the materials can be precisely tuned by atomic-level structural control. For example, it will be shown that the band gap of graphene nanoribbons can be adjusted with a periodic array of pores or structural elements with non-alternant topology.[2] Unusual regionselectivity of C-C coupling reactions through monoselective C-H bond activation will be explained based on the relevant reaction mechanisms.

COLL 386

Designing nanostructures for plasmon-enhanced spectroscopies to probe chemistry at surfaces

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Engineering plasmonic nanostructures for controlled light-matter interactions has been a major research focus for broad applications including chemical and biological sensing, photovoltaics, photocatalysis, and subwavelength optics. Much research activity has focused on elucidating the design rules for plasmonic antennas in order to control the optical responses through structure or assembly. Nanosphere template lithography (NTL) is a simple, versatile fabrication method for preparing plasmonic nanoparticles with controlled structural properties. We have used NTL to prepare gold and silver nanocrescents exhibiting broadly tunable plasmons, from the visible into the infrared spectral range. Recently we extended NTL to fabricate aluminum nanocrescents. Aluminum as a plasmonic material has gained attention because of the abundance of the material compared to noble metals. Aluminum also provides access to ultraviolet plasmon activity. When extending NTL to aluminum, the rather robust oxide layer poses a challenge, thus limiting the scope of shape control. In order to overcome this

challenge, we introduced a sacrificial copper layer into the NTL fabrication process, ultimately eliminating the need for a milling step. By combining polarization control and fabrication details such as material, structure aspect ratios through length and backbone width, the plasmons in nanocrescents may be tuned from the ultraviolet through the infrared. The ability to access unique antenna shapes as well as applications of these plasmonic structures in surface enhanced Raman, infrared absorption, and circular dichroism spectroscopy applications in analyzing surface chemistries will be discussed.

COLL 387

Neutron scattering investigations of molecular interactions with surfaces of nanomaterials

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Many of the technological challenges currently faced by society involve understanding and modifying the interaction of molecules with the surfaces of nanomaterials. Often times these issues involve familiar topics such as gas separation, lubrication and energy conversion, storage or generation. Although neutron scattering is widely viewed as a highly penetrative probe of bulk materials, both elastic and inelastic scattering methods can be effectively employed to examine the structure and dynamics of molecular interactions with nanometer scale materials. In this presentation we will demonstrate that by employing a research regime that includes novel material synthesis, adsorption thermodynamics, and computational modeling an attractive opportunity exists for observing and understanding the behavior of single and multilayer molecular adsorption on pure and metal decorated surfaces. Selected examples of these investigations will be discussed. Among them are: [1] the structure and wetting properties of normal and cyclic alkane films on MgO, graphite and h-BN, [2] the structure and dynamics of methane and hydrogen adsorbed on MgO [3] spillover of hydrogen interacting with Pd decorated ZnO. The advent of new, high-intensity, pulsed sources such as SNS in the US and ESS in Lund presents exciting possibilities for new discoveries in molecule-surface interactions and advanced materials.

COLL 388

Heterogeneous reactions on atmospherically relevant sea spray aerosols

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The surfaces of tropospheric aerosols can profoundly affect the composition of the atmosphere by serving as sites for heterogeneous reactions with trace gases. This presentation focuses on reactions occurring on sea spray aerosols (SSA) which

represent one of the most abundant surfaces in the atmosphere. When bubbles burst at the surface of the ocean, SSA particles become enriched in organic species relative to inorganic salts. Due to complex interactions between water, ions, and organic species, the interface of SSA particles is highly complex and distinctly different from the bulk composition. This presentation will describe recent studies focusing on improving our understanding of the reactivity of realistic sea spray aerosols. A discussion on how the chemical complexity occurring at chemically complex interfaces results in unexpected behavior will be presented.

COLL 389

Environmental marine interfaces: Inherent electric fields from dipole and electrolyte organization

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Ions and molecular dipoles have metastable configurations at aqueous interfaces that give rise to inherent electric fields in the surface region. This surface potential is measured as is the organization of the water, solute, and insoluble surface active components through spectroscopic means and imaging. 3D vs 2D molecular organization of marine relevant interfaces is discussed to understand the basic science underpinnings of atmospheric aerosol and ocean surface chemistry.

COLL 390

Catching the freshwater wave: Lakes, aerosols, and algal blooms

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Aerosol production from wave breaking is one of the most abundant sources of aerosol globally, but emissions from freshwater lakes are poorly understood in comparison to sea spray aerosol (SSA). In addition, harmful algal blooms (HABs) can lead to aerosolization of toxins like microcystins, which has the potential to lead to exposures to local populations. Given their small size and chemical complexity there is a significant analytical challenge when measuring these environmental contaminants. Herein, the chemical and physical properties of lake spray aerosol (LSA) from pristine freshwater and HABs are discussed. We will discuss measurements of particles along the coasts of the Great Lakes, inland, and aloft at cloud heights from flight measurements using a suite of microscopy, spectroscopy, and mass spectrometry measurements. As LSA can be generated and act as CCN, IN or eject toxic materials from harmful algal blooms, an improved understanding of LSA emission and physicochemical properties is needed to determine the impacts on meteorology, climate, and health in the Great Lakes region.

COLL 391

Integrated computational and experimental strategies to explore air-water interfaces in sea spray aerosols and related model systems

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Atmospheric aerosols have long been known to alter climate by scattering incoming solar radiation and acting as seeds for cloud formation. In particular, sea spray aerosols (SSAs) are emitted over nearly three-quarters of our planet, yet the impact of SSAs on Earth's radiation budget remains highly uncertain. Individual SSA particles containing a diversity of biological species including proteins, enzymes, bacteria, viruses and an array of organic compounds including fatty acids and sugars. In this talk, I will discuss how we have tightly coupled experimental (observational and laboratory studies) and computational (simulation-based) approaches to gain new insights into SSA and model interface chemistries, with particular emphasis on work done in collaboration with the lab of Prof. Vicki Grassian (University of California, San Diego).

COLL 392

Physical chemistry of environmentally relevant multicomponent interfaces

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Oxides and hydroxides of transition metals are key players in the heterogeneous chemistry of reactive components in atmospheric aerosols, soil particles, and pollutant removal technologies. Molecular-level understanding of surface processes at the gas/solid and liquid/solid interfaces demands using simple model systems and a suite of analytical techniques (surface-sensitive and bulk) coupled with computational chemistry and mathematical modeling tools. This talk will focus on the surface chemistry of the hematite/water interface crucial to understanding the aging of iron-containing atmospheric dust and controlling the fate of oxyanions in soil water. The significance of this research will be highlighted in relation to improving models that include atmospheric and cloud chemistry, and pollutant fate and transport.

COLL 393

Surface-mediated photochemical pathways for the formation of HONO and NO_x

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Recent field studies suggest that atmospheric nitric acid (HNO₃) and particulate nitrates may represent a significant daytime source of nitrogen oxides (NO_x) and nitrous acid

(HONO). Sunlight can initiate indirect photochemical processes on nitrated particles leading to NO_x and HONO formation. First, adsorbed nitric acid can undergo symmetry breaking, resulting in changes in its photochemical reactivity. Second, semiconductor components of atmospheric aerosols can induce photocatalytic decomposition of adsorbed HNO_3 . Finally, chromophores within tropospheric aerosols can photosensitize nitrate particles and enhance its photodecomposition. In this work, we present the role of these three indirect heterogeneous photochemical pathways in the formation of HONO, N_2O and NO_x from chemisorbed nitric acid and nitrate particles. We present a combination of vibrational spectroscopy and quantum calculations for the study of nitrated tropospheric aerosols and gaseous products generated from its photodecomposition. First, insulator components of tropospheric aerosols, such as $\gamma\text{-Al}_2\text{O}_3$, are compared to semiconductor components (TiO_2 , $\alpha\text{-Fe}_2\text{O}_3$, ZnO) to contrast the heterogeneous photochemistry via symmetry breaking to that of a photocatalytic process. Photocatalysis of HNO_3 on TiO_2 was found to have the highest photochemical rate constant, almost doubling the rate constant for the photodecomposition of HNO_3 on $\gamma\text{-Al}_2\text{O}_3$. All heterogeneous photoreactions produced HONO, N_2O and NO_x . The effect on relative humidity on the HNO_3 photocatalysis was examined spectroscopically and computationally, with water participating in the photocatalytic reaction of HNO_3 . Finally, we also present photosensitization of nitrate particles and NO_2 , an additional pathway for daytime HONO formation.

COLL 394

Surface chemistry at a primarily undergraduate institution

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Surface chemistry is the study of chemical reactions at surfaces and interfaces, which can be applied to many different types of chemistry. At state-funded Primarily Undergraduate Institutions (or PUIs), studying surfaces and interfaces can be challenging in these financially trying times as the equipment used is generally expensive and requires continual maintenance. Creative solutions, such as building your own analysis systems or using another department's equipment, is needed in order to accomplish research outcomes. Here an example of how two different surface chemistry research projects were advanced with collaborations and minimal expense will be presented. Advantages of projects like these for student undergraduate researchers, such as hands-on experience with techniques like XRD or SEM-EDX or fixing equipment, will also be discussed.

COLL 395

Thermodynamics and phase of sea spray aerosol droplets using microfluidics

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Measurements of phase and phase change events in chemically complex aqueous droplets provide valuable information for understanding the dynamic processes in these complex micro-environments. For example, atmospheric aerosol droplets regularly undergo phase changes including liquid-liquid phase separation and crystallization. The phase and mixing state of the aerosol has profound effects on particle morphology, species uptake, equilibrium partitioning, activation to cloud condensation or ice nuclei, and optical properties. Many factors play a role in determining if a droplet will liquid-liquid phase separate, as well as its resulting orientation or morphology of the two phases, such as temperature, relative humidity, and chemical composition of the respective phases. In this work, aqueous droplets containing sea spray aerosol samples and chemical mimics are generated in microfluidic channels and stored in passive traps until dehydration to study the influence of relative humidity and water loss on phase behavior. The solution volume of the droplet trapped changes with respect to time, and is calculated by image analysis and correlated with the concentration of the solution to determine water activities at each time interval. The research will help determine mixture liquid-liquid phase separation and efflorescence events of droplets that include presence of other dissolved components and tend to decrease the water activity. The measurements will also be used to parameterize statistical thermodynamic modeling for predictions of thermodynamic properties of aqueous aerosols as a function of relative humidity.

COLL 396

Nanoparticle diffusion at liquid-solid interfaces and its implications on *in situ* liquid phase TEM studies

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Liquid cell transmission electron microscopy (LC-TEM) is becoming a very powerful technique for investigating processes take place in a liquid with nanometer-level resolution. The most common implementation of this approach is to encapsulate the liquid samples in between microfabricated chips with thin, electron transparent silicon nitride windows. It is often reported that nanoparticles move very slowly within these liquid cells, orders of magnitude slower than the expected diffusion calculated from the Stokes-Einstein equation for Brownian motion. One focus of our group's research has been to explain the origin of this suppressed diffusion by pushing the temporal resolution of LC-TEM with fast frame rate direct electron detection cameras. We will show that nanoparticle dynamics in these cells do not exhibit a Gaussian displacement distribution and exhibit characteristics of anomalous diffusion, in particular, that of continuous time random walk. By comparing the motion (both translation and rotation) of nanoparticles with different shapes, we further show that the nanoparticle motion can, in fact, be explained by the localized adsorption of nanoparticles to specific areas on the silicon nitride surfaces. Next, we will describe experiments where we looked at how the motion is influenced by the electron beam flux, solution chemistry, and surface treatments. These results indicate that the electron beam induced motion of

nanoparticles in these liquid cells can be rationalized by treating silicon nitride as a chemically inhomogeneous surface where the surface charges change in response to the pH shift caused by the radiolysis of water.

COLL 397

Dynamics of fluorescein embedded to amyloid beta peptide 1-40 at nano-scale gold surface

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An electronically excited fluorescein dye embedded to the amyloid beta peptide 1-40 ($A\beta_{1-40}$) (FAB) was examined with various sizes of gold nano-colloidal particles of 20 nm in diameter. The fluorescence intensity of FAB was reduced compared to that of free fluorescein. The profile of the band was roughly the same whether the fluorescein being isolated in solution or placed in the $A\beta_{1-40}$. As the gold nano-particles were mixed, the intensity further reduced. Entire components of the fluorescence peak were explained by two components, and the peak position of each component stayed roughly the same for all pHs. The fluorescence decay time, τ , was monitored at two different band ranges A) 500 ~ 550 nm (λ_A) and B) 550 ~ 600 nm (λ_B). As pH ranged between 2 and 12, a water environment created homogeneous dynamics for fluorescein, meaning that the decay spectrum exhibited about the same decaying features (*i.e.*, similar $\tau \sim 3$ nano sec) for both monitored bands λ_A and λ_B . However, more precisely, FAB displayed two distinct groups of faster decay rate ($\tau \sim 1$ nano sec) for acidic and neutral conditions (pH 2~7) and a slower decay ($\tau = 3 \sim 4$ nano sec) for both monitored bands λ_A and λ_B . The entire dynamical profile was considered to be dominated by interaction between a fluorescein and the gold nano-particle surface but not by $A\beta_{1-40}$.

COLL 398

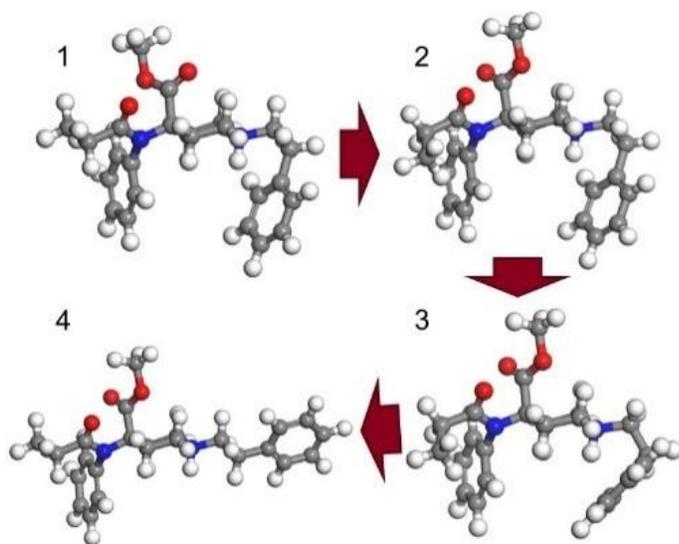
Characterization of carfentanil and remifentanil in solution and on surfaces

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Synthetic opioids are the primary contributor of drug related deaths in the United States with over 47,000 deaths in 2017, and with an additional estimated 1.7 million people suffering from substance abuse related to prescription opioids in the same year.[1] Until recently, scientific studies focused on how these opioid compounds bind to pain receptors in the human body,[2,3] and not many studies were performed outside of the medical field. As a result, the basic knowledge about the chemical interactions of these

molecules with common solvents has not been fully established. It is reasonable to believe that conformational (structural) diversity could have important implications for the binding and reactivity of this class of molecules on surfaces.

Here we study the conformational structure of two synthetic opioid molecules (carfentanil and remifentanil) in solution and their effect on binding on surfaces. We found carfentanil salts form conformers in more polar solvents such as water, whereas remifentanil salts form one conformer in water. Calculations show trends that remifentanil conformers require higher energies than carfentanil conformers. Additionally, neutral opioid structures (called the freebase) are more labile and lack stable conformers compared to the protonated opioid salt forms. Preliminary uptake studies were performed for both carfentanil and remifentanil on SiO_2 and several Zr-based metal organic frameworks, and the results show both a porosity and solvent dependence. The goal of this study was to discover a better mechanistic understanding of how these potent opioids bind to the surface, which can transition to help other fields generate better decontamination procedures, new antidotes, and protection protocols to help first responders.



Carfentanil conformers

COLL 399

Interfacial, confined, and concentrated colloidal diffusion

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This talk will present findings based on microscopy measurements and dynamic simulations to measure and model how colloidal potentials and hydrodynamic interactions together control colloidal diffusion in interfacial, confined, and concentrated systems. Particle scale trajectories are analyzed based on a modeling framework that captures the role of conservative and dissipative forces between colloids and surfaces as well as transport over a range of length scales relative to particle radii. The complexity of interactions and configurations will be presented with a systematic escalation from single spherical particles near surfaces with different chemistries to anisotropic particles, concentrated systems, and physically and chemically heterogeneous systems. Experimental measurements are obtained using a suite of optical microscopy methods to obtain three-dimensional trajectory data across a range of length and time scales necessary to quantify different mechanisms. Brownian and Stokesian dynamic simulations are performed as part of modeling particle scale interactions and as a means to identify minimally complex models that capture dominant mechanisms in a variety of systems. Results and findings will be presented to establish a foundation for what is well understood and what open questions need to be addressed in future studies of more complex systems.

COLL 400

Electrostatic barriers to nanoparticle escape from cavities in a porous matrix

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The escape of a nanoparticle or macromolecule from a cavity through a narrow constriction represents the fundamental elementary process underlying hindered mass transport within porous materials as well as many intracellular transport processes. This process could be influenced by particle-wall interaction, transient adsorption/desorption, hydrodynamic and electrostatic effects. Here, we used a three-dimensional (3D) tracking method to explicitly visualize the process of nanoparticle escape from periodic porous nanostructures in different salt concentration. Interestingly, we found that electrostatic effects played a surprisingly important role in this process; for example, increasing the Debye length by a few nm could increase the mean escape time by three-fold. A combination of computational and experimental analyses indicated that this significant increase of mean escape time was due to the energy barrier induced by electrostatic repulsion, which could be explained by DLVO theory. These findings explicitly demonstrate that the escape process under electrostatic effects is barrier-limited, and dominated by electrostatic effects.

COLL 401

From Ph.D. lab bench researcher to multi-national startup cofounder

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Folia Water Inc is a 3 year old materials chemistry startup company, whose product originated during Ph.D. research. Folia has invented a patented process to use large-scale paper machinery to manufacture low-cost nano-metal functionalized materials that unlock new mass-market consumer goods business models. Folia currently employs scientists, engineers, and marketing professionals in a fast paced environment. Folia's Chief Technology Officer will discuss her career path from Ph.D. invention through the innovation valley of death, to cofounding and running an early stage startup company. Additional discussion will include the challenges and advantages PhD scientists have in founding deep technology hardware startups. Key challenges include scaling up bench scale materials chemistry to pilot and commercial scale and finding customers half way around the world in emerging markets. Key advantages include working with a limited budget and openness to tackling difficult questions.

COLL 402

How does your academia experience support successful industrial career in colloidal science and nanotechnology?

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Many students chose to enter a STEM field with the goal of obtaining skills in school that will carry them on a long and fulfilling career. Often, students find themselves entering the industrial job market with a potential disconnect after years of academic-minded graduate school, postdoctoral, and even junior faculty work. This talk will highlight the lessons learned during the presenter's transition from a research professor to a R&D manager at a fast growing company, describing how her academic experience in a funding driven environment helped her maximize her contribution in a value driven industrial setting. This experience demonstrates how academic-based research experiences in colloidal science and nanotechnology fields can be readily translated and expanded into leading R&D efforts as well as supporting regulatory compliance, market expansion, and medical device pre-marketing authorization.

COLL 403

Colloidal science: Advancing human health

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This talk will describe how experiences researching the health and safety implications of nanomaterials has led to career opportunities performing research from the national laboratory setting to the industrial setting with a major pharmaceutical company, Pfizer. Precise synthesis of nanomaterials is required for not only nanoEHS studies, but also

for achieving goals for improved therapeutics. Highlights of research in this area, as well as lessons learned for early career success in industry will also be shared.

COLL 404

Photophysical properties of mixed-dimensional heterojunctions

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This talk will describe interfacial photophysical processes in heterojunctions comprising 0D materials (molecules, quantum dots) with 2D or layered materials, such as atomically thin metal dichalcogenides. Particular focus will be on charge and energy transfer processes between metal phthalocyanines and monolayer MoS₂, which display interfacial coupling and molecular organization that depends on the metal center of the phthalocyanine. This organization, in the case of Cu phthalocyanine, leads to exceptionally long-lived charge-separated states (70 ns) that are promising for applications in solar energy conversion.

COLL 405

Investigating the role of aliovalent doping of quantum dots: From magnetic frustration in Fe:ZnSe (CdSe) to plasmonic behavior in Sn:In₂O₃

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While stochastic incorporation of isovalent (M(II)) dopant ions into a II-VI quantum dot is well studied, the effect of incorporating an aliovalent (M(III), M(I)) metal ion can lead to immensely tunable materials. Furthermore, the doping of II-VI lattices by Sn(IV) or Fe(II) is also potentially interesting. In aliovalent doped QDs charge balance can produce antisite dimer pair inclusions leading to emergent electronic, plasmonic, optical, and magnetic properties can arise reflecting formation of donor states. Of the aliovalent dopants with potential magnetic behaviors, iron is intriguing as it can incorporate as isovalent (Fe(II)) or aliovalent (Fe(III)). In this presentation, we will explore the effect of aliovalent doping by iron centers in CdSe, ZnSe, In₂O₃ and Ga₂O₃. By correlating experimental measurements (magnetic, optical, Mossbauer) with computational methods (DFT), it is observed that Fe(III) localize as antisite in II-VI hosts. Localization at antisites leads to ferrimagnetic spin clusters within the QD lattice leading to the observation of RT-FM best described as spin-molecule like interactions within a quantum confined lattice.

COLL 406

Discovery and controlled assembly of lanthanide-doped nanoparticles for ultra-low-threshold upconversion microlasers

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Lanthanide-doped nanomaterials exhibit complex photophysical dynamics that give rise non-linear optical processes such as photon upconversion, which can be leveraged for solution-processable optoelectronics and imaging through biological tissue. I will discuss the high-throughput development and application of a new class of upconverting nanoparticle that uses an avalanche-like energy looping mechanism to non-linearly amplify the population of its excited states. This unique mechanism, excited at 1064 nm, enables such “energy-looping nanoparticles” (ELNPs) to be imaged through millimeters of brain tissue. Furthermore, by coupling ELNPs to the whispering gallery modes of polystyrene microspheres, the ELNP resonators achieve sufficient optical gain to exhibit continuous-wave, anti-Stokes lasing that is stable for hours under room temperature operation. We use correlative optical and electron microscopy to uncover the chemical and structural factors that govern the assembly of efficient upconversion microlasers. We demonstrate that microlasers with record low thresholds and high quality factors can be fabricated with high fidelity by controlling the number of layers, surface charge, and ligand coordination of the nanoparticles as they assemble onto cavity surfaces. Finally, we demonstrate that these microlasers operate and can be used to measure temperature even in complex biological media such as serum and through tissue-mimicking phantoms. These results suggest that energy looping microlasers, which are smaller than red blood cells, may be applied to in vivo sensing and optogenetic stimulation through tissue.

COLL 407

***In situ* elucidation of oxidation pathways to high quality magnetic nanoparticles**

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Magnetic nanoparticles are one of the most promising classes of particles for biomedical applications, and among these magnetite (Fe₃O₄) nanoparticles are an exciting candidate, due to their low toxicity and strong magnetic properties. During synthesis, compositional heterogeneities, surface spin disorder, or internal defects can be introduced which reduce magnetization as well as influence their field responsive behavior. Recently, it was observed that even in apparently high quality nanoparticles, reduced saturation magnetization (M_{sat}) in Fe₃O₄ could occur - directly related to the presence of antiphase boundaries. We have shown that by first synthesizing non-magnetic wustite (FeO) a nanoparticle ensemble that is single crystal, with incredibly tight size distribution, can be formed. These particles are then subjected to an oxidation

step to yield Fe_3O_4 , thus removing the uncertainty of oxidizing during synthesis. From bulk experiments we show that achieving single crystallinity is dependent on the rate of oxidation. We then investigated oxidation pathways at the atomic level using environmental transmission electron microscopy (ETEM) in order to inform the reproducible and controlled oxidation of single crystal, compositionally pure Fe_3O_4 nanoparticles.

COLL 408

Evaluating the effect of dopants on the oxygen storage behavior of bixbyite vanadium sesquioxide (V_2O_3) nanocrystals

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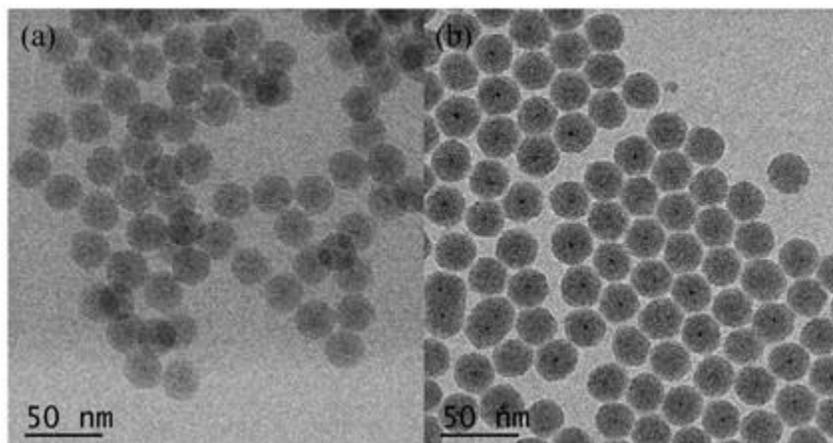
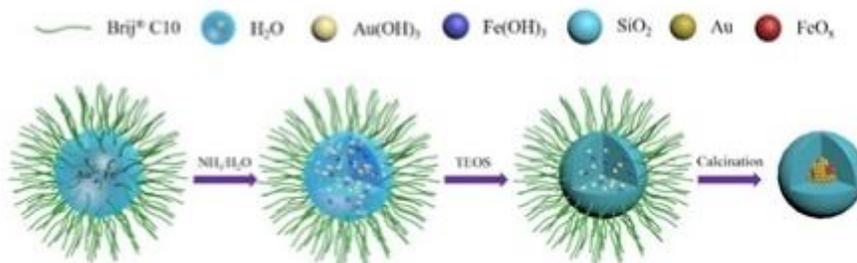
Oxygen storage materials in automotive catalysts work to maximize catalytic conversion in dynamic oxygen activity conditions. The currently commercialized materials for this purpose, ceria-zirconia solid solutions, do not function well at temperatures below 300°C , resulting in large emissions of toxic and polluting gases upon cold-start of a vehicle. In previous work, vanadium sesquioxide (V_2O_3) in the metastable bixbyite crystal phase has been shown to undergo oxygen uptake and release at very low temperatures, with oxygen uptake occurring at temperatures as low as 100°C , owing to the intrinsic oxygen vacancies in the crystal lattice. In this work, bixbyite V_2O_3 has been synthesized with two aliovalent dopants. Titanium and manganese dopants have been successfully incorporated into V_2O_3 , allowing us to investigate the effect of p- and n-type doping, respectively. Thermogravimetric analysis reveals a slight increase in oxygen storage capacity for both doped materials, along with an effect on the cycling stability after ten oxidation and reduction cycles. Ti-doped materials showed better cycling stability, while Mn-doped materials had minimal effect on cycling stability. Oxygen storage capacity drops significantly upon cycling for all tested materials, driven mainly by irreversible absorption of oxygen during the low temperature half-cycle. Ex situ X-ray diffraction performed on cycled materials show at least two mechanisms for material degradation: irreversible conversion of V_2O_3 to VO_2 and destruction of the crystals to form amorphous material. These effects are strongest for Mn-doped and undoped V_2O_3 , and density functional theory calculations show that negative lattice strain induced by the Ti^{4+} dopant decreases the formation energy of oxygen interstitials. Since these interstitials are stabilized, they are less likely to cause the formal oxidation of V^{3+} to V^{4+} , causing transformation to VO_2 , or to cause destructive strain, resulting in amorphous VO_x formation. Therefore, Ti^{4+} is a beneficial dopant for bixbyite V_2O_3 for use as an oxygen storage material in automotive catalysis.

COLL 409

One-pot construction of Au-FeO_x@SiO₂ core-shell nanostructure with both high catalytic activity and good thermal stability

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Core-shell nanostructured Au-FeO_x@SiO₂ with 3-4 nm Au-FeO_x cores and microporous SiO₂ shells were prepared by a water-in-oil (W/O) microemulsion method. A compositional control of the Au-FeO_x core was achieved by a co-precipitation method; meanwhile, microporous SiO₂ shells with tunable thickness were obtained by hydrolysis and condensation of TEOS. The obtained Au-FeO_x@SiO₂ showed a significant catalytic performance in CO oxidation, in comparison to Au@SiO₂. The synthetic strategy contained both fabrication of the active Au-FeO_x interface as well as the enhanced porosity of the SiO₂ shells, which facilitates the transpassing of reactants and products. The Au-FeO_x@SiO₂ structure provided a fine model for building up nanoreactors with both high catalytic activity and good thermal stability.



COLL 410

Stabilization and functionalization of iron oxide colloidal nanoparticles for applications at harsh environment

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Superparamagnetic iron oxide nanoparticles (SPIONs) have attracted significant attention for a wide range of applications from biomedical, environmental to oil industries in the past a few decades, including magnetic labeling and tracking, magnetic concentration and separation, hyperthermia therapy and drug delivery, bio-imaging and diagnostics, etc. Surface coating and specific functionalization of the SPIONs are crucial to improve their stability and reduce their aggregation for the successful use of the nanoparticles. Numerous methods and types of materials have been studied and used in the surface coating of SPIONs for the needs of different applications. However, many of the well-established methods and procedures of surface coating chemistry for bio-applications do not work well at harsh environment such as high temperature and high salinity for environmental engineering and oil industrial applications. We have studied different strategies to optimize the functionalization to gain long-term colloidal stability for the SPIONs at harsh environment. In this review, different coating materials (organic and inorganic) and procedures (physical and chemical) are compared, and special attention is given to the selection of molecular anchors for the coating materials. Potential applications and challenges of the functionalized SPIONs as nanoagents for oil reservoir tracers and for oil-water separation are discussed.

COLL 411

Microwave synthesis of tailored lanthanide oxide nanoparticles and their surface modification to generate homogeneous nanocomposites

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Nanocomposites have garnered great attention owing their superior chemical and physical properties over individual constituents for specific application. It is well known that the loading, spacing, type of particles, and interfacial interactions play a critical role in achieve optimal properties for nanocomposite technology advancement. Our research efforts have focused on developing tailored ceramic nanoparticles with tight size distribution and morphological features via microwave routes. To improve the dispersibility of the tailored nanoparticles, modification with silane surface ligands were investigated to understand the role of silane-moiety properties and how it effects the final property of the nanocomposites. This talk will encompass the efforts of microwave synthesis to generate lanthanide oxide nanoparticles (Ln_2O_3 -NPs) from commercial available precursors (i.e., nitrates). Various synthetic variables (i.e., precursors

concentration, temperature, surfactant) were investigated to control the tailored physical properties (i.e., crystalline phase, size, and morphology) of the Ln_2O_3 -NPs. The high quality Ln_2O_3 -NPs produced were incorporated in to various thermoset matrices by modifying their surface with different silane coupling agent to prevent agglomeration and control spacing in the polymer matrix.

COLL 412

Ultrafast charge carrier dynamics of indium-alloyed thick-shell InP/ZnSe quantum dots

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InP Quantum Dots (QDs) are being developed as an alternative to well-studied QDs that contain the heavy metal cadmium. While InP QDs offer size-tunable emission over the visible and near-infrared range and show reduced toxicity in comparison to CdSe, concerns exist about synthetically-induced broad size distributions, low photoluminescence (PL) quantum yields, and photostability. Shelling InP cores with ZnSe, a wide band gap material, has shown an increase in quantum yield up to 40% and a decrease in photodegradation. Further understanding the charge carrier dynamics of this material and correlating them to a change in structure allows for QDs to be developed for different applications. Ultrafast fluorescence upconversion spectroscopy provides valuable information about the QDs' ensemble charge carrier and trapping dynamics immediately after excitation. The obtained femtosecond decay constants and relative amplitudes show the effectiveness of the surface passivation of the ZnSe shell and allow direct comparisons to what has been previously seen for CdSe. InP/ZnSe QDs were synthesized with an alloyed interface and compared to QDs with a core/shell structure. Using ultrafast fluorescence upconversion spectroscopy, shorter decay constants were found for InP/ZnSe QDs than other previously studied CdSe-based systems indicating more favorable trapping of charge carriers.

COLL 413

Re-engineering immuno-exosome as theranostics

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Extracellular vesicles (EVs) are phospholipid and protein constructs which are continuously secreted by cells in the form of smaller (30-200 nm) and larger (micron size) particles. While all of these vesicles are called as EVs, the smaller size is normally called exosomes. Small EVs (sEVs) have now been explored as a potential candidate in

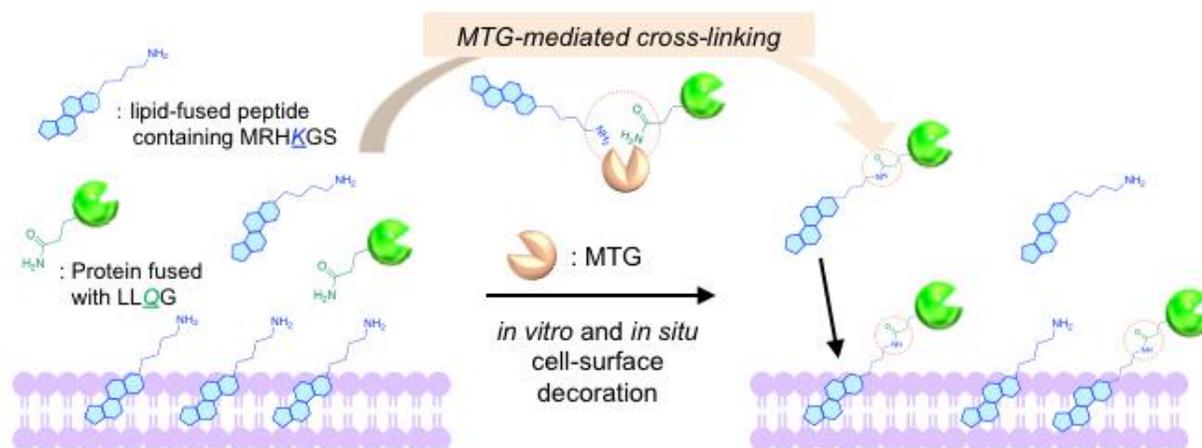
therapeutics delivery owing to their endogenous functionality, intrinsic targeting property, and ability to cooperate with a host defense system. Considering these potentials, we hypothesize that immune cell-derived sEVs can mimic immune cells to target cancer. However, different sEVs isolation technique reported poor yield and loss of functional properties. Considering these facts of exosomes, herein we hybridized sEVs with synthetic liposome to re-engineer sEVs as hybrid exosome (HE). We further envision the hybrid system could take advantage of both exosome and liposomal system thereby overcoming their respective shortcomings. To achieve this goal, sEVs isolated from immune cells were hybridized with synthetic liposomes to engineer HEs. The hybridization process was monitored using fluorescence and electron microscopy-based techniques. Exosomal functional properties in HEs were studied by tracking major protein markers and monitoring cell-based differential targeting properties against cancer and normal cells. Finally, HEs were loaded with clinical anticancer drug doxorubicin in its aqueous core and labeled with contrast agents to monitor the HEs distribution using magnetic resonance and near-infrared imaging modalities. In this presentation, we will discuss the therapeutic effectiveness of engineered HEs including its superior contrast enhancement properties, pharmacokinetics, therapy, and future perspective.

COLL 414

Transglutaminase-mediated lipid bilayer decoration with proteins using lipid-fused peptide amphiphile substrates

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Lipid modification of proteins plays a significant role in cellular signals' activation and drug delivery system for anchoring the protein on a carrier. Thus, the artificial synthesis of lipidated proteins has been developed, however, getting a high yield and purity of lipidated proteins has been challenging. Herein, we demonstrate a strategy for modifying proteins with a wide variety of synthetic lipids (fatty acids, tocopherol, lithocholic acid, cholesterol) using microbial transglutaminase (MTG). MTG catalyzes the cross-linking reaction between a specific glutamine (Q) in a protein and lysine (K) in the lipid-fused peptide. Synthesized lipid-G₃S-MRHKGS lipids as MTG substrates was successfully conjugated to a protein fused with LLQG (Q-tagged protein) by an MTG reaction, yielding > 90% conversion of the Q-tagged protein into a lipidated form. The purified lipid-protein conjugates were applied for labeling the cell membrane *in vitro*, resulting in best-anchoring ability of cholesterol modification. Furthermore, *in situ* cell-surface decoration with the protein was achieved in a simple manner: subjection of cells to a mixture of cholesterol-G₃S-MRHKGS, Q-tagged proteins and MTG.



COLL 415

Vesicle-to-sheet morphological control of lipid bilayers using polycation-chaperoned peptide system

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Controls of lipid membrane structure and property is crucial for designing lipid-based drug carrier and improving cytosolic drug delivery. We have reported that a cationic comb-type copolymer comprised of a polycation backbone and hydrophilic graft chains enhanced membrane-disruptive activity of an anionic amphiphilic peptide by chaperoning its folding through inter polyelectrolyte complex formation. To elucidate the enhancement mechanism of the copolymer upon membrane disruptive activity, effects of the peptide/copolymer complex on lipid bilayer morphology were investigated using giant vesicles (GVs). Of interest, GV underwent thorough vesicle-to-sheet morphological change upon the addition of the complex. Furthermore, reversible sheet-to-vesicle morphological conversion was controlled by turning the chaperoning activity of the copolymer off. Based on these observations, we constructed 2D/3D convertible lipid bilayer systems whose morphologies were spontaneously changed in response to particular enzymes, pH and time duration.

COLL 416

Impact of thermal annealing on physicochemical properties, serum stability, and transfection efficiency of pyridinium based lipoplexes

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The structure of the lipid-nucleic acid complexes (lipoplexes) influences the dynamic properties of the lipoplexes, their transfection activity and cytotoxicity. We optimized a protocol for the preparation of pyridinium amphiphile-based lipoplexes through thermal annealing of lipoplexes at medium-high temperature. The impact of this particular thermal treatment towards physicochemical parameters and towards biological properties of the resulted pyridinium amphiphile-based lipoplexes will be presented for several types of lipoplexes, based on different pyridinium amphiphiles.

COLL 417

New synthetic lipid chains incorporated in the structure of cationic amphiphiles for nucleic acid delivery

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Cationic amphiphiles or cationic polymers are used to compact, protect and carry nucleic acids. A fine-tuning of the physicochemical properties of the carrier must be achieved to produce lipoplexes or polyplexes that feature a compromise of stability (ideally, the nanoparticules must be stable outside the cell but not too stable after cell internalization *via* endocytosis). In particular, the endosome escape is a key point during the transfection process. In our group, we have designed synthetic phospholipids that feature a versatile synthesis [1] and with the possibility to tune the structure of the polar head group [2] and the hydrophobic chains [3]. We and others demonstrated that the use of stearyl lipid chain (C18:0) produce inefficient cationic carriers whereas oleyl chains usually produced efficient carriers.[4] This structural difference can be accounted to a less tight packing of the lipid chains within the supramolecular assemblies; the unsaturation can be view as a disorder element that increases the fluidity. In others studies, we also reported that the use of branched lipid chain (natural [5] or specially designed [6]) also favor the transfection process *via* an increase of the fluidity or by producing non-lamellar supramolecular assemblies. We explored recently the use of an alternative strategy that consist to incorporate thioether function within the structure of lipid chains.[7] All these strategies offer new possibilities to tune the formulations used for nucleic acid delivery.

COLL 418

Novel formulation strategies to overcome endosomal barriers for enhanced nucleic acid delivery

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Intracellular delivery of messenger RNA for the therapeutic production on proteins can transform modern medicine. While lipid-based nanoparticles (LNPs) remain in the forefront of delivery of nucleic acids, their endosomal sequestration remains a formidable barrier for cytosolic delivery. In studies with siRNA, even the most potent cationic lipids (the active ingredients within LNPs) enable a mere <2% release of nucleic acid to its cytosolic target. We have identified novel naturally occurring lipids that can enhance cytosolic delivery of nucleic acids and decoded structural activity relationships using analogues of these lipids to reveal the nature of endosomal escape processes. We found that these inclusions of these endosomal escape agents can lead to LNP mediated mRNA delivery (eLNPs) to about ~200-fold. 3D-Dynamic Photon Localization Tracking showed that eLNPs had improved diffusivity inside cells as compared to LNPs which remain in a mostly immobile state suggesting endosomal entrapment. eLNP-delivered mRNA also exhibited substantial cytosolic localization as visualized through single-molecule RNA-FISH. These novel lipids are a new class of endosomal agents that can boost gene delivery by overcoming endosomal barriers.

COLL 419

Colloidal quantum dot: From controllable synthesis to electrostatic-assisted self-assembly

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Colloidal quantum dot is one of the most important nano-optical materials, which has essential applications in many fields, such as display, quantum information and imaging. However, how to assemble the high quality colloidal quantum dots within nanometer accuracy is still a big challenge. Here, we have applied electrostatic force to assemble colloidal quantum dots into predetermined positions, realizing nanoxerographic printing of quantum dots. Specifically, we use conductive AFM probes to apply high pressure on the substrate, inject charge at the nanometer scale to form a charged pattern, and finally use the charged pattern to achieve high-precision assembly of quantum dots in the solution phase. By this method, we are able to organize colloidal quantum dots together over a millimeter scale in 1 minutes, with 30 nm position precision, 50 nm overlay precision, 200 nm pitch, and without any non-specific absorption.

COLL 420

Effect of surfactant on nanosynthesis of noble metal nanocrystals: Case of dioctadecyldimethylammonium chloride (DODAC)

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Controlling the nanostructures and elemental compositions of the nanocatalysts has been recognized as two prominent means to kinetically promote the (electro)catalytic performance. In this presentation, I summarized recent achievements in our group on surfactant-directed nanosynthesis strategies for nanostructured Pd-based alloyed nanocrystals in various electrocatalytic applications. By the utilization of amphiphilic dioctadecyldimethylammonium chloride (DODAC) which is composed of with two hydrophobic tails and one hydrophilic quaternary head as the surfactant template, various alloyed Pd-based nanostructures were controllably obtained in different synthetic conditions. For example, in the higher reaction temperature ($> 95\text{ }^{\circ}\text{C}$), obtained PdM were structurally ultrathin and single-crystalline, and compositionally tailorable ($M = \text{Pt, Ag, Cu, et. al.}$). By contrast, the lower temperature resulted in the formation of mesoporous nanospheres (MNSs), especially in the presence of ethanol (as the co-solvent). Our method has successfully grown size-tunable multimetallic MNSs, core-shell MNSs, and even (asymmetric) hollow MNSs. Due to synergic advantages on nanostructures and elemental compositions, the resultant materials exhibited remarkably enhanced electrocatalytic performance in both ethanol oxidation reaction and hydrogen evolution reaction. We believe our synthetic strategy will open a new avenue to rationally design multimetallic nonstructural nanocatalysts with controlled functions for a broad range of applications.

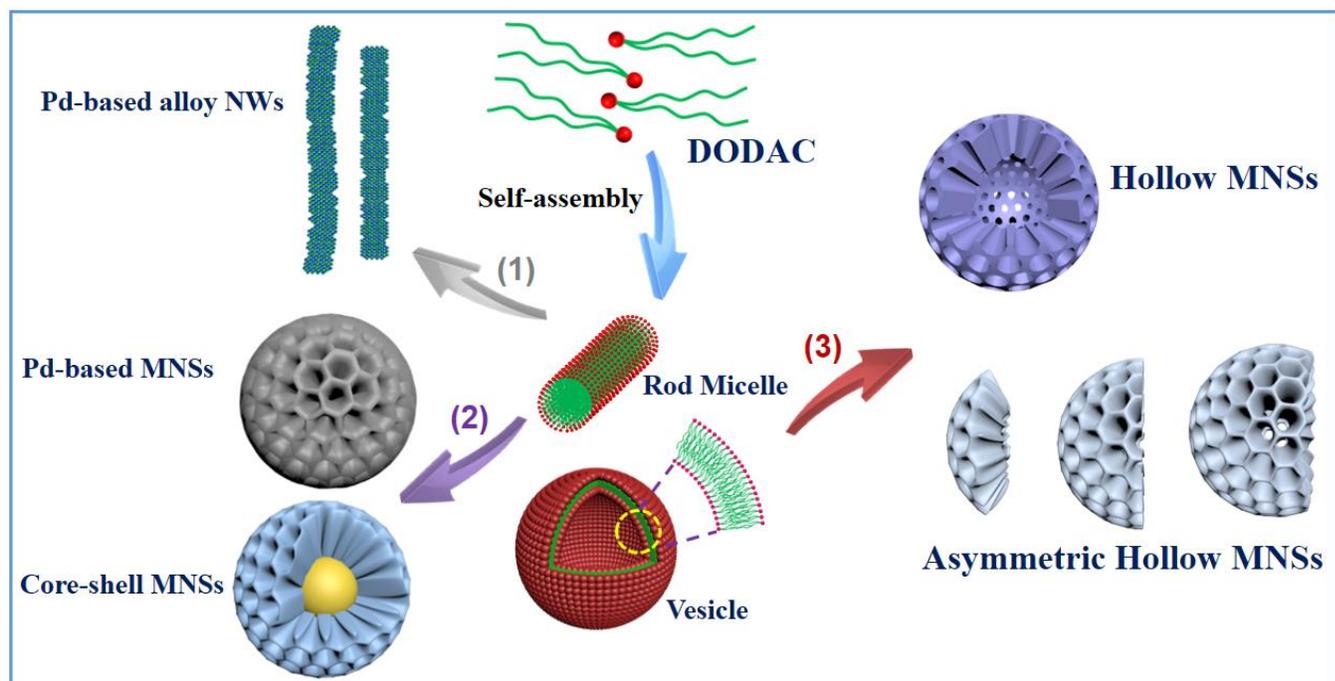


Figure 1. Surfactant-templated synthetic strategies for 1D nanowires and 3D mesoporous nanospheres.

COLL 421

Organochalcogenide reagents for the phase control of transition metal sulfides and selenides

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One of the long touted advantages of using colloiddally synthesized nanocrystals to mediate chemical reactions is the ability to control the types of surfaces exposed through the composition and shape of the nanocrystals employed. While we have made great strides in understanding the reactive surfaces of a few commonly synthesized phases of compound materials, the geologic record tells us there is a large number of “uncommon” phases that have not been explored or exploited, which will present new surfaces with new chemistries. Reliably obtaining these phases in nanocrystal syntheses is a prerequisite for further study.

Geology has the advantages of extreme temperatures, pressures, and cooling rates to achieve a dizzying array of diverse crystalline phases of metal chalcogenides. As solution phase chemists, we alternatively have access to diverse organochalcogenide precursors. Their varied chemistries provide opportunities to control crystalline phase in nanocrystal synthesis. Two cases that illustrate this synthetic tactic will be presented.

Organo-sulfur precursors can be chosen carefully to tune the crystalline phases that result in synthesis of iron and nickel sulfides. There is a correlation between the sulfur content of the resultant phase with C-S bond strength of the organosulfur reagent. However, our evidence also shows that sometimes unique organic transformations that occur at the elevated temperature of the nanocrystal synthesis also influence phase. Diallyl disulfide, in particular, undergoes allylic rearrangements in oleylamine to produce persulfide units, directly synthesizing FeS₂ pyrite.

The choice of both organo-selenium precursor and the ligand environment influences the polytype of Cu₂Se that forms in colloidal syntheses. *In situ* ¹H and ⁷⁷Se NMR during nanocrystal synthesis and XRD of reaction aliquots was used to determine the fate of the organochalcogenide precursors. The choice of alkyl-diselenide vs versus a alkylselenothiol causes the formation of either the metastable hexagonal or thermodynamic cubic Cu₂Se phase. Intermediate species, notably the formation of a copper-selenothiolate intermediate complex, or selenium-ligand complexes appear to be key to the polytype phase control.

COLL 422

Polymer-guided synthesis of asymmetric multicomponent nanoparticles with enhanced catalytical activity

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Multicomponent nanoparticles (MCNs) have multiple nanoscale domains of distinct materials within one particle. The conjugation or close placement of different components at nanoscale results in strong synergistic coupling effect that can significantly alter the intrinsic physical and chemical properties of the constituent materials. MCNs have shown emerging applications in such as solar energy harvesting, batteries, catalysis, optical and electronic devices, and biomedical imaging and delivering. In particular, the catalytical properties of MCNs are strongly dependent on not only the size, shape and composition of individual components, but also the relative spatial arrangement of these constituent domains. Moreover, recent research has shown that MCNs with asymmetric spatial distribution of constituent domains may outperform their symmetric counterparts in some applications.

Over the decade, great progress has been achieved in the synthesis of asymmetric MCNs with controlled morphology and component arrangement. Despite their initial success, most existing approaches have intrinsic limitations, such as being restricted to specific types of materials, being sensitive to small variations in synthetic conditions, and poor reproducibility in scale-up. It is therefore of paramount importance to develop effective, robust synthetic strategies for the production of asymmetric MCNs with high catalytical activity. In this talk, I will present our recent efforts on developing polymer-protected synthesis of non-conventional MCNs, as well as investigating the correlation between catalytical properties and asymmetric structures of MCNs.

COLL 423

Engineering metal-oxide interface at atomic scale in well-defined nanoparticles for catalytic conversion of small molecules

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In both heterogeneous catalysis and emerging electrocatalysis, the interfacial synergy between metal and supporting metal oxide, plays a vital role to determine the active sites and promote the catalytic reaction through cooperativity and multifunctionality. Conventionally, such interface is usually fabricated through either in situ growth or direct assembly of metal nanoparticles onto oxides, providing limited interfacial effects. In this talk, we will discuss how to precisely synthesize and tailor metal-oxide interface through a controllable surface segregation strategy and how to understand its catalytic role in conversion of small molecules, such as CO, H₂O₂, etc.

COLL 424

Heterogeneous nanostructure integration for energy conversion and production

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Three-dimensional (3-D) integration of nanostructures or nanostructure arrays into applicable platforms or devices represents the need for meeting ever-increasing demands of human beings for cost-effectiveness, structure sophistication, multi-function enabling, while simplified and efficient practical operations. Such an integration process generally involves a diverse array of nanostructured entities that include various dissimilar nanoscale building blocks such as nanoparticles, nanowires, and nanofilms made of metals, ceramics, or polymers in the nanoscale form. In this talk, I will highlight our latest research progress on the 2-D and 3-D metal oxide and metal based nanostructure integrations toward applicable energy devices, specifically on the nanoarray integrated microreactors for conversion and production of clean and renewable energies such as hydrogen and methanol. The underpinned new materials discovery and device enabling process represents a constant pursuit of ultrahigh efficiency, robustness, and improved functionality in order to practically and better bridge the gap between nanoscience and nanotechnology in energy and environmental applications. Examples as the connecting dots will depart from our decade-long effort in nano-engineered catalytic exhaust aftertreatment, nanomanufacturing, to catalytic water splitting and CO₂ transformation into methanol, intending to draw a unique nanomaterials roadmap toward multifunctional and scalable 3-D integration.

COLL 425

Metal-organic framework coated nanoparticles

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Our group focuses on incorporating nanoparticles into crystalline nanoporous materials, metal-organic frameworks (MOFs). The precise molecularly-defined pores intrinsic to the MOFs provide a new tool to control the catalytic transformations on the catalysts. We have developed methods to combine organometallic catalysts, enzymes, and nanoparticle catalysts with MOFs of precisely tuned pore structures to manipulate the reactions.

COLL 426

Biobased lubricant additives from vegetable oils and other renewable feedstocks

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Wide application of biobased lubricants is encouraged by governments worldwide because of its positive impact on the environment, wildlife and health of consumers. The reality is that biobased lubricants account for a very small slice of the global lubricant market. There are many reasons for the slow growth in biobased lubricant market share, including the shortage of suitable lubricant ingredients. Lubricant formulations are blended using two broad categories of components: baseoils and additives. While there are few viable biobased baseoils in the market, there are no commercial biobased additives. As a result, biobased lubricants currently in the market are formulated with non-biobased additives. So, there is a need to develop viable biobased additives for use in commercial lubricants. This presentation discusses the synthesis and characterization of a variety of biobased lubricant additives with promising properties.

COLL 427

Influence of surface coverage on friction performance of stearic acid on iron oxide

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The addition of friction reducing additives, or friction modifiers (FMs), to lubricants is an important strategy for improving efficiency of lubricated equipment. The performance of these additives is dependent on their surface activity and ability to form adsorbed layers on lubricated surfaces. However, the extent of surface coverage (mass per unit area) required for effective friction reduction is currently unknown. In this presentation we discuss the adsorption of stearic acid on iron oxide and compare our results to earlier studies. We show that surface coverage is affected by solvent (i.e. basestock), surface packing and free energy of adsorption. Dimerization of stearic acid is also considered, a factor which is not fully developed in earlier work. Solvent can also impact adsorption kinetics. For example, molecular dynamic simulations reveal that hexadecane tends to align on the iron oxide surface, increasing the energy barrier for the adsorption of stearic acid. Heptane does not align at the surface to create an adsorption barrier. Our results also suggest that full coverage of the surface with friction modifier is not necessary for significant friction reduction. While friction of systems lubricated with organic FMs decreases with increasing coverage, complete coverage of the surface is difficult to achieve. Moreover, full surface coverage is not necessary for effective friction reduction in the systems and conditions studied here.

COLL 428

Tricresyl phosphate reactions with ferrous surfaces: Effect of surface composition, molecular isomer, and atmospheric content

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Organophosphates have been the dominant additives for anti-wear in high-end aerospace lubricants for over half a century. Tricresyl phosphate (TCP) and similar aryl and alkyl phosphates reduce the amount of wear of ferrous materials in mechanical contacts, especially at elevated temperatures, high contact pressures, and high sliding speeds by forming thin layers of Fe-, O-, and C-containing compounds that are thought to preferentially shear and protect the underlying surfaces from material removal. These tribo-films consist of multilayered structures up to 10's of nanometers thick that contain various iron phosphates, polyphosphate, and carbon. However, the thermally- and mechanically-activated reactions mechanisms that lead to their formation continues to be debated. To elucidate initial reactions steps, we have conducted experiments to measure gaseous reaction products and corresponding simulations to compare our observations to products predicted from the hypothetical mechanisms proposed in literature. Thermal Programmed Reaction Spectroscopy (TPRS) and Gas Chromatography Mass Spectroscopy (GCMS) measurements of powders of Fe, Fe₂O₃, and Fe₃O₄ that have been exposed to TCP demonstrated that cresol is the primary gaseous product released during thermally-activated reactions under both air and oxygen/water-starved environments. Further, reactivity was observed to depend on the particular TCP isomer, reaction substrate, and atmospheric content. Reactive molecular dynamics simulations generally supported these experimental trends and provided further insight into the important role of the carbon functional groups in the reactions with the iron surfaces.

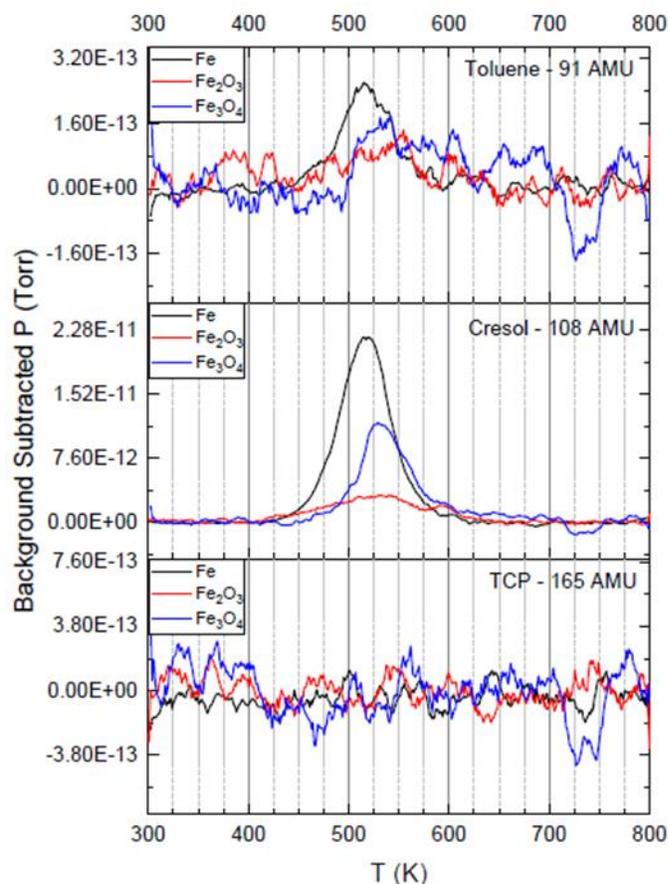


Figure 1: TPRS of Fe, Fe₂O₃, and Fe₃O₄ powders exposed to TCP. Mass spectrometer signal has been normalized to the background pressure, and a temperature ramp of 0.25 K/s was used.

COLL 429

Using ionic liquids as lubricant additives together with friction modifiers

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Boundary lubrication friction and wear are largely determined by the friction modifier (FM) and anti-wear additive (AW) in the lubricant. While ionic liquids (ILs) have recently demonstrated promising AW functionality, their compatibility with FMs is little known. Here we report the latest results for selected oil-soluble ILs when used together with either an organic FM (OFM) or a Mo-based FM. Both synergistic or antagonistic effects were observed depending on the IL chemistry. Specifically, a protic ammonium-

phosphate IL exhibited a strong synergistic effect with both FMs, yielding ultra-low steady-state friction coefficient (~ 0.02) and wear rate ($\sim 10^{-9}$ mm³/N-m), which significantly outperformed the IL or either FM alone. Surface characterization discovered distinct friction reducing and wear protection mechanisms for the synergistic IL+FM pairs in lubricating a cast iron or bronze surface sliding against a steel ball. The cast iron surface benefited from a chemically-reacted tribofilm as a result of interactions among the IL molecules, wear debris, and contact area. In contrast, the bronze surface relied on a unique physically-adsorbed surface film as a result of interconnected IL and FM molecules by hydrogen bonding.

COLL 430

Laboratory studies of spacecraft fluid lubricants

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Spacecraft mechanisms rely upon very small amounts of lubricant to survive in the harsh conditions of space. In critical applications, thin oil films must provide both low drag and longevity, with ball bearings in some devices lasting hundreds of billions of loaded mechanical contact motions. Our laboratory has developed several unique test facilities to measure the physical properties of thin lubricant films, and also to monitor their performance in realistic tests, such as ball bearings operating up to 6000 rpm. Additionally, the fluids used for these applications have unique compositions and properties (such as very low vapor pressures), which must be characterized and understood to optimize performance. We have a limited number of space rated lubricants applied across a myriad of applications, and tailoring lubricant composition requires consideration of substrate chemistry, rheology, design life and performance. This talk will provide an overview of our capabilities and highlight some unique aspects of thin film rheology and additive function.

COLL 431

Ionic liquids as environmentally friendly additives for hydraulic fluids

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Hydraulic systems provide a reliable, efficient, and cost-effective means to transmit energy than electrical or other mechanical systems, leading to the widespread use of hydraulic fluids globally. Because >50% of all lubricants sold globally end up in the environment by volatilization, spills or other loss applications, it is increasingly

recognized that in addition to meeting the rheological and tribological requirements, hydraulic fluids should also be low or non-toxic and adequately biodegradable. Here, we present our latest development of oil-soluble, low-toxicity ionic liquids (ILs) as candidate anti-wear additives for hydraulic fluids. The tribological behavior and environmental toxicity of selected ILs, at 0.5 wt.% concentration blends in a hydrophilic polyalkylene glycol (PAG), an oil soluble PAG (OSP), and a non-polar mineral base oil relative to that of a conventional anti-wear additive, primary zinc dithiophosphate (ZDDP). Tribological performance of the IL-containing lubricants were tested using a steel-steel contact under boundary lubrication at 82 °C. The candidate ILs showed lower friction coefficient and wear volume than ZDDP. Worn surface characterization revealed the microstructures and compositions of the protective tribofilms formed on the contact areas. Acute and chronic toxicity tests which exposed *Ceriodaphnia dubia*, a common aquatic bioindicator species demonstrated that most candidate ILs are more benign than ZDDP. Because of their higher thermal stability, improved lubricating functionality, and lower toxicity, these ILs may potentially be qualified for use in environmentally friendly lubricants (EALs) for hydraulics.

COLL 432

Synergistic interactions between thiolate-protected silver and palladium nanoparticles and their tribological properties

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Oil soluble, dodecanethiol protected silver and palladium nanoparticles (NPs) were synthesized as potential lubricant additives. The size distributions of AgNPs and PdNPs varied between 2-4 nm and 3-6 nm, respectively. These two organic-modified NPs were found to be very stable in both wet (organic solvents) and dry forms and the NPs could produce a stable colloidal suspension in a polyalphaolefin (PAO) base oil up to 1 wt%. Tribological bench tests were conducted using a ball-on-flat reciprocating sliding configuration at 100 °C under boundary lubrication. Addition of NPs to the lubricating oil resulted in friction and wear reductions up to 40% and 97%, respectively, with respect to the neat base oil. Further experiments revealed that the metallic core of the NPs had primary impact on both friction and wear improvement, whereas the organic ligand only contributed to the wear protection with little impact on friction. More interestingly, the Ag and Pd NPs were discovered to interact synergistically when mixed together in oil. The Ag-Pd NPs blend significantly reduced both the friction (37%) and wear (80%), compared with either NPs alone. Analysis of top and cross-section of the worn surface showed formation of two types of protective tribofilm. The electron donation ability of the Ag-Pd combination, dual tribofilm formation, and ultra-thick protective film with a unique composition are believed to be responsible for the enhanced tribological properties.

COLL 433

Sputtering-enabled intracellular X-ray photoelectron spectroscopy (SEI-XPS): New lab-based technique to investigate the biological fate of metal nanoparticles

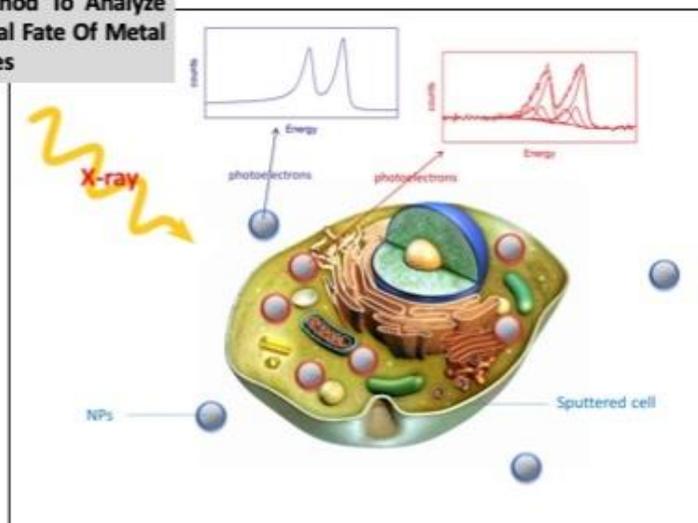
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The investigation of the toxicological profile and biomedical application of nanoparticles (NPs) requires deep understanding of their intracellular fate. Various techniques are usually employed to characterize NPs upon cellular internalization, including high-resolution optical and electron microscopies. Here, we show a new method, named sputtering-enabled intracellular XPS (SEI-XPS), proving that it is able to provide valuable information about the behavior of metallic NPs in culture media as well as within cells, directly measuring their internalization, stability/degradation, and oxidation state, without any preparative steps. The technique can also provide nanometer-scale vertical resolution along with semi-quantitative information about the cellular internalization of the metallic species. The proposed approach is easy-to-use and can become a standard technique in nanotoxicology/nanomedicine and in the rational design of metallic NPs. Two model cases were investigated: silver nanoparticles (AgNPs) and platinum nanoparticles (PtNPs) of same size and coating. We observed that, after 48 hours incubation, intracellular AgNPs are almost completely dissolved, forming nanoclusters as well as Ag-O and Ag-S complexes. On the other hand, PtNPs are resistant to the harsh endo-lysosomal environment, and only some surface oxidation was detected after 48 hours.

Sputtering-Enabled Intracellular Photoelectron Spectroscopy (SEI-XPS)

X-Ray

A New Method To Analyze The Biological Fate Of Metal Nanoparticles



Moglianetti et al, ACS Nano, 2018, 7731

COLL 434

Design near infrared absorbing triplet-triplet annihilation nanoparticles and application in tumor immunotherapy

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We present a strategy to expand anti-Stokes shifting from far red to deep blue region in metal-free triplet-triplet annihilation upconversion (TTA-UC) and demonstrate their utility in *in vivo* titrating anticancer prodrug photorelease. This new TTA system has robust brightness and the *longest* anti-Stokes shifting among all the report TTA systems. Benefiting from these properties, we developed TTA core-shell-structured prodrug delivery capsules that are able to operate with a low power density far red-LED light. These contain mesoporous silica nanoparticles preloaded with TTA molecules as the core and amphiphilic polymers encapsulating anti-cancer prodrug molecules as the shell. When stimulated by far red light, the intense TTA upconversion blue emission in our system activated the anticancer prodrug molecules and showed effective tumor growth inhibition *in vivo*. In particular, In combination with PD-1 check-point blockade anti-body, the nanocapsules are found to be highly effective against metastasis 4T₁ tumor. In sum, in this study, we not only provide a simple solution to break through

these key bottlenecks in the field of upconversion by creating the smallest and brightest organic TTA-UCNPs with surface modifications, but also provide a paradigm for metastatic cancer treatment in combination with cancer immunotherapy.

COLL 435

Orchestrating cellular organization and phenotype in small diameter bi-layered vascular grafts by heterotypic scaffold design

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Hierarchical scaffold design is a crucial parameter to develop appropriate tissue characteristics in the different layers of a vessel. The natural layers of the human vessel, e.g. the tunica intima and the tunica media, can be engineered in bi-layered tubular scaffolds. These scaffolds must permit the adhesion and formation of a confluent endothelial cell monolayer on the intimal side to avoid occlusion via thrombosis. In the medial layer, vascular smooth muscle cell (vSMC) stacking and circumferential alignment must be recapitulated to ensure the contractile function of the vessel. To date, fabrication of an dense luminal fibrous scaffold layer for endothelialization combined with an open fibrous layer for full population by vSMCs with close cell-cell contact throughout the medial layer, remains a challenge in bi-layered scaffolds.

To address these limitations, we present a fabrication approach that combines hierarchically layered scaffold design with the possibility to control structural orientation within the medial layer as guidance for biomimetic vSMC adhesion and growth. This bio-inspired scaffold design was achieved with a novel combination of conventional solution electrospinning and the new melt electrowriting (MEW) technology [1] onto cylindrical targets. The scaffolds consisted of an inner dense randomly oriented layer of single micron diameter fibers, and an oriented outer layer of one order of magnitude thicker fibers and bigger pores. We demonstrate that this vascular graft supported the organization of a continuous luminal endothelial monolayer and multiple oriented layers of vSM-like cells in the outer layer of the graft. Induction of the phenotypic morphology of the endothelium and vSM-like cells was enabled by this specific scaffold hierarchy. This study underlines the importance of the convergence of fabrication techniques to create scaffold designs that can support and control heterotypic cell organization and differentiation, improving vascular tissue engineering strategies.

COLL 436

Silica nanofibers-based extracellular matrix scaffolds with tunable nanostructure

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There is a great need in developing *in-vivo* like extracellular matrix (ECM) with tunable microstructures to precisely regulate cellular behaviors and to effectively investigate tissue-specific diseases such as cardiovascular diseases. Currently, there are only limited studies on engineering the microstructures of commonly used hydrogels as ECM scaffolds, hindering precise control of biophysicochemical cues surrounding cells. Here, we propose streamlined strategies to pattern microfluidics-fabricated silica nanofibers (SNFs) (average diameter: ~130nm, average aspect ratio: ~12) on substrates as alternate ECM scaffolds to address these challenges. SNFs are favorable for biological investigations with their good biocompatibility, flexibility towards surface modification, and resemblance to natural ECM. Their size and aspect ratio can be conveniently tuned by changing flow rates and reagent concentrations, allowing for precise structure control. Two methods are employed to deposit SNFs for ECM scaffolds: simple and effective spin-coating and spot-wise microfluidic printing. The uniformity and thickness of silica-nanofiber scaffolds depend on the concentration of SNFs, spin speed, and deposition times: 10 times of depositions (per deposition, 40ml of 2.0w/v% SNFs dispersed in dimethylformamide were spin-coated at 2000rpm for 20s) formed ECM-favorable contiguous silica-nanofiber layers. Similar scaffolds having a spot size of 400mm×600mm were obtained by microfluidic printing. These scaffolds were then immersed into 70% ethanol overnight and immobilized onto three wells of a six-well plate. ~ 3.68 × 10⁵/mL of PANC-1 (a human pancreatic cancer cell line) were seeded into the plate and cultured for 24 hours, after which their nuclei and cytoskeleton were stained. Based on fluorescent images, PANC-1 cells were observed to grow on the silica-nanofiber scaffolds with very good attachments. Compared to controls, improved cell spreading on these scaffolds was also demonstrated quantitatively by scanning electron microscope. In sum, we propose two robust approaches to deposit biocompatible and well-controlled silica nanofibers onto substrates as ECM scaffolds and demonstrate qualitatively enhanced cell attachment and spreading on these scaffolds. Further integration of the silica-nanofiber scaffolds into commercially available cellular metabolism profiling arrays promises an effective platform to study cellular behaviors for tissue-specific diseases.

COLL 437

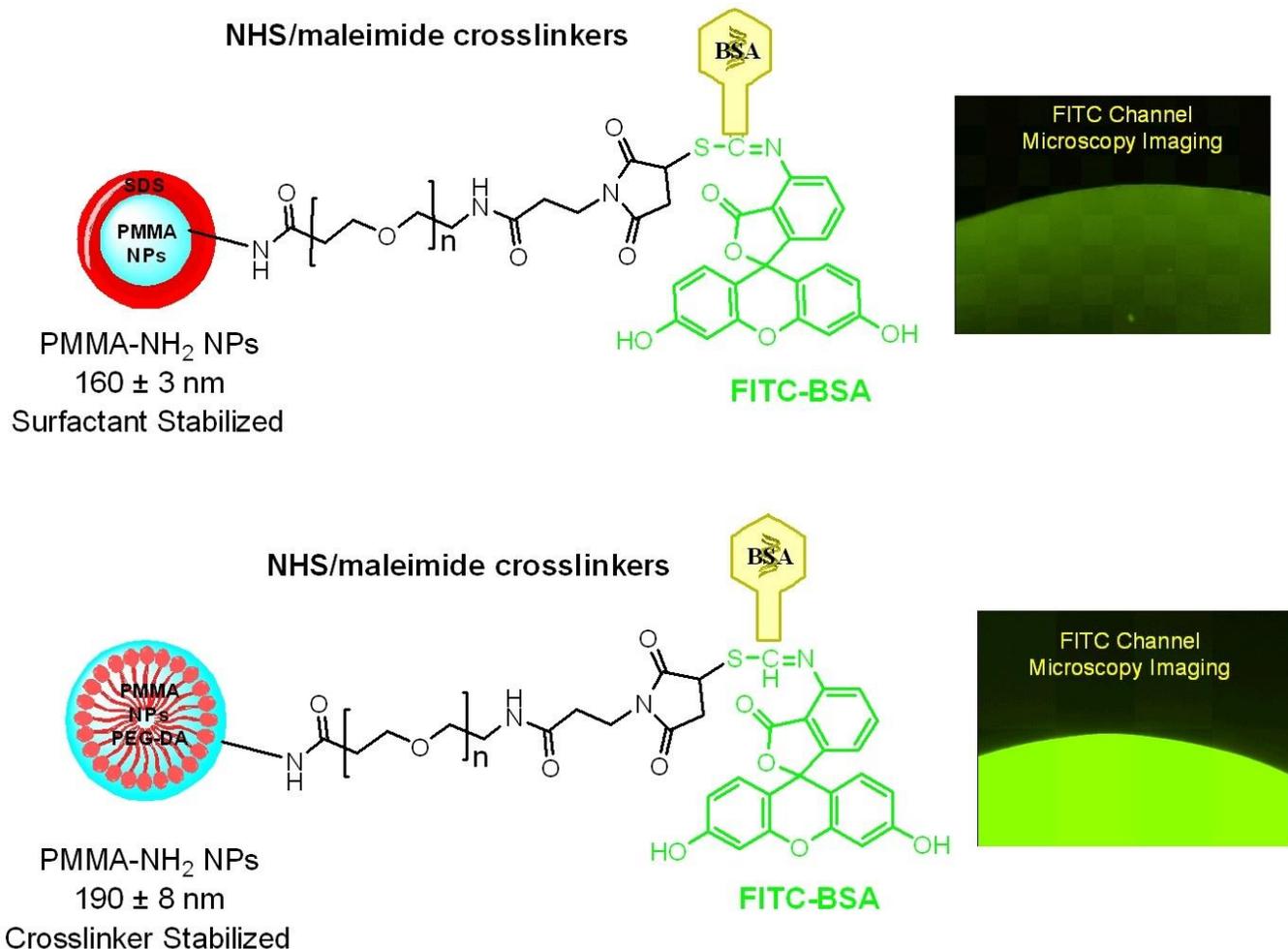
New synthesis methodology for making FITC labeled PMMA nanoparticles: Understanding effect of crosslinked vs. surfactant-stabilized nanoparticles on conjugation

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Researchers exploring personalized medicine often dose cells with targeting nanoparticles, and it is known that nanoparticle uptake can depend- on the quantity of biomarker-specific sites (e.g. protein antibodies) present on the nanoparticle surface. Hence, designing a bio-conjugation platform which produces nanoparticles that have a

high number of surface-linked biomarker-specific sites has recently attracted considerable attention.

Poly (methyl methacrylate) (PMMA) is an FDA approved synthetic polymer which has been used in biomedicine as an agent for drug/gene delivery. In this study, poly (methyl methacrylate)-co-2-aminomethacrylamide nanoparticles (PMMANPs) were synthesized and stabilized with either a surfactant (sodium dodecyl sulfate, SDS) or a cross-linker [poly (ethylene glycol) diacrylate, PEG-DA], then post-synthetically conjugated to a FITC labeled protein, BSA. Post-synthetic conjugation was accomplished using a commercially available NHS-maleimide linker system, which permits the BSA-amine conjugation. Success of post-synthetic BSA conjugation for each stabilizer was indirectly determined by measuring the fluorescence intensity of the labeled BSA. For both stabilizers, the PMMA NPs were able to conjugate to FITC-BSA, but in stark contrast, the fluorescence microscopy data reveals that crosslinker-stabilized PMMA NPs exhibit a higher FITC intensity than surfactant-stabilized PMMA NPs; this suggests that more conjugated BSA protein associated with the PEG-DA stabilized PMMA NP. Thus, stabilization via a crosslinker may be more appealing for researchers investigating personalized medicine.



Fluorescence Microscopy: Crosslinker-Stabilized PMMA NPs Exhibit a Higher FITC Intensity than Surfactant-Stabilized PMMA NPs

COLL 438

Role of core stiffness in regulating the intracellular fate of GM3-functionalized polymer nanoparticles

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Glycoprotein-independent entry of human immunodeficiency virus-1 (HIV-1) is mediated via the binding between glycosphingolipid ganglioside GM3, which is in the membrane of HIV-1 particles and CD169 (Siglec 1), a protein expressed on the surface of macrophages and dendritic cells. GM3-presenting lipid-wrapped nanoparticles (NPs) create a unique platform to fundamentally investigate the cell-NP interactions via specific ligand-receptor (GM3-CD169) binding. We use GM3-incorporated lipid-wrapped poly lactic-co-glycolic acid (PLGA), poly lactic acid (PLA), and poly glycolic acid (PGA) NPs to systematically investigate the effects of stiffness, quantified as Young's modulus, through atomic force microscopy (AFM) measurements on NP binding, uptake, and intracellular fate in THP-1 CD169 expressing macrophages. Our experimental strategy allows for a systematic variation of the NP stiffness through choice of polymer, while other properties such as size (average size of 130 nm), surface composition, and GM3 content remain the same. We characterized the successful wrapping of lipid membrane surround the polymer NPs by using different techniques including gel electrophoresis and differential scanning calorimetry (DSC). The average Young's moduli of the NPs from AFM measurements are $E_{PLGA} = 0.6 \pm 0.1$ GPa, $E_{PLA} = 1.6 \pm 0.2$ GPa, and $E_{PGA} = 4.1 \pm 0.3$ GPa. We have found experimental evidence that although the NP stiffness does not affect the binding affinity, it influences the uptake and the intracellular fate of GM3-presenting polymer NPs. PGA NPs showed a significantly higher uptake than PLA or PLGA NPs at long incubation time points (4-6 h). Furthermore, our measurements reveal that with increasing the core stiffness ($E_{PLGA} < E_{PLA} < E_{PGA}$), the number of NPs located outside of lysosomal compartments is increased as well. Our observations suggest that the intracellular fate of the NPs does not entirely depend on the GM3 ligand but also depends on the NP core stiffness. These findings improve the current understanding of how CD169-captured HIV-1 particles are sequestered in non-lysosomal compartment and highlight the role of core stiffness for virus function in infection and intracellular NP targeting.

COLL 439

Reactive oxygen species sensitive dendrimers for chronic wound healing

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Chronic wounds are characterized by its inability to complete the normal phases of wound healing. This leads to excessive levels of proinflammatory cytokines and reactive oxygen species (ROS). In addition, it has been shown that the elevated alkaline environment in these wounds provides additional hindrance to the healing process. While there are many biomaterials including hydrogels, films, alginates and foams that are being used for wound dressing, there is still a need for material that facilitates complete wound closure.

Dendrimers are hyperbranched macromolecules with a tree-like design composed of a central core and branches of repeating units. The ability to manipulate its shape, size and functional groups synthetically gives dendrimers a distinct advantage over other nanoparticles. The discovery of click chemistry and clickable asymmetric monomer synthesis has opened the possibility for highly efficient dendrimer synthesis. In this work, we utilize these click reactions to synthesize thioether linked Vanillin dendrimers. Vanillin is an antioxidant drug and while it has been shown to be helpful in wound healing, it shows toxicity at high concentrations. Our dendrimer incorporates the thioether- Vanillin conjugates via ester linkages to the internal hydroxyl groups of the dendrimer. This causes triggered and controlled release of Vanillin in response to the high levels of ROS present in chronic wounds. We will present our synthesis, characterization and *in vitro* drug release studies of Vanillin and also the resulting pH changes in the release medium caused by the hydrolyzed ester links. We also show that the released drug can successfully reduce inflammation in dermal cells. We believe these dendrimers can be incorporated into wound dressings to show controlled antioxidant drug release and temporarily decrease wound pH to promote healing.

COLL 440

Preparation and properties of POSS/HA composite film layer

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We used the sol-gel method to prepare HA sol and powder by using tributyl phosphate and calcium nitrate tetrahydrate as raw materials. We confirmed the successful synthesis of HA with XRD, FT-IR, TG/DSC analysis of the powder, and we determined that the optimum heat treatment temperature was 600 °C. The HA film layer was prepared by spin coating method. The best aging time was determined to be 30 h by the steel wool anti-friction test, LSCM(laser scanning confocal microscope) analysis and CCK-8 test of the film layer.

At the same time, amine-POSS sol and EP-POSS sol were synthesized by sol-gel

method using KH-550 and KH-560 as raw materials, and they were characterized by FT-IR. The POSS/HA composite film layer was prepared by spin coating. We have studied the effects of different functional groups, ratios and coating methods on the film-forming properties. The best film-forming process was determined by the steel wool anti-friction test, LSCM analysis and CCK-8 test. We found that the performance of the film obtained by mixing the POSS-50 sol with the POSS-60 sol at a mass ratio of 1:2 and then mixing it with the HA sol at a mass ratio of 1:5 is optimal. The anti-friction properties of the film are significantly improved and have good osteoblast biological activity.

COLL 441

Can surface science help explain biology?

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A variety of different types of surfaces (or interfaces) exist in biology. For example, the surface of a biomaterial is the interface between that biomaterial and the biological environment. State-of-the-art instrument, experimental protocols, and data analysis methods are needed to obtain detailed information about the surface structures and compositions, as well as that of the biomolecules that attach to those surfaces. Surface analysis tools such as imaging time-of-flight mass spectrometry (ToF-SIMS) can provide images of polymer biomaterials, cells and tissues with chemical and molecular specificity. These chemically specific images could revolutionize our understanding of biological processes such as the role of changes in tumor metabolism affecting the response to chemotherapy is under scrutiny. However, since many biomaterials (e.g. porous polymer scaffolds), cells and tissues are three-dimensional constructs, it is of interest to be able to characterize their chemical composition in 3D. However, it is challenging to characterize these topographically complex materials. With the use of gas cluster ion beams (GCIBs) ToF-SIMS can attain very fine z-resolution (<10 nm) in-depth profiles. In this presentation, ToF-SIMS analysis of biological samples from 2D images of tissues to 3D images of explanted porous scaffolds will be presented.

COLL 442

Aqueous-phase adsorption energies of model bio-oil compounds on Pt and Rh: Comparison between experiment and theory

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Understanding catalysis in aqueous phase is important for many applications, including energy storage and production of renewable fuels and chemicals (e.g., hydrogenation of molecules to valuable products). Compared to gas-phase catalysis, however, the link

between adsorption thermodynamics and kinetics, and between theory and experiment is not as well-studied in the aqueous phase. In this talk, we will discuss our work in measuring adsorption energies of organic molecules in aqueous conditions and the role of water and pH on the kinetics of heterogeneous catalysts. We will cover similarities and differences in the adsorption and reaction of hydrogen and organic molecules on metal surfaces in: (i) the gas-phase, (ii) thermally in the aqueous phase, and (iii) electrochemically in the aqueous phase. We have chosen hydrogenation of phenol and benzaldehyde as model molecules and reactions to simulate the upgrading of bio-oil, a water-rich waste stream from pyrolysis or hydrothermal liquefaction. If we are able to increase the activity for bio-oil hydrogenation, we enable a process to produce liquid transportation fuels from waste biomass, unlocking a renewable way to produce high-density fuels.

The talk will examine our electrochemical techniques to measure the adsorption of molecules (phenol, benzaldehyde and their products) onto metal surfaces (Pt and Rh) and the role water plays in modifying the adsorption energies. This understanding of the role of water allows us to better use density functional theory (DFT) calculations of molecules in the gas phase to predict adsorption energies that can be corrected to aqueous adsorption energies. We will discuss how these adsorption energies can be used to understand catalytic sites and observed macroscopic kinetic behavior. Taken together, we will show how we are beginning to understand the effect that water has on these hydrogenation reactions and how to interpret the observed reaction rates, and what is required to further increase rates for a system to cost-effectively convert waste products to valuable fuels and chemicals.

COLL 443

Active structures and species of modified transition metal oxide electrocatalysts for the oxygen evolution reaction

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The oxygen evolution reaction (OER) is a major cause of energy losses in a number of emergent technologies such as water splitting devices, photocatalytic systems for solar fuels, rechargeable metal-air batteries, and unitized regenerative fuel cells. Clear structure-activity correlations remain elusive for transition metal oxide (TMO) electrocatalysts sought to replace precious metal-based OER catalysts because of their complex composition and structure. We will discuss insights from two examples of our studies, which utilized a range of spectroscopic techniques for characterization of Ce-modified copper oxide and Ni-modified cobalt (oxy)hydroxides to reveal information about the OER active species and structures of these catalysts. In the case of Ce-modified CuO_x , Ce incorporation (6.9 at%) into CuO_x led to 3.3 times greater OER activity compared to pure CuO_x and this was coincident with significant structural changes due to an increasing amount of disorder. By combining X-ray photoelectron and Raman spectroscopy techniques, a strong correlation between increasing OER performance with increasing tetravalent Ce (Ce^{4+}) ions was observed up to a

concentration corresponding to CeO₂ phase segregation. In the case of Ni-modified CoO_xH_y, operando Raman spectroscopy was used to reveal a drastic transformation of a spinel Co₃O₄-like structure into a more active (oxy)hydroxide structure under applied potential. Such a transformation was only observed in the presence of uniformly distributed Ni ions. These two examples, i.e. the promoting effect of Ce⁴⁺ and the formation of active OER structures in Ni-modified CoO_xH_y, reveal the importance of chemical state and local structure considerations for the rational design of improved oxide-based OER catalysts.

COLL 444

Role of open circuit and external potentials to control electrocatalytic reductions

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Electrocatalytic reduction of organic molecules emerges as one of the critical steps in producing energy carriers in a sustainable future. Understanding the role of electrochemical potentials for sorption and ordering on metal particles is critical to interpret the behavior of metals in aqueous solution and to design catalysts for electrocatalytic reactions. Determined by pH and external H₂ pressure the open circuit potential of carbon supported Rh, Pt, and Pd has been found to vary inversely with hydrogenation rates of molecules like phenol. More negative external potentials have been found on the other hand to correlate with higher rates of hydrogen evolution and higher hydrogenation rates. The lecture discusses these apparently contradicting observations and the role of the organization of reactants electrolytes and water or hydronium ions at the surface of electrocatalysts as function of the overpotential, the hydronium ion concentration, and partial pressure of hydrogen during the hydrogenation of phenol as example.

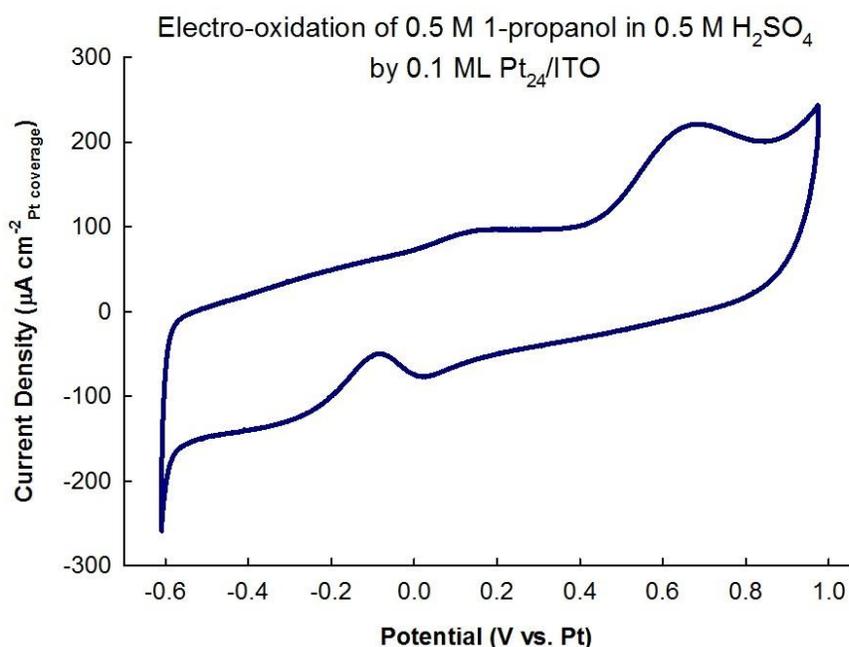
COLL 445

Electrocatalytic alcohol oxidation by size-selected Pt clusters

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We have developed a new capability to study electrochemistry of electrodes containing atomically size-selected cluster catalysts, *in situ*, without air exposure. Electrodes are prepared in ultra-high vacuum by mass-selected cluster deposition onto glassy carbon (GC) or indium tin oxide (ITO) supports, characterized by surface science methods, and then transferred in vacuum to a chamber containing a small electrochemical cell. After

venting the chamber with argon, the cell is pressed against the electrode surrounding the clusters, and electrolytes are injected. Initial studies have focused on electro-oxidation of glycerol, catalyzed by Pt_n/ITO and Pt_n/GC. Glycerol is of interest as a by-product of biodiesel production, and thus is an inexpensive raw material rich in functionalities that can be transformed into added-value products. To facilitate theoretical studies by collaborators, we have also examined propanol oxidation. Propanol is a promising fuel for direct alcohol fuel cells (DAFCs) due to its higher energy density, compared to ethanol or methanol. The work presented will include experimental cyclic voltammetry results for electrocatalytic alcohol oxidation by size-selected Pt clusters on the two electrode supports.



COLL 446

Ambient pressure X-ray photoelectron spectroscopy with application to solar water splitting materials

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The development of ambient pressure X-ray photoelectron spectroscopy (AP-XPS) has enabled photoelectron spectroscopy experiments at elevated pressures. This has made possible quantitative, chemically specific investigations of technologically relevant

surfaces and interfaces in equilibrium with realistic gas pressures. AP-XPS with soft X-rays has been used extensively to study solid/gas interfaces. However, the AP-XPS technique has recently been extended into the tender (or “hard”) X-ray regime (ambient pressure hard X-ray photoelectron spectroscopy, AP-HAXPES). AP-HAXPES provides the ability to investigate buried interfaces, including solid/electrolyte interfaces, at pressures exceeding 25 mbar. We have used both AP-XPS and AP-HAXPES to understand the bismuth vanadate (BiVO_4)/electrolyte interface used in solar water splitting devices. We have studied gas phase water adsorption onto a Mo-doped $\text{BiVO}_4(010)$ single crystal surface at pressures up to a few mbar with soft X-ray AP-XPS. Our results indicate that the surface is significantly hydroxylated by ~ 0.5 mbar. Surface hydroxylation is accompanied by reduced vanadium in the surface and occupied states above the valence band maximum which are attributed to hydroxyl induced small polaron formation. We have also investigated the effects of solar illumination on BiVO_4 /potassium phosphate electrolyte and BiVO_4 /potassium borate electrolyte interfaces at open circuit potential using AP-HAXPES. Upon illumination with a solar simulator, we observe spectral changes consistent with the formation of bismuth phosphate and significant restructuring of the electrolyte near the BiVO_4 /potassium phosphate interface. These changes were not observed upon illumination of the BiVO_4 /potassium borate electrolyte interface. These results provide fundamental information about the general behaviour of water splitting photoelectrodes under illumination and insight into how the electrolyte influences device stability.

COLL 447

Greatest hits album: Campbell group

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This talk will highlight some of the contributions from my research group that I consider to be most important, while acknowledging the many wonderful folks who made them possible.

Contributions include new experimental methods for characterizing surfaces, including the world’s most sensitive calorimeter for measuring reaction energies on single-crystal surfaces, the world’s only calorimeter for measuring metal atom adsorption energies, methods for quantitative analysis of adsorption rates in liquids using surface plasmon resonance, including simultaneous measurement on 3000 different microscopic areas. The group provided the most important collection of adsorption energies ever reported, and the only experimental heats of formation of whole classes of ubiquitous catalytic intermediates on late transition metals, including the simplest alkoxies, carboxylates, alkynes, alkenes, alkyls, -OH, aromatics and phenol on Pt(111) and Ni(111). These have served as benchmarks for theory, revealing large errors in DFT and helping to guide the development of better functionals.

The group uncovered key mechanistic details of industrially-important catalytic reactions, including methanol synthesis from CO and CO_2 , water-gas shift, ethylene epoxidation, CO oxidation, hydrocarbon conversions, and aqueous-phase

hydrogenation of aromatic oxygenates.

The group also made important contributions to theory, including simple but accurate ways to estimate entropies of adsorbates, the first correct way to extract sticking probabilities from measured rates of adsorption in liquids, a way to extract solid / solid adhesion energies from calorimetric heats of adsorption, a Gibbs-Thompson-like equation for estimating chemical potential versus particle size but now for supported particles, the 'degree of rate control' (DRC), a mathematical method for analyzing microkinetic models to determine which intermediate and transition-state energies most critically control rates, and the extension of DRC analysis into a new method for computational catalyst discovery.

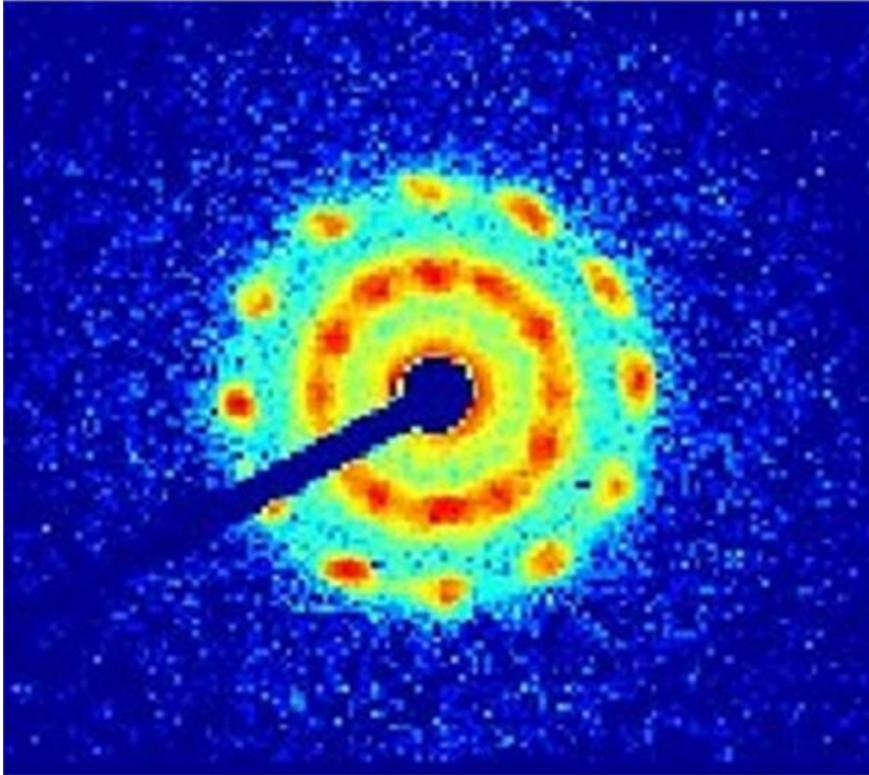
COLL 448

Self-assembly of soft colloids into quasicrystals

*Martin Dulle¹, Tobias Jurczyk¹, Thomas Gruhn², **Stephan Förster¹**, s.foerster@fz-juelich.de. (1) JCNS-1/ICS-1, Forschungszentrum Jülich, Jülich, Germany (2) Biomaterials, University of Bayreuth, Bayreuth, Germany*

Quasicrystals have a unique aperiodic order leading to diffraction patterns of 8-, 10-, or 12-fold rotational symmetry. They have been discovered in 1982 by Dan Shechtman. Since then they have been found in more than one hundred binary and ternary metal alloys. Beginning in 2004 there have been reports on quasicrystalline structures formed by soft colloids such as dendrimers, polymers and surfactants. This indicates that there might be general principles that favor the formation of quasicrystals, and if this would be the case, quasicrystals could be rationally designed using soft colloids with characteristic length scales up to the micron range for photonic applications.

We have discovered quasicrystalline phases with 12- and 18-fold rotational symmetry for soft core/shell-colloids and binary colloid mixtures in aqueous and organic solvents. Their stability range and phase transitions into FCC and BCC phases as a function of volume fraction, temperature and size have been determined by X-ray and neutron diffraction. Our studies indicate that a condition for the formation of colloidal quasicrystals is a soft repulsive interaction potential facilitating the formation of polytetrahedral particle arrangements. Using MD-simulations we have mapped the stability regions of crystalline and quasi-crystalline phases over a large range of volume fractions and core/shell size ratios. The phase diagram for the first time links previous reports of quasicrystals in nanoparticles, polymers and metal alloys as well as MD-simulations of repulsive and attractive colloid systems to provide a fundamental understanding of the structure and stability of soft quasicrystals.



SAXS-image of a dodecagonal block copolymer micellar phase in an organic solvent.

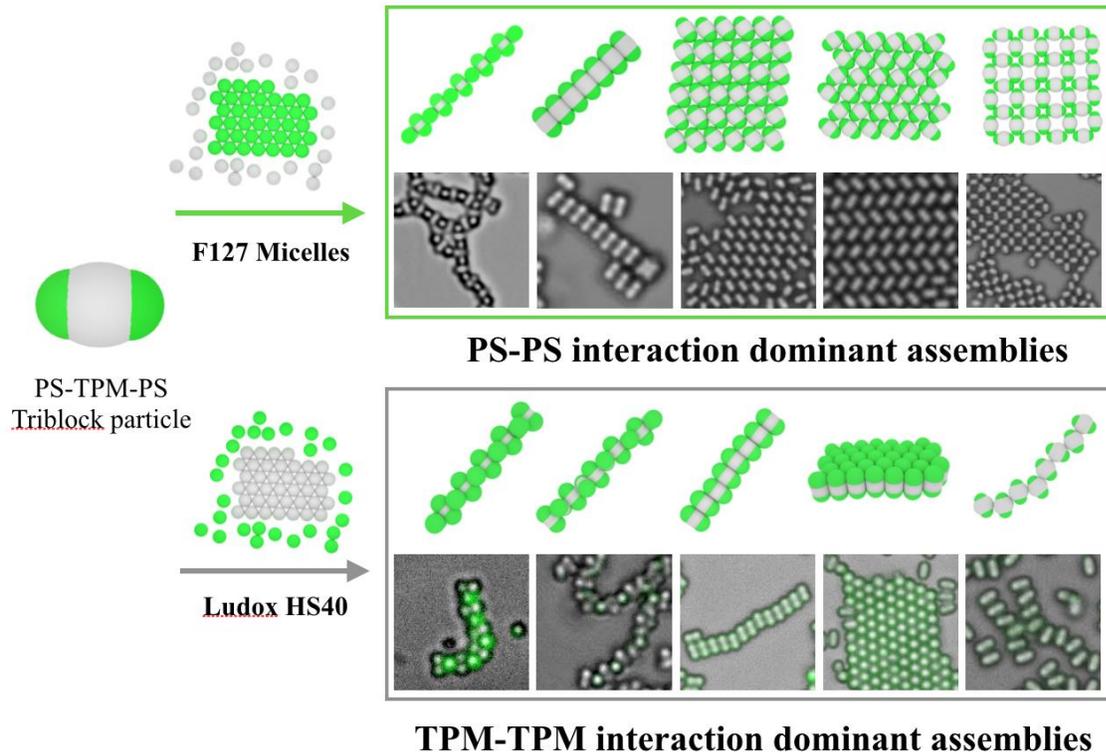
COLL 449

Switchable regioselective assemble of triblock microparticles based on surface material recognition

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Assembling colloidal microparticles with directional bonding into desired colloidal superlattice have been a long-standing challenge in the field due to the complexity of selective functionalization of particle surface and poor tunability of interactions. Herein we demonstrate that selective depletion interaction can be exploited to engineer the directional bonding and assembly of colloidal microparticles made of hybrid materials. We discover selective crystallization of spheres made of different materials in the presence of specific depletants. Inspired by that, we fabricate triblock biphasic colloids with various aspect ratios to achieve regioselective bonding and assembly. Without any surface treatment, we can assemble them into various colloidal superstructures and superlattices with polymorphic formation. Furthermore, by switching the depletion

condition, we observe a new scenario of colloidal chains and membranes featuring different site-specific interaction. Our method requires no tedious surface functionalization to realize directional interaction, which can be further adopted for other programmable colloidal assemblies and colloidal materials processing.



COLL 450

Magnetic assembly of anisotropic nanostructures into responsive photonic crystals

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Nanoscale assembly coupled with competing anisotropic interactions can produce complex structures and provide additional degrees of freedom for tailoring their collective properties. However, the on-going researches are highly limited by the poor quality of building blocks, inaccessibility of direct observation of crystal structures and lack of reliable numerical methods for analyzing their dynamic anisotropic interactions.

In this presentation, we report magnetic assembly of super uniform magnetic nanorods into responsive photonic crystals. The assembled structures are fixed during assembly by silica coating and directly characterized under electron microscopy, which suggests a body-centered tetragonal (*bct*) crystal structure. Finite-element calculations show that two magnetic nanorods approach thermodynamic equilibrium when the tangent components (orthogonal to the surface normal) of their magnetic forces is zero, showing good agreement with structures from TEM images of the assembled crystals. This method provides reliable analytical approach towards understanding the anisotropic interactions between building blocks. Thanks to the pretty good orders of the crystals, well-defined diffraction peaks are observed during SAXS measurements, which is consistent with the *bct* structures obtained by TEM images and provides detailed information about assembly kinetics. In combination with high packing density, extreme bright structural color is observed, whose intensity overwhelms other tunable photonic crystals. In addition, the diffraction peaks and structural colors can be continuously tuned across visible range by varying the directions of magnetic fields.

COLL 451

Investigation of the aggregates formation mechanism of Amyloid beta 1-40 coated nano-gold particles

Kazushige Yokoyama, *yokoyama@geneseo.edu*. Chemistry, The State University of New York Geneseo College, Rochester, New York, United States

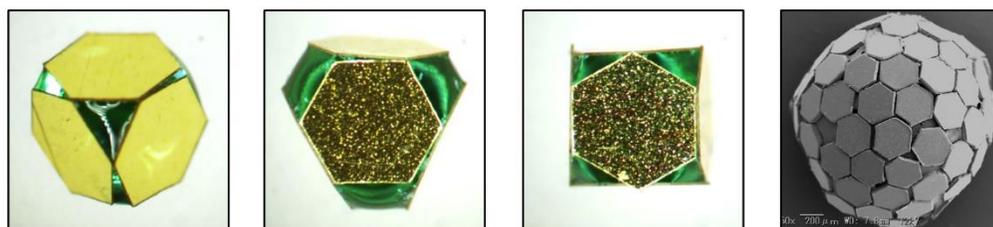
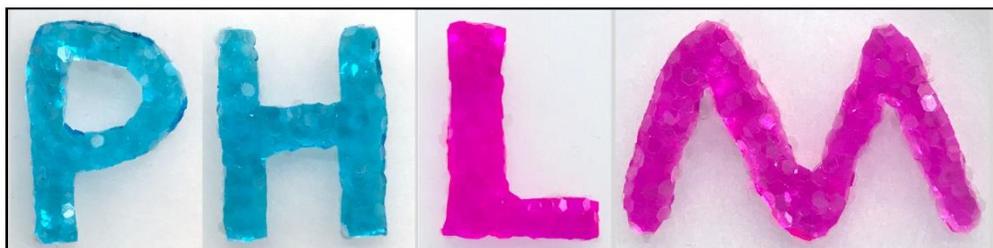
The aggregation of the Amyloid beta 1-40 ($A\beta_{1-40}$) coated nano-particles involves a networking between $A\beta_{1-40}$ at nano-scale interface. While the details of peptide conformation at the nano-scale interface has not been known, the aggregation was known to be initiated by the unfolded $A\beta_{1-40}$ monomers. An empirical peptide coverage ratio was extracted for 20 nm gold colloid and 50 nm gold colloid to be approximately 0.75 and 0.45, respectively. By adding the $A\beta_{1-40}$ to the 20 nm and 50 nm gold colloidal particles, different gold colloid aggregates formation paths were identified. For the 20 nm gold colloid particle, it had two different induction points (*i.e.*, two step-function responses) for gold's aggregation. On the contrary, there was only one moderate induction point for the aggregation of 50 nm gold colloid particles. The aggregation model based on stepwise coverage ratio is proposed to explain the difference in aggregation formation mechanism between 20 nm and 50 nm gold colloid.

COLL 452

Polyhedral liquid marbles

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A new type of armored droplets, so-called polyhedral liquid marbles are introduced in this work. These armored liquid marbles consist of liquid droplets stabilized by hydrophobic hexagonal plates made of poly(ethylene terephthalate), which adsorb to the liquid-air interface. Depending on the specific combination of plate size and droplet diameter, the plates self-assemble into highly ordered hexagonally arranged domains. Even tetrahedral-, pentahedral-, and cube-shaped liquid marbles composed of only 4 to 6 plates are demonstrated. During evaporation of the internal liquid, due to the high adsorption energy of the plates at the liquid-air interface, the overall surface area stayed constant resulting in strongly deformed polyhedral liquid marbles. In line with this, highly asymmetric polyhedral liquid marbles and letters are obtained due to the strong interfacial jamming exerted by the rigid hexagonal plates. This is particularly pronounced for larger plate sizes leading to liquid marbles with unusually sharp edges (for example, rectangular edges). The polyhedral liquid marbles exhibit various stimuli-responsive behaviors simultaneously being exposed to water, ammonia or tetrahydrofuran vapors. Air-driven polyhedral liquid marbles floating on water can reach velocities of several cm per second.



COLL 453

Block copolymer assembly of ligand stripped nanocrystals

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Block copolymer directed assembly of nanocrystals present an exciting avenue for enabling bottom up processing of inorganic materials and organic-inorganic composites

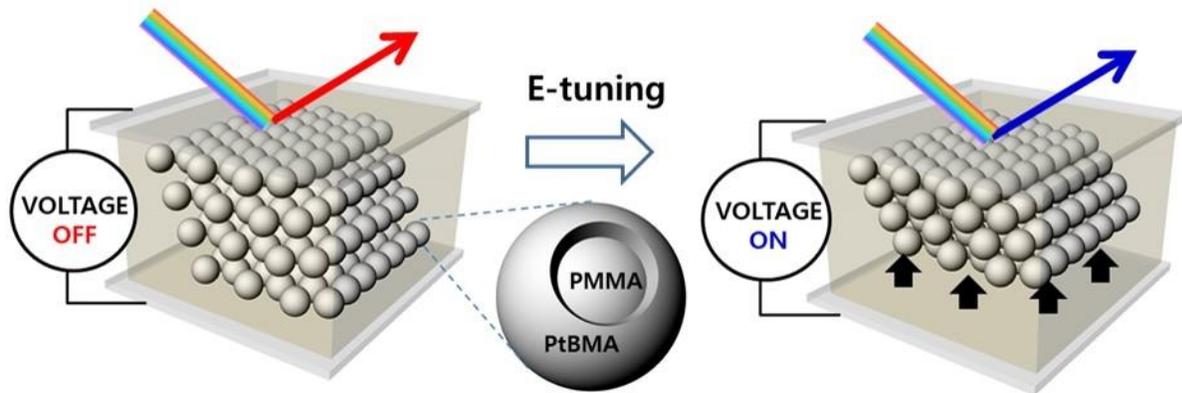
that harness the merits of both classes of materials along with precise control of structure. One limit in the approach include chemical specificity necessitating nanocrystal surface ligand functionalization prior to assembly to prevent macrophase separation of nanocrystals out of the block copolymer domain. A second limit is the ability to achieve a high loading of nanocrystals in the structure without macrophase separation or kinetic arrest due to effects such as particle jamming. Prior work on a specific polymer polystyrene-polydimethylacrylamide (PS-PDMA) where the acrylamide block preferentially adsorbs to bare nanocrystal surfaces have shown micelle assembly of nanocrystals of arbitrary composition up to high loading as long as the nanocrystals are ligand stripped of their native organic ligands. Here, we extend the extent of assembly in the morphological space by demonstrating solvent annealed microphase separated morphologies using PS-PDMA and ligand stripped nanocrystals. We also demonstrate the coassembly of binary nanocrystal systems within the same block copolymer system having uncovered the nature of the interaction between PDMA and the nanocrystals. These findings possess significant implications in regards to how ligand stripped nanocrystals may be assembled with other assembly systems such as PS-PEO and PS-P4VP.

COLL 454

All-organic crystalline colloidal array for full color electrophoretic reflective display

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The increasing demands for display devices with low power consumption and outdoor readability have stimulated comprehensive research into reflective displays that employ tunable photonic crystal technologies. Recently, color tuning of electrophoretic crystalline colloidal array (CCA) has been demonstrated as a promising candidate for full color reflective display. To overcome problematic features of water in electric field, non-aqueous liquid medium is required. Herein, CCA formed from core-shell PMMA/poly(t-butyl methacrylate) microspheres was fabricated, which was stabilized by the inverse micelles of sodium di-2-ethylhexyl-sulfosuccinate in an iso-paraffinic fluid. A highly charged all-organic CCA was found to exhibit full-color tunability with a thousand-fold reduction in the operating current under a voltage bias in comparison with the current in an aqueous system.



COLL 455

Templated capillary assembly of liquid colloidal particles

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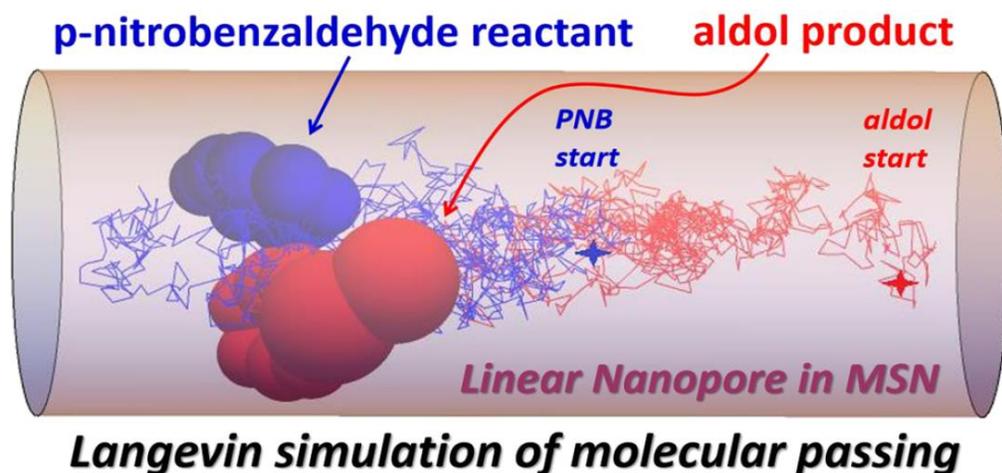
Capillary assembly of colloidal particles onto topographical substrates has dramatically accelerated the production of precisely structured colloidal arrays and superstructures. Whereby particles of numerous shapes and chemical compositions are driven into cavities by the capillary force generated when a particle suspension is dried within a patterned channel. Herein, we extend this method to assemble highly cross-linked liquid particles, in which we unite exact spatial arrangement of liquid particles with post-assembly polymerization and end-group modification to engineer functional microarrays. Successful assembly of liquid polymer emulsion droplet “particles” into surface patterns is achieved by inducing coalescence and space filling of cavities of any desired geometry by disrupting their electrostatic stabilization via solvent evaporation. Subsequent polymerization results in a solid particle that can be anisotropically functionalized with molecular recognition units such as DNA, and/or harvested from the template and used for further assembly. We envision that this innovation will enable access to polymer particles of unlimited geometries as directed by the template shape. This work will broaden the impact of capillary assembly methods for generating multicomponent arrays and tailored colloidal architectures. The fabrication schemes are robust, scalable, and will certainly be implemented in optical crystals, sensing, biomaterials, and colloidal chemistry in general.

COLL 456

Catalytic activity in nanoporous materials with inhibited transport: Pore diameter dependence of PNB conversion to aldol in MSN

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Catalytic conversion in narrow pores is inhibited as product formed in the pore interior cannot readily pass reactants near the pore openings, and thus blocks reactant from reaching interior catalytic sites. Standard mean-field treatments of reaction-diffusion kinetics fail dramatically due to the development strong spatial correlations associated with the subtle interplay of restricted transport and reaction. Behavior can however be described by KMC simulation of stochastic molecular-level models, or by generalized hydrodynamic theories [PRL 108 (2012) 228301]. A key observation is the strong dependence of catalytic activity on the propensity for reactant and product species to pass each other inside the pore. These concepts are applied to interpret the strong increase in yield with modest increase in pore diameter observed for PNB conversion to an aldol product in amine-functionalized mesoporous silica [J Chem Phys 149 (2018) 024101]. The passing propensity for PNB and aldol versus pore diameter is first determined applying Langevin simulations [PRL 113 (2014) 038301]. These must reliably treat rotational as well as translational diffusion, since species must align with the pore and with each other in order to pass in narrow pores. This information provides input to stochastic models for the overall reaction-diffusion process for which KMC simulation shows behavior consistent with experimental observations.

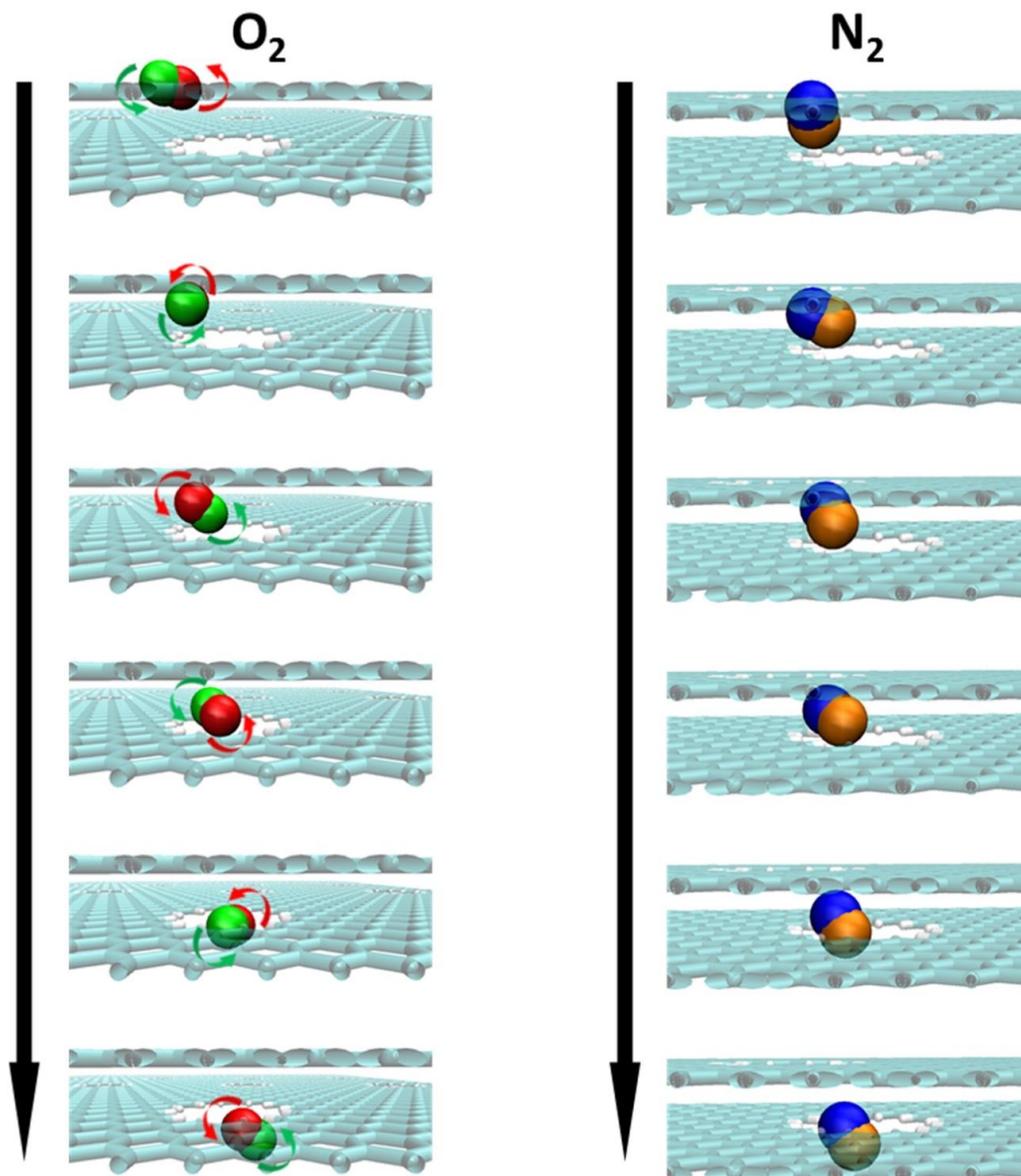


COLL 457

Enhanced selectivity in air separation by tumbling movement through a bilayer nanoporous graphene membrane

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Membranes are an energy-efficient technology for air separation, but it is difficult to control the pore size to separate N₂ and O₂ due to their similar kinetic diameters. Here we demonstrate from molecular dynamics simulations that a bilayer nanoporous graphene membrane with continuously tunable pore sizes by the offset between the two graphene layers can achieve O₂/N₂ selectivity up to 26 with a permeance over 10⁵ GPU. By analyzing the mechanism of gas passing through the pore, we find that the entropic selectivity is the main reason behind the high selectivity via the tumbling movement of the skinnier and shorter O₂ molecules entering and passing through the elliptic-cylinder-shaped nanopore. In contrast, the longer and fatter N₂ molecules wiggle through the nanopore with the rotational degrees of freedom confined. Hence, tuning the pore size and the pore shape via the offset of the bilayer nanoporous graphene membrane provides a novel way to enhance selectivity by confining molecular rotational movement.



COLL 458

Transforming the potential energy landscape to suppress deactivation pathways in surface supported catalysts

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Cambridge, Massachusetts, United States (2) Nuclear Engineering & Technology, Sun Yat-Sen University, Guangzhou, China (3) Materials Science & Engineering, MIT, Cambridge, Massachusetts, United States

The global raw material shortage and dire need for improved energy efficiency in industry have led to a resurgence of interest in the stabilization of supported catalyst systems both *in operando* and during high-temperature regeneration processes. Catalyst deactivation in supported systems generally proceeds by Ostwald ripening (OR) and particle coalescence/migration (PCM) mechanisms that depend strongly on the interaction between catalytically active surface particles and their support structure. We have employed a complimentary experimental and computational approach to study this interaction using gold nanoparticles supported on zeolite frameworks as a model system. Systematic alteration of the aluminum dopant concentration in the zeolite framework allowed the potential energy landscape of the surface to be examined both experimentally (UV-Vis & TEM) and computationally (DFT and MD), and these analyses were used to determine the contributions of the surface binding energy profiles on OR and PCM. Recent findings will be presented in the context of potential exploitation of these interactions to suppress surface-supported catalyst deactivation pathways and thereby extend catalyst lifetimes.

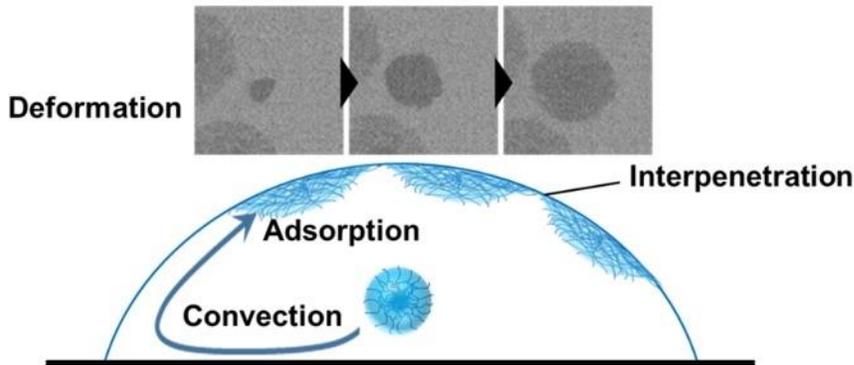
COLL 459

Self-assembly of deformable soft hydrogel microspheres at the air/water interface

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The hydrogel microspheres (microgels), which are colloidal particles of cross-linked polymeric networks, have attracted much attention in many applications due to their responsiveness to external stimuli. In order to further develop and create new applications for such microgels, understanding the interfacial behaviors of microgels is especially important. Our group has been investigating that the self-organization of dilute dispersions containing microgels during the evaporation exhibit unique drying behaviors due to their selective adsorption at the air/water interface of sessile droplets. So far, impacts of size, chemical composition and softness (degree of crosslinking) of microgels have been revealed. Additionally, it has been clarified that a single microgel is largely deformed immediately when they attached at the air/water interface, which was directly observed with an optical microscope equipped with a high-speed camera. Our findings of this study would promote further development in many applications that understanding the interfacial behaviors of soft and deformable microgels is crucial, including coating and sensors. Furthermore, recent results on self-organization of polyelectrolyte microgels and anisotropic microgels will also be discussed, and dynamics of various microgels and their assemblies that were deformed at the air/water interface will be summarized.

Size: irrelevant Softness: crucial Surface activity: crucial



summary of this study

COLL 460

Surface segregation of binary particles in photonic colloidal assemblies

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Colors are generated via one of two methods; the absorption of light by small molecules (pigmentary colors) or by the scattering of light by nanostructures (structural color). There are many examples of structural color in nature including the wing feathers of the green-winged teal (*Anas crecca*) and feathers of the wild turkey (*Meleagris gallopavo*), both of which use different types of melanosomes to generate these colors. There is great interest in synthetic materials capable of generating structural colors due to their tunability and improved resistance to bleaching (chemical and photo). Previously, our lab described the development of synthetic melanin-based core-shell particles that were assembled into three dimensional photonic balls, termed supraballs, which showed bright and noniridescent colors. When these synthetic melanin particles were combined in a binary system, we observed that they appeared to localize on the surface of the supraballs, which greatly affects their colors. However, the mechanism and properties that influence this surface segregation lacks understanding. Surface segregation in binary colloidal particle mixtures offers a simple way to control surface properties and colors of colloidal assemblies without affecting their bulk composition. In our study, we synthesized different sizes of synthetic melanin particles and silica particles, combined them in a binary mixture, and assembled them into supraballs by a facile one-pot reverse emulsion process. Interestingly, we observed that melanin-based and/or smaller particles preferentially segregate at the surface of the supraballs compared to their larger counterparts, while no such surface segregation is observed in films prepared by evaporative assembly. Coarse-grained molecular dynamics (CG-MD) simulations suggest that differences in the contact angle of particles at the liquid-liquid interface

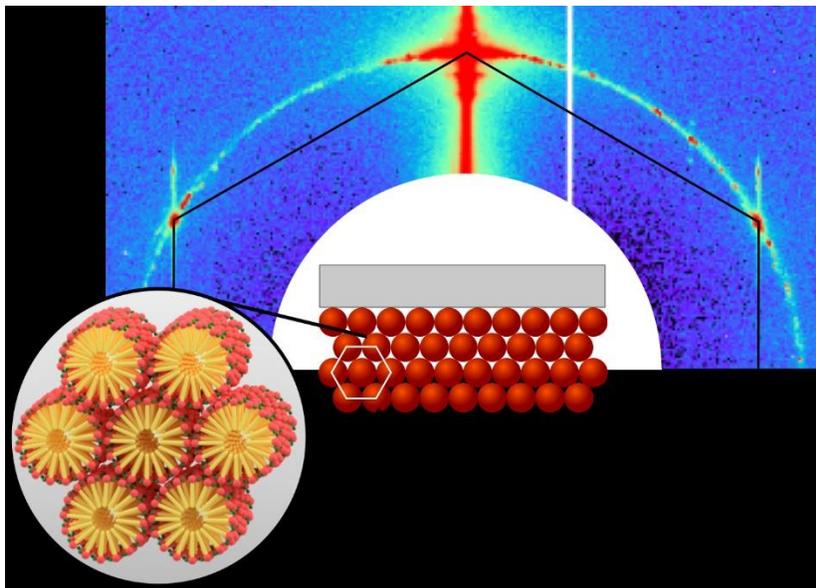
during emulsion assembly drives the observed surface segregation behavior with particles having a larger contact angle (melanin) being enriched at the supraball surface regardless of the relative strength of particle-interface interactions.

COLL 461

Structure and dynamics of a confined ionic liquid studied by an x-ray surface force apparatus

Markus Mezger¹, mezger@mpip-mainz.mpg.de, **Markus Valtiner**², **Veijo Honkimäki**³. (1) Max Planck Institute for Polymer Research, Mainz, Germany (2) TU Vienna, Vienna, Austria (3) ESRF, Grenoble, France

Structure and dynamics of confined liquids were probed by an in-situ X-ray surface force apparatus in plane-cylinder geometry. Our novel device can shear, compress and decompress soft matter within a precisely controlled slit pore confinement. Complementary structural information is obtained by X-ray scattering and simultaneous force measurements. Experiments using high energy x-rays were performed at ID31, ESRF. Here, we present results from an ionic liquid/water mixture in its columnar liquid crystalline mesophase. Defect-formation and structural relaxation processes in confinement were studied as reaction to external stimuli. The observed mesoscopic orientation induced by oscillatory shear is explained by the anisotropic mobility of the amphiphilic cations.



The X-ray scattering pattern from the confined ionic liquid indicates hexagonal arrangement of mesoscopic cylinders formed by amphiphilic alkyl-imidazolium cations (inset). Rods extending vertically from the Bragg reflections are attributed to the confinement.

COLL 462

Investigation of water adlayers confined between 2D interface

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The water/solid interfaces are of fundamental importance owing to its relevance to many physicochemical phenomena and interfacial processes. Although many studies have contributed to a rapid progression in understanding of water/solid interfaces, the exact structure and dynamic behavior of the interfacial water adlayers at ambient conditions is still unclear and many findings and theories are still under debate. Therefore, it will be extremely important to study the structure of water molecules at solid interface or confined between two solid surfaces under molecular level. By utilizing *in situ* thermally controlled AFM, we have investigated the structure and dynamic behaviors of water adlayers confined in graphene/mica and MoS₂/mica interfaces under ambient conditions. Ice-like water adlayers and fluid-like water adlayers have been identified. For the first time, ice-like water adlayers stacked on top of each other up to three layers and the transition from layers to liquid droplets was directly visualized; the dynamic behaviors of fluid-like water adlayer was recorded. Furthermore, the etching of MoS₂ by water molecules under high temperatures was also investigated. These findings of water molecules growth at the interface and water molecules etching of 2D materials will further strengthen our understanding of water behaviors at interface.

COLL 463

Ionic liquid confined between metallic surfaces: What is the role of image charges?

Samuel Ntim, **Marialore Sulpizi**, *sulpizi@uni-mainz.de*. Department of Physics, Johannes Gutenberg University, Mainz, Germany

Room-temperature ionic liquids (RTILs) are salts, liquid at room temperature because of their low melting points. Their peculiar properties in confined geometries have become essential in many fields including energy storage, catalysis and tribology. Recently, an anomalous liquid-solid phase transition of the RTIL 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄]) was reported from atomic force microscopy experiments in different confining materials, the transition being more pronounced for more metallic surfaces. Using classical atomistic molecular dynamics simulations, we provide a detailed description of the structural, thermodynamical and dynamical properties of the confined ([BMIM][BF₄]), quantifying the impact of the image charges. We find that image charges have, however, a limited influence and cannot possibly be responsible for the anomalous freezing. Further ideas on the microscopic origin of the anomalous transition will be discussed.

COLL 464

Effect of confinement on phase transitions of hydrocarbons in nanoporous materials

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The phase behavior of petroleum fluids is essential in shale oil and gas production. The fluid properties in low permeability, low porosity shales are different from those in conventional reservoirs, which have high porosity and high permeability. Shales have nano-scale pores. Due to the strong surface-fluid interactions and complex pore geometries in shale nanopores, PVT properties of fluids in shale are different than in conventional reservoirs and thus cannot be described by bulk-phase thermodynamics. In this work, we investigate phase changes in three different hydrocarbons (toluene, heptane, decane) and water with and without the effect of confinement (nano-sized porous materials) using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). SBA-15 and SBA-16 were synthesized to use as confined systems in this work. Both SBA-15 and SBA-16 have pores of about 4 nm in size. To compare the effect of confinement on phase changes, SiO₂, which has similar grain size to SBA-15 and SBA-16 but no nano-sized pores, is used under the same experimental conditions. Also, mesoporous SBA-15 has hexagonal pores, while SBA-16 has cubic pores. The effect of pore morphology on phase changes in hydrocarbons is also studied. Boiling and melting points were affected by the nano-sized porous samples, and the degree of change depends on the pore morphology, including pore volume and grain shape. Also, we studied the effect of confinement on phase transitions at high pressures. These findings can contribute to expanding our understanding of phase change/phase behavior in natural porous media, including shales.

COLL 465

Design and synthesis of inorganic nanomaterials for medical applications

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For the last 10 years, our group has been focused on medical applications of various uniform-sized nanoparticles.¹ We report on the biocompatibility evaluation and MR imaging of uniform 2 nm-sized iron oxide nanoparticles in large animal models including most clinically-relevant non-human primates. These biocompatible iron oxide nanoparticles are successfully used as T1 MR contrast agent for high-resolution MR angiography of macaque monkeys.²

I will present recent advances on the fabrication of ultraflexible & stretchable electronic & optoelectronic devices integrated with various functional nanomaterials and their applications to wearable & implantable healthcare devices.³ We reported graphene-hybrid electrochemical devices integrated with thermo-responsive micro-needles for the sweat-based diabetes monitoring and feedback therapy.^{4, 5} We introduced

electromechanical cardioplasty using an epicardial mesh made of electrically conductive and mechanically elastic Ag nanowire-rubber nanocomposite to resemble the innate cardiac tissue and confer cardiac conduction system function.

COLL 466

Aqueous stable gold nanostar/ZIF-8 nanocomposites for light triggered release of active cargo inside living cells

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A plasmonic core-shell gold nanostars/zeolitic imidazolate framework 8 (ZIF-8) nanocomposite was developed for thermoplasmonic-driven release of encapsulated active molecules inside living cells. The nanocomposites were loaded, as a proof of concept, with bisbenzimidazole molecules as functional cargo, and wrapped with an amphiphilic polymer that prevents ZIF-8 degradation and bisbenzimidazole leaking in aqueous media or inside living cells. The demonstrated molecule-release mechanism relies on the use of near-IR light coupled to the plasmonic absorption of the core gold nanostars, which creates local temperature gradients and thus, bisbenzimidazole thermodiffusion. Confocal microscopy and surface-enhanced Raman spectroscopy (SERS) were used to demonstrate bisbenzimidazole loading/leaking and near-IR-triggered cargo release inside cells, thereby leading to DNA staining.

COLL 467

Engineering metal-organic-framework nanoparticles for enhanced chemoradiation of breast cancer

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Combination cancer therapies often offer improved tumor cell kill over individual treatments, such as surgery, radiation, or chemotherapy alone. However, these multi-pronged approaches may also increase unwanted toxicities for the patient. In an effort to reduce these limiting side-effects, nanoparticle drug carriers have been investigated for site specific and controlled release of therapeutic agents. In our previous work, we have developed a variety of polymeric, inorganic, and composite nanomaterials capable of delivering hydrophilic or hydrophobic chemotherapeutic compounds to cancer cells. Here, we present a metal-organic framework (MoF) nanoparticle platform for the delivery of DNA damage repair inhibitors, such as the poly-ADP ribose polymerase (PARP) inhibitor, talazoparib, to breast cancer cells. We have engineered a carrier that is capable of loading these drugs and demonstrate their release as well as the ability of the hafnium(BDC) MoF to serve as a radiation dose enhancer. The hydrodynamic size

of the drug loaded particles were approximately 100 nm and correlated well with that observed by TEM. The resulting nanoparticles were evaluated for efficacy against a breast cancer cell line, 4T1, to assess cytotoxicity *in vitro*. Preliminary chemoradiation studies were also performed with the MoFs by assessing DNA damage via the γ H2AX assay on this cell line. In addition, short and long-term biocompatibility studies were performed, as well as the biodistribution of PEGylated MoF nanoparticles were evaluated in a mouse model by inductively coupled plasma mass spectrometry (ICP-MS). Overall, these results provide a strong foundation for the further development of this nanoparticle-based drug delivery platform for chemoradiation of breast cancers.

COLL 468

Fluorinated nanomaterials for efficient nucleic acids delivery with medium serum

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Efficient nucleic acids-based drug delivery in presence of serum is of crucial importance for effective gene therapy. Fluorinated vectors are considered to be attractive candidates for siRNA-mediated gene therapy because of their delivery efficacy in serum-containing media. However, the mechanisms driving the superior gene transfection behavior of fluorinated vectors are still not well understood and comprehensive investigations are warranted. Herein, a library of perfluorooctanoyl fluoride (PFF)-fluorinated oligoethylenimines (OEI) was fabricated. The gene silencing in serum-containing medium revealed that the f_{0.7}OEI/siRNA NAs achieved high luciferase silencing of in Luc-HeLa cells cultured in FBS-containing medium, which was almost 2-fold greater than the silencing efficacy of siRNA delivered by the commercially available vector Lipo 2000. High levels of apolipoprotein B silencing were also achieved by f_{0.7}OEI/siRNA NAs *in vivo*. *In vitro* investigations demonstrated the superior gene delivery of f_{0.7}OEI NAs with the potent endosomal disruption capability of fluorinated vectors in presence of serum, which was essentially attributed to the serum proteins adsorption resistance of the f_{0.7}OEI NAs. Therefore, this work provides an potential platform to efficient siRNA delivery as well as insights into fluorine-associated serum resistance.

COLL 469

Design and implementation of gold-nanoparticle formulations as MUC1-directed cancer vaccines

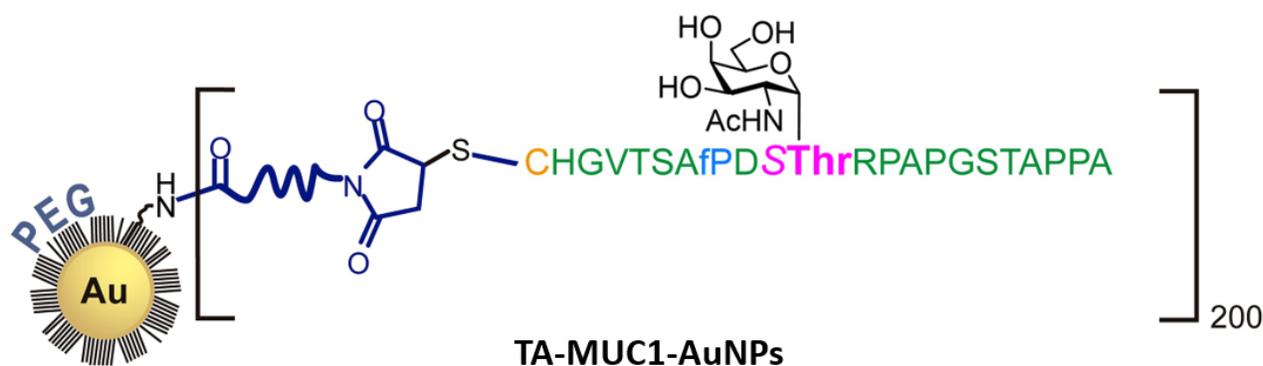
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The extracellular domain of mucin 1 (MUC1) is an attractive target for the development of therapeutic cancer vaccines.¹ In fact, the tumor-associated form of MUC1 (TA-MUC1) is markedly underglycosylated and displays new peptide and carbohydrate epitopes. Moreover, TA-MUC1 is overexpressed on a large variety of cancer cells. Thus, if properly instructed with a vaccine, the immune system may be able to recognize cancer cells based on these features killing them selectively. Although a number of vaccine design strategies have been pursued, successful anticancer vaccines are yet to be obtained.

We are developing cancer vaccines based on PEGylated gold nanoparticles (AuNPs) carrying glycopeptide antigens.²

In this contribution we describe the design, preparation and implementation of novel AuNP-based vaccine candidates carrying non-natural glycopeptides as TA-MUC1 antigen mimics. These antigen mimics present a single O/S substitution at the glycosidic linkage of a glycosylated amino acid to improve bioavailability. We have immobilized these TA-MUC1 antigen mimics on AuNPs and tested them as immunogen formulation in mice.³ A significant humoral immune response is obtained in the absence of any additional adjuvant. Moreover, the mice antisera stain with high selectivity cancer cells in biopsies of breast cancer patients demonstrating that the antibodies elicited against the antigen mimic recognize the naturally occurring antigen in its physiological context. Clinically, the exploitation of tumor-associated antigen mimics may contribute to the development of cancer vaccines and the improvement of cancer diagnosis based on antibodies.



Vaccine candidate displaying TA-MUC1 glycopeptide mimics on PEGylated gold nanoparticles

COLL 470

Modulation of precursor reactivity in colloidal syntheses of WSe₂-based nanostructures

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The development of solution-phase routes to transition metal dichalcogenides is gaining attention due to the potential to realize scalable syntheses that require relatively mild conditions. Colloidal nanocrystal syntheses offer facile control of properties such as size, shape, phase and dopant/defect incorporation by tuning of easily modulated parameters such as time, temperature, ligand identity and precursor reactivity. Here, we show that control over that size and phase of colloidal WSe₂ nanocrystals is achieved by careful choice of ligand, where increasing the coordinating strength of ligands present during synthesis favors larger nanocrystals with the 1T' phase. Specifically, oleic acid is used to coordinate W in solution, slowing down the W reactivity and yielding large 1T' WSe₂ nanocrystals. We can further exploit this modulation of the reactivity to enable one-pot synthesis of colloidal core/shell heterostructured nanocrystals. The core nanocrystals can subsequently be removed by soaking in ethylene diamine and trioctylphosphine, allowing easy access to hollow WSe₂ nanocrystals. Overall, these syntheses allow access to heterostructured or hollow nanostructures in just one or two steps and demonstrate a synthetic strategy to ultimately enable facile, solution-phase syntheses of exotic nanostructures.

COLL 471

Colloidal Pb-free halide perovskite and group IV nanomaterials

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Semiconducting nanocrystals and quantum dots have realized commercialization for several technologies, including lighting and display technologies. However, their potential is limited by issues such as inadequate stability, concerns over heavy metal content, and poor quantum yields in the blue spectral region. In this talk I demonstrate our recent progress addressing these issues through colloidal nanostructures that address each of these issues. In the case of Pb-free halide perovskites, I will show our progress in developing Bi-based halide perovskite NCs that have composition-tunable photoluminescence. I will also show how Zintl compounds can be used as a precursor to fabricate layered silicides and germanides, that can be subsequently deintercalated to form colloidal nanosheets with controllable composition and optical properties.

COLL 472

Tuning the band gap of semiconducting two-dimensional materials by changing the structure of polymer assembled on their surface

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Polyethylene glycol (PEG) assembled on the surface of two-dimensional tungsten disulfide (WS_2) into a limited number of nanoislands (NIs), nanoshell (NS), and granular nanoparticulates (GNPs) depending on its chain length. NIs assemblies showed a non-measurable shift of photoluminescence (PL) and the A and B absorption peaks of WS_2 . This confirmed that the electronic doping by thiol is not effective. PEG NS assembly displayed a smaller red-shift of the PL and a slight decrease of the energy difference between the A and B absorption peaks of WS_2 . However, increasing the dielectric function on the surface of WS_2 has a small influence on their optical properties. The PEG NPs assembly on WS_2 exhibited a significant red-shift of the PL spectrum and a large decrease of the energy difference between A and B absorption peaks. Deforming the WS_2 sheet by PEG NPs assembly decreased the orbital coupling and lowered the electronic direct band gap significantly. Raman bands of WS_2 are shifted to a higher frequency due to improving its mechanical strength after PEG assembly.

COLL 473

Effect of the heterostructure on charge transfer processes in Pbse/Cdse Janus quantum dots functionalized by Ru(II) dyes

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New photovoltaic and photocatalysis materials have been recently proposed, which are based on semiconductor quantum dots (QDs) and various organic and metal-organic dyes functionalizing the surface. Chemical functionalization of nanostructures by dyes provides an organic-inorganic interface for efficient charge separation and transfer. Additionally, complex heterostructures of Janus QDs, where a half of the QD is made from CdS(e) and another half is from PbS(e) forming an interface along a specific crystalline direction, have recently emerged as a new type of interfaces that permits more control over the charge transfer processes and the overall efficiency of energy conversion. We computationally study how the fundamental properties of the Janus QDs – specifically, electronic couplings and the energy alignment of the band offsets are impacted by the atomistic character of the PbSe/CdSe interface and its interaction with the black dye. We found that the (111) crystalline direction of the interface provides highly optically active lower energy transitions, as well as stabilizes the occupied orbitals of the dye moving them deeper to the valence band of the QD. In contrast, (100) crystalline direction of the interface leads to weaker optical transitions, and electronic couplings between the QD and the dye.

COLL 474

Spanning the atomic to the agglomerate dimensions in colloidal dispersions of 2D lead halide perovskites

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Hybrid organic-inorganic perovskites (HOIPs), such as methylammonium lead iodide (MAPbI₃), are promising semiconductors with long carrier lifetimes, synthetic tunability, remarkable defect tolerance and simple processing. Recently, 2D analogues with improved ambient stability and radiative recombination rates have been made by adding insulating cations (e.g. butylammonium) to separate the perovskite structure into sheets. These 2D materials can be formed either in thin films or as dispersed nanoplatelets of only a few PbX₆ octahedra thick. The number of PbX₆ octahedra confined between insulating layers (i.e. the '*n*-value') can be tuned by varying precursor stoichiometry, enabling discrete tunability of the bandgap through dielectric and quantum confinement. However, it is challenging to control the polydispersity of crystallites with different confinement dimensions.

We present a systematic study of the colloidal microstructure of 2D perovskite nanocrystal dispersions at multiple length scales to identify and control their dynamic evolution. Monodisperse colloids of single (*n*=1) and double (*n*=2) layered 2D nanocrystals can be grown by antisolvent precipitation, but for *n* > 2 the nanocrystal thickness is a distribution of *n*-values. Moreover, this distribution can change in both average *n*-value and variance with the choice of insulating molecules, particle concentration, dispersion aging or deposition onto a substrate. Using optical absorption and emission of dispersions, along with XRD and TEM of deposited films, we find that the selection of insulating molecules controls the distribution of *n*-values and agglomeration behavior. A mixture of shorter alkylammonium cations (e.g. butylammonium) and longer, bulkier alkylammonium cations is found to systematically narrow the distribution of *n*-values in 2D perovskite dispersions, even for *n* > 2. We present a combined transmission wide-angle x-ray scattering (WAXS) and small angle neutron scattering (SANS) study to demonstrate the role of insulating cation size, solubility and motility on the atomic structure and self-assembly of dispersed 2D perovskites. This study provides a novel framework to discuss the length-scales of growth for confined 2D perovskite colloids, and suggests new avenues to control phase, morphology and dispersion properties.

COLL 475

Synthesis and characterization of modified hydroxyapatites

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Hydroxyapatite is an inorganic nanomaterial whose modification is being explored to increase its metal ion and molecular affinities. One method of modification is through the introduction of bisphosphonates into the matrix and a second method is by the introduction of metal ions, such as Cu(II) and Cd(II), into the matrix. Characterization of products from both methods will be described, especially with solid-state NMR and UV spectra. The effect of the modifications on molecular affinities will be quantified and structure – property relationships proposed.

COLL 476

Air-stable CuInSe₂ nanocrystal transistors and circuits via post-deposition cation exchange

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Colloidal semiconductor nanocrystals (NCs) are a promising materials class for solution-processable, next-generation electronic devices. However, most high-performance devices and circuits have been achieved using NCs containing toxic elements, which may limit their further device development. We fabricate high mobility CuInSe₂ NC field-effect transistors (FETs) using a solution-based, post-deposition, sequential cation exchange process that starts with electronically coupled, thiocyanate (SCN)-capped CdSe NC thin films. First Cu⁺ is substituted for Cd²⁺ transforming CdSe NCs to Cu-rich Cu₂Se NC films. Next, Cu₂Se NC films are dipped into a Na₂Se solution to Se-enrich the NCs, thus compensating the Cu-rich surface, promoting fusion of the Cu₂Se NCs, and providing sites for subsequent In-dopants. The liquid-coordination-complex trioctylphosphine–indium chloride (TOP–InCl₃) is used as a source of In³⁺ to partially exchange and n-dope CuInSe₂ NC films. We fabricate FETs using CuInSe₂ NC thin films and encapsulate the device by Atomic Layer Deposition (ALD). The elevated processing temperatures in the ALD provide *in situ* thermal activation of the In-dopants, while the encapsulation process further passivates trap states, improves doping efficiency, and makes the FETs air-stable. We demonstrate CuInSe₂ NC FETs with linear (saturation) electron mobilities of $8.2 \pm 1.8 \text{ cm}^2 /(\text{V s})$ ($10.5 \pm 2.4 \text{ cm}^2 /(\text{V s})$) and with current modulation of 10^5 , comparable to that for high-performance Cd-, Pb-, and As-based NC FETs. We show the feasibility of CuInSe₂NC FETs for low-voltage operation and fabricate CuInSe₂ NC inverters, demonstrating their promise for fabricating low-cost, low-toxicity integrated circuits.

COLL 477

Fundamental study of graphene oxide-metal nanoparticle material hybrids for electromagnetic energy interference mitigation: Systematic structure/function analysis

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Electromagnetic (EM) energy covers a very large spectrum, from low energy radio waves to high energy gamma rays. Humankind has utilized and controlled these various energy regions for applications ranging from radio communication to molecular and atomic level characterizations. However, oftentimes unwanted and deleterious effects are observed from uncontrolled and undesired EM sources. To mitigate and minimize these potentially harmful effects, numerous materials have been studied that specifically interact with various EM energies. Such examples include IR reflective materials for passive heating and lead vests for x-ray protection. Despite these and many additional examples, fundamental understanding of EM energy mitigating interactions at the molecular level remain amiss. Here we have started using graphene oxide in combination with different metal and metal oxide nanoparticles in a systematic study to explore their interaction with microwave energy (1 to 300 GHz) as a function of molecular structure. By using systematically controlled reduction of graphene oxide, the electronic structure can be varied, resulting in different dielectric properties. By combining with metal and metal oxide nanoparticles with controllable properties (chemistry, size, concentration), the magnetic susceptibility can simultaneously be controlled resulting in tunable EM energy interactions. Using vector network analysis in combination with structural characterization, we will report our progress towards understanding the effects of material structure on microwave absorption.

COLL 478

Understanding the excipient's effects on functionality of glass and polymer pre-filled syringes

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Combination drug products, based on therapeutic proteins, are gaining popularity due to easy administration from the patient perspective. Designing and developing a combination drug product is a very complex process, and most early efforts were spent typically on the stability of the drug substance. The drug/packaging compatibility tends to be over-looked in the early stage of the development of a combination drug product, an issue which could cause serious future problems such as a device malfunction or a drug safety issue.

Glass-based pre-filled syringes (PFS) are the most commonly used PFS in many combination drug products. Silicone oil is commonly used as a lubricant in the glass PFS to control break-loose and extrusion forces. However, the stability of the sprayed silicone oil layer can be altered by drug excipients, which then will have a profound effect on the break-loose and extrusion forces. We discovered that syringe friction change is caused by dynamic interactions of formulation excipients (surfactants, tonicity agents, buffering agents, etc.) with silicone oil, water, and glass. Our data shows that different excipients affect extrusion forces differently, and that those differences can be explained/predicted by Hansen Solubility Parameters theory.

Compared to glass PFS, cyclic olefin polymer (COP) PFS showed more consistent and predictable extrusion forces. This can be explained/predicted by Hansen Solubility Parameters theory as well. Furthermore, COP PFS also showed significantly less variance in extrusion force within each injection, which is critical for certain applications such as autoinjectors.

Therefore, we demonstrated how to choose the right excipients and their compatible primary packaging materials to perform their chemical functionality, without jeopardizing the combination drug product's physical functionality and device performance. This process that takes drug/packaging compatibility into consideration at the early stage of designing and developing of a combination drug product will give drug manufacturers a tremendous advantage.

COLL 479

Protein-excipient interactions via diffusion NMR: Case study of zwitterions

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Understanding protein interactions with organic compounds and materials are paramount in improving therapeutic proteins functions and formulations. Emerging evidence indicates that the zwitterions and zwitterionic materials have biocompatibility properties that can have applications in protein stability and protein delivery. In contrast, there is little empirical information available on their mechanism, which means that the details of interactions between zwitterions and proteins are far from being fully understood. Diffusion NMR is a tool that can evaluate the dynamics of multi-component mixtures and can be applied to protein and excipient molecules in solution. In this work, we studied the interactions between model proteins and different zwitterions, including a zwitterionic surfactant, a zwitterionic inner-salt, and a zwitterionic polymer. The diffusion coefficients of the protein and the excipients were evaluated using the pulsed field gradient (PFG) stimulated echo (STE). The diffusion data were later used to quantify important parameters such as association, binding energies, and aggregation numbers using a thermodynamic analysis. Results of this study will help researchers improve

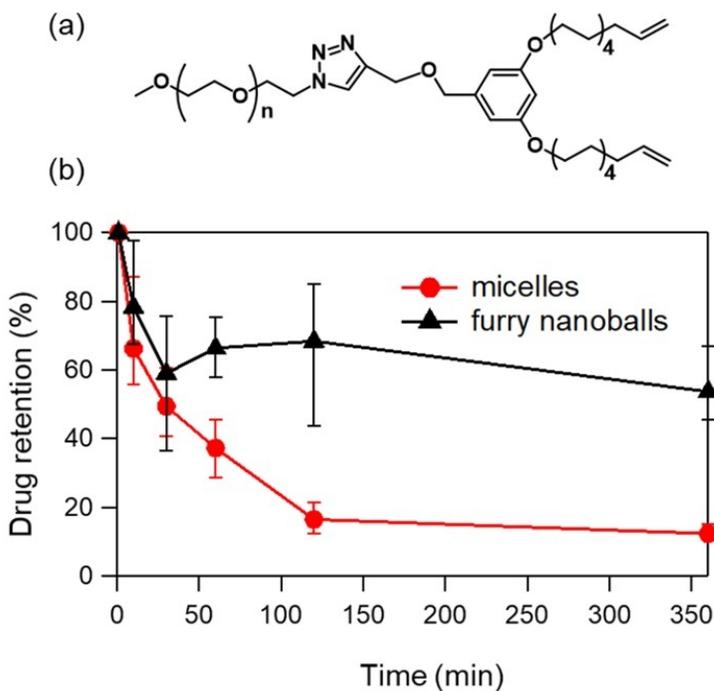
protein delivery vehicles physiochemical properties as well as improving the therapeutic protein formulations.

COLL 480

Furry nanoballs bearing D_4^H/D_4^V silicone: Synthesis, structural characterization, and their robust stability *in vivo*

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Although micelles are one of the candidates of drug carrier as nanomedicines, their structures are easily collapsed by diluting down to their critical micelle concentration and by changing environmental condition including temperature, pH, and salt concentration, which are disadvantages for the practical application *in vivo*. Further, high shear stress and interactions with plasma proteins in blood stream would induce premature drug release from micelles. Employing polyethylene glycol (PEG) on micellar shells provides prolonged blood retention *in vivo* due to the stealth character, but still the structural stability is not high enough. For preparing particles demonstrating robust stability *in vivo*, we have synthesized PEG-bearing amphiphilic compound containing a vinyl group in the end of the alkyl chain (C11). After preparing nanoemulsion composed of the PEG-based micelle and tetramethyl-cyclotetrasiloxane (D_4^H) and tetramethyltetravinylcyclotetrasiloxane (D_4^V), we carried out a hydrosilylation reaction to form D_4^H/D_4^V network structures in the micellar core. We named the obtained particle “furry nano-balls”. The nano-ball structure was characterized using small angle scattering techniques, and their retention properties in blood was compared to that of the original micelle.



(a) Chemical structure of PEG-bearing amphiphilic compound.
 (b) Drug retention in vivo of micelles (red profile) and nanoballs (black profile)

COLL 481

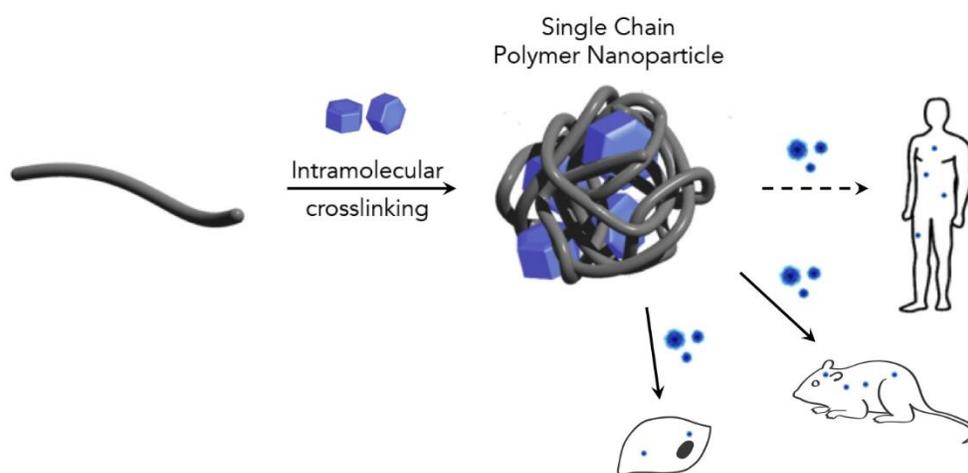
Versatile single chain polymer nanoparticles in controlled drug delivery

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As the area of controlled drug delivery is increasingly finding application in a variety of diseases, with different targeting sites and drug candidates, there is an urgent need for adjustable nanocarrier systems. Due to their chemical diversity and highly modular nature, polymers and polymeric nanoparticles in particular are popular drug carrier materials. Most polymeric nanoparticles are in the 50-200 nm size range, which is unfortunate, since proteins, enzymes and some viruses are considerably smaller in size. In order to widen the existing polymeric drug carrier systems to the sub-20 nm size regime, our research is focused on developing *single-chain polymer*

nanoparticles (SCNPs). SCNPs are prepared through intramolecular crosslinking of individual polymer chains into individual nanoparticles and thus offer tremendous control over size and dispersity. Through exclusive intramolecular crosslinks, SCNPs are an order of magnitude smaller than conventional polymer nanoparticles, easily accessible in relevant quantities and without the requirement of complex synthetic strategies.

Highly modular in nature, these uniquely sized polymer nanoparticles enable encapsulation and controlled release of drug molecules, irrespective of their hydro- or lipophilicity. Careful engineering of the nanoparticle surface provides control over distribution behavior and has enabled us to mimic proteins in terms of shape, composition and even function.



COLL 482

Chaperone effect of cationic comb-type copolymers for an amphiphilic peptide disturbing lipid membranes

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Macromolecular drugs have attracted great attention owing to their high target specificity, however, an effective method to deliver them intracellularly is demanded. As one of the intracellular delivery tools, an amphiphilic E5 peptide that mimics the N-terminal end of hemagglutinin, a membrane fusogenic protein, derived from influenza virus has been focused. E5 exhibits coil-to-helix transition with decrease in pH, resulting in disruption of cellular membranes. However, the intrinsic hydrophobicity of E5 at acidic pH makes it difficult to use as a drug delivery tool due to its poor solubility and non-specific interactions with biological components. We have reported that a cationic comb-

type copolymer, poly(allylamine)-*graft*-dextran (PAA-*g*-Dex) forms a soluble inter-polyelectrolyte complex with E5 and induces the coil-to-helix transition even at neutral pH. Moreover, PAA-*g*-Dex enhances cellular membrane disruptive activity of E5 at both acidic and neutral pH. Furthermore, we have clarified that the E5/PAA-*g*-Dex complex augmented the cellular membrane permeability of a model protein. Considering that cellular membranes are heterogeneous in lipid composition depending on cell types and growth phases, the lipid membrane composition is an important factor for interaction with the complex. Herein, we assessed the effect of the lipid composition on folding of E5 with or without PAA-*g*-Dex to explore effect of the copolymer on interaction between E5 and the membrane, and chaperoning mechanisms of the copolymer. Circular dichroism measurements at pH 7.4 indicated that partial folding of E5 took place in the presence of liposomes having liquid-disordered (L_d) phase but not having liquid-ordered phase. PAA-*g*-Dex partially folded E5 into the helical structure, and the addition of the liposomes having L_d phase further folded E5 into the functional structure to disrupt the membrane. Hence, PAA-*g*-Dex chaperones E5 while maintaining the intrinsic membrane selectivity of E5.

COLL 483

Macromolecular HPMA-based nanoparticles with cholesterol for solid tumor targeting: Synthesis, internal structure, and interaction with blood plasma proteins

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In this three-part talk, I will start by quick introduction of drug conjugates consisting of N-(2-Hydroxypropyl)methacrylamide (HPMA) copolymer, the anticancer drug doxorubicin (Dox), and a defined amount of cholesterol moieties differing in their hydrophobicity. In the second part of my talk, I will describe our research on aggregation behavior and shape of the HPMA copolymers in dilute aqueous solutions and detailed structure of nanoparticles. Using a combination of various techniques, we conclude that the most probable structure of HPMA-cholesterol nanoparticles is the pearl-necklace one where ellipsoidal pearls mainly composed of cholesterol covered by HPMA shell; the pearls are connected by bridges composed of hydrophilic HPMA copolymer chains. We have unambiguously proven that Dox moieties are not embedded inside of the cholesterol domain only but uniformly distributed around the whole nanoparticle including a hydrophilic HPMA shell surface [1]. Additionally, we performed time-resolved SAXS/SANS measurements after changing from pH values typical for blood (pH=7.4) to those typical for tumor cells (pH=5.0) to characterize drug release and particle growth. For most conjugates, nanoparticle growth was observed in the time range of several hours. It was established that the growth rate and steady-state size of nanoparticles depend on the hydrophobicity of the cholesterol derivative [2]. Finally, I will highlight our work on interaction of HPMA copolymers with blood plasma proteins. Human serum albumin (HSA), fibrinogen, Immunoglobulin G, and

apolipoproteins A-E were chosen for this study as basic proteins, which are the main component of human blood plasma. It was found that individual proteins and plasma have very low binding affinity to nanoparticles. We observed no hard corona around HPMA-based nanoparticles; with the exception of HSA the proteins showed no detectable binding to the nanoparticles. Our study confirms that a classical “hard corona–soft corona” paradigm is not valid for all types of nanoparticles and each system has a unique protein corona that is determined by the nature of the nanoparticle material

COLL 484

Quantifying drug adsorption to lipid membranes using second harmonic generation

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Studies of aqueous solutions of antipsychotic drugs clozapine and chlorpromazine adsorbed to supported lipid bilayers composed of phospholipids of varying lipid phase, head group charge and cholesterol content were conducted. The nonlinear optical method, second harmonic generation, was used to directly detect adsorbed drugs at the aqueous-lipid interface without any extrinsic tags. Binding affinities and the impact of lipid fluidity and electrostatic interactions were quantified. Temperatures were varied under biologically-relevant conditions and the relative enthalpic and entropic contributions to free energies of adsorption were found to vary based on lipid composition. These studies provide mechanistic insight into how drug structure impacts interactions with phospholipids to inform studies of lipid-based drug delivery materials.

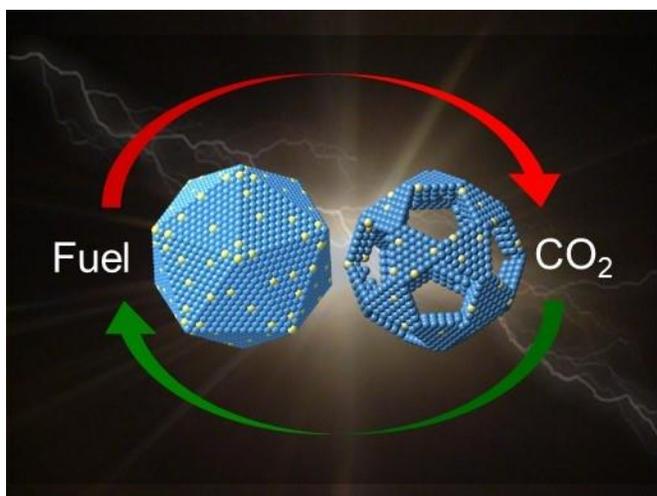
COLL 485

Modulation of surface states on bimetallic nanoicosahedra toward catalytic energy conversion

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Building bimetallic surfaces on nanocrystals renders them superior catalysts for energy-conversion reactions by virtue of the electronic effect. In the common types of alloy, core-shell, and Janus structures, the alloy forms in atom-level blending of elements while the latter two form with interfaces by contacts of different components in the structures where specific strain is generated due to lattice mismatch. The strain varies the surface states in the vicinities of interfaces and hence leads to further alterations in the catalytic behaviors of bimetallic nanocrystals. Recently, an icosahedron is known a

structure with 30 twinned boundaries that induce large tensile strain on its 20 facets, significantly improving the surface reactivity of the nanoicosahedron in a catalytic reaction. In this talk, two stories about bimetallic nanoicosahedra for liquid fuel oxidation and photoreduction of nitro-compounds will be introduced. In the first part, we will demonstrate how monodispersed AuPd nanoicosahedra with photoactivity were fabricated in one-step aqueous synthesis. With these AuPd nanoicosahedra, the performances by their variable yet controlled surface compositions in ethanol oxidation via electrocatalysis and photoreduction of 4-nitrophenol aided by visible energy had been explored and will be presented. In the second part, we will further introduce the work where unique icosahedral PdRu nanoframes were also prepared in one-step strategy and water phase. We had explored the growth kinetics of the nanoframes and looked into their performances in electrocatalytic ethanol oxidation and CO₂ reduction, that all will be presented, too.



COLL 486

Highly tunable platform for biomimetic catalysis from nanocrystal-polymer composites

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Enzymes are ideal catalysts for many important reactions. They have evolved to contain confined metal centers within angstrom distances of amino acid groups with specific functionality to direct transport of species (reactants, products) as well as to shape the

electronic landscape of adsorbates to impart high activity and selectivity for biologically relevant transformations. Most traditional catalytic approaches use extended metal surfaces as the active site for catalysis. Consequently, rational catalytic design is mostly limited to engineering metal electronic structure with alloying, surface structuring and metal oxide interface engineering. In this work we draw from enzymes to add another level of control to catalyst engineering by incorporating metal centers within amorphous polymers with tunable morphology and functionality.

In this talk, we will highlight how we employ porous organic frameworks (POFs), a class of thermally stable, microporous, and chemically functionalizable amorphous polymers, to encapsulate colloidal metal nanoparticles as a catalytic platform. We first support nanocrystals on POF, remove ligands with thermal treatment and then epitaxially grow porous polymer overlayers over the POF-metal composite to encapsulate the particles fully. This approach is tunable in the polymer chemistry, morphology as well as the metal particle composition. We synthesized an array of materials with differing POF chemistry, nanoparticle composition and morphology to demonstrate the wide range of possibilities with this system. In a second part, the catalytic properties of several materials will be discussed. We demonstrate that introducing the POF overlayer on palladium nanoparticles increases intrinsic activity as well as induces catalytic oscillations under conditions that do not induce oscillations on supported palladium catalysts for CO Oxidation, a test reaction. These catalytic changes have been demonstrated to be stable under oxidizing conditions for upwards of 40 hours. We discuss how the amorphous polymer overlayer induces changes to control transport and chemical environment of reactants, products, and intermediates at the metal active site much like in enzymes. These amorphous polymers open up avenues to explore catalytic materials with novel reactivity.

COLL 487

Nanoscale metal–organic supercontainers as biomimetic catalysts

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Our group recently discovered a new class of synthetic receptors known as metal-organic supercontainers (MOSCs). These nanoscale supercontainers can be synthesized from the reaction of divalent metal ions such as Co(II)/Ni(II)/Zn(II), carboxylate linkers of various shapes, and sulfonycalix[4]arene-based container precursors. The most attractive features of the MOSCs include their novel multi-cavity structure, enzyme-like substrate binding pocket, and a metal-bound μ_4 -H₂O molecule located within the active site. We demonstrate that the unique microenvironment of the MOSC nano-cavity readily modulates the chemical tendency of the μ_4 -H₂O species, allowing the MOSCs to promote hydrogen-bond catalysis, Brønsted-acid catalysis, and Brønsted-base catalysis, respectively. We show that the catalytic efficacy of the MOSCs can be further mediated through both cation- and anion-regulation, a concept we termed “electrostatic regulation”. In addition, we describe how MOSCs can be imparted water-solubility through surface functionalization to facilitate “catalysis on water”. Together,

these results highlight the exciting potential of MOSCs as a new class of biomimetic catalysts.

COLL 488

Hierarchical nanocrystal assembly driven by structural transformation of biomolecules

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The hierarchical control in biogenic minerals ranging from precise morphology control at a nanometer scale to their subsequent assembly into a macroscopic scale remains a formidable challenge in artificial materials syntheses. Although considerable efforts have been devoted to exploring effects of biomolecules in the biomineralization, the studies to date are largely limited to atomic/molecular scale crystallization processes. On the other hand, the high order structures of biomolecules play important roles on the long arrange assembly of biominerals but remains a largely untouched topic. Here we demonstrate a biomimetic route that explores higher order peptide structure (beyond primary) on guiding nanocrystal formation and their subsequent anisotropic assembly into hierarchical structures. We demonstrate the secondary structure (ST-turn) in a crystallographic specific peptide molecule can drive the formation of nanocrystals with specific facets and their other higher order structure (β -sheet) can further guide the long-range 0D nanocrystal assembly into 1D arrays and 2D sheets along the specific crystallographic direction. This study demonstrates for the first time an entire growth and assembly process of non-biogenic material that is driven by biomolecular specificity and governed by tunable and reversible non-covalent hydrogen bonds, analogous to hierarchical structures self-assembled in biological systems.

COLL 489

Mechanically initiated free radical polymerization

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Mechanical initiation of polymerization offers the chance to generate polymers in new environments using an energy source with unique capabilities. Recently, a renewed interest in mechanically controlled polymerization has yielded many techniques for controlled radical polymerization via ultrasound. However, other types of polymerizations induced by mechanical activation are rare, especially for generating high molecular weight polymers. Herein we show the example of using piezoelectric ZnO nanoparticles to generate free radical species that initiate chain-growth

polymerization and polymer crosslinking. The fast generation of high amounts of reactive radicals enable the formation of polymer/gel via ultrasound activation. We envision that this chemistry can be used to harness mechanical energy for constructive purposes in polymeric materials and for controlled polymerizations for bulk-scale reactions.

COLL 490

Coupling magnetic and plasmonic anisotropy in hybrid nanorods for mechanochromic films

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Mechanochromic response is a key desirable function for designing bionic robot systems. Unfortunately, compared to mimicking motions of natural creatures, we are far from successful in fabricating mechanochromic systems with responsive colorimetric changes. Herein, we report the development of novel mechanochromic films based on hybrid nanorods integrated with magnetic and plasmonic anisotropy. Magnetic-plasmonic hybrid nanorods have first been synthesized through a unique space-confined seed-mediated process, which represents a new platform for fabricating next-generation complex nanostructures. By coupling magnetic and plasmonic anisotropy, the plasmonic excitation of the colloidal hybrid nanorods could be collectively regulated using magnetic fields. Such magnetic manipulation facilitates the convenient incorporation of the hybrid nanorods into solid matrices such as polymer films with a well-controlled orientation to enable colorimetric changes when mimicking linear (rotating and bending) and non-linear (twisting) motions. The potential of these hybrid nanostructures is further demonstrated by configuring the 3D orientation of nanorods and quantifying the localized mechanical distortion by deconvolution of excitation states from space-resolved extinction spectra.

COLL 491

3D-porous plate-like Ag nanostructures for efficient CO₂ electroreduction

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Developing an efficient and cost-effective catalyst is of the highest interests for electrochemical reduction of CO₂. Nanostructured silver (Ag) represents one candidate due to its efficiency of selective formation of CO that is comparable that of the well-known expensive gold (Au) catalysts. However, the mass-specific efficiency and suppression of the competitive hydrogen evolution reaction (HER) of the available Ag nanostructured catalysts are not ideal yet for electrochemical CO₂ reduction. In this

presentation, we demonstrate a new type of porous Ag nanostructures with two-levels of porosity, exhibiting the larger hollows for efficient electrolyte diffusion and the smaller pores for exposing the highest surface area. The porous Ag nanostructures are synthesized from in-situ electrochemical reduction of silver benzenethiolate nanoboxes constructed from the well-organized nanoplates. Such synthesis results in the Ag surfaces to be covered with benzenethiolate, which influences the adsorption energy of active species involved in both CO₂ reduction and HER to improve the selectivity of CO₂-to-CO conversion. The results reveal tremendous enhancement of mass efficiency reaching upto 500 A/g for CO₂ reduction. In the presence of surface benzenethiolate adsorbates, the electrochemical CO₂-to-CO conversion efficiency maintains as high as close to the unity even at high overpotentials, where HER is usually difficult to suppress. This work highlights a promising way to design a cost-effective catalyst toward an efficient and selective electroreduction of CO₂.

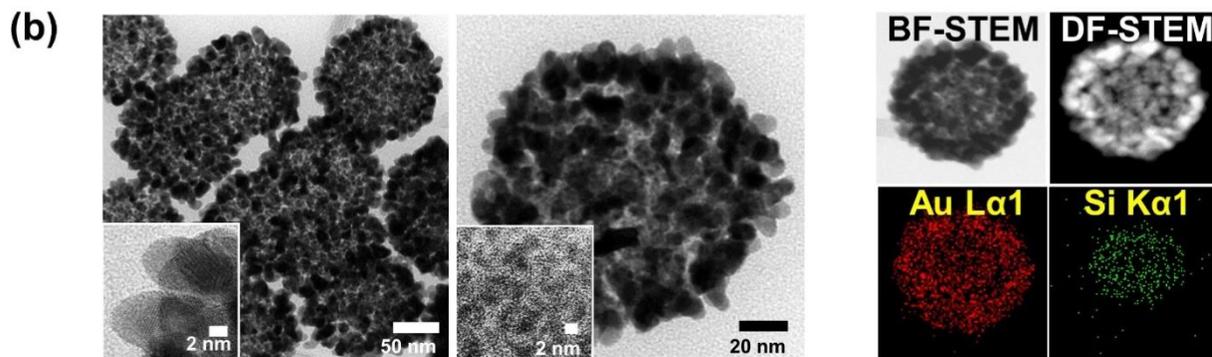
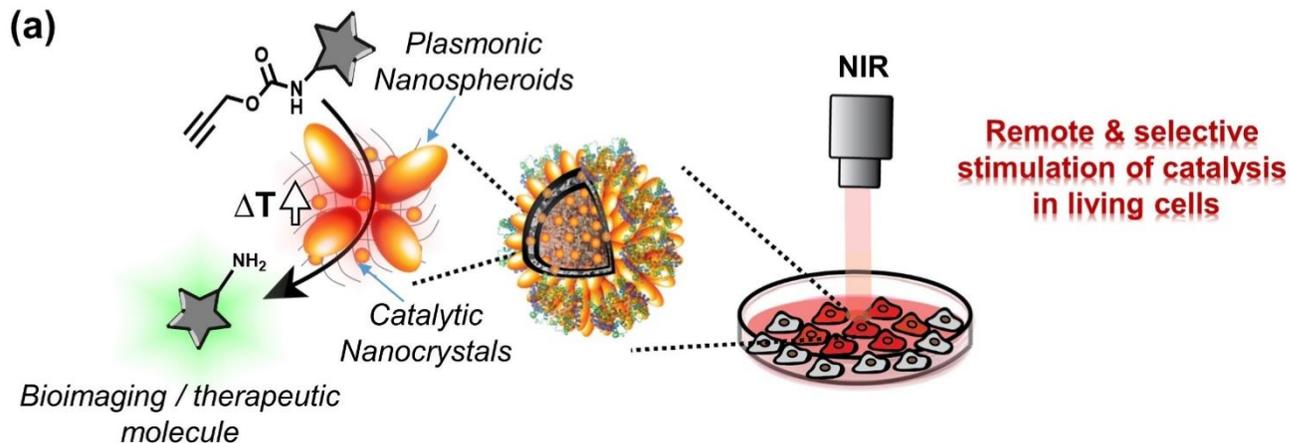
COLL 492

Remotely operable and highly functional plasmonic nanoreactors for NIR-light-induced bioorthogonal catalysis in living cells

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Nature uses its own sophisticated catalysts, namely enzymes, to carry out numerous biochemical reactions sustaining life. Besides enzymes, innovative man-made catalysts — capable of synthesizing functional molecules such as therapeutic drugs and bioimaging probes locally inside living cells from simple and non-toxic precursors via various bond forming/breaking reactions — can lead to the discovery of side-effect-free drugs and ultraprecise diagnosis and also contribute as synthetic toolkit to chemical biologists. To realize such versatile and efficient bioorthogonal reactions — rational, customizable and biocompatible designs of catalysts which can provide high catalytic efficacy, tolerance to complex biological media and facility to remotely control or stimulate reaction rates should be synthesized. Unfortunately, most of the reported bioorthogonal catalysts take rather long reaction times and realize the products in poor yields and don't offer any plug-in to remotely trigger or promote sluggish intracellular reactions, which is a serious bottle-neck for their advancement to extensive applications. Our new plasmonically integrated nanoreactors (PINERs) can perform highly accelerated catalytic reactions in living cells by using NIR-light as harmless and efficient energy source. The bi-component design of PINER (overall size ca. 100 nm) consists of compartmentalized and selectively accessible noble metal (Au/Pd/Pt) catalytic nanocrystals (size ca. 2 nm), proximally interfaced with a plasmonic corona having multiple closely spaced Au-nanospheroids (size ca. 15 nm). Plasmonic Au-nanospheroids act as optical nano-antennae which can efficiently concentrate remotely exposed NIR light and convert the absorbed photonic energy to highly localized heat and generate reactive charge-carriers; and these plasmon-induced effects dramatically

stimulate the reactions taking place on proximal catalytic nanocrystals in PINER, without any unintentional adverse effects on living cells.



Structure and intracellular catalysis by PINERs.

COLL 493

Enhanced virus removal in a practical sand filter

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The purpose of this paper is to report an unprecedented, high virus removal observed in a practical sand filter and the corresponding mechanism of removal. Fecal contamination of drinking water and related health burden is a global challenge. Among the pathogens present in contaminated water, viruses are especially difficult to detect and treat leading to frequent outbreaks worldwide. No definitive solution exists for this problem due to the limitations with the current technologies. Disinfection is effective but can be prone to failure as currently practiced while boiling is considered a last resort intervention. We found that simple functionalization of sand (f-sand) filters, using a water extract of *Moringa oleifera* (MO) seeds, can enable $\sim 7 \log_{10}$ virus removal efficiency. These tests were conducted with MS2 bacteriophage, a surrogate for human enteric viruses. A surprising discovery from experiments was that the origin of MO seeds used to prepare f-sand filters critically affect the virus removal. This led us to probe the composition of proteins adsorbed on f-sand to identify the source of virus removal activity. A combination of gel electrophoresis and mass spectrometry indicated the presence of two proteins (MoCBP and MO2.1) adsorbed on f-sand. Molecular docking simulations of these proteins with virus (MS2) capsid proteins suggested that favorable interactions between MoCBP and MS2 drives the virus removal. MoCBP is known to exhibit antifungal and chitin binding activity. Our simulations indicated that chitin monomers and MS2 interact with MoCBP through similar binding regions. Further column experiments guided by simulations revealed that the specific interactions of MS2 capsid with the chitin-binding region of MoCBP is the molecular mechanism of removal in f-sand filters. We propose f-sand filters as a highly effective, energy-efficient, and practical technology for virus removal applicable to both developing and developed countries. The removal mechanism based on specific molecular interactions between virus capsid and plant-based protein provides a molecular basis for screening and engineering plant-based proteins to filter viruses in water, medicine and agricultural applications.

COLL 494

Use of rotifers as self-propelling biohybrid microcleaners

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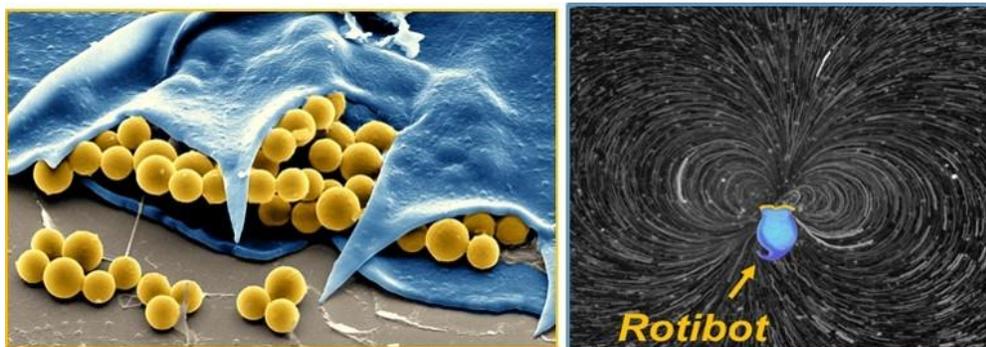
The contamination of water resources with biological and chemical pollutants could have long term negative effects on aquatic ecosystems and human health. Current pollutant neutralization methods for environmental remediation involve the use of adsorbent materials and chemical degradation. However, these methods have several

deficiencies, including slow /adsorption degradation rates, and localized activity due to limited spatial displacement based on diffusion.

Here, I will present the development of self-propelled biohybrid microrobots, employing marine rotifers as their engine, named “rotibot”, and demonstrate their practical utility and advantages for environmental remediation. Functionalized microbeads have been attached electrostatically within the rotifer mouth and aggregated inside their inner lip. The reactive particles confined around the rotifer’s lip are thus exposed to a high flow rate of the pollutant solution, resulting in dramatically accelerated decontamination processes, without external mixing or harmful fuels. Theoretical simulations, modeling the greatly enhanced fluid dynamic associated with such built-in mixing effect, correlated well with the experimental observations.

The rotibot thus proved to be an effective, versatile and robust dynamic microcleaning platform for removing diverse environmental pollutants. Microbeads functionalized with lysozyme and organophosphorus hydrolase enzymes were shown extremely useful for enzymatic biodegradation of *E. coli* and the nerve agent methyl paraoxon, respectively, while ligand (meso-2,3-dimercaptosuccinic acid) modified beads for chemical adsorption of heavy metals in solution.

Rotifer-based biohybrid microrobots hold considerable promise as self-propelling dynamic pumps for diverse large-scale environmental remediation applications.



Functionalized marine rotifers serve as microengines of self-propelling biohybrid pumps, acting as efficient environmental microcleaners. The functionalized particles, confined around the rotifer’s mouth, are exposed to a strong vortex flow field of the pollutant solution, resulting in dramatically accelerated decontamination processes. Such a biohybrid platform holds a considerable promise for environmental remediation and defense neutralization applications.

COLL 495

Determining the properties of flocs made of aluminum oxide particles and lignin-acrylic acid polymers

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Flocculation process is widely used for separating particles from suspension systems. In this study, the experimental evaluation of flocculation systems of aluminum oxide particles and kraft lignin-acrylic acid (KL-AA) polymer was exploited. Advanced tools, such as focused beam reflectance measurement (FBRM), vertical scan analyzer and gravitational scan analyzer were extensively used. A novel statistical framework was also developed, for the first time, to model the experimental results based on the mixture distribution theory, which led to a more in-depth analysis of shape and size of flocs in heterogeneous suspensions. The results revealed that the flocculation process of aluminum oxide suspension was altered by the salinity of the medium as well as the size of aluminum oxide particles. It was found that the flocs formed with KL-AA at a higher NaCl concentration had smaller sizes and exhibited higher shear resistance than the flocs formed in the absence of salt. Furthermore, the impact of pH of the colloidal suspension on the structure, fractal dimension and shape of flocs will be comprehensively discussed. This presentation will also elaborate on the impacts of stirring and gravitational force on the properties of flocs and their settlement. This is the first report on the analysis of lignin-based flocs in colloidal systems with experimental and modeling investigations.

COLL 496

Bioinspired nanomaterials for water remediation

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Porous materials such as silica, carbons, metal organic framework materials, porous polymers and others, are used in a variety of environmental remediation applications such as removal of toxic pollutants from water. However, these materials are generally prepared under environmentally damaging conditions, leading to secondary pollution – this only shifts the pollution problem. Taking inspiration from biomineralisation, we have developed green nanomaterials (GN) synthesis. This green method (mild, one-pot and rapid synthesis in water, at room temperature and neutral pH) offers substantial reductions in resources, time and energy usage when compared to traditional routes, yet offers excellent control over the properties and function of the materials. With the examples of (A) anthraquinone dyes and (B) arsenic removal from water (detailed below), we demonstrate the applications of GN in water treatment.

(A) The increased release of harmful dyes in water has placed under greater pressure to safely and effectively treat wastewater effluents. Anthraquinone dyes, used the textile industry, are resistant to breakdown and hence need specialised removal methods. In this presentation, we will show results from using GN to remove/destroy dyes via either adsorption or enzymatic action. It was found that dye adsorption on GN occurs

spontaneously and the adsorption capacity (334 mg/g) is higher than other that reported in the literature. Separately, when GN were used to immobilise Peroxidase for enzymatic degradation of dye, the operational stability and reusability of the enzyme was improved but the immobilisation created mass transfer barriers.

(B) For water treatment, bioinspired green synthesis was used to prepare, for the first time, a family of iron supported on GN. For arsenate ion removal, they exhibited high extraction efficiencies, high adsorption capacities and superior kinetics (threefold higher than the highest removal rates reported to date). Moreover, a method was developed to regenerate GN allowing for full recovery and reuse of the adsorbent in subsequent extractions; strongly highlighting the potential technological benefits of these new green materials.

It is clear from the results presented herein that GN, which can be prepared with a substantial reduction in secondary pollution, form a viable alternative to traditional porous materials in separations.

COLL 497

Space-confined seeded growth of black silver nanostructures for solar steam generation

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Plasmonic metal nanostructures have attracted considerable attention for solar energy harvesting due to their capability in photothermal conversion. However, the narrow resonant band of the conventional plasmonic nanoparticles greatly limits their application as only a small fraction of the solar energy can be utilized. Herein, a unique confined seeded growth strategy is developed to synthesize black silver nanostructures with broadband absorption in the visible and near-infrared spectrum. Through this novel strategy, assemblages of silver nanoparticles with widely distributed interparticle distances are generated in rod-shaped tubular spaces, leading to strong random plasmonic coupling and accordingly broadband absorption for significantly improved utilization of solar energy. With excellent efficiency in converting solar energy to heat, the resulting black Ag nanostructures can be made into thin films floating at the air/water interface for efficient generation of clean water steam through localized interfacial heating.

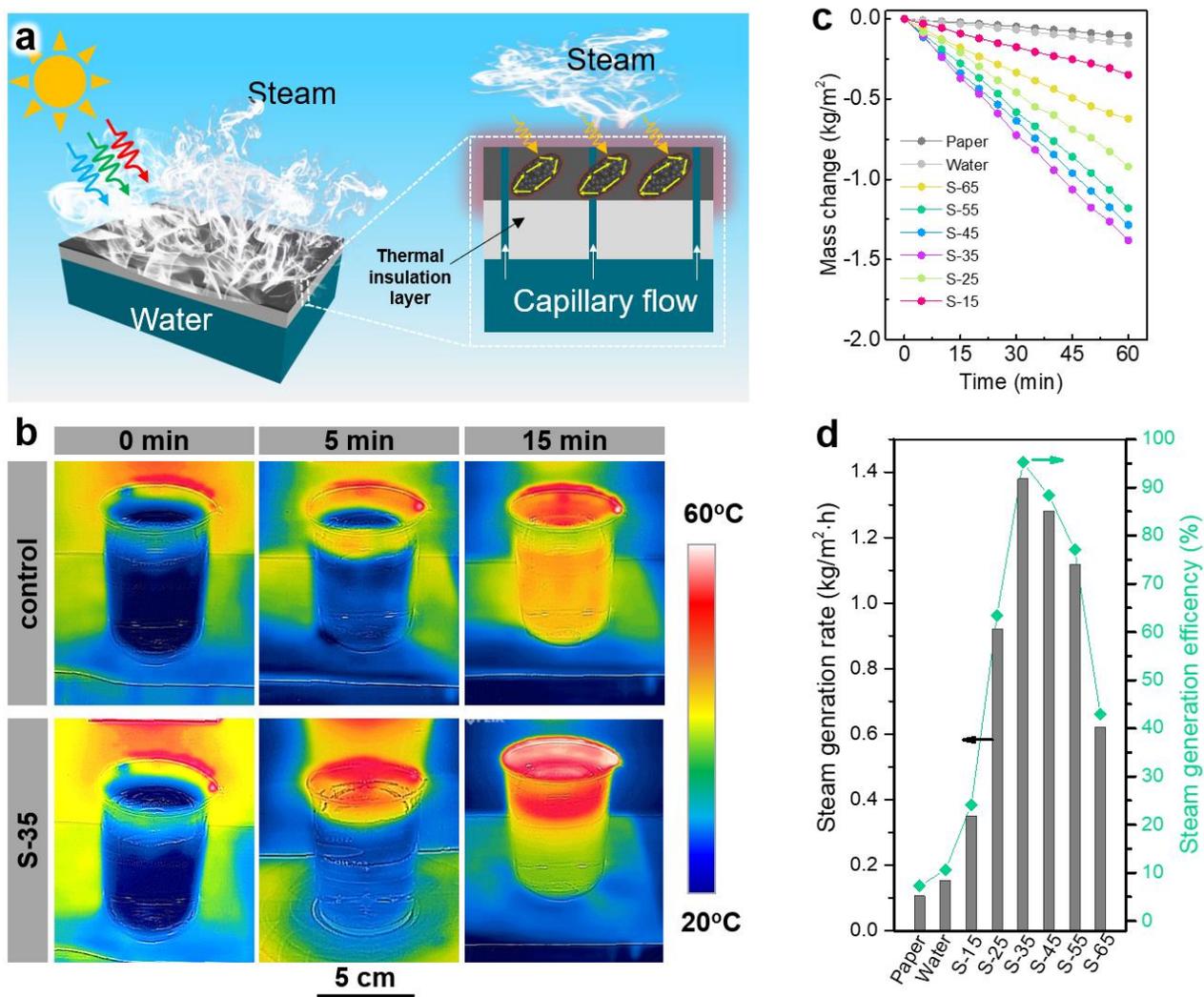


Figure 5. (a) Schematic illustration of the solar steam generation process. (b) IR thermal images of water beakers recorded by a thermal camera after being irradiated with a Xenon light (300 W) for different periods of time without (top panel) and with (bottom panel) a black film of AgNP assemblages. (c) Time course of water evaporation performance under various conditions. (d) Dependence of the steam generation rate and efficiency on the amount of AgNO₃ precursor used in the seeded growth.

COLL 498

Remediating aqueous waste with supramolecular gels to create smart materials with high-tech applications

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Supramolecular gels are soft materials, self-assembled from low-molecular-weight building blocks, and comprise ca. 1% of a solid-like network assembled in 99% of a solvent phase. Hydrogels assemble in water and therefore have great potential for environmental remediation. They are compatible with the aqueous medium, which can rapidly diffuse in and out of the gel, and they possess very high internal nanostructured surface areas, which, if they can interact with pollutant species within the water, have the potential to achieve very high levels of uptake.

This talk presents an overview of the ways in which supramolecular gels can be used to remediate different pollutant species from water. It then focuses on our own recent results using commercially-relevant, low-cost, environmentally benign supramolecular hydrogels based on dibenzylidenesorbitol, to remediate waste. In particular, we focus on pollutant dyes, acid-functionalised pharmaceuticals and precious heavy metals and in each case demonstrate the high levels of uptake that can be achieved using this strategy. In the case of precious heavy metals, we demonstrate very high levels of remediation, suitable for the treatment of e-waste. The precious metals are converted into nanoparticle form during remediation, and the resulting nanocomposite materials have high value. We demonstrate that they can be used as conducting materials (in the case of Au or Ag waste), and as catalysts for reactions of value to the pharmaceutical industry (in the case of Pd waste). In this way, we demonstrate a simple strategy based on supramolecular soft materials chemistry that converts waste-to-wealth and could be of value in a variety of different settings.

COLL 499

Imprinted copolymer/SiO₂ hybrid for selective adsorption of bisphenol A

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A molecularly imprinted hybrid (MIH) which wraps imprinted linear copolymer with SiO₂ moieties was fabricated for selective adsorption of bisphenol A (BPA). Styrene (St) and methyl methacrylate (MMA) monomers were selected to specifically interact with BPA molecules via π - π interaction and create hydrophobic microenvironment of the copolymer, respectively. The copolymer was then covalently coated with SiO₂ clusters with a coupling agent, 3-methacryloxypropyltrimethoxysilane (MPS), in order to preserve the imprinted conformation. In addition, the external SiO₂ shell also suppressed non-specific hydrophobic interactions and promoted the water compatibility of the MIH. The optimal BPA/St/MMA/MPS/tetraethyl orthosilicate molar ratio for the desired adsorption performance was 1/2/5/5/15. The resulting MIH exhibited a high BPA adsorption capacity of 40.3 mg/g, an extraordinarily high imprinting factor of 14, and a large association constant of $3.8 \times 10^4 \text{ M}^{-1}$. On the top of that, it quickly reached an adsorption equilibrium within 20 min and showed a high selectivity factor of 2-24 for

BPA molecules over the other three endocrine disrupting chemicals according to their sizes and geometries. These outstanding adsorption features suggested that the MIH is promising to be a target-selective adsorbent for advanced water purification

COLL 500

Electrospun nanofibrous poly-cyclodextrin membrane for efficient removal of polycyclic aromatic hydrocarbons (PAHs) and heavy metals from water

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Several sorbent materials have been developed to scavenge the toxic pollutants of polycyclic aromatic hydrocarbons (PAHs) and heavy metals in water sources. These pollutants are generally discharged in industrial wastes and severely affect human and animal health at concentrations above their acceptable limits. Cyclodextrins (CD) are non-toxic cyclic oligosaccharides representing various application opportunities due to their toroid-shaped molecular structure. The production of CD functional nanomaterials has grown significantly in the last decade for environmental applications. Since, the high surface to volume ratio and highly porous structure of nanomaterials are being integrated with the unique molecular structure of CD and this enhances the sorption performance of ultimate material. Here, electrospun CD nanofibers were prepared by electrospinning of hydroxypropyl- β -CD molecules in the presence of a tetracarboxylic acid functional cross-linker. Insoluble and hydrophilic nanofibrous poly-CD membrane were obtained which were used for the scavenging of several PAHs (*i.e.*, Ace, Flu, FluA, Phe, and Pyr) and heavy metals (*i.e.*, Pb^{2+} , Ni^{2+} , Mn^{2+} , Cd^{2+} , Zn^{2+} and Cu^{2+}) from water over time. The sorption performance of the PAHs was explored over batch sorption experiments by GC-MS analysis, while ICP-MS was used to monitor the removal of the heavy metals by the poly-CD membrane. Furthermore, the filtration performance of the membrane for both types of pollutants was tested through a dead-end filtration system which showed that the PAH removal efficiencies were high as 92.6 ± 1.6 and $89.9 \pm 4.8\%$ in 40 s for the solutions of 400 and 600 $\mu\text{g/L}$ PAHs, respectively. On the other hand, the removal efficiencies for heavy metals during the filtration were 94.3 ± 5.3 and $72.4 \pm 23.4\%$ for 10 and 50 mg/L solutions, respectively, suggesting rapid and efficient filtration of heavy metals and PAHs by the nanofibrous poly-CD membrane.

COLL 501

Core-shell Fe-SiO₂-polyamine magnetic nanoparticles for metal recovery using a continuous flow pipeline reactor

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Magnetite nanoparticles made by the co-precipitation method or using commercially available magnetite nano-particles were coated with silica by reaction with tetraethyl orthosilicate (TEOS). The TEOS coated particles were then treated with a mixture of methyltrimethoxysilane (MTMS) and chloropropyltrimethoxysilane (CPTMS) to provide an organic surface to which a polymeric amine could be grafted. The resulting inorganic-organic hybrid nanoparticles were then used to capture metals such as Cu, Zn, Mn and Hg. Metal capacities were quite good being $\geq 0.5 \text{ mmol g}^{-1}$. The particles could be magnetically recovered, stripped, regenerated and used many times over without significant loss of capacity. The particles were characterized by DLS, TEM, elemental analysis and infrared spectroscopy. Adsorption was well modeled by the Langmuir adsorption isotherm and TEM clearly showed core-shell nature of their structure. The particles were designed for use in a continuous flow doubly looped reactor equipped with electromagnets to capture the particle after adsorption and after metal removal and particle regeneration. Operation of the reactor and use of the particles in the reactor on waste streams will be presented.

COLL 502

Hydrophobic-force-driven removal of organic compounds from water by reduced graphene oxides generated in agarose hydrogels

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Each day, copious amounts of household chemicals and industrial chemicals enter world's water supply as result of the disposal of industrial and agricultural waste and inadequately treated sewage. The discharge of human and animal excrement has also led to introduction of antibiotics in ground water, compounding the current antimicrobial resistance crisis. Despite the concentration of organic compounds present in natural waters is sufficiently low in most cases to cause immediate, acute health effects, their long-term impact on public health and aquatic life is a growing public concern. In most cases, furthermore, organic compounds co-exist with various salts at high concentration in industrial wastewater, in which results in significant deterioration the technical performance of conventional treatment processes.

Herein, Hydrophobic reduced graphene oxides (rGOs) were generated in agarose hydrogel beads (AgarBs). The resulting rGO-loaded AgarBs could effectively adsorb organic compounds in water at concentrations as low as $1 \text{ ng} \cdot \text{ml}^{-1}$ through the attractive hydrophobic force between rGOs and organic compounds dissolved in aqueous media. The adsorption capacity of the rGOs was fairly high even toward reasonably water-soluble organic compounds (Rhodamine B, $321.7 \text{ mg} \cdot \text{g}^{-1}$; aspirin, $196.4 \text{ mg} \cdot \text{g}^{-1}$). Moreover, this hydrophobic force-driven adsorption approach is more efficient as the salinity in water increases, therefore offering great operational flexibility and versatility for many wastewater treatment processes, when salt is inevitably present at high concentrations.

We also wish the work will increase awareness in the role of long-range, attractive hydrophobic forces in many other processes occurring in aqueous media.

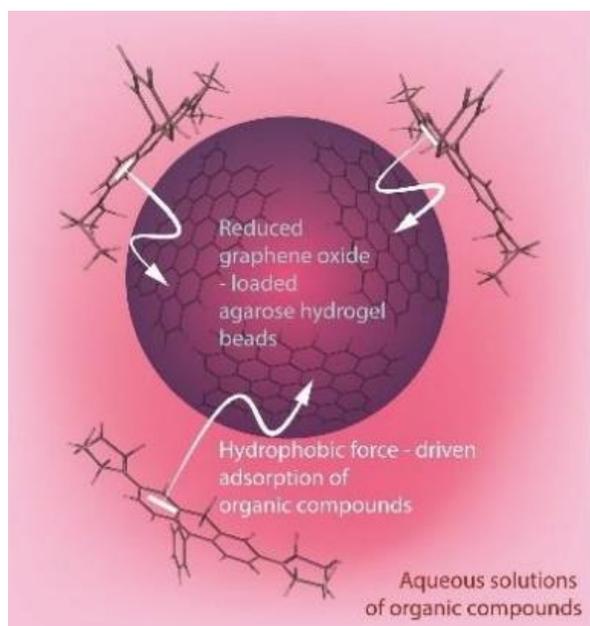


Figure 1: Hydrophobic reduced graphene oxides are introduced into agarose hydrogel beads to effectively remove various organic compounds from water through adsorption driven by the hydrophobic attraction.

COLL 503

Surface modified magnetic nanoparticles as efficient adsorbents for heavy metals removal from wastewater: Progress and prospects

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The great amount of research on magnetic nanoparticles for application in wastewater decontamination has generated new and exciting materials in recent times. The effect of magnetic nanoparticles must be known to show low cytotoxicity and be ascertained prior to their use for wastewater treatment. Synthesized chelating ligands considerably improve the adsorbing capabilities of magnetic nanoparticles in wastewater. This paper evaluates the influence of surface modification on the efficiency of magnetic nanoparticles for the removal of heavy metals in wastewater. The progress made on or/and prospect of magnetic nanoparticles functionalization for wastewater decontamination are also extensively highlighted. This article is specifically targeted at discussing the different strategies that could be employed for surface modification of magnetic nanoparticles for application in the removal of heavy metals from wastewater.

COLL 504

Visualizing the inner architecture of poly(ϵ -caprolactone)-based biomaterials and its impact on performance optimization

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For poly(ϵ -caprolactone) (PCL)-based materials, the crystalline skeleton and its structural integrity determine the strength and toughness of the materials. Meanwhile, the amorphous regions actually serve as the nano/microscale compartments that can host functional ingredients (e.g., drugs, inorganic additives, etc) excluded from the PCL crystallites. Thus, the distribution and the size of these amorphous compartments play a key role in the materials' performance. The goal of our study is to directly visualize the internal architectures (i.e., spatial distribution of amorphous and crystalline phases) of PCL-based materials (e.g., nanofibers, microfibers, and composite fibers). By using PCL thin films as model systems, we first demonstrated that, when the *Candida antarctica* lipase B (CALB) enzyme is used at very low concentrations (e.g., approximately 0.01-0.075 mg \times mL⁻¹), it preferentially breaks down amorphous chains prior to crystalline chains, suggesting its high degradation selectivity. Top-down dissection using the CALB enzyme was then performed on other PCL-based systems including nano/microfibers, nanofibers, and composite fibers. Hierarchically assembled crystalline domains (e.g., in the case of thin films) or hierarchically nanostructured crystalline skeletons (e.g., in the case of fibers) were clearly revealed using scanning electron microscopy (SEM). This finding allows top-down direct visualization of nanoscale lamellae using high resolution SEM, providing an easily-accessible route to study the internal structures of semicrystalline PCL and the hierarchical self-assembly of nanoscale lamellae. By using low concentrations of CALB enzyme, the structural differences in the crystalline skeletons of PCL nanofibers and microfibers were clearly captured, which allowed mapping out the spatial distribution of amorphous compartments that can potentially host functional ingredients.

COLL 505

Substrate-independent micropatterning of polymer brushes using chemical vapor deposition-based polymerization initiator films

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Precise microscale arrangement of biomolecules and cells is essential for tissue engineering, microarray development, diagnostic sensors, and fundamental research in the biosciences. Biofunctional polymer brushes have attracted broad interest in these applications. However, patterning approaches to creating microstructured biointerfaces based on polymer brushes often involve tedious, expensive, and complicated procedures that are specifically designed for model substrates. We report a substrate-independent, facile, and scalable technique with which to prepare micropatterned biofunctional brushes with the ability to generate binary chemical patterns. Employing chemical vapor deposition (CVD) polymerization, a functionalized polymer coating decorated with 2-bromoisobutyryl groups that act as atom-transfer radical polymerization (ATRP) initiators was prepared and subsequently modified using UV light. The exposure of 2-bromoisobutyryl groups to UV light with wavelengths between 187 and 254 nm resulted in selective debromination, effectively eliminating the initiation of ATRP. In addition, when coatings incorporating both 2-bromoisobutyryl and primary amine groups were irradiated with UV light, the amines retained their functionality after UV treatment and could be conjugated to activated esters, facilitating binary chemical patterns. In contrast, polymer brushes were selectively grown from areas protected from UV treatment, as confirmed by atomic force microscopy, time-of-flight secondary ion mass spectrometry, and imaging ellipsometry. Furthermore, spatial control over biomolecular adhesion was achieved in three ways: (1) patterned nonfouling brushes resulted in nonspecific protein adsorption to areas not covered with polymer brushes; (2) patterned brushes decorated with active binding sides gave rise to specific protein immobilization on areas presenting polymer brushes; (3) and primary amines were co-patterned along with clickable polymer brushes bearing pendant alkyne groups, leading to bifunctional reactivity. Because this novel technique is independent of the original substrate's physicochemical properties, it can be extended to technologically relevant substrates such as polystyrene, polydimethylsiloxane, polyvinyl chloride, and steel. With further work, the photolytic deactivation of CVD-based initiator coatings promises to advance the utility of patterned biofunctional polymer brushes across a spectrum of biomedical applications.

COLL 506

Is hydroxyl functionality a prerequisite for inducing stasis in human pluripotent stem cell colonies immersed within block copolymer worm gels?

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Current technologies for the transportation and storage of human pluripotent stem cells (hPSCs) usually involve cryogenic freezing protocols, but these methods are somewhat problematic because they can dramatically reduce hPSC harvest yields and cell viability. In principle, one solution to this problem is to immerse hPSC colonies in a

synthetic diblock copolymer worm gel composed of poly(glycerol monomethacrylate)-poly(2-hydroxypropyl methacrylate) (PGMA₅₅-PHPMA₁₃₅), whereupon they enter stasis for up to 14 days at 37 °C. These PGMA-PHPMA worm gels act as synthetic mimics for natural mucins, offering similar gel strength *and* hydroxyl functionality. The research question addressed in the present study is whether the hydroxyl functionality of the PGMA stabiliser block is essential to induce hPSC stasis. To examine this hypothesis, non-hydroxylated diblock copolymer worms based on poly(ethylene glycol)-poly(2-hydroxypropyl methacrylate) (PEG₅₇-PHPMA_y) are prepared *via* reversible addition-fragmentation chain transfer (RAFT)-mediated polymerisation-induced self-assembly (PISA). A phase diagram is constructed to determine the relationship between diblock copolymer composition and nanoparticle morphology, and the thermoresponsive properties of the worm gels are examined. More importantly, a specific diblock copolymer is identified to exhibit the desired physical properties in the commercial cell culture medium *Nutristem*. Live/dead cell-staining experiments confirmed that the hPSC colonies survive immersion within the PEG₅₇-PHPMA₆₅ worm gel for 7 days. However, the well-known cell cycle markers ki67 and nuclear envelope statin (NES) indicated continued cell proliferation, rather than cell stasis. Interestingly, retrieved live cell colonies stained positive for the neural differentiation marker b3TUB.

COLL 507

Upper critical solution temperature (UCST) behavior of core cross-linked polymer micelle in water

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A random copolymer ((U/A10)₁₆₅) bearing pendent ureido and a small amount (10 mol%) of primary amine groups shows an upper critical solution temperature (UCST) in water. We prepared a diblock copolymer (M₂₀(U/A10)₁₆₅) composed of water-soluble poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC) and (U/A10)₁₆₅ blocks via reversible addition-fragmentation chain transfer radical polymerization and post reaction. In the abbreviation, M is PMPC block, as well as U and A are ureido and primary amine group-containing units, respectively. Subscript numbers are degrees of polymerization of each block. Although M₂₀(U/A10)₁₆₅ dissolved in water as a unimer state above the UCST phase transition temperature (T_p), it formed polymer micelles composed of dehydrated (U/A10)₁₆₅ core and hydrophilic PMPC shells. Nanogel was prepared by cross-linking the pendent primary amines in the micelle core using (hydroxymethyl)phosphonium chloride below T_p . NMR and light scattering data suggested that the nanogel core dehydrated to shrink below T_p and hydrated to swell above T_p . Nanogel can encapsulate into the core guest molecules such as hydrophobic fluorescence probe and bovine serum albumin (BSA) mainly owing to hydrophobic interactions below T_p . Encapsulated BSA can be kept in the nanogel core below T_p and BSA can be released above T_p .

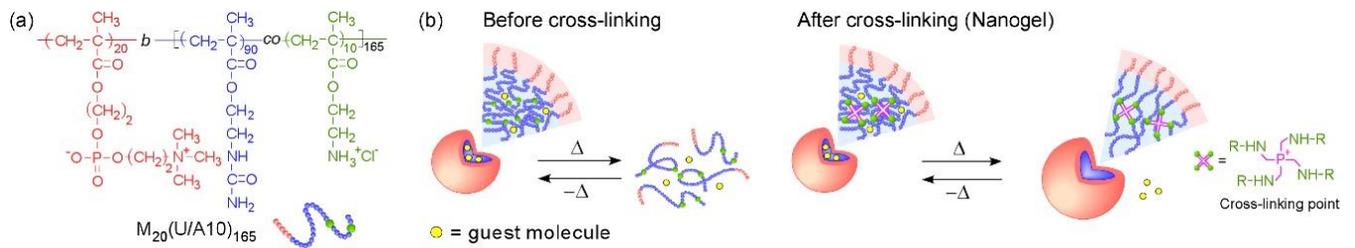


Figure 1. (a) Chemical structure of $M_{20}(U/A10)_{165}$ and (b) thermo-responsive behavior of $M_{20}(U/A10)_{165}$ and nanogel in water.

COLL 508

Tailoring surfaces of silk fibroin films to control protein adhesion

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Silk fibroin, extracted from *Bombyx mori* silkworm cocoons, is a fibrous protein that contains alternating blocks of hydrophilic and hydrophobic amino acids. The hydrophilic blocks allow the protein to be processed and chemically modified under aqueous conditions, while the hydrophobic blocks form beta sheet secondary structures via hydrogen bonding. The inducible self-assembly of the protein gives rise to impressive mechanical properties and tunable degradation rates. The formation of secondary structures also allows silk fibroin to be prepared in different formats such as hydrogels, sponges, and films. Due to its biocompatibility and versatility, silk fibroin finds utility in a wide variety of applications such as drug delivery, wound dressings, and tissue engineering. Though silk fibroin can be chemically modified, the low degrees of functionalization remain a challenge for many applications. To address this issue, surface-initiated polymerizations were used to modify the hydrophilicity and charge of silk surfaces, where the goal was to tailor the degree to which proteins adhere to the silk biomaterials to tailor their biocompatibility. Monomers that possess different charges were selected to generate polymer grafts extending from the surface of silk films using living polymerization methods. These monomers were selected to lower protein adhesion to the surface of implanted materials, which may help improve compatibility with tissues as well as reduce potential infection. Water contact angle measurements show a reduction in contact angle after polymerization, indicating successful polymer grafting. ATR-FTIR spectra was also used to characterize the films before and after grafting, and the formation of new peaks confirmed successful reaction. Protein deposition was reduced on more hydrophilic films, however the charge of a surface

appears to play a more significant role compared to its hydrophilicity. This new approach to modify silk fibroin is anticipated to enable tailoring of silk-protein interactions to enhance compatibility and fouling of implanted biomaterials.

COLL 509

Mechanochemical phenomena in free and constrained polyacrylamide hydrogels induced by osmotic swelling

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Hydrogels are water-swollen, hydrophilic polymer networks that are popular materials for cell culture matrices and bone scaffolds. Hydrogels placed in water experience mechanical stress due to competing effects of osmotic swelling and network modulus. Such forces can lead to chemical changes at the bonds within the matrix. Here, we show that osmotic stress can initiate covalent mechanochemical reactions that produce reactive oxidative species (ROS), which are known to influence differentiation and proliferation of certain stem cell phenotypes. In particular, hydrogen peroxide (H₂O₂) is known to affect cell signaling and cellular protein structure, and it has been found to be generated in stressed PDMS. Thus, the relationship between hydrogel stress and ROS production should be studied in more depth.

In this work, mechanochemical production of ROS in polyacrylamide hydrogels by osmotic swelling was investigated. A simple enzymatic assay was developed using horseradish peroxidase (HRP) and amplex ultrared (AUR) to quantify the amount of H₂O₂ formed via a chromogenic readout. Colorless AUR reacts with H₂O₂ in the presence of HRP to form resorufin, a bright pink compound. Crosslinkers with varying linkage strengths were used to fabricate hydrogels and it was observed that when a crosslinker containing a weak disulfide linkage, such as bis(acryloyl)cystamine (BAC) is used, the H₂O₂ produced is observed to be in the 12-25 μM range, whereas incorporation of a stronger polyethylene glycol diacrylate (PEGDA) crosslinker resulted in significant lowering of overall H₂O₂ production.

Next, mechanical strain was increased via constrained swelling by chemically conjugating the gel to a glass substrate and swelling in water. Consequentially, biaxial compressive forces developed in the gel, leading to a significant increase in ROS concentration regardless of the crosslinker structure, achieving up to 30 μM H₂O₂ in the swelling media. The impact of this work is important for the general biomaterials community, especially groups that focus on using hydrogels for stem cell culture.

COLL 510

Catechol-modified poly(oxazoline)s with tunable degradability facilitate cell invasion and lateral cartilage integration

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Poly(2-alkyl-2-oxazoline)s (POx) are a promising candidate for biomedical applications due to their good cyto- and hemocompatibility. They are also very versatile polymers due to the variety of available functional monomers including vinyl [1] or thiol functionalities [2]. These groups can be used to perform thiol-ene chemistry for further functionalization or to produce hydrogels. We have previously described the introduction of cysteines via thiol-ene chemistry for biopolymer-coupling via native chemical ligation [3].

Here we exploit the thiol-ene coupling to introduce catechol-functionalities as mussel-inspired adhesion moieties for the development of tissue adhesives. Tissue adhesives play an important role in clinical applications and may aid in the treatment of cartilage defects for improved cartilage integration. However, many fail to satisfy the demand for adequate adhesive strength on wet tissue surfaces and to facilitate sufficient cell migration and extracellular matrix (ECM) deposition at the defect site. Utilizing poly(2-alkyl-2-oxazoline) (POx)-based polymers equipped with catechol groups and combining them with the natural wound sealant fibrinogen, we fabricated an adhesive biosynthetic hydrogel with tunable mechanical properties and improved bonding strength.

Degradation of the hydrogels could be adjusted by the ratio of amide to ester linkages of the catecholic functional group at the POx side chain. In an in vitro disc/ring model for lateral cartilage integration, a benefit in long-term integration was observed with enhanced degradation of the adhesive without the expense of bonding strength. Incorporation of degradable ester linkages in the polymer facilitated cell invasion and strong deposition of cartilaginous ECM at the defect site.

COLL 511

Scalable synthesis of on-demand degradable hydrogel particles

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We describe a straightforward and scalable strategy to synthesize size-controlled and fully-degradable hydrogel particles. Through a chemically programmed biocompatible degradation reaction, we can induce the degradation of these particles into low molecular weight fragments upon addition of an exogenous trigger. By incorporating these particles into a secondary matrix, we can readily tune the properties of the resulting materials in a spatially and temporally controlled manner with minimal impact

on cellular viability. We demonstrate the utility of this approach in addressing some fundamental challenges in the tissue engineering space.

COLL 512

Effect of the shape on phagocytosis: Phagocyte type matters!

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Neutrophils are the most abundant phagocytic immune cells in human blood and first responder in case of an injury and inflammation. Particle shape has recently emerged as a new design parameter for the micro/nanocarriers, and directly affects immune clearance and phagocytosis. Different studies have demonstrated that increasing the aspect ratio of micro/nanoparticles will reduce their clearance by macrophages, and long enough particles can avoid clearance by macrophages. However, the impact of the aspect ratio of particles on uptake by neutrophils is not well understood. Herein, we examine that the effect of the shape on phagocytosis is the direct consequence of the phagocyte type. In contrary to the observed trend for macrophages, we found that increasing the aspect ratio of the particle increased their uptake by primary human and mouse neutrophils. The difference between particles of varying aspect ratios becomes most prominent for mid-sized microparticles with an equivalent spherical diameter of $1\ \mu\text{m}$, and ellipsoidal rods can have up to 3.5-fold higher uptake by neutrophil compared to spheres of the same volume. This difference between the response of various phagocyte groups to aspect ratio can introduce shape as a new parameter to selectively target neutrophils while having minimal effect on other phagocyte groups.

COLL 513

Fantastic voyage: Designing self-powered nano/microbots

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Self-powered nano and microscale moving systems are currently the subject of intense interest due in part to their potential applications in nanomachinery, nanoscale assembly, robotics, fluidics, and chemical/biochemical sensing. One of the more interesting recent discoveries has been the ability to design nano/microparticles which catalytically harness the chemical energy in their environment to move autonomously. These "bots" can be directed by chemical and light gradients. Further, our group has developed systems in which chemical secretions from the translating micro/nanomotors initiate long-range, collective interactions among the particles. This behavior is reminiscent of quorum sensing organisms that swarm in response to a minimum threshold concentration of a signaling chemical. In addition, an object that moves by

generating a continuous surface force in a fluid can, in principle, be used to pump the fluid by the same catalytic mechanism. Thus, by immobilizing the nano/micromotors, we have developed nano/microfluidic pumps that transduce energy catalytically. These non-mechanical pumps provide precise control over flow rate without the aid of an external power source and are capable of turning on in response to specific analytes in solution.

COLL 514

Langmuir science teaches everything: Molecular machine operation, nanocarbon synthesis, and life regulation at liquid interfaces

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Langmuir science teaches everything: molecular machine operation, nanocarbon synthesis & life regulation. This concept can be realized at dynamic two-dimensional medium such as thin films at the air-water interface, i.e., Langmuir monolayer because this medium possess both features of bulk and molecular dimension. For example, we successfully manipulated molecular machines at the air-water interface upon bulk (10-100 cm size) motion of the entire monolayer and realized “capture and release” of aqueous guest molecules using molecular machine, steroid cyclophane. In addition, mechanically controlled chiral recognition of amino acid and discrimination of nucleosides by the supramolecular monolayer was successfully demonstrated. As Langmuir protocol for nanocarbon synthesis, a new bottom-up method for carbon nanosheet fabrication using a newly designed anisotropic carbon nanoring molecule, will be also presented. The carbon nanoring was self-assembled at a dynamic air-water interface with a vortex motion to afford molecular nanosheets, which were then carbonized under inert gas flow. Their nanosheet morphologies were retained after carbonization, which has never been seen for low-molecular weight compounds. Furthermore, adding pyridine as a nitrogen dopant in the self-assembly step successfully afforded nitrogen-doped carbon nanosheets containing mainly pyridinic nitrogen species. For life regulation, we demonstrate the regulation of myogenic differentiation on fluid substrates by using a liquid-liquid interface as a scaffold. C2C12 myoblast cells were cultured using water-perfluorocarbon (PFC) interfaces as the fluid microenvironment. We found that, for controlled in vitro culture at water-PFC interfaces, expression of myogenin, myogenic regulatory factors (MRF) family gene, is remarkably attenuated even when myogenic differentiation was induced by reducing levels of growth factors, although MyoD was expressed at the usual level (MyoD up-regulates myogenin under an elastic and/or viscoelastic environment).

COLL 515

Interfacing polymer materials with microbiology

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By fundamentally understanding the interactions between microorganisms and engineered materials, we can reduce the spread of microbial resistant genes and the use of commercial antimicrobials in applications from biomaterials to water purification membranes. In this presentation, I will discuss a story from each of my lab's two synergistic research thrusts. First, I will discuss the effect that the fundamental properties of polymer hydrogels (i.e., molecular architecture, stiffness, and thickness) have on the surface-associated transport of bacteria and on the adhesion of bacteria under quiescent conditions. By decoupling the effects of molecular architecture, stiffness, and thickness from hydrogel chemistry, we have unlocked specific structure-property relationships that can be tailored to control the initial stage of bacterial adhesion. As an example of our work on green chemistry, I will highlight our development of a universal surface modification strategy that relies on dopamine and antifouling polymers to repel microbes. When viewed together, the structure-property relationships and smart fouling-resistant chemistries developed in this work offer alternative approaches to mitigate the risk of bacterial infections without relying on antibiotics.

COLL 516

End-group ionisation enables the use of poly(N-(2-methacryloyloxy)ethyl pyrrolidone) as an electrosteric stabiliser block for polymerisation-induced self-assembly in aqueous media

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A series of near-monodisperse poly(N-2-(methacryloyloxy)ethyl pyrrolidone) (PNMEP) homopolymers was prepared via reversible addition-fragmentation chain transfer (RAFT) solution polymerisation of NMEP in ethanol at 70 °C using a carboxylic acid-functional RAFT agent. The mean degree of polymerisation (DP) was varied from 19 to 89 and acid titration indicated end-group pK_a values of 5.07-5.44. Turbidimetry studies indicated that homopolymer cloud points were significantly higher at pH 7 (anionic carboxylate) than at pH 3 (neutral carboxylic acid). Moreover, this enhanced hydrophilic character enabled PNMEP to be used as a steric stabiliser for aqueous polymerisation-induced self-assembly (PISA) syntheses. Thus, a PNMEP₄₂ precursor was chain-extended via RAFT aqueous dispersion polymerisation of 2-hydroxypropyl methacrylate (HPMA) at 44 °C. A series of PNMEP₄₂-PHPMA_x diblock copolymers were synthesised using this protocol, with target PHPMA DPs of 150 to 400. High conversions were achieved and a linear increase in M_n with increasing PHPMA DP was observed. Dynamic light scattering (DLS) and transmission electron microscopy (TEM) studies confirmed a spherical morphology in all cases. The nanoparticles flocculated either below pH 4.5 (owing to protonation) or on addition of 60 mM KCl (as a result of charge

screening). Thus the anionic end-groups on the PNMEP stabiliser chains make an important contribution to the overall colloidal stability. Similarly, a PNMEP₅₃ macro-CTA was chain-extended via RAFT aqueous emulsion polymerisation of 2-ethoxyethyl methacrylate (EEMA) at 44 °C. Again, a neutral solution pH was critical for the synthesis of colloidally stable nanoparticles. High conversions were achieved as the target PEEMA DP was varied between 100 and 600 and a linear evolution in molecular weight with PEEMA DP was confirmed by chloroform GPC studies. DLS experiments indicated a monotonic increase in nanoparticle diameter with PEEMA DP and TEM studies confirmed a spherical morphology in each case. In summary, PNMEP can be used as a water-soluble steric stabiliser for aqueous PISA syntheses provided that it contains an anionic carboxylate end-group to enhance its hydrophilic character.

COLL 517

Hydrodynamic instabilities in fatty acid/surfactant self-assembling systems

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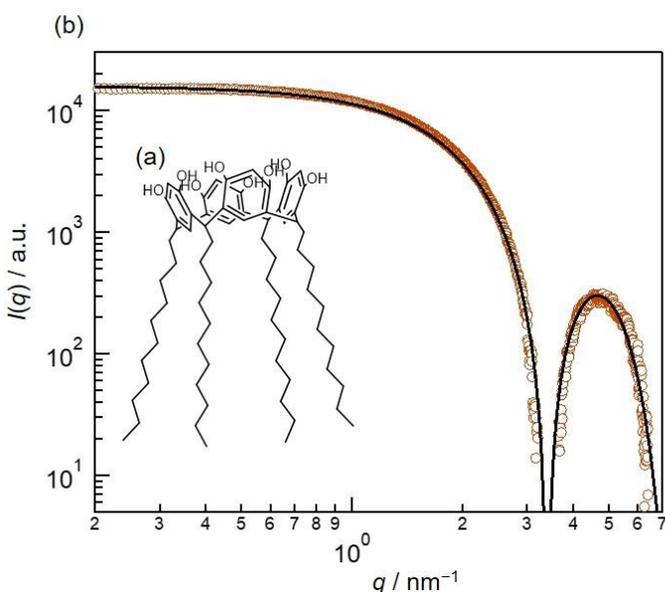
Multicomponent amphiphilic systems containing oil, water, and surfactants have been widely utilized in applications ranging from oil recovery and drug delivery, to food and personal care products. The main role of surfactants in those systems is to increase emulsion stabilities and control colloidal morphologies. Here, we present a method for the in situ formation of a nanostructured interface between an aqueous cationic surfactant (cetylpyridinium chloride) solution and a fatty acid (oleic acid, OA). We study the underlying mechanisms for the formation of the surfactant/fatty acid self-assembly at the interface, and characterize the nanostructure using small-angle X-ray scattering (SAXS). We show that the interfacial layer can undergo hydrodynamic instabilities with interplaying component concentrations and flow conditions. It is evidenced that the hydrodynamic instabilities of the interfacial layer are highly influenced by the phase equilibria of three-component amphiphilic system, even though the interfacial layer forms far from equilibrium conditions. The correlation between characteristics of the in situ interfacial layers and those of equilibrium phases can help to predict the interfacial instabilities. The work presented here has implications for controlling and optimizing the morphology in wide variety of complex fluid systems including surfactant mixtures, emulsions, and colloidal domains.

COLL 518

Rediscovering micelle-like behavior of resorcinarene capsules and their unique aggregation number corresponding to Platonic structures

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The hexameric capsule-like structure of resorcinarene assembly was elucidated in 1997, which has been accepted as an indisputable structure formed in any apolar solvents over the past couple of decades. This paper presents the solvent dependence in the aggregation number (N_{agg}) of the C-undecylresorcinarene capsule and their micelle-like behavior in apolar solvents, whose structures were characterized with small angle X-ray scattering and analytical ultracentrifugation methods. The resorcinarene forms octameric structures in toluene, which demonstrated the temperature dependent morphological transition from spherical to cylindrical. This could reasonably be understood by packing parameter theory used in predicting micellar structures. Further, we determined the N_{agg} in toluene, chloroform, and mixture solvent of toluene/cyclohexane (vol/vol, 2/8) to be 8, 6, and 4, respectively. Interestingly, they showed perfect monodispersity in the N_{agg} . The aggregation behavior demonstrating monodispersity in the N_{agg} whose values are consistent with vertex or face number of regular polyhedral structures (i.e., Platonic solids) is known as that of Platonic micelles, suggesting that the resorcinarene capsules are the first example of Platonic “reverse” micelles.



(a) Chemical structure of Undecylcalix[4]resorcinarene.
(b) SAXS profile of the reverse micelle composed of Undecyl-calix[4]resorcinarene in toluene (red points) and fitting curve calculated using spherical model (black solid line).

Dynamic self-assembly and rheological behaviour of light-responsive surfactants

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Azobenzene photosurfactants (AzoPS) can isomerise between *cis* and *trans* forms upon illumination with light of certain wavelengths (Fig. 1a). Photoisomerisation changes the surface activity, polarity and shape of the surfactant on demand, which has led to the exploration of AzoPS in applications from photofoaming, to transport in microfluidic devices. The interplay between these properties also affects the concentration-dependent self-assembly of AzoPS into micelles or even higher order structures such as lyotropic liquid crystals.

Despite the myriad of applications, there is limited understanding of the structure-function-self-assembly relationships in this family of materials, particularly when probed out of equilibrium. Here, we report a new approach using integrated UV/Vis absorption spectroscopy with small-angle neutron scattering (SANS) that enables the time-resolved self-assembly of AzoPS to be monitored. We have investigated a model neutral AzoPS, **C₈AzoOC₈E₄**(tetraethylene glycol mono(4',4-octyloxy, octyl-azobenzene)), using this technique, which allows the scattering profile to be correlated with the extent of photoisomerisation in real-time. It was observed that the AzoPS could switch between wormlike micelles (WLMs, blue light) and fractal aggregates (UV light), with the time to change structure lagging behind the time taken to reach the photostationary state. The formation of photoresponsive WLMs in a single component system is in itself unusual, and rheology studies have shown that these WLMs result in a shear-thinning AzoPS solution, which can be reversibly switched to a low viscosity, Newtonian fluid using UV light. We anticipate that this ability to simultaneously monitor and control photoisomerisation and track structural changes *in-situ* will aid in the development of tailored AzoPS structures that will enhance their uptake into light-responsive surfactant-based technologies.

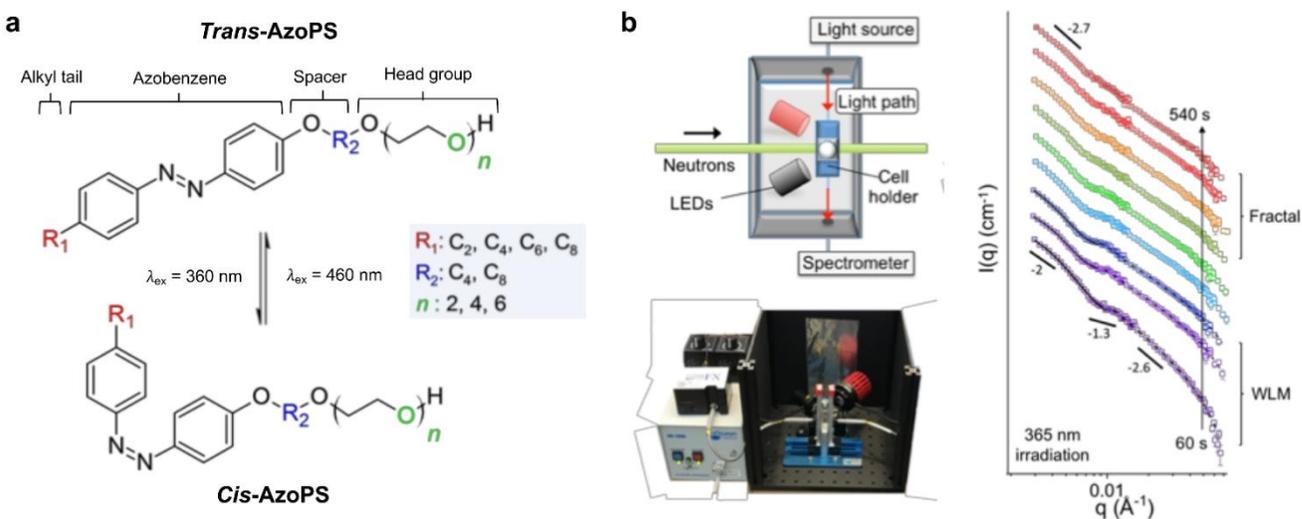


Figure 1. a) Structure and photoisomerisation of neutral AzoPS. b) Combined UV/Vis spectroscopy-SANS sample environment enables the light-dependent self-assembly process to be followed in real-time.

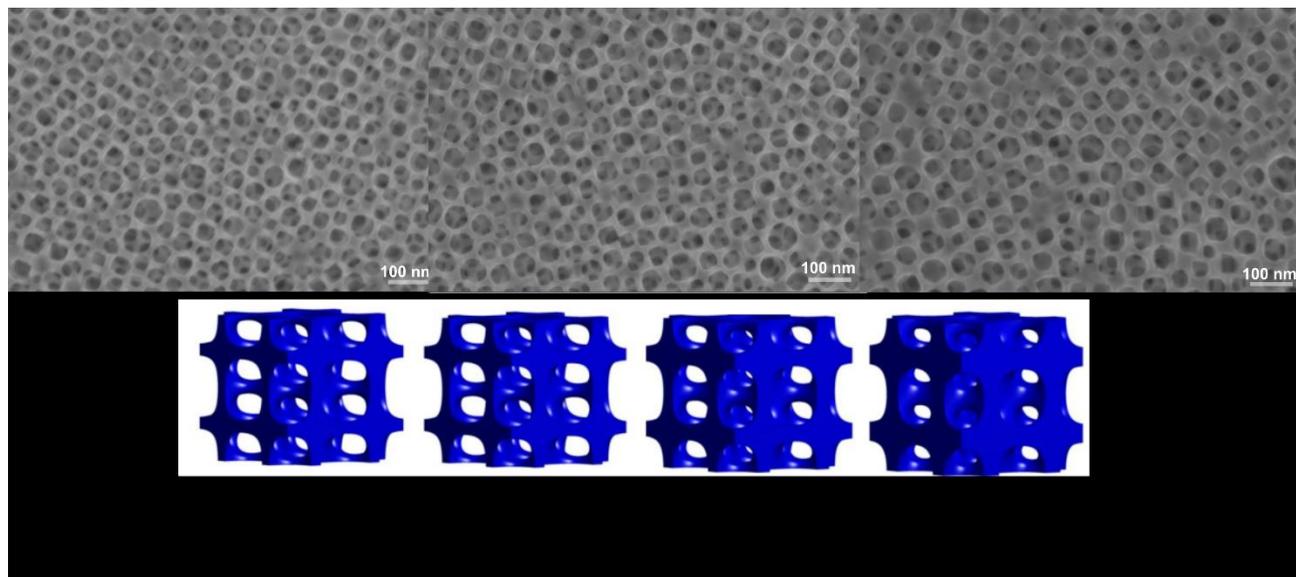
COLL 520

Kinetic-control effects towards persistent micelle templating

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Porous nanostructured materials are essential to power high-performance energy conversion and storage devices. Block copolymer self-assembly plays a very important role in achieving that. However, fully tunable nanostructured materials with decoupled effect on each architectural feature remains elusive. Recently, we introduced a new approach, persistent micelle templating (PMT) to develop tunable nanomaterials with architecture control where pore size and wall-dimension tuned independently. PMT is rather known as a kinetic-controlled process where constant template sizes are maintained despite the shifting equilibrium as material precursors are included. We have demonstrated PMT concept with atomic-level precision, by introducing a custom-made block copolymer poly(ethyleneoxide-*block*-hexyl acrylate) and a solution processing guideline. PMT is primarily governed by the micelle kinetic entrapment process that is regulated by adjusting cosolvent amount. However, the unrestricted amount of cosolvent (e.g. water) may cause the formation of secondary pores into the material wall that may affect device performance. Therefore, we came up with the idea of controlling PMT development via adding major solvents of higher Hildebrand

solubility parameters and minimizing the cosolvent addition. This not only avoids the formation of secondary pores, also expands the PMT window tunability. PMT development under kinetic control with different solvents including THF, methanol, and ethanol will be presented.



COLL 521

Tuning of the aggregation number of platonic micelles with binary mixture of calix[4]arene surfactants

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The mixture ratios were used as a factor for aggregation number determination in binary mixtures of calix[4]arene surfactants. Platonic micelles having different aggregation number were prepared by adjusting the ratio of oppositely charged compounds. In this presentation, we will introduce two calixarene-derived molecules having sulfonic groups (SC5) and quaternary amine groups (QA7).

COLL 522

Magnetite-loaded biocompatible diblock copolymer vesicles

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It is well-known that polymerization-induced self-assembly (PISA) enables the efficient preparation of a wide range of block copolymer nano-objects. For example, the RAFT aqueous dispersion polymerization of 2-hydroxypropyl methacrylate (HPMA) using zwitterionic poly(2-(methacryloyloxy)ethyl phosphorylcholine) (PMPC) or non-ionic poly(ethylene glycol) (PEG) precursors produces spheres, worms or vesicles, depending on the precise reaction conditions. Similarly, relatively small vesicles with narrow size distributions can be prepared using a pair of long and short poly(methacrylic acid) precursors for the RAFT dispersion polymerization of benzyl methacrylate in ethanol. Herein we seek to integrate these earlier studies in order to take advantage of observations made by Blanazs et al., who reported that (i) the mutual incompatibility between PMPC and PEG is sufficient to produce a biphasic aqueous solution and (ii) double-hydrophilic PEG-PMPC diblock copolymers form nanostructures in concentrated aqueous solution. Thus we utilize a judicious binary mixture of PEG and PMPC precursors to conduct the RAFT aqueous dispersion polymerization of HPMA at 50 °C. The resulting $[x \text{ PEG}_{113} + (1-x) \text{ PMPC}_{28}]$ -PHPMA₄₀₀ diblock copolymers self-assemble *in situ* to form various copolymer morphologies depending on the PEG/PMPC molar ratio and the overall copolymer concentration. We target vesicles and exploit enthalpic demixing between the PEG and PMPC stabilizer blocks to drive their segregation across the PHPMA membrane. More specifically, the shorter PMPC block is preferentially expressed at the inner leaflet, while the longer PEG block is preferentially expressed at the outer leaflet. Moreover, using a carboxylic acid-functional RAFT agent to prepare the PMPC precursor ensures that the vesicle lumen contains a relatively high concentration of such acid groups. Such vesicles can be utilized as nanoreactors for the spatially-controlled nucleation of magnetite crystals within the lumen. In principle, they may be useful for anti-cancer therapies based on hypothermia treatment.

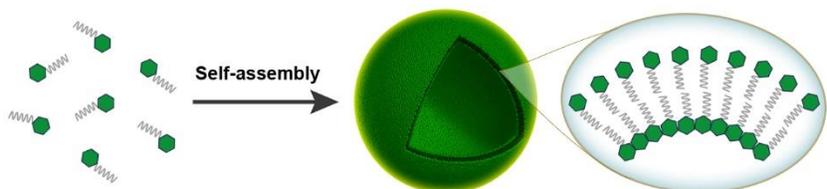
COLL 523

Construction of artificial cells from galactopyranose-derived single-chain amphiphiles

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Single-chain amphiphiles (SCAs) are attractive components of synthetic cells because of the simplicity of bilayer formation and increased membrane permeability. However, SCAs suffer from restricted working pH ranges, instability to divalent cations, and the inhibition of biocatalysts. Therefore, it would be valuable to develop robust biocompatible membranes that enjoys the benefits of SCAs but without the aforementioned limitations. Here we describe the construction of highly stable vesicles

from a new class of uncharged galactopyranose-derived SCAs. The compatibility of these amphiphiles with biomolecules makes possible the encapsulation of functional enzymes and nucleic acids during the vesicle generation process, enabling membrane protein reconstitution and compartmentalized nucleic acid amplification, even when charged precursors are supplied externally. Our studies demonstrate that single-chain glycolipid-based amphiphiles could serve as robust building blocks for artificial cells and have potential applications in drug delivery and microreactor design.



COLL 524

Model predictions of phase transformation sequence in Al-oxide-hydroxide system in pure water by bulk and interface thermodynamics

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Phase transformation sequence in Al – oxide – hydroxide system occurring on a surface of crystalline aluminum substrate placed in pure water in a temperature range of 298 – 373 K (liquid) and 373 – 500 K (steam) was predicted on the basis of bulk and interface thermodynamics. Different competing oxide (amorphous Al_2O_3 and crystalline $\gamma\text{-Al}_2\text{O}_3$) and hydroxide (amorphous $\text{Al}(\text{OH})_3$, AlOOH and crystalline gibbsite, bayerite and boehmite) phases were taken into account. The first stage of film formation on a crystalline aluminum surface in water, as predicted by interface thermodynamics, is the development of an amorphous oxide layer Al_2O_3 . However this initial oxide film is not stable in water and it is predicted further to transform to amorphous oxide hydroxide phase AlOOH . This phase is also not stable in water and tends to transform into the crystalline trihydroxide phase bayerite in a temperature range below approximately 350 K. Above this temperature, the amorphous oxide hydroxide AlOOH is assumed to transform directly to the crystalline boehmite. The model predictions are in good agreement with experimental observations reported in the literature.

COLL 525

Measuring the surface potential at water and pure liquid surfaces

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Considering the ubiquity of air/liquid interfaces for chemical and biological processes in nature and industry, the surface electrical potential across the air/liquid interface provides insight into the molecular organization and electrical fields generated by molecules present at the interface. Using a custom-built Air Surface Electrical Potential (ASEP) instrument, we measure the surface potential of water, several pure solvents, and inorganic electrolyte solutions without disruption to the liquid surface. Alpha particle radiation from an ionizing source reduces the resistivity of the air gap above the liquid sample, establishing a closed electrical circuit for voltage measurements. From the measured surface potential, we show (i) the orientation of interfacial solvent molecules in pure solvents, and (ii) ascertain the propensity of specific aqueous ions with respect to the air/solution boundary.

COLL 526

Probing mixed octadecanol/stearic acid monolayers at the air/water interface

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The pKa values for stearic acid in mixed monolayers with octadecanol were determined from direct measurement of the symmetric carboxylate stretch by vibrational sum frequency spectroscopy (VSFS). The measurements were determined at the air/water interface on a Langmuir trough. As the density of the carboxylate groups at the interface increased, the pKa also increased, in agreement with theory. Pressure-area diagrams were obtained to determine the carboxylate density at the interface, which remained consistent for fully deprotonated and fully protonated carboxylate at all concentrations below 40% stearic acid. VSFS was used to determine the response of the carboxylate symmetric stretch peak with changing subphase pH, and the fraction of deprotonated carboxylate was obtained by fitting the spectra. The results are in good agreement with the Grahame Equation, derived from Guoy-Chapman theory.

COLL 527

Do monovalent anions preferentially adsorb to extended hydrophobic surfaces exposing methyl groups?

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The preferential affinity of selected anions to interfaces exposing organic hydrophobic moieties plays, in connection to the incompletely understood Hofmeister effects, a vital role in a number of complex biological processes. The prototypical model surface for studying ion adsorption has been the air/water interface, where potential effects of the

nature of the hydrophobic surface have been neglected. Here, we investigate the interactions of the monovalent anions Cl⁻, Br⁻, I⁻, and SCN⁻ with a hydrophobic solid surface exposing methyl groups to the solution. Molecular information is obtained using vibrational sum frequency spectroscopy by targeting water molecules in the first monolayer as well as the C≡N stretch of the adsorbing SCN⁻ anion. Although the relative affinity for the interface follows the Hofmeister ordering with SCN⁻ > I⁻ > Br⁻ > Cl⁻, chlorine, and bromide are found to be expelled from the interfacial region, with thiocyanate showing a net enrichment. Molecular dynamics simulations of NaSCN solutions at the interface with air and with an alkane monolayer provide additional quantitative insight and confirm the comparatively higher affinity of SCN⁻ anions to methyl-terminated hydrophobic surfaces.

COLL 528

Tracking the molecular organisation of water and alcohol mixtures at hydrophobic solid interfaces

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Mixtures of water and alcohol play vital roles in many fields such as catalysis, surface treatments and in fuel cells. We have recently shown that at hydrophobic interfaces such as highly oriented pyrolytic graphite (HOPG), water-methanol mixtures spontaneously nucleate self-assembled stable supramolecular monolayers consisting of both molecules at room temperature. Despite only being physisorbed on the surface, these structures are robust due to a stabilising extended network of hydrogen bonds. Their presence can dramatically affect the properties of the interface, leading to significant consequences for applications using graphitic material immersed in aqueous solutions where we have recently shown that methanol can spontaneously form. There is hence a need to better understand the properties, evolution and molecular arrangement of these structures, as well as their stability in different environments.

Computational analysis indicates that the alcohol-water assemblies have a wide variety of energetically favorable configurations with low free energy barriers for transitions between them. In this work, we demonstrate that by doping the system in a controlled manner it is possible to direct the self-assembly to create reproducible structures unique to the composition of the interfacial liquid. Using atomic force microscopy to map these structures with high-resolution we identify supramolecular patterns and gain insights into the molecular arrangements. Three-dimensional scanning force microscopy (3D-SFM) is used to explore the hydration profile of the interfacial liquid and demonstrate the 3D structure of the multi-molecule assemblies. The experimental results are complemented by molecular dynamics simulations to verify our 3D picture of the interfacial assembly.

Our results reveal the importance of the alcohol structure in the molecular assemblies and an interesting competition between the hydrogen-bonded network within the monolayer and interactions with the surface. We believe that this research will have an

exciting impact on the ever-evolving field of controlled molecular self-assembly and nanoscale surface treatments.

COLL 529

Dilution effects on the behavior of thin ionic liquid films probed with electrochemistry and vibrational spectroscopy

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Ionic liquids are (ILs) akin to common salts such as sodium chloride (table salt), but unlike table salt which melts at approximately 800° C, ILs are liquid below 100° C with many of them being liquid at room temperature. This behavior is due to ILs being composed of bulky asymmetric anions and cations, which due to steric effects prevent ILs from readily forming crystal structures. Because ILs are liquid at room temperature and contain no solvents, they have several unique properties including negligible vapor pressure, high thermal stability, and moderate conductivity. As such ILs have found use in a variety of applications such as energy storage, solvents in extractions and separations, and lubrication.

Our work investigates effects of co-solvents on interfacial IL behaviors. We present *in situ* analysis of IL thin films, analyzed by electrochemistry and surface sensitive spectroscopic techniques such as infrared reflection absorption spectroscopy (IRRAS), and spectroscopic ellipsometry. We previously presented results showing IL films' long ranged ordering in these thin film environments. This significantly changes interfacial molecular ordering, as evidenced by significant changes in the spectral absorption profiles. Here, we show data for IL systems in the presence of co-solvents and analyze changes in the dynamics of the interfacial region's ordering process. Specifically, we study 1-alkyl-3-methylimidazolium trifluoromethanesulfonate ($[C_nMIM][OTf]$) ILs with varying alkyl chain lengths and varying amounts of co-solvents (water, acetonitrile). Special attention is given to the effects of decreasing viscosity on the rates of diffusion and ordering of the films. We find that the length of the alkyl and the concentration of co-solvent in the IL film dramatically alter the electrochemical transport properties of the film, with longer alkyl chains exhibiting slower diffusion through the IL film. We also find that the rate at which the mixed IL-co-solvent film matures increases dramatically when compared to a neat IL film. We believe these results hold valuable information useful in the design of new classes of ILs to better fit their applications in energy storage, extraction, and lubrication.

COLL 530

Dual-responsive fluorinated ionic liquid infused slippery surfaces

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Smart slippery surfaces are highly desirable due to the potential application in liquid transportation, water collection and dropwise condensation.¹ Although, many intelligent responsive slippery surfaces with controllable wettability switching are developed. There challenges remain in fabricating novel and multiple responsive slippery surfaces with regulatable wettability based on new kinds of phase-transition lubricants. Here, a magnetic-thermal and photo-thermal responsive slippery surface was fabricated by employing the fluorinated ionic liquid (FIL), a new type of thermo-driven phase-transition materials, as the lubricants and the cross-linked fluoropolymer film as the underlying substrates. The substrates showed good self-repairing property and efficient magnetic-thermal and photo-thermal heating effects. The precisely adjustment of droplet motion on the slippery surfaces was achieved by tuning the surface temperature. The driven temperature could be easily revised by replacing the cationic groups. Besides, the FIL-1H3M infused slippery surfaces presented excellent anti-icing performance. The freezing time was prolonged by 3605s. It is worth mentioning that employing the FIL as the lubricant to accomplish the wettability switching of slippery surfaces has rarely been reported and the FILs presented here are first reported. The findings provide a novel phase-transition lubricant oil to prepare smart slippery surfaces, thus advancing the application of slippery surfaces in microfluidic devices and biomedical systems.

COLL 531

Functional solid surface with liquid-like slippery feature for bubble/drop transport and self-assembly of nanoparticles

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Functional slippery surfaces have broad applications in engineering processes, such as mineral flotation, lubrication, wastewater treatment and food industry. In this work, for the first time, we have fabricated one type of functional solid surfaces, achieved by one-step chemical grafting, which show liquid-like slippery feature but are different from the conventional slippery surfaces composed of oil-infused lubricant. The as-prepared functional surfaces can transport bubbles in aqueous solutions as well as water droplets in oil media, and can also facilitate the self-assembly of nanoparticles from their suspensions. The transport of bubbles/liquid drops is driven by the buoyancy force or gravity force, against the resistance sliding force associated with the bubble-solid or drop-solid contact during transport. Functional surfaces with lower surface energy show higher velocity of transporting bubbles/drops. The as-prepared functional surfaces allow the three-phase-contact-line (TPL) to move more freely as compared to the pristine substrates. The evaporation of sessile drops of silica nanoparticle suspension on the functional surfaces could lead to the self-assembly of these nanoparticles with controllable sizes, which offers a facile approach for particle assembly and nano/micro-scale reactions. Our research provides a new and facile approach for the fabrication of slippery coatings on different substrates, with potential applications for bubble/drop transport and self-assembly of nanoparticles.

COLL 532

Highly thermally stable hybrid coatings by fluoride rearrangement of phenylsilsesquioxanes and methyltrimethoxysilane

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Phenylsilsesquioxanes (PhenylSQ) have very high thermal stabilities (>400 °C/air). However, the most common phenylSQ exhibits very poor solubility. This disadvantage limits their use. The aim of this study was to investigate a simple route to making PhenylSQ/methylsilicone coatings with good thermo-oxidative stability. The reaction of fluoride catalyzed rearrangement between PhenylSQ and Methyltrimethoxysilane was used to improve the solubility of PhenylSQ and fabricate coatings. The thermal stability of coatings was measured by Thermogravimetric Analysis. It was found that these coatings have high thermal stabilities due to the siloxane network. Thermal degradation temperature about 600 degree centigrade. This indicates that we can obtain Highly Thermally Stable Coatings and further broaden the scope of PhenylSQ's applications by Fluoride Rearrangement.

COLL 533

Understanding the fate and behaviour of nanoparticle in biological system

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Many nanomaterials are promising in biological detection, diagnosis, and therapy for diseases and have shown great potential for biomedical applications. Therefore, the toxicity of nanomaterials becomes an increasing concern. Nanotoxicology is an emerging field to characterize and categorize the interactions of nanoscale materials with biologic systems, and consider the potential health and environmental effects caused by engineered nanomaterials.

Both in vitro and in vivo studies were applied to evaluate biological consequence of nanomaterials. The underlying mechanisms were investigated including induction of oxidative stress, inflammation and autophagy. The intrinsic physicochemical properties of nanomaterials have decisive influence on their biological consequences and toxicity. These properties include size, shape, surface charge, chemical composition, surface modification, metal impurities, agglomeration and dispersion, degradation, as well as the formation of "protein corona". It is important to obtain a better understanding of the uptake, trafficking, pharmacokinetics, clearance, and role of nanomaterials in biological systems, so that their possible undesirable effects can be avoided.

We will discuss the analytical methodology and techniques developed for the quantification of the ADME processes of nanomaterials in vivo, focusing on those used for nanomaterials quantification in different bio-matrices, such as blood, tissues, organs and biomedical processes. To understand the full picture of nanomaterials metabolism in the liver, it is crucial to monitor in situ the dynamic changes in their concentration, composition and precise location with time, and to accurately quantify the metabolite products. Chemical speciation analytical techniques is highly necessary to study the chemical process and fates of nanomaterials, such as X-ray absorption spectroscopy (XAS) and high performance liquid chromatography (HPLC)-coupled ICP-MS (HPLC-ICP-MS), which can sensitively reveal the chemical structures and states of nanomaterials in the liver.

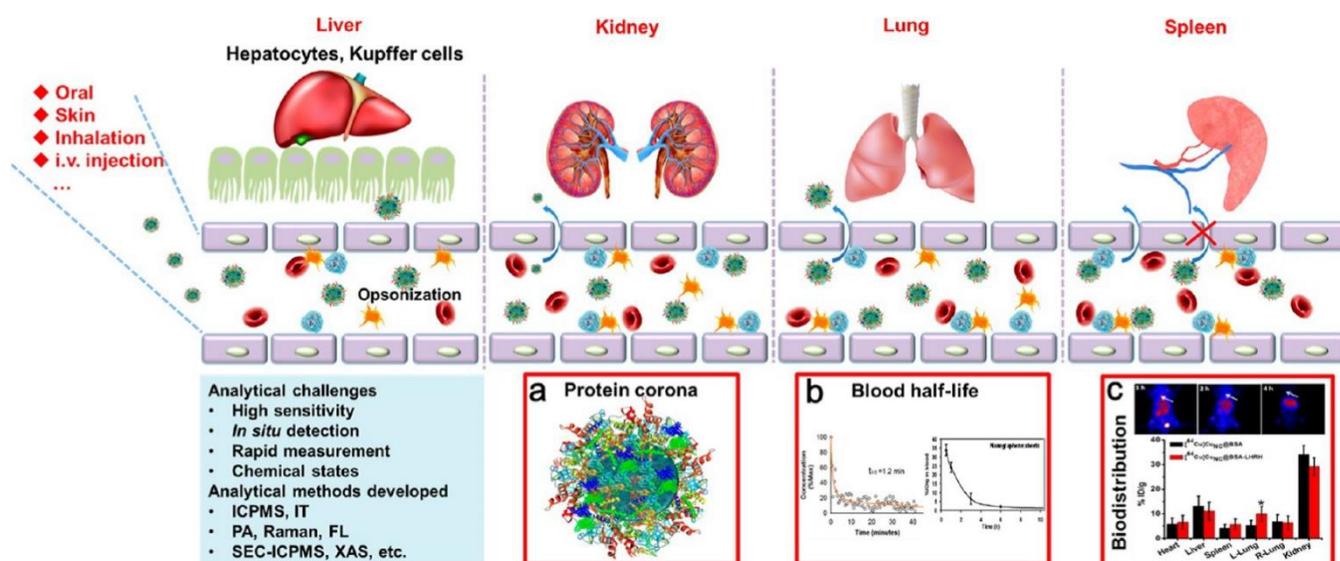


Figure Quantitative Analysis of Nanomaterials in vivo

COLL 534

Silver nanoparticles toxicity and nanomedicine

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The widespread use of silver nanoparticles (AgNPs) has raised substantial health risks to human beings. Despite a wealth of progress on toxicity studies, the understanding of the adverse effects on fetuses, embryos, and early stage cells is still rather limited, particularly under low-dose exposure settings. Moreover, nearly all previous studies

ascribed AgNP-induced toxic effects to oxidative stress. Differently, we here unearthed a mechanism, namely, interruption of X chromosome inactivation (XCI) in female mouse embryonic stem cells (mESCs). Albeit with no observable cytotoxicity, significant differentiation retardation was found in female mESCs upon low-dose AgNP exposure. Mechanistic investigations uncovered expedited inactivation for the inactive X chromosome (Xi) and attenuated maintenance of the active X chromosome (Xa) state during mESC differentiation upon the challenge of low-dose AgNPs, indicative of disordered XCI. Thereby, a few X-linked genes (which are closely involved in orchestrating ESC differentiation) were found to be repressed, partially attributable to reinforced enrichment of histone modification (e. g., histone 3 lysine 27 trimethylation, H3K27me3) on their promoter regions, as the result of disordered XCI. In stark contrast to female mESCs, no impairment of differentiation was observed in male mESCs under low-dose AgNP exposure. All considered, our data unearthed that AgNPs at low concentrations compromised the differentiation program of female mESCs through disturbing XCI. Thus, this work would provide a model for the type of studies necessary to advance the understandings on AgNP-induced developmental toxicity.

COLL 535

Use of polymeric nanoparticle platform targeting the liver to induce Treg-mediated antigen-specific immune tolerance in a pulmonary allergen sensitization model

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Nanoparticles can be used to accomplish antigen-specific immune tolerance in allergic and autoimmune disease. The available options for custom-designing tolerogenic nanoparticles (NPs) include the use of nanocarriers that introduce antigens into natural tolerogenic environments, such as the liver, where antigen presentation promotes tolerance to self or foreign antigens. Here, we demonstrate the engineering of a biodegradable polymeric poly (lactic-co-glycolic acid) (PLGA) nanocarrier for the selective delivery of the murine allergen, ovalbumin (OVA), to the liver. This was accomplished by developing a series of NPs in the 200-300 nm size range as well as decorating particle surfaces with ligands that targets scavenger and mannose receptors on specialized tolerogenic liver sinusoidal endothelial cells (LSECs). LSECs represent a major antigen presenting cell (APC) type in the liver capable of generating regulatory T-cells (Tregs). In vitro exposure of LSECs to NPOVA induced abundant TGF- β , IL-4 and IL-10 production, which was further increased by surface ligands. Further animal experiments showed that in the chosen size range, NPOVA was almost exclusively delivered to the liver, where the co-localization of fluorescent-labeled particles with LSECs could be seen to increase by surface ligand decoration. Moreover, prophylactic treatment with NP^{OVA} in OVA-sensitized and challenged animals (aerosolized inhalation), could be seen to significantly suppress anti-OVA IgE responses, airway eosinophilia and TH2 cytokine production in the bronchoalveolar lavage fluid. The suppression of allergic airway inflammation was further enhanced by attachment of surface ligands, particularly for particles decorated with the ApoB peptide, which

induced high levels of TGF- β production in the lung along with the appearance of Foxp3+ Tregs. The ApoB peptide coated NPs could also interfere in allergic airway inflammation when delivered post-sensitization. The significance of these findings are that liver and LSEC targeting PLGA NPs could be used for therapy of allergic airway disease, in addition to using their tolerogenic effects for other disease applications.

COLL 536

Towards tracking stem cells and macrophages with gold and iron oxide nanoparticles: Choice of the best suited particles

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Nanoparticle (NP)-based cell imaging offers good potential for future diagnosis tools in medicine. Gold and iron oxide NPs can be used as contrast agents for imaging by computed tomography (CT) and magnetic resonance imaging (MRI), respectively. Thus, also cells which have been labeled with these NPs may be tracked. This may be important for in vivo tracking of administered or transplanted cells. In this work, we optimized the conditions to label stem cells and macrophages with a library of gold and iron oxide NPs of different sizes (5–100 nm core diameter) and shapes. We investigated the amount of NPs which can be delivered to different cells, as well as their related toxic effects, in relation to the physicochemical properties of the NPs. Our study revealed that in general, when cells are exposed to NPs at similar elemental concentration (e.g., Au or Fe), bigger NPs lead to higher internalized elemental amounts as compared to exposure with smaller sized NPs. While the exposure concentrations are limited concerning the onset of toxicity, bigger NPs lead to better labeling than small NPs, resulting in improved contrast for imaging with enhanced biocompatibility.

COLL 537

Drug delivery via polymer-drug conjugates for pancreatic ductal adenocarcinoma

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Chemotherapy agents, attack not only to cancer cells but also all fast reproducing cells, most being the crucial cells for continuation of life. In an effort to save the rest of the body from the undesirable effects of the cytotoxic agents, they are packaged in a delivery system, grandiosely termed as nanomedicine. The carrier should carry its cargo till the tumor and release only after it is next to or inside the target cell. This fundamental requirement is simple yet not easy to achieve. Since the result of premature release of the payload is almost as good as administering the free drug, there is enormous effort in trying to optimize the voyage and release at destination. This, of course, requires various adjustments according to the drug and the site of delivery. The presentation will

highlight different linkers on a polymeric carrier system for delivery to pancreatic ductal adenocarcinoma (PDAC). Only a limited number of patients can be treated surgically, which is the only curative treatment option for PDAC. A distinct feature of PDAC is its abundant fibrotic stroma, a nightmare for any delivery platform trying to reach the tumor. The polymeric carriers are ornamented with drug molecules with different linkers, aiming to sail through the stroma and deliver the precious cargo inside in order to effect both the tumor and the pancreatic stellate cells.

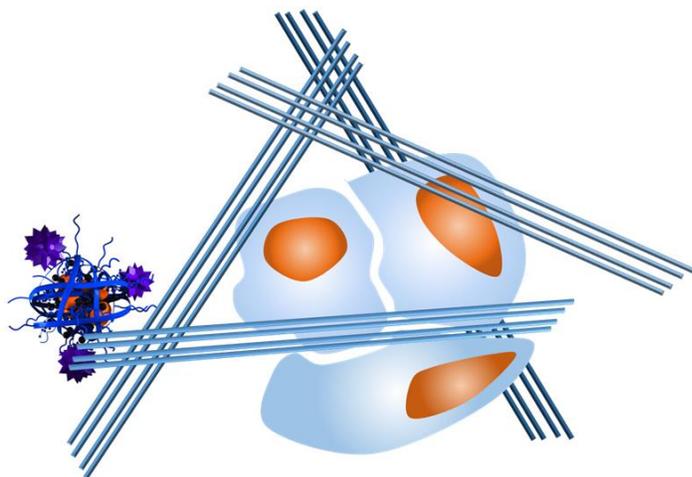


Figure. Polymeric carrier trying to deliver its cargo through extra cellular matrix.

COLL 538

Surface pressure-induced crystallization behaviour of poly(caprolactone)-based mixed monolayers at the air/water interface

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In the past, we have reported the crystallization of poly(caprolactone) (PCL) from metastable monolayer at the air/water interface. When PCL/poly(t-butyl acrylate) (PtBA) mixed monolayers were dynamically compressed past the collapse transition of liquid-expansion phase, compositional PCL dendrites were observed. To grow PCL crystals at well-controlled surface pressure values, a series of isobaric area-relaxation experiments were performed for PCL/PtBA monolayers at the A/W interface. PCL crystals obtained from isobaric area relaxation experiments at different P values demonstrate a striking morphological transition from highly branched symmetric dendrites to six-arm dendrites, four-arm dendrites, seaweedlike crystals, and distorted rectangular crystals, indicating

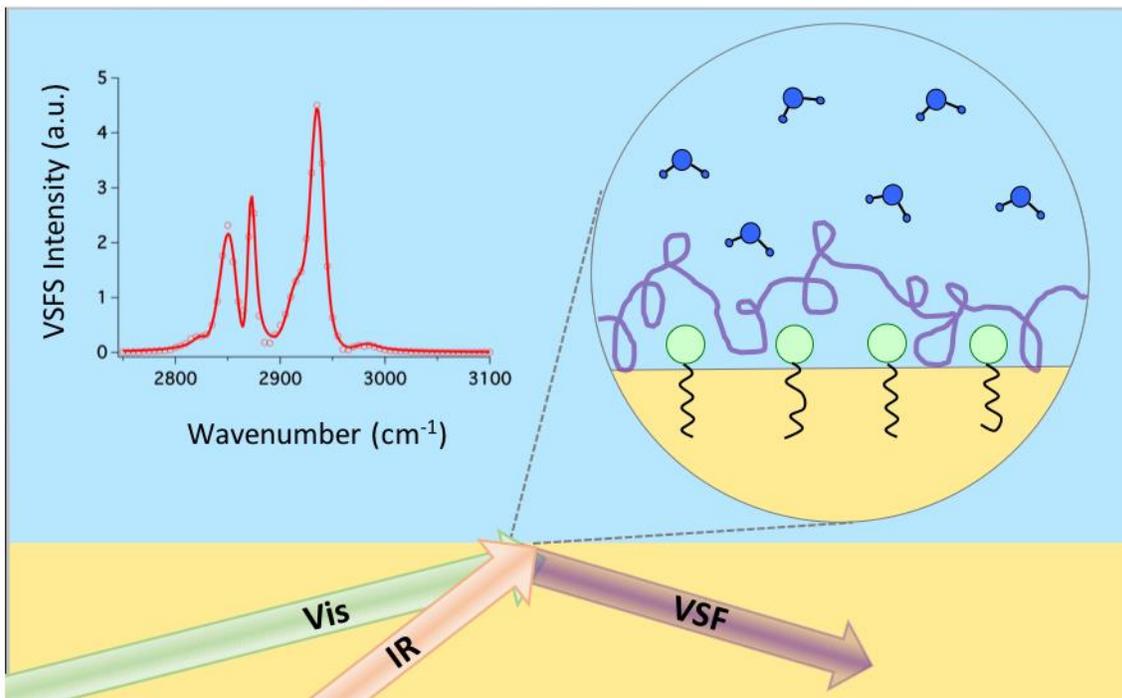
that the degree of undercooling (i.e., the surface pressure values) plays a key role for controlling crystal morphologies through the interplay of the diffusion coefficient, surface tension, and surface tension anisotropy. The overall growth rate of these quasi-2D dendrites was also found to increase with increasing surface pressure. The gross morphology of PCL dendrites was primarily controlled by the number, the location, and the growth rates of dendritic fingers developed on the {100} face. Increasing P results in a smaller diffusion length in the LE phase and therefore a decreased stability length, which favours the propagation of interfacial instability, leading to highly branched PCL dendrites. In addition, the noise level (compositional fluctuations) varies with crystallization P and the blend composition, which can be considered as another effective parameter for morphological selection in the diffusion-limited growth regime.

COLL 539

It takes two to tangle: Nonionic polymer aggregation behavior at the oil/water interface as affected by varying surfactants

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The controlled functionalization of polymer/surfactant adsorbates at the oil-water interface is crucial to applications dependent on its surface chemistry, including targeted drug delivery methods, environmental remediation techniques, and the formation of functionalized polymer films. Because the efficacy of these systems is highly dependent upon the properties of molecules present at the interface, molecular-specific information about complexes at the buried liquid-liquid interface is needed. This study uses the surface-specific nonlinear experimental technique, Vibrational Sum Frequency Spectroscopy, to observe the chemical structure and behavior of polymer/surfactant complexes at the oil-water interface. Combinations of biologically inert nonionic polymer and surfactants are found to interact synergistically both in molecular population and orientation at the oil/water interface. Where the polymer does not adsorb to the oil-water interface alone, its adsorption and orientation at the interface is heavily influenced by the hydrophobic and electrostatic properties of co-existing surfactants. The surfactants' electrostatic properties are found to affect polymer interfacial order and their hydrophobic properties influence polymer interfacial population.

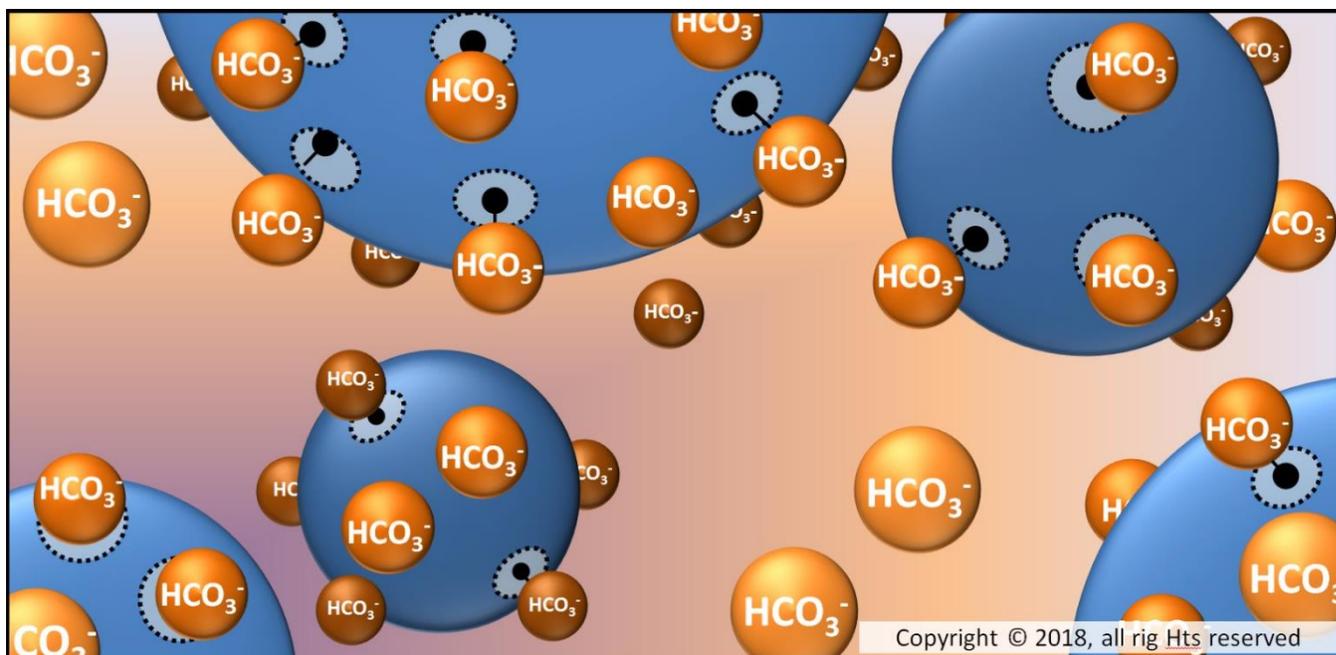


COLL 540

Bicarbonate charging of hydrophobic/water interfaces

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Most surfaces in contact with water are negatively charged. The reason for that has long been debated in the physics community as arising either from hydroxide ion adsorption or water reorganization towards a hydrophobic interface. We have recently proposed another explanation coming from the carbonation of water. Bicarbonates, which in distilled water are the most present ions at intermediate pHs (from 5 to 10), are chaotropic ions that stick to interfaces. We made use of a combination of interfacial tension measurements of oil droplets in water, and nanoprecipitation assays of polymers in a large range of pH, to show such affinity of HCO_3^- for hexadecane oil and PMMA. This preferred adsorption of bicarbonate allows also explaining why freeze/thaw cycles contribute to emulsifying oil/water mixtures



COLL 541

Ion interactions with carboxylic acid monolayers: Surface charge, reversed affinities, and contact ion pairing as revealed by non-linear vibrational spectroscopy

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Fatty acid Langmuir monolayers are used as model systems to study the interactions of the carboxylic acid functional group with various cations in solution. A molecular insight is obtained using vibrational sum frequency spectroscopy and complemented with MD simulations. Emphasis is made on targeting headgroup vibrations of both its charged and uncharged forms as well as water molecules in the interfacial and diffuse double layers. The surface charge of the monolayer as a function of cation concentration and pH is experimentally determined and theoretically rationalized. While at low ionic strengths the results are consistent with the predictions of the Gouy-Chapman model for charged interfaces, at higher ion concentrations the surface charge departs from this behavior and becomes dependent on the identity of the cation, highlighting the appearance of ion-specific effects. The sum frequency spectra also give direct information on the type of ion pairs formed between the different cations and the carboxylic acid headgroup. The results provide exciting new insights into the complex interactions of metal cations with the biophysically relevant carboxylic acid moiety.

COLL 542

Effect of polymer charge and interface concentration on structure of isotactic poly(acrylic acid) PAA and isotactic poly(methacrylic acid) PMA at oil-water interface

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Adsorption behavior of *isotactic* Poly(acrylic acid) (*i*-PAA) and *isotactic* Poly(methacrylic acid) (*i*-PMA) at CCL₄-H₂O interface was studied by all-atom molecular dynamics simulations with varying charge density f and concentration of the polyelectrolyte. *i*-PAA as well as *i*-PMA chains exist a planar extended conformation at the interface shows a different from its coiled conformation in bulk water. Orientation distribution of carbonyl and hydroxyl groups show characteristic aspects specific to these groups. Adsorption occurs only for low values of degree of ionization ($f < 0.2$) in agreement with experimental observations. Uncharged *i*-PAA and *i*-PMA, and charged *i*-PMA chains undergo structural change from extended planar conformation to random coiled conformation with increase in interface concentration. This conformational change is reflected in torsion angle distribution of backbone dihedrals and orientation distribution side groups. The preferential orientation of backbone and side groups disappear with increase in interface concentration. The morphological properties of adsorbed film such as film thickness and interface coverage were calculated. *i*-PMA exists in an extended and ordered conformation at interface as compared to the random coil conformation in bulk water. The analysis of the distributions of orientation of carbonyl, methyl, hydroxyl groups with respect to the interface-normal, showed characteristic orientations for $f = 0$, which disappear at higher f . Although such conformational changes are expected from interpretation of pressure-area isotherms, MD simulations add strength to these arguments along with providing additional molecular level information. Interface pressure-area isotherms obtained from our simulations were compared with limited available experimental data in literature for PMA at low pH. The structural changes associated with increase in interface concentration are reflected in conformational properties. 90% of COOH groups are involved in the formation of a single H-bond between hydrogen of O-H group and water and 50-60% of these groups also form H-bond with oxygen of the C=O groups. Along with the detailed structural analysis, the solvation behavior of COOH groups in water as characterized by hydrogen bonding interactions will be presented.

COLL 543

Dual actions of hydrotropes in bulk solution and at interface

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Hydrotropes are substances containing small amphiphilic molecules, which manifest a striking duality in bulk water and at water/oil interface. Typical examples of nonionic hydrotropes with well-balanced amphiphilicity are tertiary butanol and 3-methyl pyridine. Hydrotropes do not form stable micelles in aqueous solutions, but they may form reversible dynamic clusters (less or about 1 ns lifetime) with water molecules; such clusters can be viewed as “pre-micelles” or as fluctuations of aqueous solution structure. Molecular dynamics simulations demonstrate that the origin of the clustering is the formation of strong hydrogen bonds between the water and nonionic hydrotrope molecules. This molecular clustering causes pronounced thermodynamic anomalies, experimentally observed in dilute and semi-dilute aqueous solutions of nonionic hydrotropes. In particular, the isobaric heat capacity, the measure of entropy fluctuations, exhibits a lambda-like cusp in semi dilute aqueous solutions of tertiary butanol, resembling a second-order phase-transition anomaly. Most recently, experimental and simulation studies of water-hydrotrope-oil ternary solutions have revealed remarkable consequences of the duality of hydrotropes. In bulk, a spectacular phenomenon, “mesoscale solubilization”, intermediate between molecular solubility and macroscopic phase separation, is observed. It has been proved that mesoscale solubilization is a kinetically stabilized phenomenon, though extremely long-lived. Making practically stable colloids from small hydrotrope molecules has an untapped potential for applications in material science and medicine. At water/oil interface, a nonionic hydrotrope at small concentrations (prior the region of pronounced structural fluctuations) acts as a surfactant, while at higher concentrations (after the interface is saturated by the hydrotrope) it acts as a co-solvent toward complete water/oil miscibility. Crossover between these limits is described by a universal function interpolating the Gibbs-Langmuir adsorption theory and scaling theory of a smooth near-critical interface.

COLL 544

Molecule dynamics simulations of the trisiloxane surfactant monolayers at air-water and heptane-water interfaces

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To develop fluorine-free surfactants for effective fire suppression, molecular dynamics (MD) simulations are performed to study the effect of surfactants on the structural properties and stability of monolayers at the air/water and heptane/water interfaces. Experiments showed that siloxane-polyoxyethylene surfactants (undefined distribution of molecules with varied chain length) with hydrophilic terminal groups OH or OCH₃ improve lamellae stability especially when combined with alkyl polyglycoside surfactants due to synergistic effects. By applying the simulation method that we developed previously, the most probable surface area per molecule, surface tension, and maximum Gibbs elasticity of pure siloxane-polyoxyethylene and mixtures with alkyl glycosides are calculated for varied chain length of the polyether and number of glycosides. The simulation results show that the surface tension of trisiloxane at

air/water interface exhibits a minimum value (about 20 dyn/cm at oxyethylene chain length 12 to 14) with increasing chain length qualitatively similar to the experimental data. There are two peaks in Gibbs elasticity, which are around oxyethylene length of 6 and 13. High Gibbs elasticity and low surface tension suggest high stability of the monolayers to dilatation and changes in surfactant packing density. By comparing the MD simulated trisiloxane/alkyl-glycoside mixture to the pure trisiloxane at the heptane/water interface, the results show that the surface area per molecule of the mixture is significantly smaller than the pure trisiloxane because of tighter packing. The simulations of pure and mixed surfactants at air-water and heptane/water interfaces indicate that when the oxyethylene chain length is greater than 8, the difference in the hydrophilic terminal group (OH, OCH₃) does not affect the structural properties of the interface.

COLL 545

Surface dipoles give rise to the largest odd-even effects ever reported: Structure and wettability of CF₃-terminated *n*-alkyl xanthic acid self-assembled monolayers

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A series of CF₃-terminated *n*-alkyl xanthic acids (AXAs) possessing chain lengths of the form CF₃(CH₂)_nOCS₂H (*n* = 11-18) were synthesized and used to generate self-assembled monolayers (SAMs) on gold surfaces. The wettability of these terminally fluorinated, progressively alkylated self-assembled monolayers (FSAMs) was examined, with specific attention paid to odd-even effects, using a variety of contacting liquids having a wide range of polarities. The organization and packing of the adsorbates within these unique films were evaluated by ellipsometry, X-ray photoelectron spectroscopy, polarization-modulation infrared reflection-absorption spectroscopy (PM-IRRAS), and density functional theory (DFT). Moreover, these FSAMs were compared to SAMs generated from analogous CH₃-terminated AXAs, CH₃(CH₂)_nOCS₂H (*n* = 11-18), and alkanethiols, CH₃(CH₂)_nCH₂CH₂SH (*n* = 11-18) in efforts to elucidate the influence of the CF₃-tailgroup and OCS₂H-headgroup on the interfacial properties of the SAMs. Measurements of wettability as a function of chain length revealed the largest odd-even effects ever reported for monolayer systems (e.g., ± 15°).

COLL 546

NSF's ChemMatCARS: National facility for liquid surface X-ray scattering

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Synchrotron X-ray surface scattering is the most powerful probe of the molecular and mesoscale structure at liquid-vapor and liquid-liquid interfaces. The precise and flexible design of the liquid surface and interface reflectometer at NSF's ChemMatCARS and the high brilliance and wide x-ray energy range (5-70 keV) offered in this third generation insertion device beamline provides a world-leading capability for the study of liquid surfaces and buried liquid-liquid interfaces. A full suite of x-ray surface scattering techniques is provided to measure atomic, molecular, and mesoscopic ordering at liquid interfaces, including resonant and non-resonant reflectivity, grazing-incidence diffraction and small-angle scattering, surface fluorescence, surface diffuse scattering, and fast techniques, such as grazing incidence diffraction in the 1D pinhole geometry. It has been used to investigate a wide range of chemical and materials interfacial phenomena, including those relevant to the environment, biomolecular materials, life processes, self-assembly, and directed assembly for tailored functionality.

COLL 547

Five-isotope approach to tracking the origin and evolution of life

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One of the most important parameters needed to define the origin of life and track it from the oldest record of the earth to present is the ability to define the rise of oxygen and quantify its evolution. A mechanism to provide this information had been sought for decades but was notoriously difficult to define. The discovery of mass independent isotopic anomalies of the four stable isotopes of sulfur in the earth's earliest rock record provided definition of the origin of life from the emergence of oxygen. It has been shown by experiments and quantum chemical theory that this arises from tropospheric UV photolysis of sulfur dioxide. Tropospheric UV photolysis in today's troposphere does not occur due to UV filtration by stratospheric ozone. The occurrence of the mass independent UV isotopic anomaly in the early earth occurs due to significantly lower oxygen and ozone levels and penetration of UV light to the troposphere to photolyze SO₂, consequently providing a measure of atmospheric oxygen levels. Providing deeper understanding of the photochemistry of sulfur dioxide at the most basic quantum chemical level allows more precise definition of the Archean sulfur isotopic anomalies and calculation of atmospheric oxygen levels and associated chemistry. Recently, we added measurement of a fifth sulfur isotope, radiogenic ³⁵S, a cosmic ray produced radionuclide with a 87 day half life. From measurements of all five isotopes in the present day atmosphere we have been able to provide significantly deeper chemical mechanistic information during the Pre Cambrian as well as the present atmosphere. The radiogenic and stable isotope uniquely defines the stratospheric UV contribution and a new significant tropospheric component. These measurements, plus measurements of polar ice sulfates and volcanic upper atmospheric processes provides

a combined powerful approach to interpreting the ancient atmosphere, oxygen origins and levels as well as definition of sulfur chemical processes in today's atmosphere.

COLL 548

Multiphase chemistry of reactive oxygen species in indoor environments and human surfaces

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Multiphase chemistry plays a vital role in the atmosphere and indoor environments. Reactive oxygen species (ROS) play a central role in adverse health effects of air pollutants. Respiratory deposition of fine air particulate matter can lead to the formation of ROS in epithelial lining fluid, potentially causing oxidative stress and inflammation. Secondary organic aerosols (SOA) account for a large fraction of fine particulate matter, but their role in adverse health effects is unclear. We quantify and compare the ROS yields and oxidative potential of various types of SOA in water and surrogate lung fluid. Multiphase reactions of ozone with human skin oils impact indoor air quality by depleting ozone and forming volatile and semi-volatile organic compounds, which can be respiratory and skin irritants. We investigate the impact of clothing on indoor air composition and human exposure by integrating indoor chemistry modeling over a wide range of different spatial and temporal scales, from sub-nanometer to tens of meters and from sub-nanosecond to days. The kinetic multi-layer model is developed to explicitly resolve mass transport and chemical reactions in the clothing, at the skin, and in the gas phase, and reproduces experimental measurements of ozone and major squalene oxidation products upon ozone exposure to soiled and laundered clothing. Our kinetic modeling approach, combined with molecular dynamics simulations, was also applied to kinetic experiments of adsorption of limonene on to SiO₂.

COLL 549

Interfacial dissolved O₂ consumption by photolyzed aqueous pyruvic acid

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The photochemistry of chromophoric pyruvic acid in water generates ketyl and acetyl radicals that contribute to the production and processing of atmospheric aerosols. The photochemical mechanism is known to be highly sensitive to dissolved oxygen content, [O₂(aq)], among other environmental conditions. This work explores how the photolysis ($\lambda \geq 305$ nm) of 10-200 mM pyruvic acid at pH 1.0 consumes initial dissolved O₂ concentrations in the range 0.11-1.3 mM (Figures 1 and 2). The rapid consumption of dissolved oxygen by the intermediate photolytic radicals is also monitored in real time at air flow rates from 30.0 to 900.0 mL min⁻¹. Under air saturated conditions and 30 mL min⁻¹ flow of air, the estimated half-lives of O₂(aq) consumed by the photolytic radicals is

in the range 3-22 min. Therefore, the corresponding depths of penetration of $O_2(g)$ into water, $x = 4.3$ and $1.6 \mu\text{m}$, are determined. Thus, accumulation and small coarse mode aqueous particles should not be O_2 -depleted in the presence of sunlight photons impinging this kind of chromophore. These results are of major tropospheric relevance for understanding the formation and growth of secondary organic aerosol.

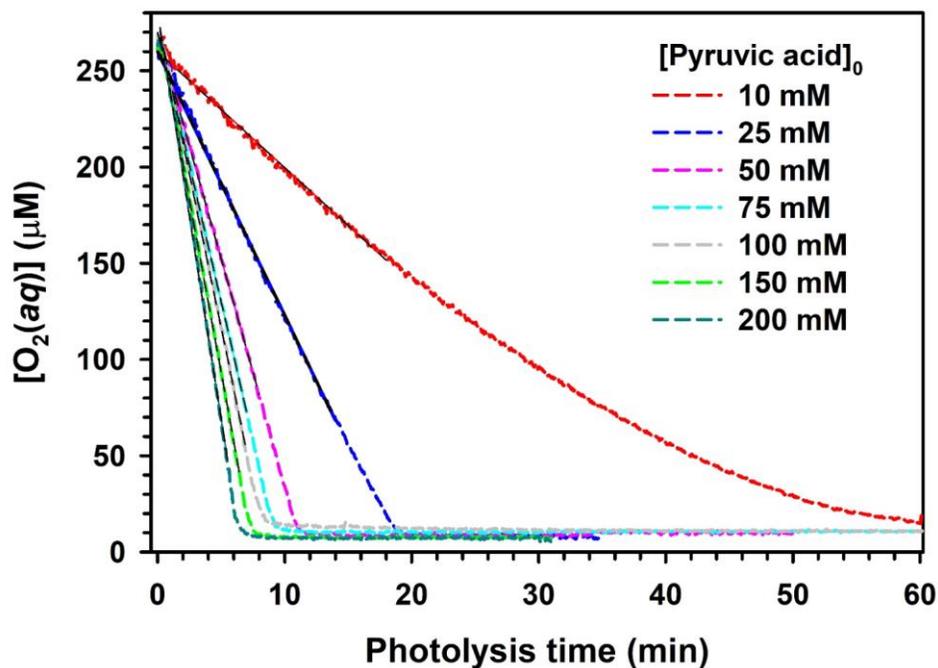


Figure 1. Dissolved oxygen consumption during the photolysis ($\lambda \geq 305 \text{ nm}$) of $10.0 \leq [\text{pyruvic acid}]_0 \leq 200.0 \text{ mM}$ (as color coded in the figure) at pH 1.0 and $25 \text{ }^\circ\text{C}$ under continuous air sparging of 30.0 mL min^{-1} .

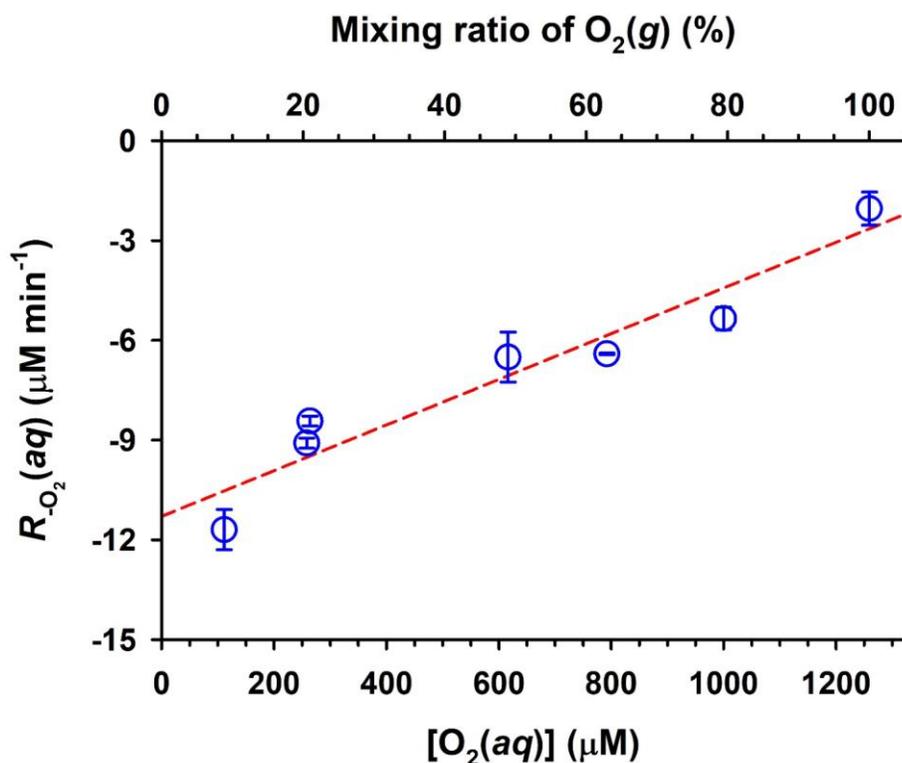


Figure 2. Rate of dissolved oxygen decay ($[R_{-O_2(aq)}]$) vs $[O_2(aq)]$ during irradiation of 20 mM pyruvic acid with continuous gas sparging at $100.0 \text{ mL min}^{-1}$

COLL 550

Aerosol spectroscopy and the dynamics of nanoparticle collisions

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Two new directions for the characterization of aerosol chemistry and dynamics will be reviewed in this presentation. In the first instance, a new single-particle dust accelerator/decelerator will be discussed.¹ This apparatus allows the examination of the impact dynamics of micron and sub-micron-sized nanoparticles. The mass and charge of single nanoparticles can be measured using charge detection mass spectrometry and particles are then accelerated or decelerated to controlled final velocities for studies of particle impact with surfaces. Results on measurements of the coefficient of restitution for polystyrene latex spheres, tin nanoparticles, and ice and mixed ice/organic solute particles will be presented. Applications to contamination mitigation in semiconductor processing and validation of environmental and planetary probes will be discussed.

In the second instance, a new electrodynamic balance apparatus optimized for the study of the spectroscopy and phase-change dynamics of aqueous particles relevant to sea-spray aerosol will be discussed. Approximately 50 micron sized droplets of model compounds are trapped with atmospheric control for the relative humidity, gas composition and temperature with this device. Initial measurements examining the translational diffusion of D₂O through H₂O in sucrose, citric acid and ternary sucrose-salt solutions will be presented, illustrating the extremely slow kinetics that are exhibited by highly viscous aerosol.

COLL 551

Condensed-phase photochemical processes in atmospheric particulate matter

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This presentation will describe our recent experiments on condensed-phase photochemistry of organic compounds, which are commonly found in primary and secondary organic aerosols. The exposure of organic aerosols to solar radiation produces a number of important effects: the chemical composition of aerosols changes; the particles tend to lose material due to the preferential photodegradation of larger, less volatile compounds leading to smaller, more volatile products; the light absorption properties of the organic material changes. These effects have important consequences for understanding the effect of aerosol particles on climate and health.

COLL 552

Molecular origin for cloud activation

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By integrating organic synthesis, secondary organic aerosol synthesis and collection, density functional theory (DFT) calculations, and vibrational sum frequency generation (SFG) spectroscopy, we identify close spectral matches between the surface vibrational spectra of β -caryophyllene-derived secondary organic material (SOM) and those of β -caryophyllene aldehyde and β -caryophyllonic acid at various interfaces. Combined with the record high surface tension depression these compounds elicit, we discuss possibilities for an intrinsically chemical origin for cloud activation by terpene-derived surfactants. Although we do not unequivocally identify the synthesized and analyzed oxidation products on the β -caryophyllene-derived SOM surfaces, these two compounds appear to be the most surface active out of the series and have also been foci of previous β -caryophyllene field and laboratory studies. An orientation analysis by phase-resolved SFG spectroscopy reveals a "pincer-like" configuration of the β -caryophyllene oxidation products, albeit on a model quartz surface, that somewhat

resembles the orientation of inverse double-tailed surfactants at the surfaces of biological systems. The structural information suggests that the less polar moiety of a surface-localized oxidation product, such as those studied here, may be the first site-of-contact for a gas-phase molecule approaching an SOA particle containing surface-active β -caryophyllene oxidation products.

COLL 553

Study of 3D morphology, phase state and viscoelastic properties of individual substrate-deposited particles

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Significant uncertainties still remain over our ability to accurately predict the overall aerosol effect on the climate and atmosphere. One reason originates from a limited number of direct physical-chemical data for submicrometer-sized aerosol particles that can be in different physical phase states. One of the important challenges is development of innovative tools to study individual submicrometer particles as a function of relative humidity under ambient pressure. Here, we present atomic force microscopy (AFM) methodologies on a series of model aerosol systems that provide the capability to identify and correlate the 3D morphology, phase state and viscoelastic properties of aerosol particles on a single particle basis. We establish quantitative framework using AFM force spectroscopy towards differentiation of the physical phase states of individual particles without prior knowledge of their chemical identity. We show the aspect ratio of individual particles can be used as a measure of the extent of the particle spreading due to impaction with the solid substrate and in turn assess their phase state. Therefore, we introduce the ability to identify the phase state of individual substrate deposited particles, irrespective of the microscopy technique used, which can subsequently be further validated by more quantitative AFM force spectroscopy.

COLL 554

Chemistry of atmospheric brown carbon

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Fundamental understanding of the complex chemistry of light absorbing atmospheric aerosols (aka Brown Carbon - BrC), their physico-chemical properties and environmental impacts is a challenging task because no single method of analytical chemistry is capable of providing the full range of analytical chemistry information. Micro-spectroscopy approaches can visualize individual particles and their internal structures; however, they largely exclude molecular-level information, and are limited to elemental and chemical bonding characterization. Contemporary methods of high-resolution mass spectrometry can provide detailed information on the molecular content

of BrC, but these methods use bulk particle samples and provide no knowledge of the individual particle composition. Therefore, application of complementary analytical methods of chemical analysis is necessary for comprehensive characterization of aerosol properties ranging from bulk molecular composition of BrC constituents to microscopy level details of individual particles. Combined assessment of the results provided by complementary analytical chemistry techniques offers unique insights to understand the composition and physico-chemical properties of BrC aerosols determining their effects on air quality and climate. This presentation will give an overview of recent field and laboratory studies of BrC with an overall goal to understand fundamental relationship between chemical transformations of airborne particles and their environmental and climate impacts.

COLL 555

Old and new insights of heterogeneous and multiphase oxidative processes affecting the lifetimes of toxic organic substances in biomass burning and sea spray aerosol

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Airborne exposure to toxic organic substances (TOS) in atmospheric aerosol, including nitrophenols from wildfire and biomass burning, and bisphenols from plastic incineration and degradation of plastics in sea spray aerosol, pose a potential significant risk to humans and the environment, and may be exacerbated in the future because of more frequent intense droughts and continued poor waste management practices. In our work, we study the heterogeneous and multiphase photochemical and oxidative degradation reactions and kinetics that affect the lifetimes of TOS in aerosol. Our previous work showed that the OH radical uptake by nitroguaiacol, a toxic byproduct of lignin decomposition, is suppressed at longer OH exposures (i.e., [OH]×time) and the oxidative degradation rate of methyl nitrocatechol, a biomass burning secondary organic aerosol marker, is suppressed at higher relative humidity, both due to competitive coadsorption of OH radicals and water at the surface. We also demonstrated that heterogeneous OH oxidation enhances the hygroscopicity of methyl nitrocatechol aerosol but the effects of oxidation on the hygroscopicity of the particles is masked in the presence of more hygroscopic inorganic salts. More recently, we have been investigating the degradation kinetics and lifetimes of the persistent plastic pollutant, bisphenol A (BPA) in the presence of OH and in the presence of a photosensitizer under solar-simulated light in an aerosol flow tube employing (extractive electrospray ionization) high resolution time-of-flight chemical ionization mass spectrometry. We study BPA degradation in simple single- and binary-component aerosol as well as complex representative sea spray aerosol produced from a marine aerosol reference tank with controlled biology. In honor of the work of Prof. Vicki Grassian, I will discuss

highlights from these works and new insights into the analysis of plastic degradation in sea spray aerosol.

COLL 556

Tuning surface properties in self-assembled monolayers of multi-functional boron clusters

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Self-assembled monolayers (SAMs) provide an avenue for creating surfaces with defined chemical and physical properties. We are interested in an icosahedral cage boron cluster, the carborane, as a building block for SAMs with properties that we can tune to advantage. Carboranes have several favorable traits, including variability in the functionalization of the molecule. A thiol group used for surface attachment can be linked to both carbon and boron vertices in the carborane cage. We have probed bifunctional carboranes with both a thiol and a carboxylic acid functional group, in either a *para* or a *meta* orientation. Additionally, isomers of carboranethiol have distinct dipole moments in orientation and magnitude. This leads to the formation of long-range dipole-dipole networks within the SAM, which can stabilize the SAM and also modify the local work function of the material. Thus, by using one or multiple isomers in the formation of a SAM, we can tune the work function at the substrate-monolayer interface. Using STM, we have visualized SAMs composed of two *meta*-carboranethiolate carboxylic acid isomers. Despite the presence of increased steric demands in the lateral direction, these monolayers are relatively pristine and defect free. We probed the chemical behavior of the exposed carboxylic acid group and found that the pK_a is shifted approximately two pH units higher. We confirmed that the carboxylic acid moiety is available for additional reactions with metal ions and organic molecules. This latter trait allowed us to modify the exposed functional group directly on the surface and thereby tune the molecular dipole and alter the local work function. It also enabled us to use chemical lift-off lithography for patterning for further surface modification. This work demonstrates that carboranethiolate carboxylic acid SAMs allow us to simultaneously modify both chemical and physical properties of a material.

COLL 557

Probing the electrochemical reductive stability of decanethiol/triazole-ferrocene mixed self-assembled monolayers on Au

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Understanding the critical factors that affect the electrochemical stability of functionalized mixed self-assembled monolayers (SAMs) is a cornerstone to improving the reductive stability of electroactive monolayers on transition metal electrodes. It is well-known that van der Waals forces play a large role in contributing to the electrochemical stability of SAMs, but less is known about how bulky terminal groups affect SAM packing in mixed-monolayers. In this presentation, we propose the reductive stability of mixed-SAMs on Au composed of ferrocene-terminated C11-thiol (Fc-C₁₁-SH) and a C10-thiol (C₁₀-SH) diluent as a model system for evaluating the electrochemical stability of electroactive mixed-monolayers with bulky terminal groups. Fc-C₁₁-SH coverage is modulated by controlling the ratio of azide-terminated C11-thiols to the C₁₀-SH diluent in the deposition solution followed by “Click” chemistry with ethynyl-ferrocene to form 1,2,3-triazole-ferrocene terminated SAMs. Reductive stability is probed by applying constant potentials followed by measuring the change in Fc-C₁₁-SH coverage. Isotherms constructed from constant potential desorption were compared to desorption peaks from linear sweep voltammetry which is traditionally used to measure SAM electrochemical stability. The desorption potential was measured as a function of the fractional coverage of the Fc-C₁₁-SH in the mixed monolayer. The SAM reductive stability was also measured under hydrodynamic flow using rotating disk electrodes to help reduce SAM re-adsorption, and the resulting desorption isotherms under hydrodynamic flow are compared to those measured in quiescent solution. Insights gained from this system will be applied to measuring the stability of SAMs on other transition metals (Cu, Ni) where traditional cyclic voltammetry fails to produce clear desorption peaks due to interference from the hydrogen evolution reaction.

COLL 558

Surface chemistry for modification and tuning of polymer CORALS

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CORALs (CoOrdinated Responsive Arrays of surface-Linked islands) represent a novel approach in the field of responsive surfaces. Polymer CORALs are composed of polymer chains covalently grafted to a solid substrate in a regular manner: islands of densely grafted chains homogeneously separated by a distance on the order of a chain length. Each island of the array is capable of conformational switching in a sharp and coordinated manner. In relaxed state upon exposure to a good solvent CORALs isolate substrate surface from the environment (gas or liquid). In a weak solvent, they adopt a compact conformation thus exposing the surface. This unique behavior distinguishes polymer CORALs from homogeneous polymer brushes and low-density

adsorbed/grafted polymer coatings. Thus, polymer CORALs may find applications for responsive heterogeneous catalysts, electrodes, and adsorbents. The control of the switch parameters may be conveniently tuned by the chemical composition of the substrate surface and the parameters (state) of the polymer. We demonstrate it both in the experiment and by the means of coarse grain molecular simulations. We show that proper chemical modification of the substrate surface significantly shifts the switching conditions, e.g. polarity of the binary solvent. A similar effect has modification of the grafted polymer. In particular, transesterification of poly(tert-butyl methacrylate) with N,N-dimethylaminoethanol results in poly(2-(N,N-dimethylamino)ethylmethacrylate) (PDMAEMA) CORALs. Such CORALs demonstrate conformational response to both temperature and pH

COLL 559

Exploration of variables involved in surface pK_a shifts of carboxylated carboranethiol self-assembled monolayers

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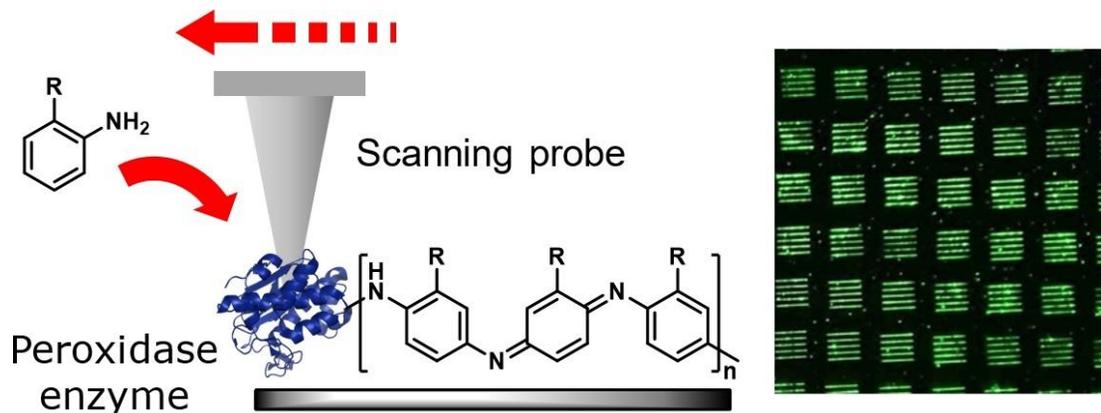
Integration of functionalized 2D materials into structured devices requires in-depth understanding of the structure, reactivity, and acid-base properties of the adsorbed molecules at the junction. Self-assembled monolayers (SAMs) have been used extensively to probe and to tune the properties of these interfaces. Alkanethiols or other functionalized alkyl chains with acidic moieties have been used to probe interfacial acid-base behavior. Here, we examine self-assembled monolayers (SAMs) of carboranethiolate molecules functionalized with carboxylic acid groups. Due to the high axial symmetry and robust nature of these molecules, many of the common defects observed in *n*-alkanethiolate monolayers are eliminated, enabling controlled platforms to study the properties at substrate/environment interfaces. Self-assembled monolayers of carboranethiolates with carboxylic acids attached in the *meta* position have pK_as ~2 pH units higher on the surface. In this study, we explore the effects of the position of the carboxylic acid functional group and the curvature of the surface on both structure and surface pK_a of the functionalized monolayer. By exploring these different conditions with contact angle titration and scanning tunneling microscopy (STM) we elucidate the roles of environmental conditions and their effects on the underlying mechanisms of surface pK_a shift. We hypothesize that the position of the functional group results in surface pK_a shifts of lesser magnitude the closer it is to the substrate/environment interface. This shift is enhanced with greater curvature of the surface as the acidic moieties become more exposed. This work creates platforms to tailor the acid-base properties of different monolayers in addition to the surface wettability of substrates. This work also has applications in functionalizing surfaces of multilayer devices with solution-processable techniques that have interfaces modulated to control chemical reactivity.

COLL 560

Biocatalytic parallelized scanning probe lithography for the additive fabrication of conjugated polymer structures

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Scanning probe lithography (SPL) offers an accessible alternative to conventional photolithography for surface nanofabrication. In principle, the synthetic scope of SPL could be greatly enhanced by combining the precision of scanning probe systems with the chemical synthetic scope offered by enzymatic catalysis. Here we report the development of multiplexed SPL employing probes functionalized with horseradish peroxidase, and its subsequent use for the constructive fabrication of polyaniline features on both silicon oxide and gold substrates. This polymer is of particular interest due to its potential applications in organic electronics but its use is hindered by its poor processability, which could be circumvented by direct *in situ* synthesis at the desired locations. Using parallelized arrays of probes, the fabrication of polymer features over 1 cm² areas was demonstrated with individual feature widths as small as 162 ± 24 nm. The identity of the deposited materials was confirmed by Raman spectroscopy, and it was further shown that these polyaniline features could be chemically derivatized postlithographically by Huisgen [2 + 3] “click” chemistry, when 2-propargyloxyaniline was used as the monomer in the initial lithography step.



COLL 561

Combined experimental and triple-mode sorption modeling approach for sorption and diffusion in polymeric materials

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Sorption and diffusion in polymeric materials is of great interest in wide range of applications. To many application, moisture sorption and diffusion can be catastrophic due to the change in chemical and mechanical properties of materials over time. The uptake and outgassing of moisture is also associated with aging and compatibility issues in a system, which can directly alter the lifetimes and viability of system assemblies and screening new materials for future designs. The process is dynamic and consists of different sorption modes and varies dramatically in different materials. Therefore, a detailed understating of the moisture uptake and diffusion is crucial. In this study, we investigate the moisture sorption and diffusion phenomena using a combined experimental and modeling approach. Polymeric materials (for example: KaptonH and Kapton HN) are investigated over a wide range of temperatures and relative humidities (RH) to quantify the moisture transport mechanism as shown in the figure 1 below. Gravimetric type dynamic vapor sorption (DVS) experiments were employed to measure the moisture uptake and used for the modeling. A reactive transport model is used which includes a triple-mode sorption model that includes absorption, adsorption, and pooling of species, molecular diffusion, and chemical reaction kinetics. Our sorption experiments and modeling results quantify the differences between the two example materials and demonstrate a substantially larger adsorption capacity and moisture affinity for Kapton HN compared with Kapton H. A distinct pooling mode can be seen above 70% RH in both materials, however the pooling mode is larger in Kapton HN. Density functional theory calculations are performed to investigate the impacts on moisture uptake due to CaHPO_4 filler, which is present only in Kapton HN.

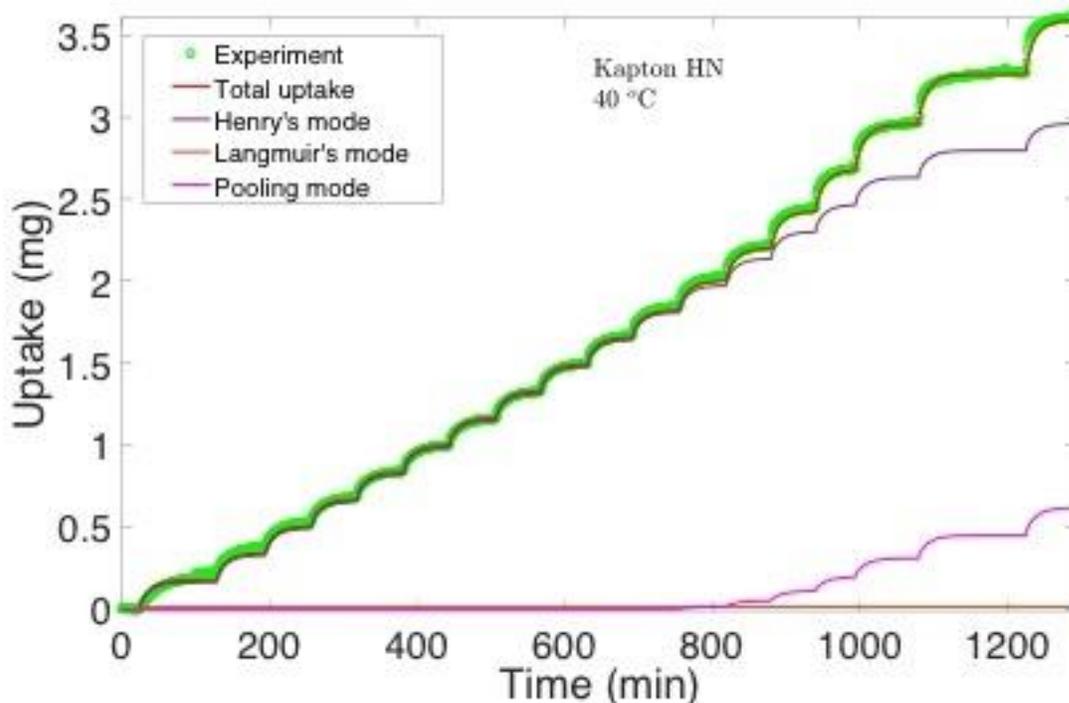


Fig 1: Experiments and modeling results of dynamic moisture uptake by Kapton HN at a range of relative humidities at 40°C.

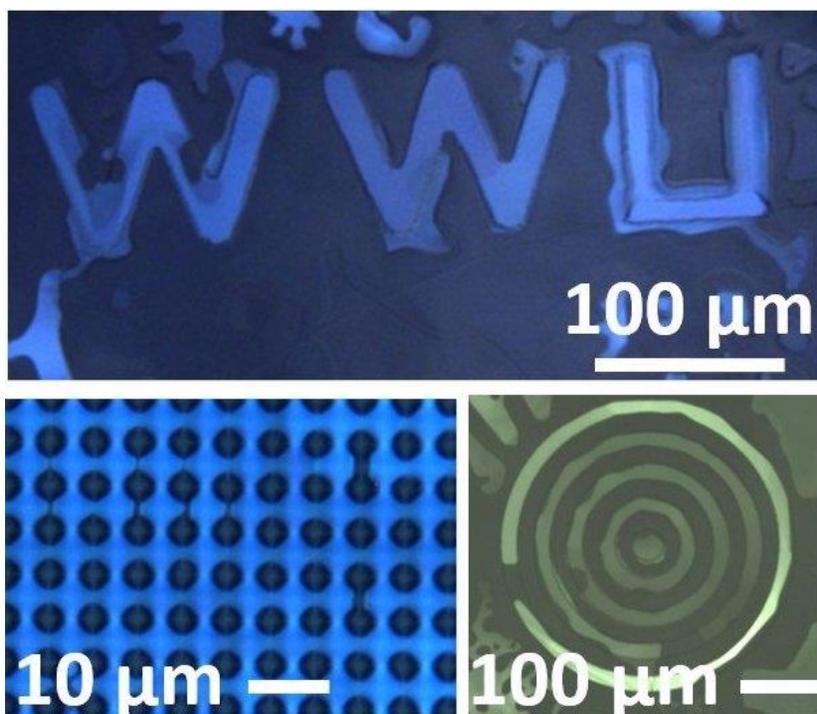
COLL 562

Bottom-up shape engineering of molecular single-crystals

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The ability to fabricate complex submicron-scale components from inorganic crystalline semiconductor materials such as c-Si enables countless modern technologies, from microelectromechanical systems to integrated circuits. For single-crystal molecular materials on the other hand, comparable approaches to defining micron- and submicron-scale structure are much less well developed, in part because weak intermolecular binding forces make molecular crystals vulnerable to damage by conventional techniques such as photolithography and energetic beam milling. Here we show how the same weak forces that are problematic for top-down patterning of

molecular crystals can be exploited to enable controlled bottom-up growth, by leveraging shape plasticity. We describe a new approach to molecular single-crystal engineering based on bottom-up growth of single-crystals on sacrificial templates by vapor-liquid-solid (VLS) deposition. We demonstrate that, under the right conditions, these templates can essentially serve as a mold for crystal formation, enabling growth of molecular single-crystals with complex, even extraordinary shapes. The resulting new class of materials may help unlock functional features for molecular single-crystals previously reserved for inorganic solids, via microstructural control over their photonic, thermal, charge transport, mechanical, and other fundamentally interesting and technologically valuable properties. Results are presented demonstrating a wide range of shape- and size-control modalities, including crystal topology, bounding perimeter shape, and nucleation position, for several families of small-molecule organic semiconductor and pharmaceutical compounds.



COLL 563

Controlling assembly of layer-by-layer films via a small hydrogen-bonding molecule

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We present a study of the effect of dimethyl sulfoxide (DMSO) on the interaction between poly(methacrylic) acid (PMAA) and polyvinylpyrrolidone (PVP) in aqueous solution at low pH and on its self-assembly in layer-by-layer (LbL) films. As a hydrogen bond acceptor, DMSO perturbs hydrogen-bonding network of water and hydrogen bonds to PMAA, competing with polymer-polymer binding in solution and strongly affecting assembly of PVP/PMAA LbL films. An increase in DMSO content in the mixed DMSO-aqueous solutions from 0 vol % to 60 vol % significantly weakened PVP-PMAA binding, leading to deposition of 2.5-fold thicker 20-bilayer films. Reversible inclusion of DMSO within the films was demonstrated by a combination of Fourier-transform infrared spectroscopy (FTIR) and ellipsometric measurements. Neutron reflectometry (NR) studies which involved deuterated PMAA showed strong effect of DMSO present in the deposition solution on polymer chain intermixing within LbL films. Isothermal titration calorimetry (ITC) revealed that binding between PVP and PMAA switched from endothermic to exothermic as content of DMSO in the mixed solvent increased, reflecting a transition from polymer-polymer binding dominated by release of water from polymer solvation shell to the one controlled by interpolymer hydrogen-bonding.

COLL 564

Multifunctional biocompatible nanocoatings of ionic fluorinated polyphosphazenes

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Water-soluble, ionic polyphosphazenes (PPzs) are promising, versatile building blocks for biomaterials. This work explores hydrophobic coatings of ionic fluorinated polyphosphazenes (FPzs) made using the layer-by-layer (LbL) assembly technique. Specifically, anionic FPzs with either carboxylic or sulfonic acid groups can be deposited with a variety of cationic molecules including cationic polymers (branched polyethylene imine), enzymes (lysozyme) and bioactive small molecules, such as antibiotics (gentamicin, polymyxin B). Film growth and morphology were monitored with spectroscopic ellipsometry, AFM, and SEM, while antibiotic content within the film was analyzed using mass spectrometry. We found that control over the degree of fluorination and charge density on PPz chains enabled programmed response/delivery of antibiotics from the coatings in response to localized pH lowering which mimicked the biofilm environment. A wide spectrum of localized delivery scenarios ranging from complete retention of functional molecules to pH-responsive delivery of variable doses of bioactive molecules could be achieved. Moreover, biocompatibility of coatings was monitored in terms of whole blood hemolysis and protein adsorption studies for coatings of varied hydrophobicity, which was controlled through fluorination degree of FPz and

top layer of the coating. Importantly, coatings containing antibiotics and enzymes demonstrate that both remain active while in the film, and can be either delivered in response to local pH variations at pre-programmed doses, or permanently retained within the coatings to achieve long-term effects.

COLL 565

Enzyme-responsive actively tumor-penetrating nanomedicine overcomes tumor diffusion barriers and produces potent anticancer efficacy

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The tumor microenvironment imposes strong barriers to passive paracellular diffusion of molecules, blocking the movement of nanomedicines in tumor tissue and making distal cells inaccessible. Tumor penetration is therefore an unresolved obstacle to effective anticancer drug delivery. To this end, we demonstrate an active tumor-penetration nanomedicine that exploits transcytosis among tumor cells to distribute throughout the tumor tissue, overcoming the paracellular diffusion obstacle and leading to significantly enhanced therapeutic efficacy. The nanomedicine is a γ -glutamyl transpeptidase (GGT)-responsive cationizing macromolecular drug, γ -glutamyl-based polymer–camptothecin (CPT) conjugate, which is zwitterionic and has a long blood circulation. When the drug conjugate passes on the luminal endothelial cells of tumor blood-vessels or extravasates into the tumor cell interstitium, the overexpressed GGT on the cell membrane cleaves off the conjugate's γ -glutamyl moieties to generate primary amines, turning it positively charged. The resulting cationic conjugate undergoes fast caveolae-mediated endocytosis and transcytosis, enabling transendothelial and transcellular transport of the conjugate and uniform distribution throughout the tumor. As a result, this conjugate shows much more potent antitumor activity than non-GGT-sensitive controls, leading to complete eradication of small solid tumors ($\sim 100 \text{ mm}^3$) and dramatic regression of large established tumors of clinically relevant sizes ($\sim 500 \text{ mm}^3$). It also significantly extends the survival of mice bearing orthotopic pancreatic tumors compared to the first-line drug gemcitabine. Thus, the active tumor penetration provides an effective approach for anticancer nanomedicine to circumvent the tumor passive diffusion barriers and enhance their therapeutic efficacies.

COLL 566

Immunoreactions in the presence of nanostructures

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The benefit of medical application of nanoparticles is related to the surface they present to the healthy and diseased environment in the body. Macrophages are involved in the recognition and clearance of foreign materials and initiate the subsequent steps of the cellular and humoral immune response. Their plasticity allows the polarization into different subtypes which plays roles in proinflammatory (M1 macrophages) and in antiinflammatory (M2 macrophages) processes. We investigated the interaction of cells with nanostructures in a co-culture model of HUVECs and macrophages of the peripheral blood and macrophages alone. We were demonstrating a significant change in cellular behaviour induced by the structure rather than the biochemical properties of the surfaces. In another project a therapeutically approach for the treatment of Generalized Arterial Calcification of Infancy (GACI) by new developed nanoparticles will be presented. Thus, novel nanotechnological setups and concepts for medical applications will be presented here.

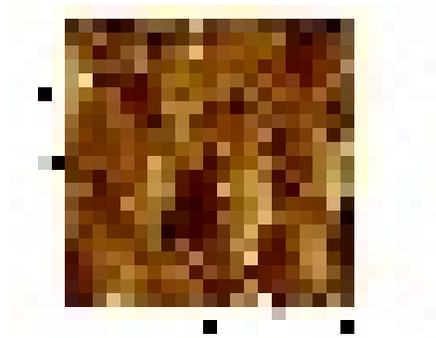


Figure 1A: Surface structure of normal HUVECs (AFM).

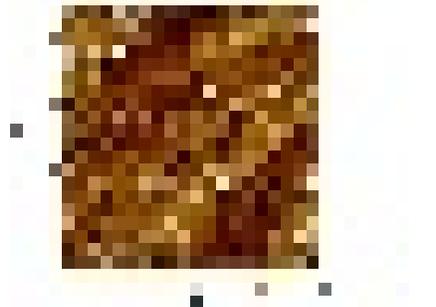


Figure 1B: Surface structure of inflammatory activated HUVECs (AFM).

COLL 567

Combination of cowpea mosaic virus and PD-1 blockade works synergistically to improve therapeutic efficacy

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Immune checkpoint inhibitor therapies currently benefit only a subset of patients in the clinic because the majority of patients bear “cold” tumors with low pre-infiltration of effector T cells and low expression of checkpoint inhibitors. Therefore, there is a critical need for an effective strategy that can not only recruit effector T cells into tumor microenvironment, but also broaden the repertoire of T cells engaged in the existing checkpoint inhibitor therapies that stimulate antitumor activity. Here, we hypothesized cowpea mosaic virus (CPMV) could induce effector CD4⁺ and CD8⁺ T cells infiltration into tumors and induce PD-1 expression on effector T cells, leading to more susceptible targets for anti-PD-1 immunotherapy. We demonstrated that in situ CPMV administration recruited both CD4⁺ and CD8⁺ T cells to the tumor site and induced the expression of PD-1 on those T cells using an immunocompetent murine ovarian cancer model, therefore, enhancing the targeting performance of PD-1 blockade and triggering robust local cytotoxic T cell immune responses. The combination of CPMV and anti-PD-1 worked synergistically to delay tumor growth and prevent tumor relapse. This work may lead to new design principles for plant virus nanoparticles as novel immunotherapeutic adjuvants and provide new treatment option for ovarian cancer patients.

COLL 568

Designed Au-TiO₂ nanoreactors for spatiotemporal controlled, NIR-promoted photocatalytic transformations inside living cells

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Herein, we introduce a novel approach based on the use of synthetic chemical nanoreactors for achieving control over chemical transformation inside a living cell. Such functionality is attained through the design of a hybrid nanocomposite in which plasmonic Au nanorods and TiO₂ nanoparticles are synergistically integrated within a mesoporous hollow silica capsule. This architecture permits to exploit the hot-electron injection process from the metal to a semiconductor photocatalysts by means of the use of NIR light. Additionally, the mesoporous silica shell of the reactor acts as a molecular sieve, leading just to the transformation of molecules than can reach the inner cavity of the reactor. As a proof of concept of this powerful approach for the performance of photochemistry in side living cells, the nanoreactors where internalized through an endocytosis process into the lysosomes of HeLa cells. Then, the chemical transformation of Rhodamine B was performed by means of a NIR laser without affecting the viability of the cells.

COLL 569

Comparison of drug delivery strategies for enhancing efficacy of intravesical therapy for bladder cancer

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A major shortcoming associated with current intravesical chemotherapy for bladder cancer is the short residence time of the instilled drug or drug delivery system (DDS) in the bladder since much of it is lost upon the first voiding of urine. Strategies to improve the efficacy of DDS for intravesical chemotherapy are greatly needed since about ~50-70% of patients with non-muscle invasive bladder cancer will develop tumor recurrence, and ~25% will suffer from progression to the muscle-invading stage. As a result of the necessity for long-term follow-up and repeat interventions, bladder cancer is the costliest cancer to treat on a per patient basis. Our work focuses on developing strategies to enhance delivery of chemotherapeutic agents for bladder cancer treatment. Three different strategies are compared. The first strategy employs cationic mucoadhesive nano DDS that promotes cellular uptake via electrostatic interactions with the negatively charged components on the cell membranes. The DDS also demonstrates a high degree of retention on the bladder wall due to similar interactions with the negatively charged glycosaminoglycan layer. In the second strategy, chemotherapeutic agents or nano DDS are conjugated with peptides that target receptors that are highly expressed on bladder cancer cells, whereas in the third strategy, sugar moieties are conjugated to the chemotherapeutic agents or nano DDS to capitalize on cancer cells' avidity for sugar. From in vitro and ex vivo experiments, the relative advantages of using these formulations in intravesical chemotherapy are identified. Preliminary animal model studies have also been carried to assess the potential of these three strategies in potentiating drug efficacy in intravesical chemotherapy for non-muscle invasive bladder cancer treatment.

COLL 570

Nanoscale colocalization of fluorogenic probes reveals the role of oxygen vacancies in the photocatalytic activity of tungsten oxide nanowires

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Defect engineering is a strategy that has been widely used to design active semiconductor photocatalysts. However, understanding the role of specific defects, such as oxygen vacancies, in controlling photocatalytic activity remains a challenge. In this talk I will discuss the use of chemically triggered fluorogenic probes to study the spatial distribution of active regions in individual tungsten oxide nanowires using super-resolution fluorescence microscopy. Through quantitative, coordinate-based colocalization of probe molecules activated by the same nanowires, we demonstrate that the nanoscale regions most active for the photocatalytic generation of hydroxyl

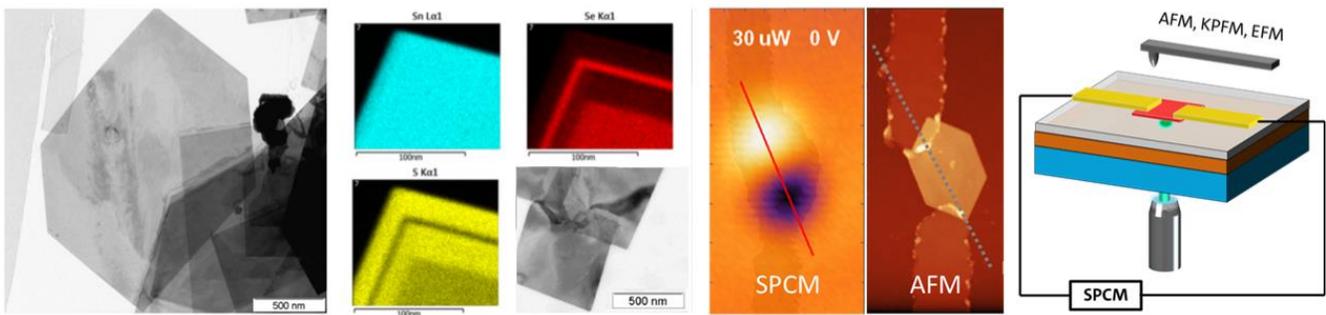
radicals also possess a greater concentration of oxygen vacancies. Furthermore, we show how the distribution of active regions in a tungsten oxide nanowire is altered based on the ligands bound to its surface. These findings indicate that oxygen vacancies activate water molecules adsorbed onto the semiconductor surface to catalyze the generation of hydroxyl radicals, an important chemical intermediate in the production of fuels from sunlight.

COLL 571

Synthesis and electrical properties of photoactive, two-dimensional SnS nanosheets

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Tin(II)sulfide nanosheets with lateral sizes in the range of several micrometers and thicknesses of only tens of nanometers are synthesized by injection of S-oleylamine into a hot solution of oleylamine, oleic acid, HMDS and tin chloride. We will present structural data to follow the nanosheets growth and show how additional octadecene can influence the lateral growth direction to form either rectangular or hexagonal nanosheets. In addition we present results on lateral SnS/SnSe heterostructures. In the second part we focus on the electrical properties of individual hexagonal SnS/SnSe-nanosheets. Here we present data from combined Kelvin Probe Force Microscopy (KPFM) with simultaneous Scanning Photocurrent Measurements (SPCM), where the illumination is either achieved by an optical microscope or an X-ray nanoprobe. Here we attribute the electro-optical properties to mutual interaction between locally generated charge carriers and electric potentials. For example the occurrence of zero-bias photocurrent can directly be attributed to changes of the band bending due to the optically generated charge carriers.



TEM images of hexagonal SnS nanosheets and rectangular SnS/SnSe hetero sheets. SPCM and AFM images of one individual contacted SnS nanosheet to investigate electrical optical properties.

COLL 572

Metal nanoclusters: New light harvesting antenna for solar energy conversion

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Noble metal nanoclusters (NCs) with molecule-like behavior have emerged as a new light harvester in solar energy conversion systems. Despite several important strides made recently, efforts toward the utilization of NCs as a light harvester have been primarily restricted to proving their potency and feasibility. A complete characterization of metal cluster-sensitized solar cells (MCSSCs) is still lacking, and hence comprehensive understanding of the interfacial events and limiting factors that dictate their performance remains elusive. In this presentation, the utilization of Au and Ag NCs in MCSSCs and in-depth spectroscopic and electrochemical investigation on electrode/electrolyte interface is discussed.

COLL 573

Space-confined seeded growth of Au nanostructures for highly efficient photo-induced cancer therapy

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Plasmon coupling occurs when two or more excited plasmonic nanoparticles approach each other to a distance below approximately one diameter's length. Once the coupling happens, the electromagnetic field in the interparticle gap to be boosted by several orders of magnitude, which enables many exciting applications in areas such as bioimaging and phototherapy. The current challenges for designing plasmonic coupling nanostructures remain in terms of the relatively complicated synthesis and fabrications. In this presentation, we propose a highly efficient confined seeded growth strategy for the preparation of metallic nanostructures with complex plasmon coupling, using Au as a representative demonstration. Specifically, the growth of Au is confined to a narrow tubular space of preformed rod-shaped polymer nanocapsules, which uniquely enables the automatic clustering of Au nanoparticles during the growth processes, thereby avoiding the complex self-assembly involved in the conventional synthesis. The flexibility of this method has been demonstrated by producing Au nanoparticles clusters (AuNCs) with varying plasmon coupling frequencies from visible to near infrared by precisely controlling the interparticle distance through adjusting the amount of precursors. The strong coupling of AuNCs to the incident light successively transfer the incident energy to generate heat with ultrahigh photothermal conversion efficiency (~78%), and can effectively excite triplet oxygen to singlet oxygen by Förster resonance energy transfer, which results in enhanced performance in photo-induced cancer therapy.

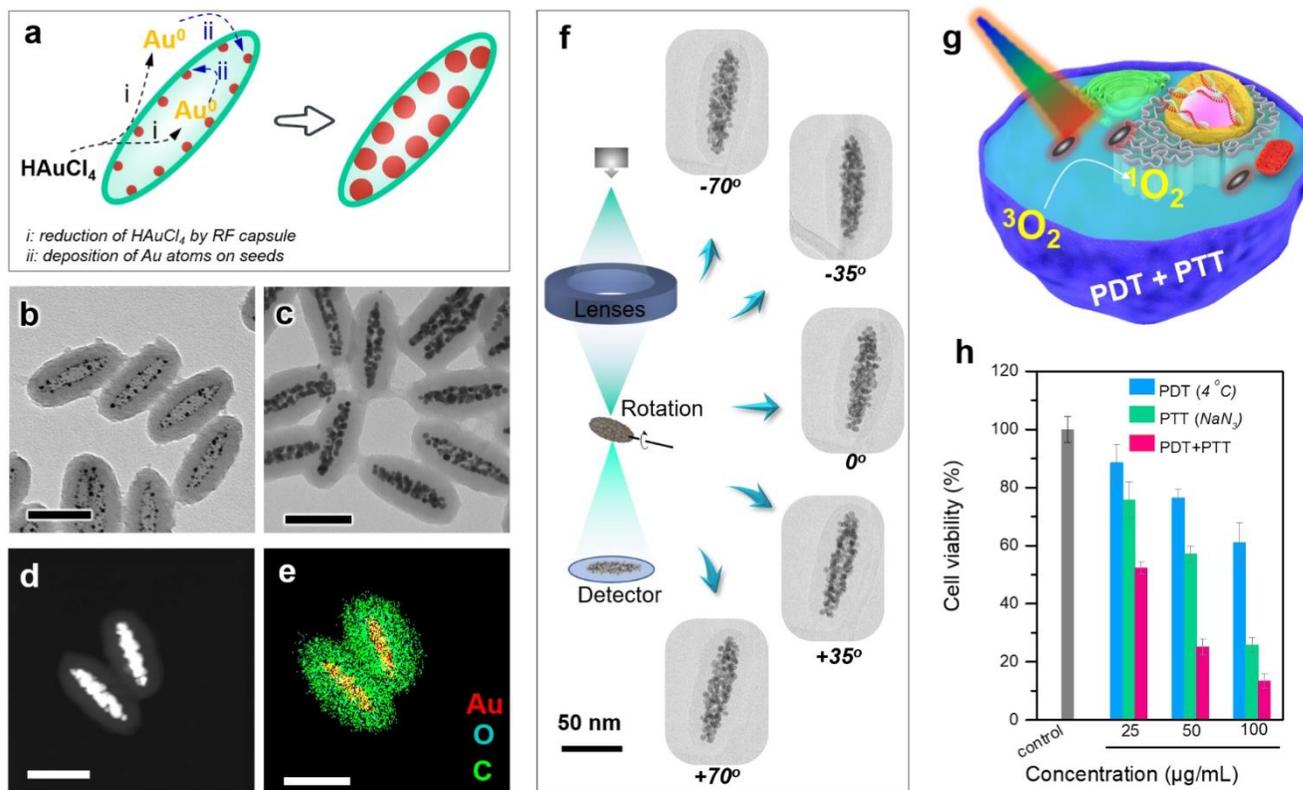


Figure 1. Schematic demonstration of confined seeded growth of AuNPs cluster by template-induced reaction (a). TEM images of hollow Au@RF nanoparticles (b) and AuNCs (c). The HADDF-STEM image (d) and the energy dispersive X-ray spectroscopy (EDS) elemental mapping (e) of AuNCs. Schematic diagram of 3D electron tomography by tilting a sample to many different orientations (f). Schematic illustration of photothermal and photodynamic therapy (g). Viability of Hela cells in vitro after treatment with varying concentration of AuNCs (h).

COLL 574

Solid plasmonic substrates synthesized using TFF purified colloidal silver for cancer detection by means of SERS analysis of blood plasma

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Surface Enhanced Raman Spectroscopy (SERS) is a very promising vibrational technique able to provide specific molecular information that could have a major impact in a plethora of biomedical applications. Amongst these applications, SERS-based early cancer detection could represent a breakthrough. Being a surface technique, SERS requires the presence of a suitable plasmonic substrate able to generate specific, enhanced and reproducible spectra when using an excitation laser line ranging from visible to near infra-red domain. The major obstacle that hampers its implementation in clinical practice is the synthesis of a proper plasmonic suitable for measurements on biofluids. In this paper we propose a new approach for the synthesis of a solid SERS substrate using as building blocks spherical silver nanoparticles purified and concentrated using the Tangential Flow Filtration (TFF) method. The capacity of the here proposed Silver Solid Plasmonic Substrate (SSPS) to generate reproducible and enhanced Raman signals in a manner that can allow cancer detection has been tested on blood plasma samples collected from 37 healthy donors and 34 breast cancer (BC) patients. The SER spectra collected from the two groups have been analyzed by means of Principal Component Analysis (PCA) combined with Linear Discriminant Analysis (LDA). Our results allowed the discrimination between the healthy donors and breast cancer (BC) patients with very high sensitivity and specificity (90% sensitivity and 89% specificity). The here reported diagnostic accuracy of 89%, obtained by performing SERS measurements directly on blood plasma samples without performing any other purification or deproteinization step, is a direct consequence of SSPSs ability to generate diagnostic relevant spectral information. Our results suggest that this type of solid substrates could be also employed for the detection of other types of cancer or other diseases.

COLL 575

Electromagnetic field confinement in self-assembled anisotropic plasmonic nanoparticle superlattice

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Plasmonic nanoparticles exhibit extraordinary optical properties due to their resonant interaction with light. Their unique optical properties can be tuned through their size, shape and composition. When coupled, they behave as optical antennas, focusing electromagnetic fields to enable surface enhanced spectroscopies. Properly engineered, these optical antennas are capable of enabling field enhanced spectroscopic detection that is orders of magnitudes more sensitive than the analogous conventional spectroscopies. This makes the plasmonic sensors an attractive option for trace analyte detection in security applications. Through self-assembly process, we have fabricated vertically aligned superlattice arrays for the detection of various analytes. In this presentation, we will present computational simulation study of such plasmonic superlattice arrays made of anisotropic nanoparticles (e.g. Au nanorods). We will present the field confinement effect in plasmonic superlattices through finite difference time domain simulation. The electric field confinement tends to located at the

expected interparticle junction in the single layer nanoparticle array. In larger plasmonic superlattices, field enhancement can come from structural resonances in addition to the gap coupling modes between the immediately coupled plasmonic nanostructures. Surprisingly, field strength tends to diminish towards the centre of the superlattice, possibly due to the screening effect. We will discuss the implication of field enhancements from both modes and its uses as surface enhanced Raman spectroscopy (SERS) sensors for the detection of small molecules. We will also present experimental measurement obtained from plasmonic nanocluster assemblies and correlate their SERS characteristics with their structural morphology.

COLL 576

Hierarchical assembly of gold nanoparticles on graphene nano platelets: Synthesis and characterization

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Hierarchical assembly of plasmonic gold nanoparticles (AuNPs) into two-dimensional materials (graphene) is of significant interest for nearfield imaging, sensing, and inducing a photo-thermal response in a material. However, decorating AuNPs onto graphene nano platelets (GNP) uniformly is a significant challenge. This is because GNPs tend to aggregate easily *via* van der Waals force to form graphite which perturbs uniform decoration of nanoparticles on its surfaces. In this work, we discuss a simple solution-based technique to exfoliate graphite into graphene platelets, followed by reacting graphene surfaces with gold acetate precursors. By carefully controlling a reaction optimization, we were successful in maintaining the structural integrity of GNPs and simultaneously decorating it with AuNPs uniformly. These nanohybrids were characterized by various microscopic and spectroscopic techniques. Powder X-ray diffraction and scanning electron microscopy (SEM) indicated that the size of the Au NPs is dependent on the amount of Au loading. High-resolution transmission electron microscopy (TEM) and high-angle annular dark-field imaging (HAADF-STEM) showed thin GNPs were decorated with AuNPs uniformly. Plasmon-phonon interactions of these hybrid structures will be discussed with the support from spectroscopy results including Raman, UV-Vis, and IR.

COLL 577

Physical stability and fibrillation kinetics of teriparatide: Influence of conformational structure, product formulation, and the Hoffmeister ions

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FDA, Silver spring, Maryland, United States (2) Upstream Manufacturing Sciences and Technology, Bristol-Myers Squibb, Syracuse, New York, United States

Teriparatide is a single-chain polypeptide used for the treatment of osteoporosis in post-menopausal women. Unlike most peptides, the structural conformation of teriparatide in solution is reported to correlate with its biological activity. For this reason, teriparatide is an ideal candidate for studying the impact of a peptide's conformational structure, formulation and product handling on the peptide's aggregation mechanism and kinetics. Computational analysis performed indicated that the folded regions of teriparatide were "hot spots" of aggregation. Further, both computational and experimental approaches indicated that teriparatide has higher propensity of undergoing fibrillation than amorphous aggregation. However, the underlying mechanism and kinetics of the aggregation process was affected by product formulation and handling. Teriparatide's fibrillation propensity was enhanced at higher peptide concentration, ionic strength and pH. Further, although the extent and stability of the teriparatide's conformational structure may impact the kinetics of fibrillation, the coulombic interaction between the peptide monomers may have a stronger impact on the nucleation rate. This observation was further corroborated by the impact of pH and ionic strength on the fibrillation kinetics.

Both Hoffmeister and ion-specific effects were observed when the impact of anions on the fibrillation kinetics of teriparatide was studied. Further, contrary to well held opinion, the cationic form of the salt had an impact on the fibrillation kinetics. The addition of osmolytes (α and β cyclodextrin, sucrose and mannitol) retarded the nucleation rate with cyclodextrins the most effective in this regard. Finally, no correlation was found between the impact of ions and osmolytes on the nucleation rate and on the elongation rate of teriparatide.

COLL 578

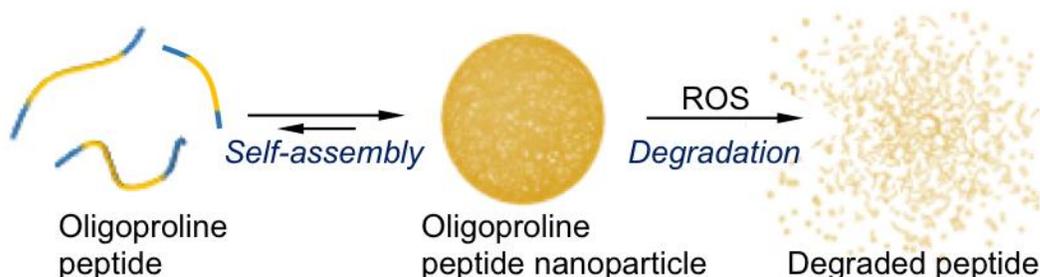
Development of ROS-triggered degradable nanoparticles using oligoproline peptides as biomolecule delivery platform for plant cells

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Peptides are promising candidates to design biomaterials due to their excellent biocompatibility and bioavailability. Furthermore, their structure and function can be easily modified by varying the number and constitute of amino acid residues and chemical modification. With surfactant activity, enzyme resistance, and reactive oxygen species (ROS) responsiveness, oligo-proline containing peptides are promising to develop ROS-triggered degradable nanoparticles. Stimuli-responsiveness is robust approach to attain efficient controlled release and targeting *in vivo*. ROS are well-known marker of inflamed tissues and cancer tissues in mammalian cells. In contrast, plant cells show higher ROS level compared to mammalian cells due to photosynthesis via

chloroplasts. From this point of view, ROS responsive nanocarriers are powerful means to attain effective and selective delivery in plant cells. Here, we designed several types of oligoproline-containing peptides with varying the number of proline residues and evaluate their availability as ROS-triggered degradable nanocarriers.

Several types of oligoproline-containing peptides, tri-, tetra-, and penta-peptides, were synthesized via liquid phase synthesis to evaluate the effect of proline residue number on ROS-responsiveness and formulation of nanoparticles. First, ROS-sensitiveness was evaluated and tetra- and penta-peptides were degraded by exposing to hydrogen peroxide containing copper. Dynamic light scattering measurement revealed that these two peptides formulated submicron-sized nanoparticles in aqueous solution and the nanoparticles showed high colloidal stability. In addition, the nanoparticles were gradually degraded by exposing to ROS. Finally, we demonstrated their dye loading capacity and controlled release capacity as ROS-triggered degradable nanocarriers using fluorescent dye as a model molecule. The fluorescent dye was efficiently trapped by these nanoparticles by providing hydrophobic nanodomain in each nanoparticle. Furthermore, the encapsulated dyes were released by responding to ROS and the time scale in releasing was corresponding to the time in degrading. For these results, oligoproline-containing peptides can be available not only for ROS-triggered degradable nanocarrier.



COLL 579

Quantifying hyaluronic acid and metal-organic framework for biomedical applications using gas-phase electrophoresis

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We report a facile, high-resolution aerosol-based electrophoretic approach to quantitatively study (1) hyaluronic acid (HA) and study its crosslinking reaction, and (2) metal-organic framework (MOF) as molecular drug carrier. Electrospray-differential

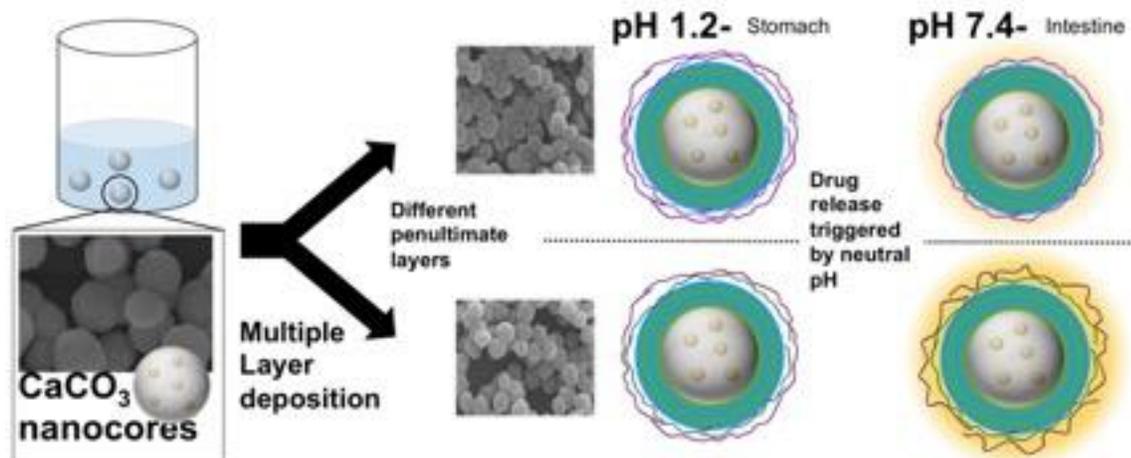
mobility analysis (ES-DMA) was employed, where mobility size distributions, number concentrations, molecular mass distributions and polydispersity index of HA and MOF were obtained successfully by ES-DMA. Orthogonally, size exclusion chromatography (SEC) was employed for data comparison on a semi-quantitative basis. Using ES-DMA, the 1,4-butanediol diglycidyl ether (BDDE)-induced crosslinking of HA was also able to be successfully characterized through a time-dependent study. Electro-spray-differential mobility analysis coupled to aerosol particle mass analyzer (ES-DMA/APM) was employed to successfully develop metal-organic framework (MOF)-based targeted drug delivery platform. A direct quantification of the loading of isoprofen (the representative molecular drug) on individual MOF particles achieved using the ES-DMA/APM. The interaction with phosphate ions in the medium and the corresponding drug release was successfully identified through a time-resolved study. The corresponding methodology provides a proof of concept for the study of formulation strategies to drug delivery systems.

COLL 580

Controlled synthesis of calcium carbonate nanoparticles and stimuli-responsive multilayered nanocapsules for oral drug delivery

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Stimuli-responsive layer-by-layer (LbL) capsules are appealing drug carriers for oral drug delivery owing to their abilities to utilize environmental differences to trigger changes in particles properties. LbL capsules typically have micrometer diameter ranging between 1-5 μm . The opportunity to use LbL for the modification of particles in the nanorange may provide enhanced benefits and properties for drug delivery. In this work, we used multiple polyelectrolytes to prepare novel stimuli-responsive multi-layered nanocapsules with submicron diameters. A systematic study was conducted to investigate the influence of various experimental parameters on the formation of calcium carbonate nanoparticles (CaCO_3) as nanocores. The resultant nanocores were then used for the assembly of LbL nanocapsules and the variables that influenced the diameter of capsules were investigated. Finally, novel stimuli-responsive multi-layered nanocapsules made of four polyelectrolytes including Eudragit L100, chitosan, sodium alginate, and poly-L-arginine were prepared and characterized. The stimuli-responsive multi-layered nanocapsules loaded with a model drug, curcumin were assessed for drug release under pH conditions that mimic gastrointestinal tract. These data demonstrate the potential for nanocapsules to be designed to protect the drug in the stomach and release it lower in the gastrointestinal tract.



Abstract figure: calcium carbonate nanoparticles loaded with curcumin were modified by layer-by-layer to form stimuli responsive nanocapsules. *In-vitro* drug release at different pH conditions mimicking gastrointestinal transit showed that the design of the structures of the layers in the nanocapsules can be used to protect the drug in the stomach and release it in the intestine.

COLL 581

Hard nanoparticles as tools for understanding controlled drug delivery

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The use of nanoparticle (NP) materials for the improvement of drug delivery and drug efficacy continues to be an active area of research. Critical to success in this area is our furthered understanding of the rational design of NP-drug formulations and how that relates to cellular drug targeting, uptake, release, and metabolism. This talk will focus on these themes in the context of various 'hard' NP carriers such as semiconductor quantum dots and gold NPs. The goal of this talk is to provide several recent examples from our laboratory that highlight how NP-drug design critically affects these aforementioned parameters.

COLL 582

Improving the therapeutic efficacy of nucleic acids and small molecule drugs using stimuli-responsive nanostructures

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Many small molecule drugs are hydrophobic in nature, thereby enhancing their passage through lipid bilayers for gaining access to cells. In contrast, nucleic acids carry a negative charge and have considerable mass, making their entry into cells significantly more challenging. Attempts to deliver both small molecule drugs and nucleic acids in a single construct therefore poses several practical hurdles. Here we present chemical strategies that enable the co-delivery of such disparate molecules by modifications to our recently developed nucleic acid nanocapsule (NAN) delivery platform. Using NANs, we demonstrate the delivery of a hydrophobic gold(III) metallodrug alongside an siRNA against an apoptosis regulating gene, showing that their combined delivery enhances the overall cytotoxic effects of the metallodrug in cancer cells at lower concentrations of the drug (from micromolar to nanomolar). Additionally, we show the advantages that arise when such formulations are built from chemistries that can accommodate stimuli responsive elements, including temperature and pH responsive chemistries. The NANs enable a route to exogenous nucleic acid delivery and improved solubility of small molecule drugs that are normally prone to aggregation in aqueous conditions. We show that they achieve enhanced therapeutic efficacy in the form of improved cytotoxicity at lower drug doses and more potent gene regulation at lower concentrations of therapeutic nucleic acids delivered. Lastly, we demonstrate the versatility of the platform for 1) functionalization with cell surface targeting agents including RNA aptamers, showing that they can bias the localization of these nanostructures, and 2) offer insights into the mechanism by which these materials are able to enhance cytosolic access for their nucleic acid cargo.

COLL 583

Formulation of carbonic anhydrase IX: Targeted drug delivery systems against hypoxic tumors

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We will present the most recent advances from our team towards formulation of several drug delivery nanosystems aimed at the carbonic anhydrase IX isozyme that is over-expressed in hypoxic tumors. Special emphasis will be placed on the design and optimization of the targeting moieties, linkers, carrier nanoplatfoms and we will present how different formulations strategies were adapted to the particular nanocarrier selected for delivery.

COLL 584

Surfactant-induced reorganization of the hydrophobic phase at nanoemulsion interfaces

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The stabilization of nanoemulsions, emulsions with diameters ~100's nm, is most often achieved by surfactant adsorption to the droplet surface. The idealized picture of surfactants at the nanoemulsion surface is one where the surfactant alkyl chains interdigitate with the alkyl chains of the interfacial hydrophobic molecules. Whereas initial surface spectroscopic measurements of nanoemulsions observed an invariance of the hydrophobic phase structure to the presence of some surfactants at the droplet surface, our recent studies have shown those same surfactants perturb the interfacial structure of the hydrophobic phase. In this talk the surface assembly of several surfactants at nanoemulsion surfaces will be discussed alongside the structural perturbations they exert on the hydrophobic phase. This work takes advantage of the surface specificity of vibrational sum-frequency scattering spectroscopy to isolate the nanoemulsion interface and provide molecularly specific details of surfactant adsorption.

COLL 585

Oil-in-oil Pickering emulsions stabilized solely by diblock copolymer nanoparticles

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Reversible addition-fragmentation chain transfer (RAFT) dispersion polymerization was used to prepare spherical diblock copolymer nanoparticles comprising a silicone methacrylate-based stabilizer block and a poly(benzyl methacrylate) (PBzMA) core-forming block directly in dimethicone 5 (DM5), which is a linear polydimethylsiloxane with a viscosity of 5 cS. The resulting nanoparticles had diameters ranging from 30 nm to 123 nm and were evaluated as Pickering emulsifiers for ten non-polar oils, producing three examples of relatively stable oil-in-DM5 Pickering emulsions. When utilizing the larger nanoparticles, optical microscopy studies indicate that such Pickering emulsions were stable to coalescence for at least two months. Moreover, the mean emulsion droplet diameter can be adjusted by varying either the emulsifier concentration or the oil volume fraction. In an attempt to produce a generic Pickering emulsifier that could stabilise the broadest possible range of oil-in-oil emulsions, varying amounts of lauryl methacrylate (LMA) were statistically copolymerised with BzMA to modify the core-forming block. The former monomer was selected to enhance the wettability of the resulting nanoparticles towards the droplet phase and hence ensure stronger adsorption at the oil/silicone interface. Optical microscopy studies indicated that, when the nanoparticle cores comprise relatively small amounts (5 – 12.5 mol %) of LMA, the resulting Pickering emulsions are stable up to at least six months. In addition, a significantly broader range of non-polar oils that can be utilized. However, when the

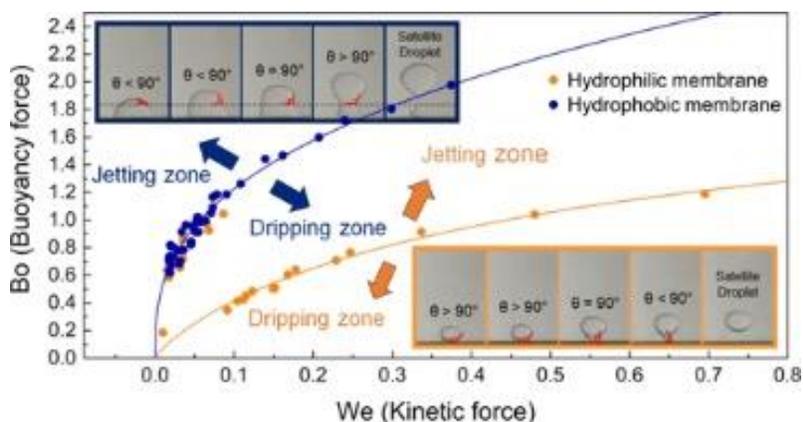
nanoparticles comprise greater than 18 mol % LMA within their cores, the resulting emulsions become highly aggregated. This suggests that there is an optimum LMA content that confers maximum Pickering emulsifier performance.

COLL 586

Understanding uniform, fast, and scalable buoyancy-driven macro-sized drop generations

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Generating uniform drops with fast production rate and tunable volume in a high-throughput way is important in various academic and industrial disciplines. In this study, we propose a strategy to produce milliscale drop in a size-tunable way and model its formation processes. The size of generated drops is uniform (<1% of the standard deviation) and tunable by controlling the flow rate, the pore diameter in membrane, and the surface hydrophobicity of membranes in the dripping regime. Also, their production rates range from ca. 0.1–2.1 Hz. The drop formation is successfully investigated by our five-force balance model. On hydrophobic membranes, the range of the dripping regime for uniform drops is wider (from ca. 5.7 to 10.4 mm) than that on hydrophilic membranes (from ca. 3.8 to 7.0 mm). Also, in the dripping regime in hydrophilic membranes, the production rates of the drop are faster than those of the hydrophobic membrane.



COLL 587

Phase stability and miscibility in alcohol microemulsions: Do reverse micelles form in ethanol/AOT/*n*-heptane systems?

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We describe the effects of ethanol on the phase behavior of sodium bis(2-ethylhexyl) sulfosuccinate (AOT), and in particular its ability to form reverse micelles, in *n*-heptane. Using dynamic light scattering and molecular dynamics simulations, we investigate the aggregation behavior of AOT across a wide range of ethanol/AOT/*n*-heptane compositions. We conclude that reverse micelles do not form at any of the investigated concentrations, but find other surfactant aggregate morphologies and behaviors unique to this system which vary significantly with changes in ethanol concentration. When the concentration of ethanol is 20 wt.% or below, the system is inhomogeneous with varying sizes of AOT, ethanol, and AOT + ethanol aggregates present. At the lowest ethanol concentrations in this behavior regime, ethanol exhibits co-surfactant behavior almost exclusively, binding at the surface of AOT aggregates. With increased ethanol, the number of independent ethanol clusters increases, and eventually extended interpenetrating networks of AOT and ethanol form. With ethanol concentrations of 20–35 wt.%, increased numbers of ethanol clusters are observed which leads to a more distinct separation of AOT aggregates. These aggregates increase linearly with increased AOT concentration when the system heptane concentration is below 40 wt.%. Most significantly, when the ethanol concentration is raised above 35 wt.%, the solvent environment polarity is high enough such that AOT Na⁺ counterions dissociate from the headgroups and are dissolved in the ethanol. As a result, ethanol hydrogen bonding increases and unique spherical structures of ethanol surrounding AOT aggregates form. These spherical structures continue to increase in size linearly with increased AOT concentration. We use these results to construct a preliminary phase diagram for the ethanol/AOT/*n*-heptane system.

COLL 588

Two's company, three's a crowd: How ions tag along for the ride with SDS and PEI on a nanoemulsion surface

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Nanoemulsions are tiny oil droplets dispersed in water. As tiny as they are, they have captured the interest of scientists and industry alike due to their application in nanocarrier technology. Nanocarriers are made up of nanoemulsions coated by polymer/surfactant (PS) systems to provide stability and functionality to the droplet. The surface structure of the PS system can influence specific interfacial behavior and properties important for the controlled and targeted release of the encapsulated cargo, but determining interfacial structural information has been limited due to the experimental difficulty of selectively probing the curved surface. We have overcome this hurdle by employing vibrational sum frequency scattering spectroscopy to better

understand PS interfacial behavior at the droplet surface. This study seeks to determine how pH governs the interfacial behavior and structure of polyethylenimine (PEI) and sodium dodecyl sulfate (SDS) mixtures to elucidate how nanocarrier surfaces respond to different physiological conditions at the molecular level. Interestingly, there is a stark contrast in PEI/SDS adsorption behavior and ordering between acidic and basic conditions, which raises questions about how the interplay between electrostatic and hydrophobic forces dictate the way PEI and SDS interacts with these tiny oil droplets.

COLL 589

Effects of low-temperature hydrothermal treatment on the properties and removal of fine solids from nonaqueous extraction (NAE) bitumen

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Nonaqueous extraction (NAE) is a potential process to replace water-extraction process and eliminate the problems associated with it. However, the high solids content of NAE product bitumen remains a major challenge. In the present work, a process of low-temperature thermal treatment coupled with water addition, or hydrothermal treatment, was investigated to remove solids from treated NAE bitumen mixture. Laboratory hydrothermal treatment was conducted at 200-300°C for a reaction time of 30 min at 200 psi initial pressure. The filterability of fine solids was quantitatively characterized by room-temperature filtration of toluene-diluted treated bitumen mixture. Thermal treatment alone at 200°C and 250°C yielded products that were unfilterable, but treatment at 300°C yielded a filterable product. However, thermal treatment coupled with water addition facilitated fines removal by filtration by yielding a filterable product at 200°C and 250°C and decreasing the filtration time at 300°C. The effects of the sub-critical water on the filtration were studied.

COLL 590

How does end-group charge on the steric stabilizer block affect the formation and stability of Pickering nanoemulsions prepared using diblock copolymer nanoparticles?

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Reversible addition-fragmentation chain transfer (RAFT) solution polymerization is used to prepare well-defined poly(glycerol monomethacrylate) (PGMA) bearing either carboxylic acid, tertiary amine or neutral end-groups. These PGMA precursors were

then chain-extended *via* RAFT aqueous emulsion polymerization of 2,2,2-trifluoroethyl methacrylate (TFEMA) to form PGMA₄₈-PTFEMA₅₀ spherical nanoparticles of approximately 20 nm, as confirmed by TEM studies. Zeta potential studies confirmed that the amine-functional nanoparticles became cationic (~ +25 mV) at low pH owing to end-group protonation. In contrast, carboxylic acid-functional nanoparticles became anionic (~ -25 mV) at pH 10 owing to end-group ionization. Finally, the nanoparticles bearing neutral end-groups exhibited almost zero zeta potential (0 to -10 mV) over a range of solution pH. High shear homogenization of such nanoparticles in the presence of *n*-dodecane led to the formation of oil-in-water Pickering *macroemulsions* of 30 - 50 μm diameter. High-pressure microfluidization was then used to prepare the corresponding three Pickering *nanoemulsions*. Each Pickering nanoemulsion was characterized by TEM studies and analytical centrifugation. The nanoparticle adsorption efficiency at the oil-water interface was assessed by gel permeation chromatography (GPC) for all three nanoparticles at both pH 3 and 7 using a UV detector (set to λ = 305 nm, which corresponds to the absorption maximum of the RAFT end-groups). Nanoparticles with charged end-groups exhibited relatively low adsorption efficiency, whereas neutral nanoparticles had efficiencies of around 90%. Analytical centrifugation was used to evaluate the colloidal stability of the aged Pickering nanoemulsions. Pickering nanoemulsions stabilized with nanoparticles bearing charged end-groups proved to be significantly less stable than those prepared using neutral end-groups.

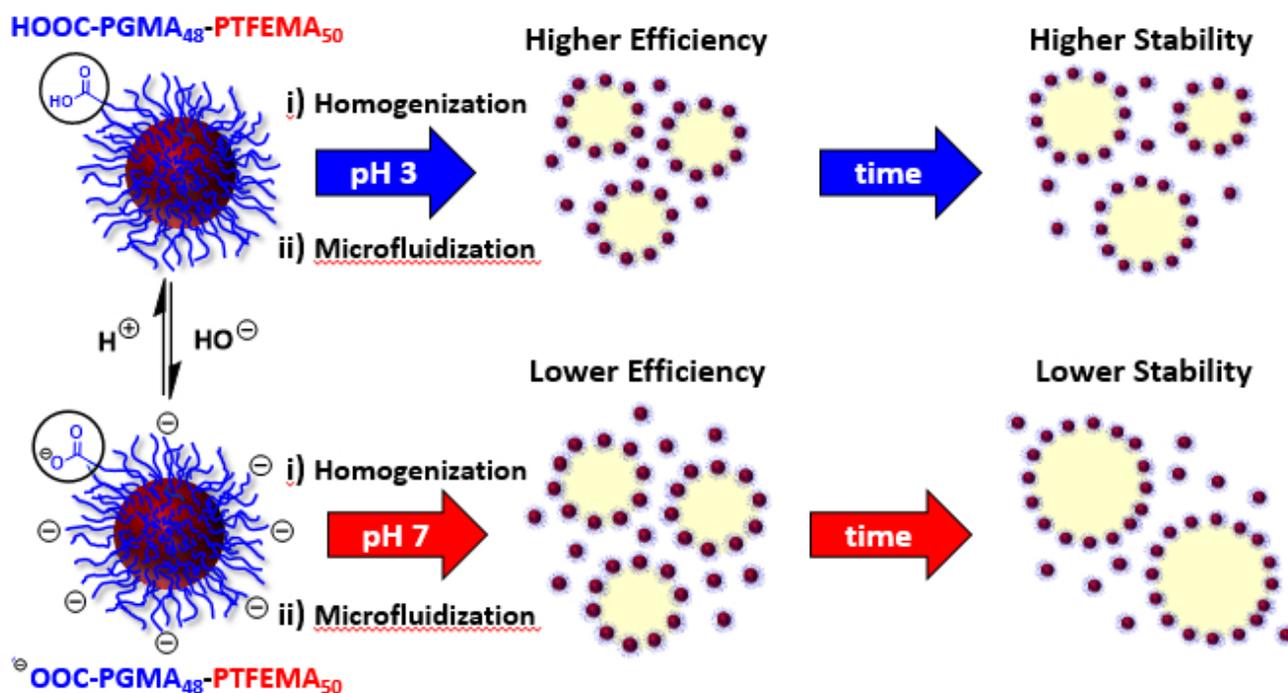


Figure 1. Schematic representation of Pickering nanoemulsion formation and stability when prepared using diblock copolymer nanoparticles with either neutral (pH 3) or anionic (pH 7) end-groups.

COLL 591

Simple creams, complex structures

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Objectives

Topical creams used to treat various skin conditions are typically semi-solid emulsions in which oil droplets are dispersed throughout a continuous aqueous phase containing an 'excess' of emulsifier – a mixture of surfactant and co-surfactant(s), which form lamellar structures and give “body” to the cream. Historically, structural details of creams have been inferred largely from *indirect* observations and the exact composition and structure of the lamellar phases present remain poorly characterized. Here we report studies conducted to secure a detailed understanding of the molecular structure of a simple cream and how this is influenced by additives like preservatives.

Materials and Methods

Aqueous creams containing cetyl and stearyl alcohol (co-surfactants), sodium dodecyl sulfate (surfactant, SDS), water and liquid paraffin were prepared as specified in the British Pharmacopoeia. The concentration of emulsifier was varied as either 4% or 10% (w/w), with the latter prepared with and without preservative, 1,5-pentanediol. The macroscopic properties of the creams were studied using rheology and microscopy and their molecular architecture determined via small-angle neutron and X-ray scattering (SANS and SAXS) and wide-angle X-ray scattering (WAXS) experiments.

Results

Evidence of a lamellar structure was seen in the 10% but not the 4% emulsifier creams – both directly as Bragg-peaks in SANS and SAXS profiles and indirectly as Maltese crosses in polarised-light micrographs. For the 10% emulsifier creams with and without preservative, the lamellar *d*-spacings varied as ~240 vs ~270 Å, with bilayer thicknesses of ~48 Å in both cases. The use of individually perdeuterated cream components showed that the co-surfactants along with the preservative co-locate in the lamellar bilayers. The surfactant (SDS) however, appears to arrange (primarily) as a monolayer surrounding the oil droplets and also seems to combine with one or both of the co-surfactants to form mixed micelles. WAXS measurements indicated hexagonal close packing of the emulsifier alkyl chains, with the paraffin forming a liquid-crystalline phase. Rheological measurements showed that both the 4% and 10% emulsifier creams are *shear-thinning* with consistency indices of 58 and 113 Pa.s, respectively.

Conclusions

Details of the molecular architecture of a simple cream have been deduced, revealing the packing arrangements and loci of the component surfactant, co-surfactants, and preservative.

COLL 592

Desiccant-based food drying for reduced carbon generation and improved food security

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Cereal grains (rice, maize, wheat) provide 70% of the global food supply. The ability of these grains, and many other food commodities, to be dried to low water activities enhances their storage life and preserves their nutritional content. However, the common practice of using heated air, generally based on burning natural gas, to dry commodities accounts for a significant fraction of the carbon footprint of the agricultural and the food system. In addition, in many tropical countries, such drying systems are largely unavailable, and high ambient humidities result in high moisture contents of stored commodities. This enables growth of molds and insects, causing losses and the accumulation of mycotoxins such as fumonisin and aflatoxin, which present a dietary health threat for more than 4 billion people around the world. A solution to these issues is to implement the Dry Chain (www.drychain.org), which is simply to dry commodities to safe levels (<65% relative humidity to prevent fungal growth) and then store in moisture-proof packaging. Use of modern desiccants such as Drying Beads TM (www.dryingbeads.org) could shift drying systems to use of renewable electrical power, reducing carbon generation, and provide efficient drying methods for humid climates in which heated-air drying performs poorly.

COLL 593

NMR characterization of dehydration of zeolites by three heating methods

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Dehydration of fully hydrated zeolites through heating with microwaves, electric furnace and hot air is investigated. The zeolites are commercially available and the three drying apparatuses are either commercially available or built in the lab. The amounts of energy consumed in the three apparatuses to partially dehydrate the samples are compared, and at each dehydration stage the samples are characterized using solid-state NMR spectroscopy. The results are presented and discussed.

COLL 594

Discerning the fundamental interactions of water with porous catalysts by *in situ* MAS NMR

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The ubiquity of water in catalytic systems introduces additional complexity in understanding the interactions between the substrate and active center. The presence of water not only often modifies the observed reactivity, but poses challenges in understanding the mechanistic details of the chemical transformation since water molecules may significantly alter the method by which substrates interact with catalytic surfaces. *In situ* magic angle spinning nuclear magnetic resonance (NMR) offers a non-destructive means to observe the chemical environments of constituent species at the molecular level under conditions relevant to catalysis. Employing our recently-developed gas-tight NMR rotors enables the study of such systems under relatively harsh conditions (up to ~100 bar and ~250°C). With this capability, we probe the interactions of water with solid acid catalysts (e.g., silica-supported Al-polyoxometalate and zeolite H-ZSM5) to identify the consequences of water on the active sites and other system components. Density functional theory-based theoretical calculations are implemented to aide in the interpretation of the spectroscopic observations. The recent results presented will offer a unique perspective on understanding the fundamental interactions of water with porous catalysts.

COLL 595

Drop manipulation on superhydrophobic surface with dielectrowetting

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Controlling the interactions of drops on surfaces is essential to not only the basic understanding of various processes but also a variety of viable applications. Recently, the superhydrophobic surface has attracted much attention from researchers, due to its advantages on the contamination-free property and low adhesion between drop and surface during manipulation. However, the properties of such superhydrophobic surface are determined after fabrication, making the surface inapplicable to situations when on-demand behaviors of the drop are required, which is especially important in the applications of digital microfluidics. In this study, we utilized liquid-dielectrophoresis force to manipulate the drop on a superhydrophobic surface. Such control is found to be fast-response, bio-friendly, convenient, repeatable, and energy efficient. Adhesion force and rebounding for both static and dynamic interactions between drop and surface under electric field have been explored. To demonstrate the possible applications of the dielectrowetting on the superhydrophobic surface, we demonstrate a proof-of-concept experiment of drop sorting. The electric-field dependent drop manipulation enables

potential applications for digital microfluidic, micro-reactor and advanced lap-on-a-drop platform.

COLL 596

Electrified membranes for water treatment: Toward new experimental and theoretical tools

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Because of the high operational costs required to perform water purification, radical new treatment approaches are being considered beyond traditional pressure-driven membrane separations. The development of electrified membranes is one promising approach toward improving performance, as applied voltages can be used to mitigate biofouling while simultaneously enhancing the removal of ions and other charged contaminants. Many processes have been explored to leverage applied voltages for separations, such as in: (1) electrofiltration, where conductive membrane surfaces are charged to mitigate the adhesion of contaminants, (2) capacitive deionization, where high surface area electrodes electrophoretically draw contaminants from water, or (3) ion concentration polarization / shock deionization, where faradaic currents generate a depletion of ions near an ion exclusion membrane, creating a pure water stream.

Despite the rapidly growing potential for these and other technologies that rely upon electrified membranes, there is a significant need for an improved understanding of the effect of ion and water electrostatics within these porous materials while under the effects of an electric field. In particular, the origin of exotic transport behaviors of ions within micro- and nanoporous channels, such as high streaming mobilities, overlimiting currents, and the competition between surface conduction and electro-osmotic flow, is still relatively unexplored. In this presentation, we discuss the many factors that affect the use of electric fields to enhance separations, focusing on the fundamental transport of ionic species and our work to leverage those effects for improved separations. First, we describe our own work to make existing membrane materials conductive using organic and inorganic coatings combined with laser pyrolysis. The resulting laser-induced graphene-based membranes show excellent conductivity, an important characteristic for reducing electrical resistance losses, and can be scalably and cost-competitively produced when compared to current membrane technologies. We also describe our work to further enhance the separation of charged contaminants by leveraging surface coatings to create trans-membrane electric fields. Together, these works demonstrate how electrified porous materials can be used to enhance separation processes and highlight the need for improved fundamental understanding of the transport behaviors involved in their operation.

COLL 597

Water in the deterioration of porous building materials

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Water is a key factor in the deterioration of porous building materials as it may have synergistic interactions with other factors such as the presence of air pollution, soluble salts biocolonization, and freeze-thaw cycling. The nature of the porous building material(s) will define their interaction with water. Points to consider include: 1) How does water enter the porous material; 2) What happens once it enters the masonry; 3) Which other factors will contribute to the deterioration. In general, the most important source of water is rising damp, ground water rising through capillary action, and this water will include some soluble salts. The distribution of pore sizes in the building material will affect the transport mechanism(s) within the material. The rate of wetting, time-of-wetness, and drying of the material, are fundamental for the interactions with other co-factors. The balance of cohesive forces between water molecules, and adhesive forces between the water molecules and the mineral surfaces, are the source of the water-porous inorganic material interaction.

COLL 598

Charge and structure quantification of peptides at aqueous interfaces

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We integrate state-of-the-art non-linear spectroscopic and mass sensing techniques with atomistic simulations to quantify the charge state and structure of peptides at aqueous interfaces. We reveal explicitly how the charge state and structure of peptides change upon binding to charged surfaces, such as lipid membranes, as well as natural and engineered oxides, leading to new insights into the physical and chemical factors that dictate binding affinity and selectivity at charged aqueous interfaces. The results provide guidance to the design of novel biomaterials with desired surface activity and specificity. Special attention is given to the role that interfacial water has in regulating the super- or sub-charging of peptides at interfaces.

COLL 599

Dynamics of cellular membranes and their interactions with nanomaterials

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The expanding production of nanoparticles (NPs) has led to serious concerns regarding their impact on human health and the environment in general. Indeed, nanoparticles are easily dispersed in air and inhaled because of their nanoscale size. In this work, we present a new theoretical model to predict the average permeation time of nanoparticles in biological membranes, using only four molecular and membrane properties. By separating the contributions that depend only on NPs' characteristics (size, shape), membrane properties (density distribution of the membrane) and mixed factors (solubility), the model allows the combination of both experimental and computational data in the rapid estimation of large numbers of nanoparticles/membranes combinations. We validated our model comparing the results with data obtained from molecular dynamics simulations of the permeation of three different carbonaceous NPs and with experimental measures of NP leakage from lipid vesicles.

COLL 600

Force spectroscopy measurement of the adhesion of galactose to the human pathogen *Leishmania mexicana*

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Force spectroscopy, a variant of atomic force microscopy (AFM), was used to characterize the adhesive properties of the glycocalyx of the single cell (protozoan) parasite, *Leishmania*, in order to understand the structural features of attachment in its sand fly vector. In the case of *Leishmania mexicana* and *Leishmania major*, parasitic protozoa responsible for cutaneous leishmaniasis, an important adhesin is lipophosphoglycan (LPG), an outer membrane glycoprotein containing carbohydrates that adhere to the sand fly midgut epithelium. Adhesion of *Leishmania* promastigotes, the flagellated insect-borne forms, to the sand fly midgut is crucial for colonization of the vector and transmission, since parasite–midgut attachment must be of sufficient strength to resist the peristaltic action of the sand fly gut during defecation of digested bloodmeal. Here, the interaction of an analog of *N*-acetyl-D-galactosamine, a carbohydrate present on the surface of permissive sand fly vectors, with *L. mexicana* LPG was investigated. AFM tips were first functionalized with grafted layers (brushes) of poly(methacrylic acid), grown using atom-transfer radical polymerization. Immersion in aqueous solutions of *N*-(3-dimethylaminopropyl)-*N*-ethylcarbodiimide hydrochloride and *N*-hydroxysuccinimide readied the brush for functionalization with 2-aminoethyl- β -D-galactopyranoside, producing AFM tips coated with a poly[*N*-2-(β -D-

galactosyloxy)ethyl methacrylamide] brush. These carbohydrate-functionalized AFM tips revealed that nectomonad promastigotes had adhesive molecules distributed across their surface, but that these were largely absent from the infective, metacyclic stage of the parasite, and from LPG-deficient parasites (mutants). Consequently adhesion to infective parasites was substantially less than those to the nectomonad promastigotes. Furthermore, up to half of the wild-type promastigotes analyzed displayed a line of high adhesive force along the cell body, indicating a highly adhesive subpopulation. The selectivity of the *N*-acetyl-D-galactosamine analog to the parasites was compared with an antibody (anti-LPG) adsorbed to an AFM tip, which did not effectively differentiate between the different lifecycle stages of the parasite. Again, in LPG-deficient mutants, antibody adhesion was not observed. The molecular specificity afforded by coating AFM tips with polymer brushes enables key molecular roles to be identified, and the technique can be extended to other biological problems.

COLL 601

Synthesis, characterization, and evaluation of a zwitterionic microgel for therapeutic protein delivery

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Advancement of therapeutic protein therapy has been hindered by the poor stability and short half-life of proteins *in vivo*. There is emerging evidence that biocompatible zwitterionic materials can prevent non-specific interactions within proteins systems. Here, a form of zwitterionic hydrogel is synthesized from poly sulfo-betaine methyl acrylate (SBMA) using an inverse emulsion, radical polymerization reaction. The zwitterionic microgel reaction was characterized using ¹H NMR. Microgel particles were loaded with a model protein, serum albumin, and the protein loading efficiency was studied. Furthermore, the release rates of the protein from the synthesized microgels were studied at different monomer to crosslinker ratios. The microgel particles were analyzed for their size, regenerative characteristics, protein stability, and delivery properties. Furthermore, *in vitro* studies were carried out to evaluate toxicity and immunogenicity of the microgels.

COLL 602

Photodegradable hydrogels for retrieval of bacteria cells from screening interfaces

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Retrieval of cells from interfaces after microscopic observation for follow-up “omics” measurements is a critical but often overlooked step that limits many cell-based assays. In this work, photodegradable hydrogels are developed to non-destructively recover cells from screening interfaces in order to couple an observed phenotype with genomic information. Polyethylene glycol (PEG)-based hydrogels are formed using thiol-acrylate Michael-type addition reactions to first immobilize individual bacteria cells from a heterogenous population for culture and/or microscopic observation. PEG molecules are modified with *o*-nitrobenzyl chromophores, allowing for controlled degradation of hydrogel areas with high spatial precision using a patterned illumination tool and a 365 nm light source. Patterned light exposure triggers the efficient release of targeted bacteria cells into solution for retrieval, enrichment, and sequencing. Using this methodology, photodegradable hydrogels have been developed as a light-responsive membrane for cell culture and retrieval from a microwell platform designed to screen and discover microbial interactions in root and soil microbiomes. This approach can also be used to recover and sequence strains showing rare or unique function during high-throughput screening of transposon mutant libraries. We aim to further develop this method towards precision extraction at the single cell level, and expect that the approach will be useful in a variety of high-throughput screening applications that aim to connect cellular function with genomic, proteomic, or metabolomic measurements.

COLL 603

High throughput creation of water-in-water droplets in a microfluidic flow-focusing device

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The generation of water-in-water droplets have recently received great attention because of their highly biocompatible nature, but the controllable formation of such droplets is still challenging based on conventional flow-focusing microfluidic approaches. Several alternative microfluidic techniques have been introduced with either active perturbation or passive formation. The first approach requires external components to perturb the flow, such as a piezoelectric disc to oscillate channel walls, a vibration table to oscillate the flow, or a peristaltic pressure pump to pulsate the fluid pressure. These approaches enable high throughput formation of water-in-water droplets but necessitate additional perturbation modules. The second approach simplifies the formation system by eliminating the external component requirement but suffers from droplet size-selectivity and throughput.

Here, we introduce a simple modification to the passive system of water-in-water

droplets. The modification involves the integration of a microneedle into the conventional flow-focusing geometry. The integrated microneedle induces 3D flow focusing of the dispersed phase fluid, which significantly improves the formation of water-in-water droplets. With the microneedle-assisted microfluidic scheme, we are able to generate water-in-water droplets in a high throughput manner with great control over their size, ranging from 5 to 65 μm .

COLL 604

Thermophoretic manipulation of the mechanical properties of biomaterials in microfluidics

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The optimization of cell-substrate and cell-cell interactions is of great importance for tissue engineering and biomedical applications such as tissue repair and wound healing. These could be greatly improved using extracellular matrices that accurately mimic the in vivo tissue microenvironment and modulate cell behavior. Biomaterials exhibiting a gradient of mechanical properties can regulate cell activity which is dependent upon the elasticity of the substrate. However, the possibility to fabricate these materials is still limited especially with a control over the mechanical properties at the micron scale. By carefully imposing and controlling temperature gradients across a microfluidic channel and exploiting the phenomenon of thermophoresis, we demonstrated the generation of gradients with tuneable properties in colloidal systems. Particularly, a microfluidic device consisted of the main microchannel and two side channels acting as hot and cold thermal sources, are used to apply the temperature gradient and fabricate biocompatible gellan gum hydrogels exhibiting stiffness gradients. Moreover, we effectively control the stiffness gradient of the biomaterials by regulating the temperature difference across the device and altering the concentration of the gellan gum. Using Atomic Force Microscopy we characterized the biomaterials by evaluating locally Young's modulus across the 600 μm width of the hydrogels, obtaining values ranging from 20 to 100 kPa. Furthermore, we monitored cell behavior over time by seeding MC3T3 osteoblasts on the surface of the biomaterial. Cell migration and mineralization are observed on the surface of the material at different stiffness areas and time points, using live/dead assays and x-ray fluorescence technique. The results obtained gave us valuable information for the design and improvement of future 3D scaffolds.

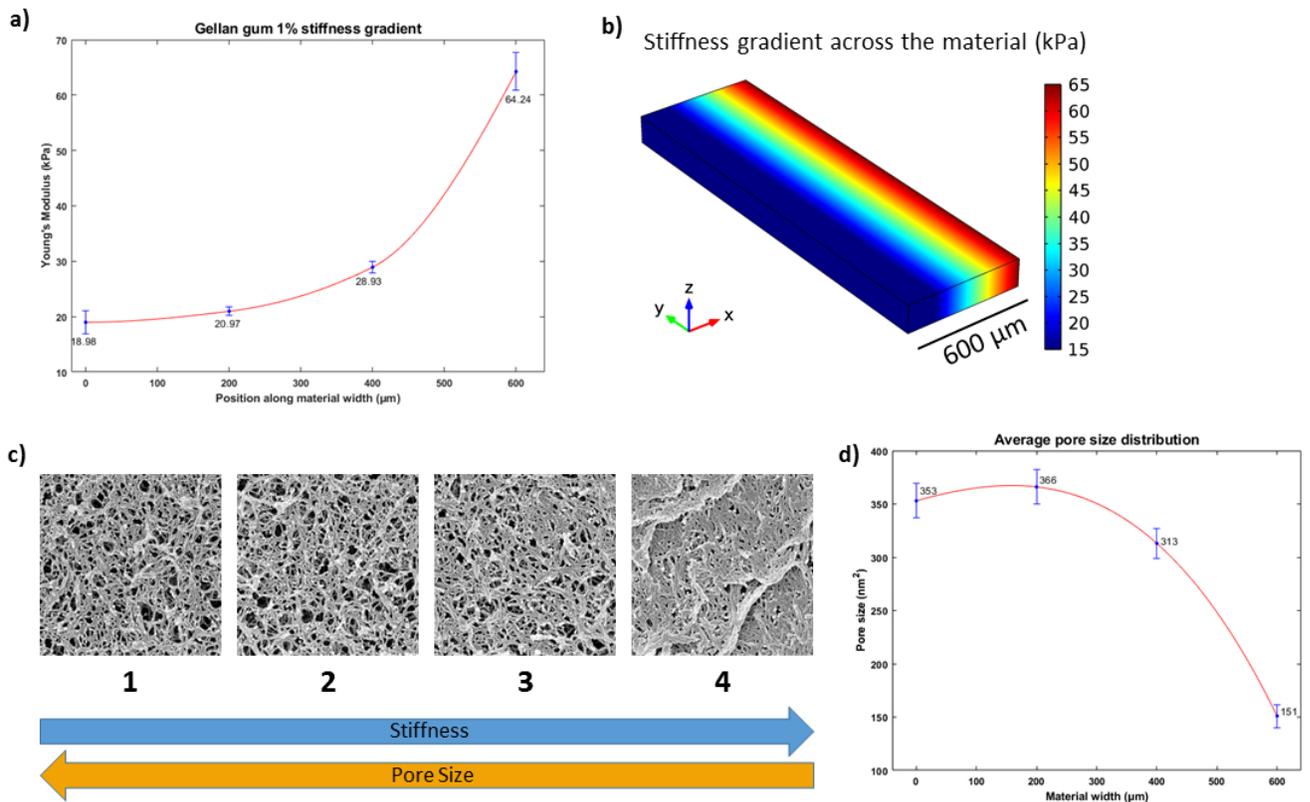


Figure 1: a) Young's Modulus across the material width, b) Schematic of the stiffness gradient, c) SEM images of the hydrogel surface, d) Pore size distribution across the material width

COLL 605

Tuning surface charge as a general approach to improving immobilized enzyme function on mixed lipid bilayers

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The design of synthetic surfaces that maintain the structure and function of immobilized enzymes is of fundamental importance in many biotechnological applications. As quintessential biomimetic surfaces, lipid bilayers (LBs) have been proposed as useful supports for protein immobilization. However, the design of such supports has, to date, remained elusive. Here, we present a rational approach to significantly improve the conformational stability and activity of immobilized enzymes by tuning the LB charge with respect to that of the enzyme. LB charge is varied by mixing different ratios of zwitterionic 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC) lipid with either 1,2-

dioleoyl-sn-glycero-3-phospho-(1'-rac-glycerol) (DOPG), which is negatively charged, or with 1,2-dioleoyl-sn-glycero-3-ethylphosphocholine (DOEPC), which is positively charged, resulting in LBs with zeta potential values ranging from -85 mV to 30 mV. Using dynamic single-molecule tracking in combination with Förster resonance energy transfer, we find that the stability of four enzymes (nitroreductase, lipase, organophosphorus hydrolase, and lysozyme), which have different net charge, is significantly enhanced on LBs that match the enzymes' charge. In fact, extraordinary folded fractions greater than 0.95 are observed for all enzymes on LBs with optimized composition. Correspondingly, the activity of enzymes also shows significant enhancement on such LBs, with as much as a three-fold increase over enzymes immobilized to 100% DOPC LBs—the most widely used LB composition for protein immobilization. Measurements of folding and unfolding rates suggest that optimum bilayers facilitate the rapid re-folding of unfolded enzymes by a chaperone-like mechanism. Interestingly, by correlating the enzymes membrane diffusivity, LB composition, and conformational state, we find that the composition of the membrane influences the interactions with enzymes differentially, providing a possible rationale for the stabilization effect. Combined, these results suggest that by tuning the extent of interactions with the surfaces, an optimum lipid composition that enhances enzyme stability and activity can be obtained.

COLL 606

Molecular interactions at the cellulose-lignin interface explored via molecular simulation

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Lignin and cellulose are found ubiquitously in plant cell walls, making them two of the most abundant biopolymers on Earth. In spite of their ubiquity, comparatively little is known quantitatively about their interactions within native biomass, and by extension how their interaction may play a role in biomaterials. The possible binding faces for lignin on crystalline cellulose I- β and the heterogeneous chemistries found in native lignin typically preclude the isolation of specific interactions for quantitative comparison in the laboratory. In this study, we use molecular simulation to examine individual combinations of binding face and lignin chemistry to quantify lignin-cellulose interactions, including contributions from both specific hydrogen bonds and nonspecific van der Waals interactions. For all lignin chemistries simulated, the hydrophobic 200 face is the preferred for cellulose interactions. For hydrophilic crystalline faces, lignin is found to bind most effectively to the 110 face. The affinity between lignin and cellulose increases as additional lignin methoxy groups are added. These groups increase the lignin-cellulose contact area, increasing the binding affinity. These trends are extended to larger lignin polymers, where the relationships between lignin polymer size and binding affinity are quantified through biased simulation. In this case, the binding surface area between the lignin polymer and the cellulose surface dictates the interaction strength.

COLL 607

Preparation and properties of fluoroalkyl end-capped vinyltrimethoxysilane oligomer/magnetite nanocomposites

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Much attention has been devoted to well dispersed magnetic colloidal particles owing to their wide potential applications in the fields of ferrofluids, disks and toner in printing, and magnetic resonance imaging (MRI). Heretofore, we have been comprehensively studying on the synthesis and applications on the ABA triblock-type two fluoroalkyl end-capped oligomers $[R_F-(M)_n-R_F]$; R_F = fluoroalkyl groups; M = radical polymerizable hydrocarbon monomers. These fluoroalkyl end-capped oligomers can form the nanometer size controlled self-assembled molecular aggregates through the aggregation of terminal fluoroalkyl segments in aqueous and organic media. The fluorinated oligomeric aggregates thus obtained can interact with a variety of inorganic guest molecules such as silica, titanium oxide, hydroxyapatite, gold, silver, copper, palladium, zinc oxide, calcium carbonate, calcium silicide, magnesium carbonate, magnesium oxide, and talc to afford the corresponding fluorinated oligomeric aggregates/guest molecules nanocomposites. In fact, fluoroalkyl end-capped oligomeric nanocomposites - encapsulated gold nanoparticles can provide linear arrays of these fluorinated nanocomposite particles to afford the extremely red-shifted plasmon absorption band at around 960 nm. Thus, it is of particular interest to explore novel fluoroalkyl end-capped oligomeric nanocomposites by using magnetic nanoparticles as the guest molecules from the developmental viewpoints of new fluorinated functional materials.

Here we report that fluoroalkyl end-capped vinyltrimethoxysilane oligomer/magnetite nanocomposites can be prepared by the sol-gel reactions of the corresponding oligomer in the presence of magnetic nanoparticles under alkaline conditions. The obtained fluorinated nanocomposites were found to afford a good dispersibility toward the traditional organic media except for water. Transmission electron microscope (TEM) image shows that the magnetic nanoparticles can be effectively encapsulated into the fluoroalkyl end-capped oligomeric nanoparticle cores to provide the expected $R_F-(VM-SiO_2)_n-R_F$ / magnetite nanocomposites. Interestingly, it was demonstrated that these fluorinated nanocomposites can exhibit a superoleophilic/superhydrophobic characteristic on the modified surface and these obtained nanocomposite powders are applicable to the adsorbent for removing oil in water by using the permanent magnet.

COLL 608

Synthesis of hybrid polystyrene-poly(organosiloxane) particles with complex architectures through use of organotrialkoxysilanes as surfmer

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Surfactants are often used for the synthesis and stabilization of nanoparticles in dispersion. A large share of the applied surfactant, however, is not bound to the particle surface after synthesis. This unbound surfactant can cause problems in further functionalization of the nanoparticles with e.g. a metal or metal oxide shell, and hinders the application of the nanoparticles in e.g. coatings. Through use of surfmers, i.e. polymerizable surfactants, the above mentioned limitations can be avoided. Surfmers with vinyl groups suited for radical polymerization are well known, and applied for the synthesis of polymer particles from micelles, vesicles and emulsions. Here, we present a class of surfmers suited for the emulsion-based synthesis of sub-micron sized particles based on silica sol-gel chemistry: organotrialkoxysilanes. We noticed that, when bringing organotrialkoxysilanes, e.g. phenyltrimethoxysilane, in contact with aqueous ammonia, an emulsion is formed spontaneously after a couple of minutes reaction time. Based on that observation, we concluded that a surfactant must be formed under these conditions. We studied the formation of the emulsion in detail, and extensively characterized the properties of the surfactant. Using the obtained insights, we applied these surfmers for the synthesis of hybrid polystyrene-poly(organosiloxane) particles with complex architectures. When performing both the radical polymerization of styrene and the sol-gel reaction of organotrialkoxysilanes simultaneously in one pot, we obtained hybrid spheres. The distribution of domains of polystyrene and poly(organosiloxane) could be tailored through variation of the ratio of styrene to organotrialkoxysilane. When performing both reactions sequentially in one pot, we obtained non-spherical hybrid particles with complex Janus-type or raspberry architectures. The formation mechanism of the obtained particles, and its relation to the applied surfmers, will be discussed in detail.

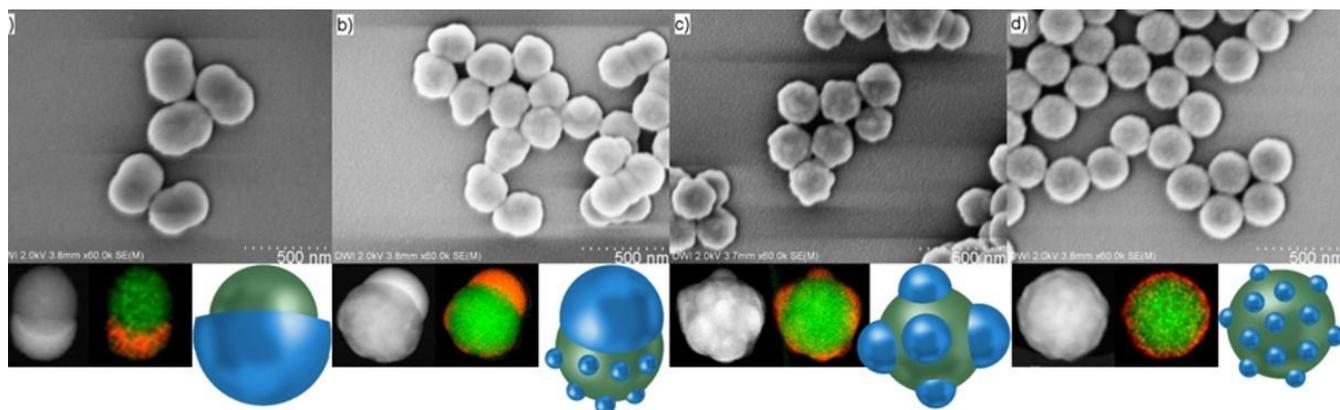


Fig. 1: Hybrid polystyrene-poly(organosiloxane) particles with Janus-type or raspberry architecture, obtained through sequential radical polymerization of styrene and sol-gel reaction of organotrialkoxysilanes in one pot.

COLL 609

Cracking and self-healing of shrinkable, granular materials

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Shrinkable, granular materials—materials composed of hydrated grains that individually shrink when dried—arise in many diverse settings; prominent examples include clays, soils, biological tissues, foods, and coatings. In many cases, these materials crack during drying, critically hindering applications. By combining experiments with hydrogels, discrete-element simulations, and poroelasticity theory, we reveal how grain shrinkability dramatically alters crack evolution during drying—in some cases, even causing cracks to spontaneously self-heal. Moreover, we elucidate the rich physics underlying cracking, and develop new strategies to controlling crack evolution and patterning.

COLL 610

Preparation and application of fluoroalkyl end-capped vinyltrimethoxysilane oligomer/hexagonal boron nitride nanocomposites

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Hexagonal boron nitride (h-BN) nanoparticle is one of the most promising inorganic nanomaterials in recent years, due to exhibiting a wide variety of unique properties such as high mechanical stiffness, excellent thermal conductivity, high corrosion resistance, and chemical inertness. On the other hand, fluoroalkyl end-capped vinyltrimethoxysilane oligomer $[R_F-(CH_2CHSi(OMe)_3)_n-R_F]$ $[R_F-(VM)_n-R_F]$ can undergo the sol-gel reaction under alkaline conditions to provide the corresponding fluorinated oligomeric silica nanocomposites possessing an oleophobic/superhydrophobic characteristic. Thus, it is of particular interest to develop novel fluorinated oligomer/h-BN nanocomposites possessing not only the surface active property imparted by fluorine but also the unique characteristic related to h-BN.

Here we report that fluoroalkyl end-capped vinyltrimethoxysilane oligomer /hexagonal boron nitride (h-BN) nanocomposites $[R_F-(VM-SiO_2)_n-R_F/h-BN]$ can be prepared by the reactions of the corresponding oligomer with h-BN nanoparticles (mean diameter: 50 nm) under alkaline or acidic conditions at room temperature, respectively. These fluorinated h-BN nanocomposites thus obtained were applied to the surface modification of PMMA [poly(methyl methacrylate)]. Interestingly, each modified PMMA film surface treated with these nanocomposites, which were prepared under acidic conditions, can

give a good oleophobic characteristic imparted by fluoroalkyl segments in the nanocomposites on the surface side and reverse side. On the other hand, the nanocomposites, which were prepared under alkaline conditions, can give an oleophobic property on the only surface side. These findings will be demonstrated in detail in this conference.

COLL 611

Synthesis of nanoparticles in dispersion: Flow cell coupled analytics as a way to follow particle growth

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Control of the exact size and morphology of nanoparticles is key to their successful application in optical grade composites. In this work, dynamic light scattering (DLS) and ultrasound nanoparticle sizing (UNPS) have been used to follow the growth of nanoparticles from molecular precursors in a pilot scale reactor.

DLS is a standard tool for sizing of nanoparticles in solution. The principle is based on the correlation of photons scattered from the sample and detected by a suitable photon detector. It requires that only single scattered photons arrive at the detector. While the criterion of single scattering imposes no problems for solutions of low turbidity, it renders measurement of turbid solution impossible, because this results in undetectable systematic errors. Since dilution may modify the sample this needs to be reduced as much as possible. This can be done with the 3D modulation technology which suppresses multiple scattering to filter out only the single scattering. We show that real-time measurements of particle size, using a bypass loop and flow cell, can be performed directly on turbid reaction mixtures without need for dilution, as a result of the design of the setup.

Nanoparticles in dispersion change the speed and attenuation of ultrasonic waves in the dispersion. The size of the change depends amongst others on the particle size and concentration of the nanoparticles. This dependency is used in the developed measurement method. Using the known values of the speed and attenuation of the ultrasonic wave in the dispersing medium, the frequency dependent change in speed and attenuation can be obtained. An inversion process tries to fit these changes in speed of sound and attenuation by estimating the mean particle size and concentration of the particles. Figure 1 shows the basics of both the DLS and UNPS methods used.

We show that real-time measurements of particle size and concentration using a bypass loop and flow cell can be performed directly on turbid reaction mixtures without need for dilution, by using the newly developed analytical tools. This is demonstrated using a size-tunable reaction system of nano-silica in dispersion.

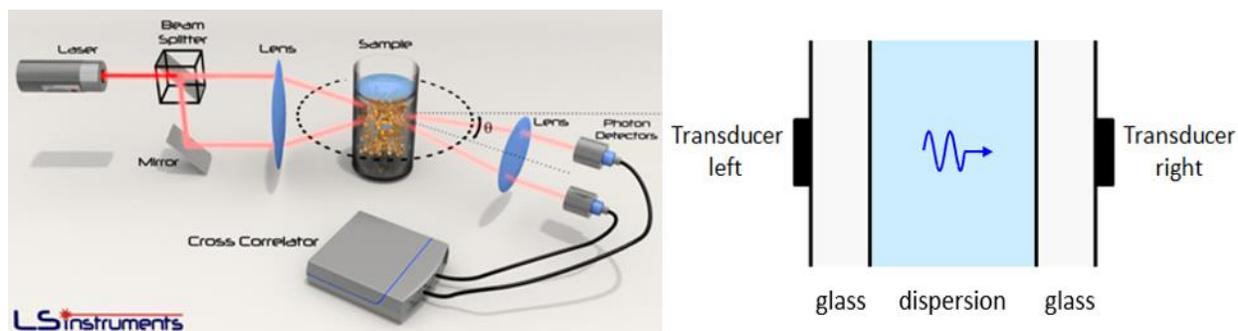


Figure 1: Left: Basics of 3D modulated DLS, **Right:** Method to measure speed of sound and attenuation of ultrasonic waves in dispersion.

COLL 612

Measuring the accessible surface area within the nanoparticle corona using molecular probe adsorption

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The corona phase, the adsorbed layer of polymer, surfactant or stabilizer molecules around a nanoparticle, is typically utilized to disperse nanoparticles into a solution or solid phase. Unfortunately, few methods can directly probe the structure of this corona phase due to issues with dilution, molecular mobility, and total radiation cross section. In this work, we introduce a Molecular Probe Adsorption (MPA) method for measuring the accessible nanoparticle surface area using a titration of a quenchable fluorescent molecule. As an example, riboflavin is utilized to measure the surface area of Au nanoparticle standards, as well as corona phases on single walled carbon nanotubes and on graphenes. A material balance on the titration yields the surface coverage parameters, including the ratio of the surface area to dissociation constant of the fluorophore, q/K_D as well as K_D alone. Total 14 different nanoparticle corona phases, on

AuNP, SWNT and graphene are chosen and studied with the new method. Uncertainty and precision are discussed, as well as the correlation of these parameters across different experiments. This rapid, quantitative technique should prove useful to elucidating the structure-property relationships of the nanoparticle corona.

COLL 613

Polymer-based energetic composites with improved thermal conductivity through bioinspired interfacial engineering strategy

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Thermal management has become a critical issue to enhance reliability and performance in many research areas including aerospace, electronic devices, and military applications. However, conventional nanocomposites incorporated with highly thermally conductive nanofillers can hardly achieve a desired value, due to the existence of large interfacial thermal resistance (*ITR*) which constitutes a primary bottleneck. Herein, we report on a bioinspired interfacial engineering strategy to construct a multi-dimensional filler structure composed of 2D GNPs, 0D AgNPs and bioinspired interfacial PDA layer, namely pGNPs@Ag. The experimental results revealed that a high-efficiency thermal conductivity enhancement was achieved by this strategy, due to that the bridging connections of decorated AgNPs could facilitate the heat transfer across the interfaces. By theoretical simulation and calculation, we also quantitatively demonstrated a decrease of *ITR* by pGNPs@Ag, leading to a contribution to improve the *k* of composites. This approach for constructing multi-dimensional thermally conductive fillers potentially provides a creative opportunity for design and fabrication of high thermally conductive composites in the near future.

COLL 614

New insight into the role of Ag in the seed-mediated gold nanorods synthesis

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The role of silver ions in seed-mediated gold nanorod (AuNR) syntheses has been investigated. The key silver intermediate which controls the AuNR aspect ratio was identified as a CTA-Ag-Br complex instead of CTA-AgBr₂ due to the low solubility of CTA-AgBr₂ under the reaction conditions. We systematically studied the AuNR growth solution preparation process and determined that the solubility of this CTA-Ag-Br complex intermediate is the limiting factor (with a limiting solubility of 0.12 mM) in the preparation of AuNR. Additional AgNO₃ does not influence of the aspect ratio (length-to-width) of the resulting AuNR. The reagent addition sequence is also observed to be important. Addition of ascorbic acid before the mixing of AgNO₃ results in the formation of large quantities of (spherical) gold nanoparticles. This confirms the crucial role of the

formation of CTA-Ag-Br complex during the AuNR synthesis. This result sheds light on the understanding of the role of silver ions in AuNR syntheses and helps the design of new synthetic approaches to produce AuNR with large aspect ratios.

COLL 615

Protection of organic molecular microcrystals encapsulated under two-dimensional materials

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Graphene, a layer of hexagonal carbon lattice, only allows photons, electrons and protons to pass through but impermeable to any other chemical species. The impermeability and atomic thickness make it an ideal candidate for the protective coating of target materials, which could be air sensitive, photo-unstable or volatile. One series of material, which might be benefited from this application is polyaromatic hydrocarbon (PAH) crystals. Due to their appealing electronic structure and photophysical properties, PAHs are one of the most extensively studied organic semiconductors, with a variety of applications in organic light emitting diodes, field effect transistor and photovoltaic devices. However, the properties of PAHs are sensitive to the presence of impurities, like oxygen. Organic molecular crystal can also be dissolved easily in the organic solvent, or sublime at elevated temperature or in the high vacuum, making them unprocessable under many standard device fabricating processes. Here we report a method to encapsulate one of the polyaromatic hydrocarbon semiconducting microcrystals, perylene, using CVD single-layer graphene. The conformal coating of graphene layer around the crystal surface offered complete protection from organic solvents and prevents crystals from subliming at elevated temperature. Raman spectroscopy measurement indicated that the graphene is slightly perturbed by the underlying crystal due to the strain effect. The time-resolved photoluminescence measurements show limited excimers quenching of perylene crystal by graphene. This encapsulation strategy can be extended to other 2D materials, and preliminary experiments using hBN nanosheet to protect molecular crystals will also be described. The encapsulation provides new possibilities for the molecular crystals in various electronic and photonic applications.

COLL 616

Understanding interfacial interactions to unlock the potential of bioinspired nanomaterials

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Porous nanosilica is a technologically important material with potential applications in the catalysis, medicine and separations sectors. These applications demand specific porosity, surface chemistry and/or particle size. Current methods to attain these features are extremely complex and/or unsustainable, leading to significant barriers to commercialisation. Taking inspiration from biomineralisation, we have developed bioinspired synthesis. This green method (mild, one-pot and rapid synthesis in water, at room temperature and neutral pH) is sustainable when compared to traditional routes, yet offers excellent control over the properties of the materials. In this presentation, we will discuss new results relevant to bioinspired synthesis which highlight the importance of interfacial interactions for controlling the (A) synthesis, (B) purification and (C) surface modification of nanosilicas (detailed below).

(A) The knowledge of the specific interactions between these additives and inorganic species has enabled green synthesis of nanosilicas of a range of properties e.g. monodisperse silica nanoparticles and mesoporous silica – this is a significant step-change compared to traditional syntheses.

(B) Using recently developed molecular dynamics force-fields, we have investigated the extraction of additives from silica surfaces for the first time. This has enabled the modulation of additive-surface interaction leading to a rapid room-temperature solution method for complete extraction of organic additives. Once extracted, additives can be directly reused for further silica synthesis. Estimates of the environmental benefits of our new method compared with previous purification techniques show significant improvements in sustainability.

(c) Finally, using extensive NMR analysis, we have identified the ability of the additives to catalyse condensation at silica surfaces even after the formation of silica is complete. Such surface-adsorption-then-catalysis reactivity has not been previously considered in studies of organic-inorganic surface interactions.

Taken together, this presentation will show that by studying the organic-inorganic interface, we have developed a cleaner, cheaper, and readily scalable method for production of bespoke nanosilica. This is a significant technological advance which is enabling sustainable and economical scale-up of these materials for commercial applications.

COLL 617

Changes in the physiochemical properties of MoO₃ nanoparticles in aquatic systems

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The understanding of nanoparticle dissolution and behavior in aquatic environments is essential in environmental chemistry since it can directly affect the aquatic ecosystem and human health. Different parameters, such as nanoparticle size, aquatic pH and ionic strength among others, can affect the stability of nanoparticles in terms of dissolution and aggregation. Recently, MoO₃ nanoparticles have shown photocatalytic properties under visible light making them capable of degrading water contaminants. In this study, we investigate the physiochemical properties and pH-dependency of MoO₃ nanoparticles with different sizes and morphologies (nanorods, nanowires, and nanosheets). Furthermore, we examine the aggregation behavior of the MoO₃ nanoparticles in the presence of monovalent or divalent salt solutions and the applicability of Derjaguin, Landau-Verwey-Overbeek (DLVO) theory in predicting the range of critical coagulation concentrations for these nanoparticles (CCC).

The solubility at different pH values showed that at basic pH, the dissolution of the nanoparticles is higher than at acidic pH. We have also shown that depending on the pH, the production of reactive oxygen species can vary. Additionally, the aggregation rates can vary drastically depending on the nanoparticle size and structure. The presence of natural organic matter as well as changes in pH can have different effects on particle stability depending on the particle's morphology. While CCC values between the different structures are similar, size and morphology dependent differences can be observed. Furthermore, we observed a weak trend between the solubility of the nanoparticles and resulting CCC. Despite the complexity of nanoparticle dissolution and kinetic behavior in water, we found that DLVO theory can be used to approximate the CCCs for the different salt solutions allowing us to predict particle behavior in a variety of water chemistries.

COLL 618

Accelerating nano-EHS research: Applications in nano-chemistry and nano-toxicology

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The field of nanotechnology related environmental health science is vast and evolving. It encompasses studies with engineered nanomaterials (such as particles, fibers, and composites) as well as nanotechnology processes (such as lithography, self-assembly, and targeted delivery). Few people have been able to contribute a significant amount of data to both of these areas; Professor Vicki Grassian is one of those scientists. Over the past 15 years, research efforts performed by Grassian and her team have resulted in hundreds of research manuscripts and perspective pieces that address critical concerns related to nanotechnology health and safety. This talk will highlight some of those most cited works as they relate to novel R&D efforts in nanomedicine and nanotoxicology.

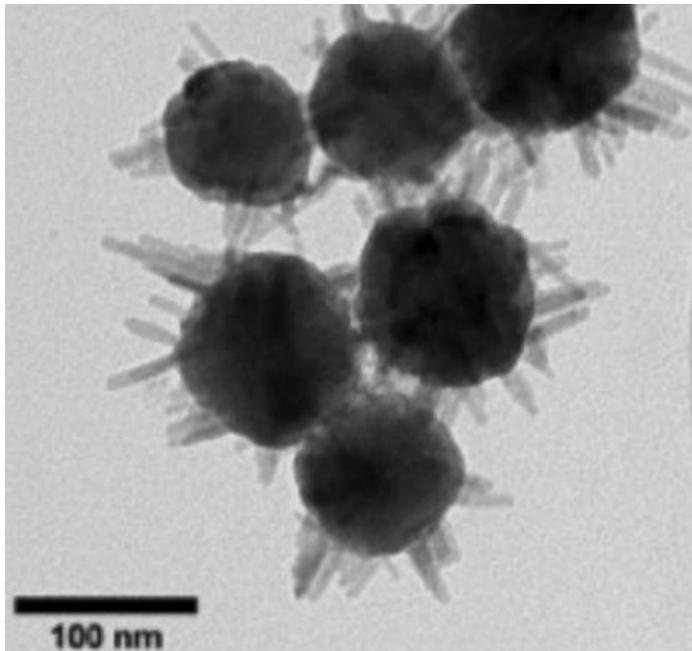
For example, principles guiding basic and complex surface chemistry provide sound insights into successful development of homing beacons tethered to the surfaces of drug delivery nano-carriers. In addition, using combinations of soft and hard “shells”, it is possible to engineer pharmaceuticals that target specific tissues (via cell surface receptors) and deliver a payload (cytotoxic dose) of active pharmaceutical ingredients, while decreasing unwanted side-effects induced by the nano-excipient. Lastly, surface chemistry (charge and absorbed functional group) play a crucial role in nanoparticle transformation and eventual fate; and, in some case, this role is more pronounced than either particle composition or the surrounding environmental conditions. Conclusions reached in Grassian’s research efforts have informed many subsequent studies and accelerated our collective knowledge in nano-EHS.

COLL 619

Mineral growth, dissolution, and beyond: Iron oxide nanoparticles

*Jeanette Voelz¹, Clare Johnston¹, Maetzin Cruz Reyes¹, Adel Soroush⁵, Jennifer A. Soltis², Jennifer H. Strehlau¹, Nathan D. Burrows³, Amanda M. Vindedahl⁴, William Arnold⁵, **R Lee Penn¹**, rleepenn@umn.edu. (1) Chemistry, University of Minnesota, Minneapolis, Minnesota, United States (2) Pacific Northwest National Lab, Richland, Washington, United States (3) Department of Chemistry, Pennsylvania State University, State College, Pennsylvania, United States (4) University of Minnesota, North Saint Paul, Minnesota, United States (5) Univ of Minnesota, Minneapolis, Minnesota, United States*

Crystal surfaces are reactive in both natural and engineered aqueous systems, and mineralogy and crystal size and shape evolve substantially as a function extent of reaction. We quantitatively compare reactivity of materials in both reductive dissolution and oxidative mineral growth. We extensively characterize solid-state materials before, during, and after reaction as well as track the loss or production of dissolved species. Furthermore, the phases formed and evolution of mineral particle shape depend on solution conditions during oxidative crystal growth on iron oxide nanocrystals. For example, the presence of organic matter (e.g., Suwanne River Natural Organic Matter) slows oxidative mineral growth on goethite nanocrystals, with greater suppression observed on the tips as compared to the sides of the acicular crystals. In a second example, oxidative mineral growth on hematite nanocrystals leads to the formation of hematite or goethite depending on pH, concentration of aqueous ferrous ion, and the presence (and concentration) of organic matter. The presentation will highlight several examples of our ongoing work studying the reactivity of iron oxide nanoparticles in aqueous systems.



COLL 620

Molecular level studies of carbon-based nanomaterials in aquatic environments

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Carbon based nanomaterials include for example, carbon nanotubes, fullerenes, graphene, carbon dots and nanocellulose. In aquatic environments, these carbon based nanomaterials are an integral component of many next generation environmental technologies (e.g. membranes), but concerns remain about their potential negative environmental implications (e.g. toxicity). In common with all nanomaterials, surface chemistry plays an important role in regulating the properties and behavior of carbon based nanomaterials due to their extremely large surface area to volume ratios. In my presentation I will show how molecular level information on the surface properties of carbon based nanomaterials can be used as the basis to understand environmentally relevant properties, ranging from particle stability and contaminant sorption properties, to photochemistry, biodegradation and sustainability.

COLL 621

Interfacial energy: Key to controlling calcium carbonate formation on environmentally-abundant surfaces

Young-Shin Jun, *ysjun@wustl.edu*, Qingyun Li, Yaguang Zhu. *Energy, Environmental and Chemical Eng., Washington University in St. Louis, Saint Louis, Missouri, United States*

In many engineering processes at the water-energy nexus, we often observe calcium carbonate (CaCO_3) formation, which plays important roles in carbon dioxide utilization and mineralization, pipeline scaling, water purification membrane processes, and energy-related subsurface operations. In this talk, I will discuss new experimental ways to quantify the interfacial energy at CaCO_3 -on-quartz substrates *in situ* and explore their roles in CaCO_3 nucleation in environmental systems. We have utilized synchrotron-based *in situ* grazing incidence small angle X-ray scattering, along with complementary water, interface, and solid characterization methods, and have quantified the nucleation kinetics of CaCO_3 at different salinities and temperatures. Through this experimental work and by applying classical nucleation theory, we obtained the effective interfacial energy (α) for each salinity, as well as the thermodynamic and kinetic activation nucleation barriers. By improving reactive transport models, this information is particularly useful in better predicting the crucial fate and transport of contaminants and nutrients in the environment. The results can also be applicable to controlling scale formation in pipelines and on desalination membranes.

COLL 622

Applications of nanotechnology for water treatment: Electrospun nanofibers as a platform for integrated treatment and monitoring

David M. Cwiertny, *david-cwiertny@uiowa.edu*. *Civil and Environmental Engineering, University of Iowa, Iowa City, Iowa, United States*

This talk will focus on the development and application of electrospun nanofibers for water treatment and sensing applications. Specific examples include the fabrication of functionalized polymer-nanoparticle composite fibers for ion exchange, sorption and photooxidative treatment. Recent efforts have integrated spectroscopic and electrochemical methods so that point of use water treatment applications can also be used for sensing and water quality monitoring.

COLL 623

Insight into the interactions of biomolecules and natural organic matter with mesoporous silica nanomaterials

Sarah C. Larsen, *sclarsen@uh.edu*. *Chemistry, University of Houston, Houston, Texas, United States*

Mesoporous silica nanomaterials are silica-based porous materials with pore diameters of greater than approximately 1 nm. Due to their high surface areas and the ease with which these materials can be functionalized, many current and emerging applications

have been identified including heavy metal and radioactive contaminant adsorption, drug delivery and imaging. As biomedical and environmental applications for mesoporous silica nanomaterials are increasingly developed and deployed, it becomes critically important to understand the interactions of these nanomaterials with natural and biological systems. Therefore, it is of great interest to investigate how the adsorption of biological and environmental media on mesoporous silica nanoparticles occurs on a molecular level and how this impacts nanoparticle transformations, such as agglomeration and dissolution, along with other parameters including the chemical properties of biological and environmental molecules. The studies discussed in this talk focus on understanding the molecular level interactions of biomolecules and of natural organic matter with mesoporous silica surfaces under conditions of varying pH, functionalization and surface charge. These results suggest that the interactions are mediated by the properties of the mesoporous silica nanomaterials, such as porosity and surface functionality, as well as other factors, such as pH and the solvent/media present.

COLL 624

Physical chemistry of environmental interfaces

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History, developments and achievements of Prof. Vicki Grassian in surface science of complex environmental interfaces will be highlighted. Topics include but are not limited to heterogeneous atmospheric chemistry of sea spray and mineral dust; aerosol impacts on climate; applications and implications of nanoscience and nanotechnology.

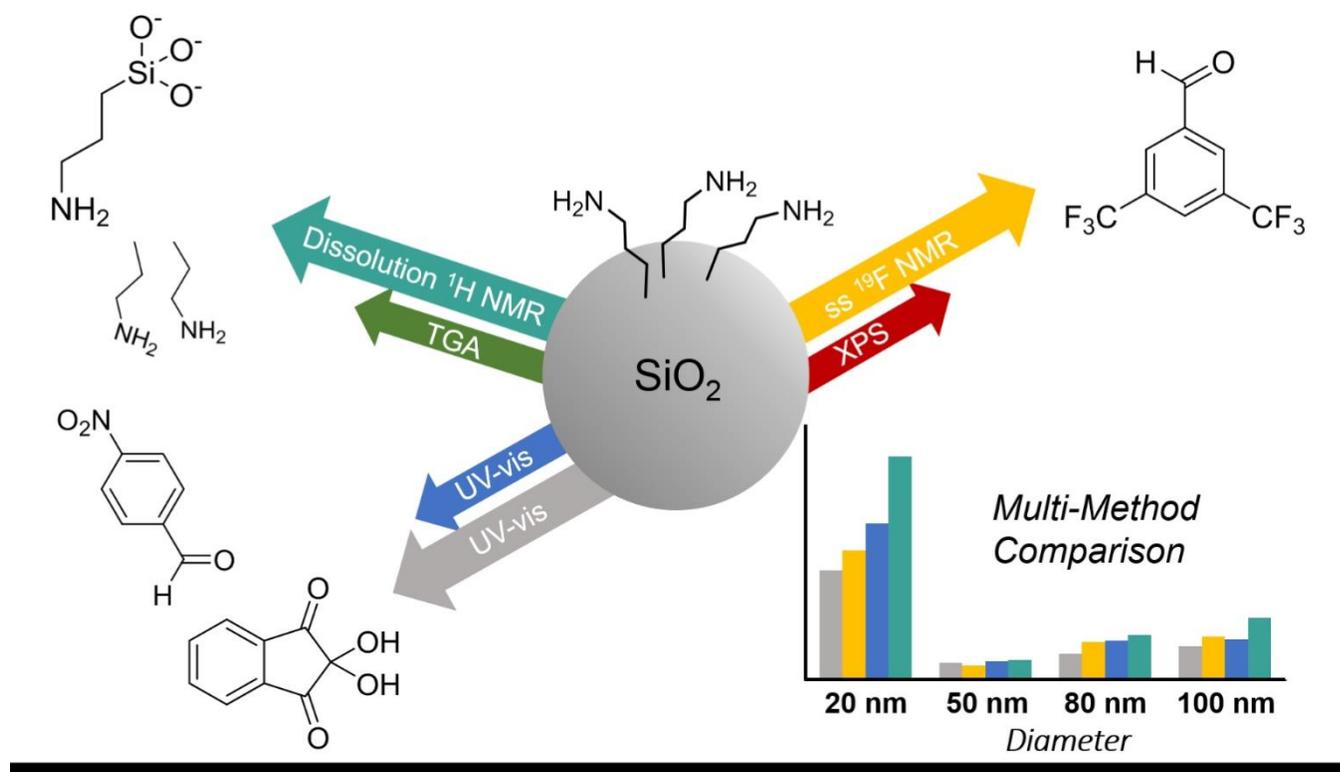
COLL 625

Multimethod quantification of nanomaterial surface functional groups

Filip Kunc, filip.kunc@nrc-cnrc.gc.ca, Ying Sun, Andreas Brinkmann, Gregory Lopinski, Linda Johnston, Vinod Balhara. Metrology, National Research Council Canada, Ottawa, Ontario, Canada

Surface-modified nanomaterials have been commonly used in a number of research applications, and are increasingly used in commercial composite materials as well. Silica and other metal oxides nanoparticles can be purchased in large quantities from a number of suppliers, but the important information on the density of surface groups is typically not provided. This is surprising because it can directly impact parameters such as toxicity, biodegradability or reproducibility in manufacturing. Reliable surface-chemistry characterization methods are therefore necessary to establish adequate quality control and regulatory frameworks. In our work, we address this complex problem by the detailed study and the cross-validation of various methods for the quantification of functional groups and their stability. Two colorimetric approaches were

used to assess the reactivity and accessibility of frequently used propylamine moiety. The first assay uses ninhydrin and the reporting dye is continuously generated. The other assay is a two-step reaction based on the conjugation and the subsequent release of 4-nitrobenzaldehyde as the reporting chromophore. In addition, fluorine-labeling reactions were used to probe the extent of surface groups coupling *via* ss ^{19}F -NMR and XPS. These results are compared to the total amount of functional groups on the material determined by 'dissolution' ^1H qNMR and TGA coupled with FTIR detection. These two methods can also inform about the chemical structure and allowed to quantify additional functional groups (C_{11}COOH , stearate, methacryl, PEG). Further substrate materials (Fe_2O_3 , TiO_2 , ZnO) were tested as well and the applicability/limitations of mentioned methods were critically assessed. Additionally, we are going to showcase that samples procured from various commercial suppliers can widely range in the functional group content, and can also contain impurities that interfere with some quantification methods. We believe that our findings can be highly relevant and practical for nanomaterials businesses as well as regulators and researchers from across many disciplines.



Convergence of ensemble and single-molecule techniques to understand protein liquid chromatography

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Optimization of protein separation and purification is an empirical process that lacks predictability and is known to be the bottleneck in downstream processing of protein-based drugs, also called biologics. One of the most widely used methods of protein purification and separation is chromatography. Despite the wide industrial usage and intensive development, there is still no detailed molecular-scale picture of protein dynamics during chromatographic separation. The lack of a predictive chromatographic theory is rooted in the absence of an in-depth understanding of interactions occurring inside a chromatographic column. To advance the understanding of underlying phenomena responsible for successful chromatographic separation of biologics, a microscopic, single-molecule picture of the elution process is necessary. The macroscopic picture of chromatography is dictated by processes at the single-molecule level. However, ensemble methods inherently average underlying heterogeneity and, therefore, are not able to yield a full understanding of chromatography on a microscopic level. This work focuses on ion-exchange chromatography (IEX) which separates proteins based on their net surface charge. By using both ensemble and single-molecule techniques we want to develop a mechanistic understanding of IEX. We use Circular Dichroism (CD) to show that negatively charged ligands in cation exchange column cause surface-induced unfolding of the proteins. Using 3D single-molecule fluorescence microscopy we observe increased linear velocities of protein molecules at increased ionic strengths. From our chromatographic profiles, single-molecule results and CD spectra we conclude that lower salt concentrations of a mobile phase lead to stronger surface-induced protein unfolding and lower linear velocity of the protein molecules inside chromatographic column. This work allows us to resolve the details of protein dynamics inside chromatographic column, providing a molecular-scale picture of protein chromatography.

COLL 627

Co-optimization of multifunctional surfaces using high-throughput surface patterning assays

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The development of multi-functional surfaces with orthogonal functionalities necessitates co-optimization, in which the improvement of one function may come at the detriment of others. As a common example of this competition, the combination of functional biomolecules (which tend to be hydrophilic) and mitigation of wetting (which requires hydrophobic surfaces) poses a major challenge. Here, we report a novel high-throughput strategy for studying the effect of patterning surface chemistry on the collective properties of surfaces using wetting and the activity of immobilized biomolecules as model properties. In particular, surface-immobilized enzymes are patterned on surfaces using a combination of top-down patterning and small molecule self-assembly processes amidst a non-binding, hydrophobic background. Vital to this experimental scheme is the design of a system that enables highly-parallelized fabrication and characterization with built-in controls to confidently sort through the essentially unlimited surface patterns and immobilization conditions. Due to the high-throughput and parallel nature of this system, we are able to study hierarchical arrangements of enzymes with independent control over the microscopic patterns of binding domains and the enzyme density within these patterns. Through a combination of high throughput activity assays, quartz crystal microbalance experiments to quantify immobilization conditions, and dynamic roll-off measurements, we co-optimize surfaces for enzyme activity and wetting properties. Additionally, these experiments provide a direct assessment of enzyme activity vs. immobilization density, which is both a challenging property to measure due to variability inherent to enzyme-based measurements and critically important to the numerous applications of immobilized enzymes in green energy and biosensing. Taken together, these methods and the proof-of-concept studies that they have enabled, illustrate that concepts from high throughput chemistry can be impactful in the study of multi-functional surfaces.

COLL 628

Using non-standard N-heterocyclic carbenes to functionalize gold surfaces and analysis of their binding via SERS

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Due to their high binding affinity for noble metals, amines and thiols have frequently been used as ligands for surface modification. However, there are many challenges for using these functional groups as linkers, ranging from the synthesis to instability once applied to the surface. Recently, N-heterocyclic carbenes (NHCs) have come to the fore as an improved ligand for surfaces modifications due to their enhanced chemical stability. To date, the NHC ligands used to functionalize noble metal surfaces are simple benzimidazoliums and imidazoliums. One method to broaden the scope of NHCs on noble metal surfaces is to employ non-standard NHCs, such as the saturated imidazolium, imidazolinium, and a six membered ring variant, perimidinium. These non-standard carbenes have the potential for even greater stability on the surfaces than typical NHC ligands. Furthermore, these non-standard NHCs can be more effective for

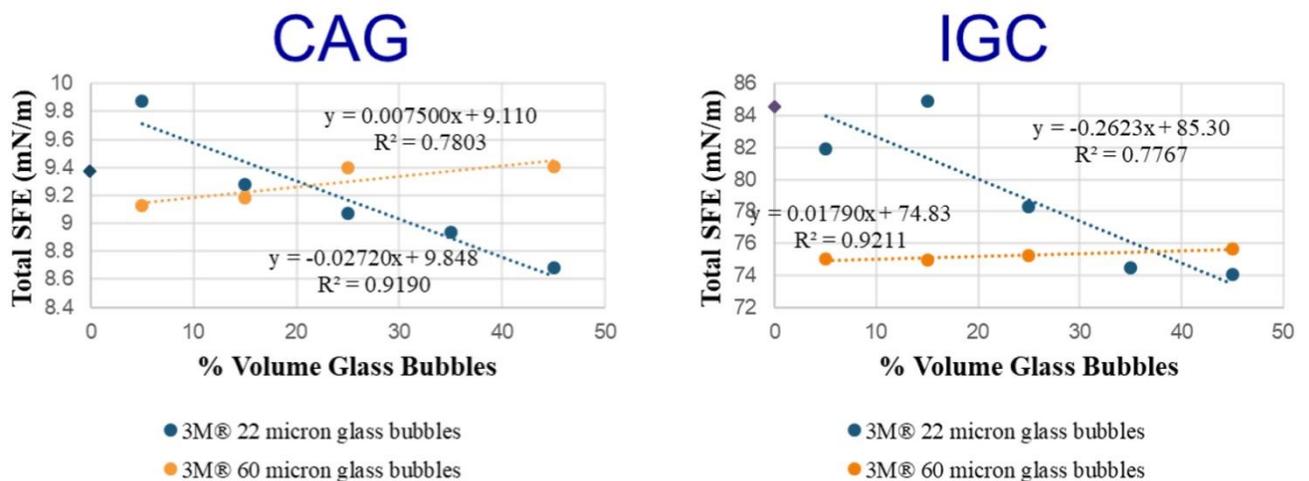
analyte binding due to their different geometries at the surface. We will present the initial results for functionalization of gold surfaces with non-standard NHCs ligands as well as their verification and characterization using Surface-enhanced Raman Spectroscopy (SERS).

COLL 629

Surface energy determination comparison: Inverse gas chromatography and contact angle goniometry

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Inverse gas chromatography was utilized to provide the surface [total surface energy (γ_s), dispersive (γ_s^d) and specific (γ_s^{sp}) components] characteristics of simple Sylgard 184® and hollow glass bead samples. Contact angle goniometer measurements were utilized for comparison of the surface free energy of the solid binder sample and the interfacial tension (surface tension) between a liquid probe material and the solid binder surface. Results include an increased understanding of the surface energies utilizing different measurement methods and the development of methods to characterize and evaluate new binder systems. Final success and progress was measured by the ability to reproducibly measure various surface energies, interactions and other properties of a series of binder systems by inverse gas chromatography and compare to contact angle measurements from both the laboratory and literature.



COLL 630

Computational study of mechanism of different amino acids binding to Graphene sheet in gas phase with DFT

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Interaction of proteins with graphene sheet is crucial to study the exfoliation mechanism of graphene by proteins as well as to use graphene for biological applications. In this present study, we have computationally explored the interaction of a number of amino acids with the graphene sheet by employing Density Functional Theory (DFT). Counterpoise binding calculations under DFT was used to calculate the binding energies of different amino acids. The results indicate that positively charged amino acids bind better to the neutral graphene sheet in the gas phase in comparison to negatively charged amino acids. These observations are consistent with the experimental results where the logarithm of the association constant (K_a), determined from Surface Plasmon measurements, can be linearly correlated to the isoelectric points of various proteins. We have also observed that polarization of graphene sheet and different charged amino acids after the optimization of these structures. The neutral amino acids, on the other hand, show no polarization and hence the binding energy is low for them.

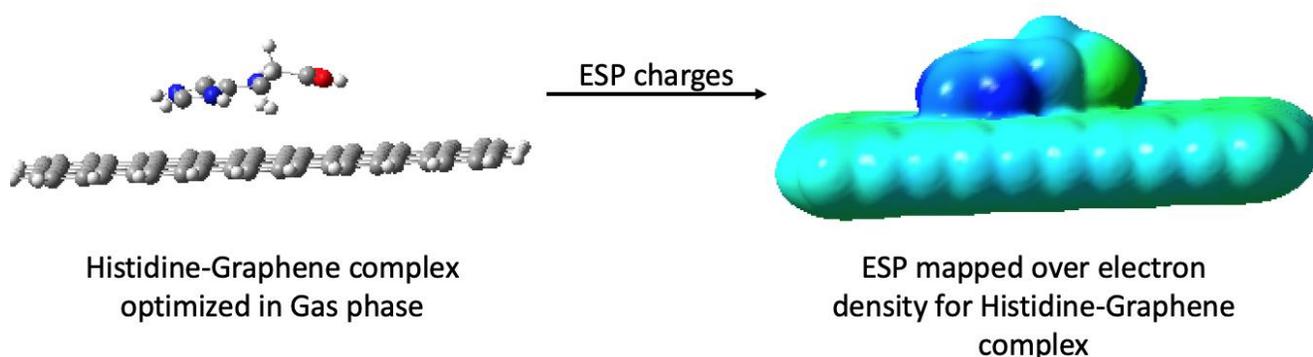


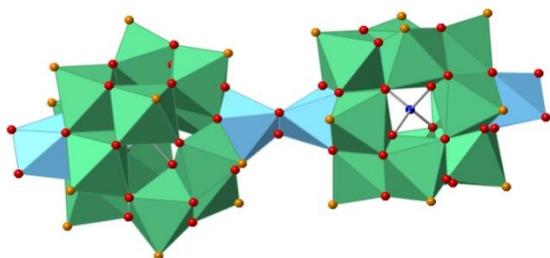
Figure 1: Electrostatic potential mapped on electron density for the optimized structure depicting binding of positively charged histidine to graphene sheet.

COLL 631

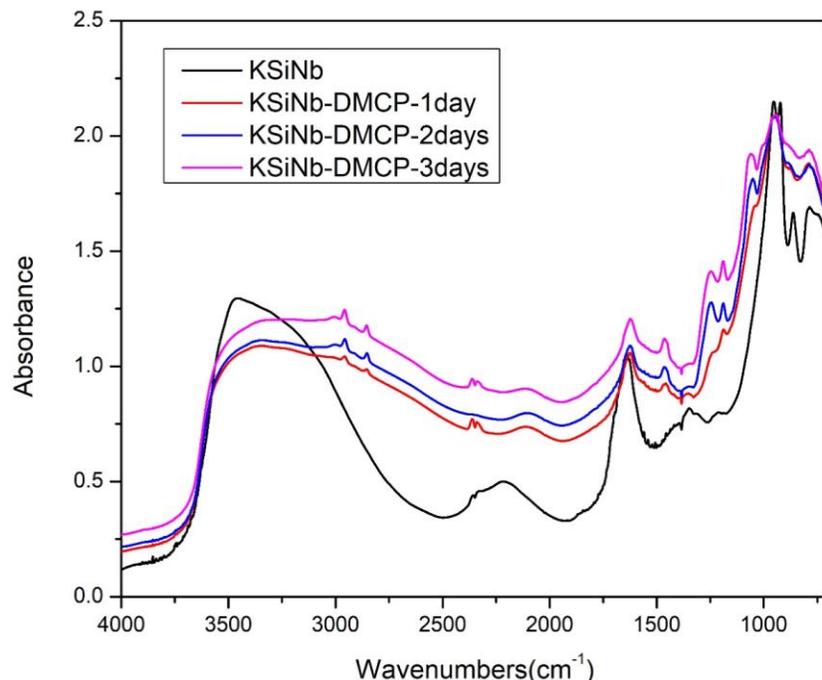
Nerve-agent decomposition by polyoxometalates utilizing a correlated multimodal approach

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Development of technologies for protection against chemical warfare agents (CWAs) is critically important. Recently, polyoxometalates (POMs) have attracted attention as potential catalysts for CWAs decomposition. However, several challenges limit our understanding of CWAs decomposition on POMs, including structural changes of both catalysts and agents, uncertainty in the active sites, and scarcity of experimental methods that are sensitive to changes. We tackled these challenges by utilizing a multimodal approach specific for gas-surface reactions, combining spectroscopies and calculations, to investigate a reaction of gaseous DMCP, a CWA simulant, with a Zr-based POM. We were able to detect the structural changes, determine the active sites and understand the nucleophilic hydrolysis. Here, we present our findings on a one-dimensional polymeric polyniobate (KSiNb) for the decomposition of DMCP. Raman and DRIFTS data indicate the adsorption and decomposition of DMCP on KSiNb. XAFS data of DMCP exposed KSiNb samples shows that while the Ti linkage keeps intact, the shortest Nb-O bonds, located at the perimeter of polyniobates, are the ones most responsive to the interaction with DMCP. By further employing in-situ XAFS, Raman, and DRIFTS, we are expecting to understand how the shortest Nb-O bonds interact with DMCP as DMCP exposure time increases.



Polyhedral representation of the one-dimensional polyanion chain of KSiNb. Color code: green: NbO₆; blue: TiO₆; dark blue center: Si; orange: the nearest O bound to Nb



DRIFTS data of KSiNb under DMCP exposure for 0, 1, 2, and 3 days. The background is KBr powder at room temperature

COLL 632

Functionalized porous silicon for the capture and detection of organophosphates from air

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The capture and detection of organophosphate (OP) chemical warfare agents generally involves a sorbent-based pre-concentrator. However, typical sorbents offer only broad-spectrum uptake capabilities, allowing them to become saturated with background contaminants prior to target exposure, substantially reducing their efficacy. Additionally, the target analyte may only be present at low concentrations and for short periods of time, further complicating capture. In order for a sorbent to be left unattended in the field until it encounters the analyte of interest, it must demonstrate: (i) a high affinity for the target molecule, (ii) selectivity for the target over background interferences, (iii) post-exposure retention of the analyte, and (iv) a remotely measureable indication of uptake.

This work describes the design of a chemically selective one-dimensional photonic crystal for OP detection using electrochemically etched mesoporous silicon. In these

devices, adsorption of the target within the silicon mesopores alters the composite refractive index and measurably shifts the reflectance stop-band. Porous silicon interferometers have been previously used in the detection of various analytes, such as HF, NH₄, and DNA fragments. In the present work, the functionalization of the silicon surface with an oxime functional group (typically used as OP poisoning antidotes), imparts chemical selectivity toward OPs relative to a mixture of common interferents. The materials are shown to selectively uptake OPs in air at 1 ppm concentrations under humid conditions, with retention of the analyte under subsequent N₂ flow, while the specific capture event is signaled by a shift in the reflectance pattern of the device. The successful incorporation of the oxime surface functionality is confirmed spectroscopically, and the identity of the captured warfare agents is verified by thermal desorption and GC-MS.

COLL 633

Adsorption of Sarin on dry, wet, and doped TiO₂(110) using density functional theory

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Sarin is a chemical warfare agent that has been used against military and civilian populations by nation states and non-state terror groups. Different metal oxides including TiO₂ have shown promising properties for the adsorption and decomposition of Sarin. In this work, we have used density functional theory to explore the adsorption and dissociation of Sarin on dry, wet and doped TiO₂(110) and determine the stability and structure of the systems. The computational results show that the dissociative adsorption of Sarin is more stable than the molecular adsorption for all the systems considered here. In addition, the calculation of the energy barrier for the adsorption of Sarin on dry TiO₂(110) showed that Sarin is initially adsorbed with a molecular configuration followed by a dissociative process. In the case of the adsorption of Sarin on wet TiO₂ there was a higher stability for the surface with 0.5 monolayer of H₂O compared to the dry and other wet surfaces explored. The adsorption of Sarin on Hf doped TiO₂ showed lower adsorption energy values and higher charge transfer compared with the Zr and Ge doped TiO₂ systems, as well as, the undoped systems. The results obtained in this work suggest that there could be an important effect of the hydroxylation, hydration and doping of TiO₂(110) for the adsorption and decomposition of the Sarin molecule on this metal oxide, which ultimately could contribute to the decontamination process of Sarin.

COLL 634

Transition metal oxide nanostructures for a magnetic goal in nanomedicine

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Nanoparticles of magnetic materials are very useful in different bio-related applications, on which the combination of chemistry and magnetic performance will determine their final purpose. In particular, some transition metal oxide nanocrystals have become a versatile tool in the field of biomedicine, by keeping the cytotoxicity low while offering a wide range of tunable magnetic properties, to be used in magnetic separation, heat delivery or as therapeutic or contrast agents for imaging. These applications of magnetic nanoparticles rely on their capability: to be moved by an inhomogeneous magnetic field, to be detected based on the local magnetic field they generate, or to locally heat their environment.

Each one of these bio-related applications depends on different magnetic parameters such as the coercive field, the remanence, the saturation magnetization and the magnetic susceptibility, which are related to the different anisotropy contributions ruling the nanocrystal magnetic behavior. Thus, a fundamental motivation for studying transition metal oxide nanocrystals is the control of their effective magnetic anisotropy, which determines a preferred magnetization direction within the material, and consequently, the final bio-related application.

Accordingly, examples of these magnetic nanoparticles and nanostructures synthesized and manipulated by wet-chemistry methods will be detailed to demonstrate how to exert control over the final magnetic behavior and over their ultimate functionalities, considering heat delivery, magnetic separation and guidance in bio-related applications.

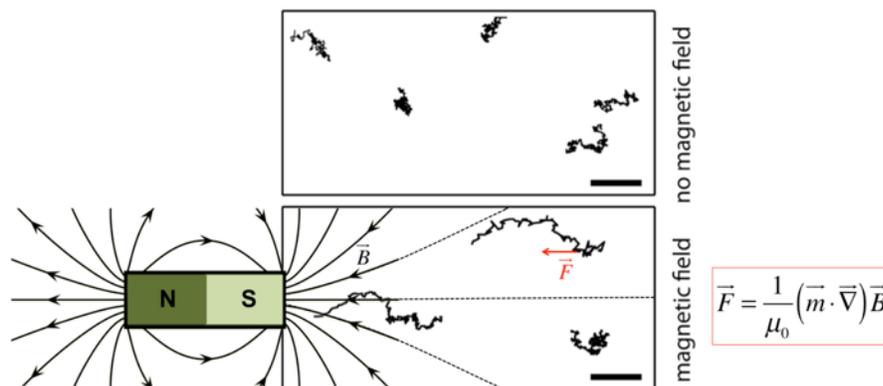


Figure 1. Representative trajectories of magnetic swimmers in the absence and presence of an applied magnetic field.

Fabrication of 3D plasmonic micro-structured super-crystals arrays

Nicolas Pazos-Perez², *nicolas.pazos@urv.cat*, **Ramon A. Alvarez-Puebla^{1,2}**. (1) *ICREA, Barcelona, Spain* (2) *Universitat Rovira i Virgili, Department of Physical and Inorganic Chemistry and EMaS, Tarragona, Spain*

In this work, we report novel methods to produce arrays of nanoparticles, either as continuous or as isolated supercrystals made with plasmonic nanoparticles. These macroscale organizations were created via confinement controlled drying and spin coating. SERS studies on the supercrystals shape and size were conducted. Moreover, the produced structures were effectively use for SERS sensing showing very good reproducibility among big areas. This fact make them perfect candidates as ultrasensitive substrates for SERS due to the controlled formation of hot spots. Which provide high and uniform SERS enhancement over extended areas.

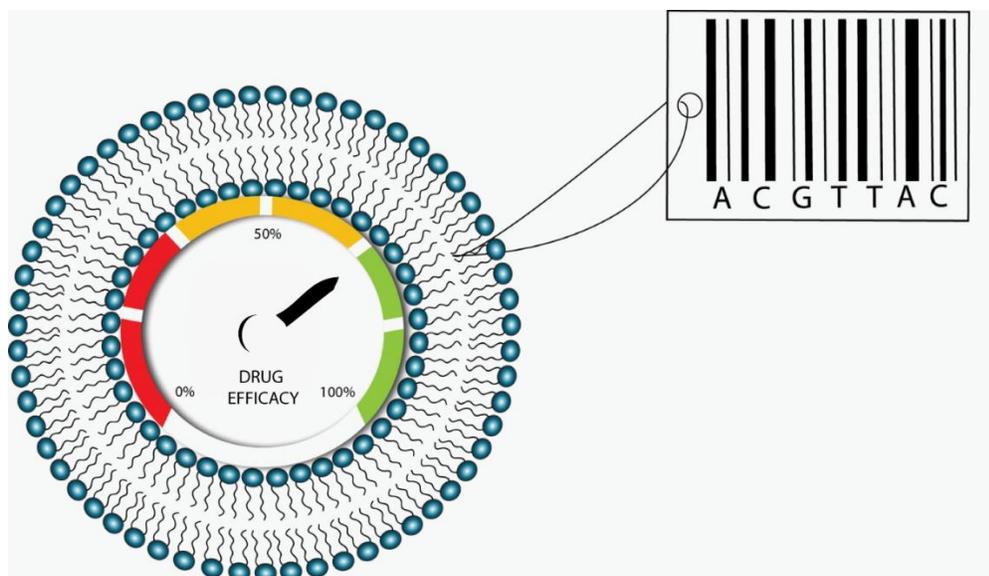
COLL 636

Theranostic carcoded nanoparticles personalize cancer medicine by predicting the drug response in the primary tumor microenvironment and in brain metastasis

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Personalized medicine promises to revolutionize cancer therapy by matching the most effective treatment to the individual patient. Using a nanoparticle-based system, we predict the therapeutic potency of anti-cancer medicines in a personalized manner. We carry out the diagnostic stage through a multi-drug screen performed inside the tumor, extracting drug activity information with single cell sensitivity. By using 100-nm liposomes, loaded with various cancer drugs and corresponding synthetic DNA barcodes, we found a correlation between the cell viability and the drug it was exposed to, according to the matching barcodes. Based on this screen, we devised a treatment protocol for mice bearing triple-negative breast-cancer tumors, and its results confirm the diagnostic prediction. Interestingly, we found that differernt We show that the use of nanotechnology in cancer care is effective for generating personalized treatment protocols.

Furthermore, different cell types in the tumor microenvironment responded differently to medication, each susceptible to different types and doses of the medicine. Metastasis, responded to medication depending on their biological site, but, in general, were more resistant to treatment compared to the primary tumor cells.



DNA was used as a barcode for labeling and detecting drug activity in single cells inside tumors and metastasis. Synthetic DNA strands were embedded in 100-nm liposome together with a corresponding drug to detect the most effective medicine for treating triple-negative breast cancer in a personalized manner.

COLL 637

Multimodal nanostructures as theragnostic agent in Alzheimer disease at early stages: PANA project

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Nowadays Alzheimer's disease (AD) is the main cause of dementia in developed countries. The rise in life expectancy and the progressive ageing of the population are leading to an increased social and economic burden due to this illness. Unfortunately, this data is expected to increase in the upcoming years.

Abnormal accumulation of intracellular tau protein and the extracellular aberrant deposits of beta-amyloid protein are the classic hallmarks of this disease. Traditionally the diagnosis and therapy efforts in this field were focused to one of these paths. All of these attempts failed to provide a suitable treatment because most of them, despite

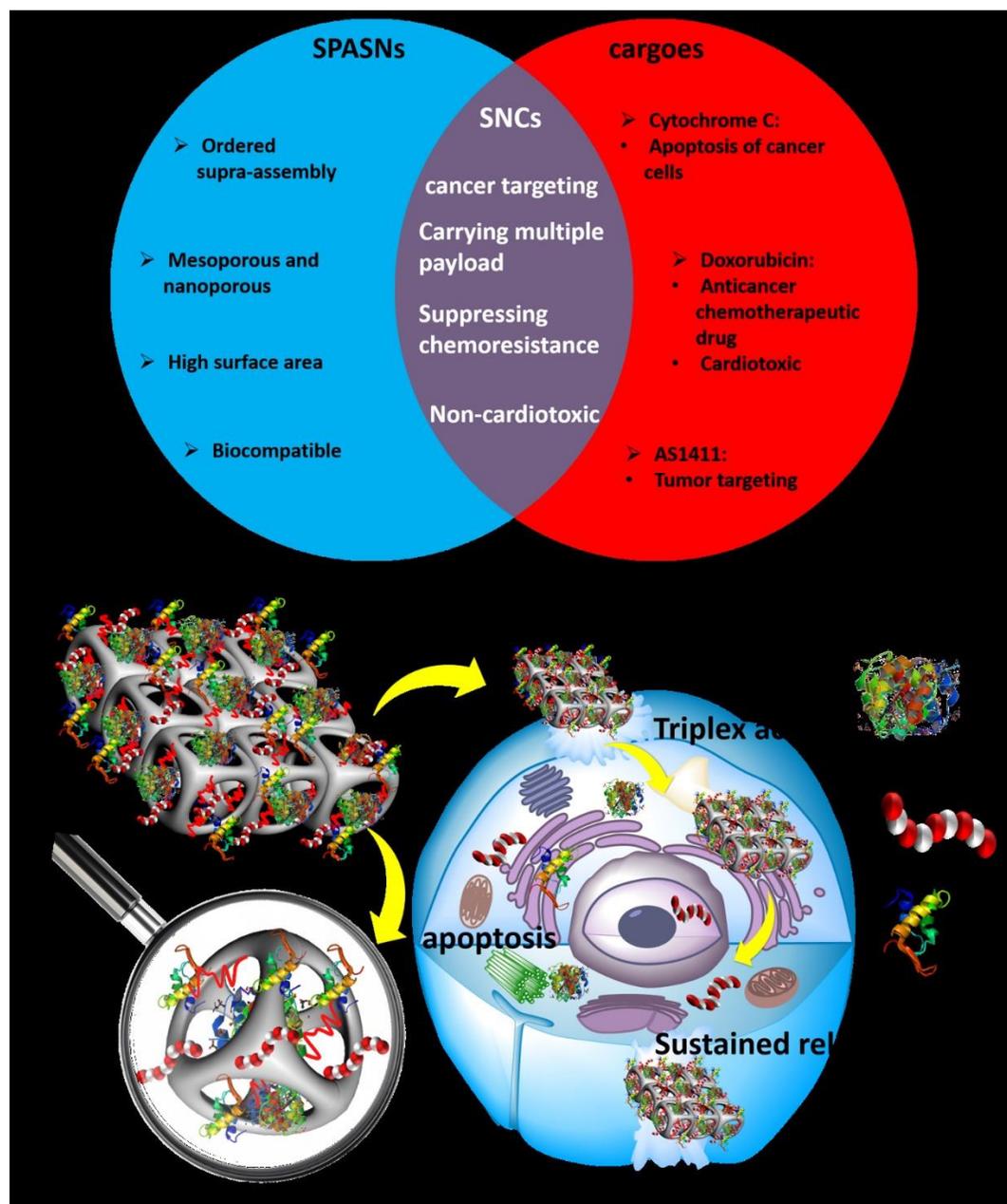
being a good strategy, were raised in an inappropriate time. Here we propose a theragnostic approach to overcome these limitations. Our goal is to achieve a multimodal and versatile nanoplatform compatible with several functionalizations which can be vectorised to an AD early stage biomarker, and used in non-invasive technologies as MRI and PET. Our aim is to take advantage of the iron oxide nanoparticles, which has been largely proved in biomedical applications due to their suitability as contrast agent and biocompatibility. For that purpose our nanoparticles are doped with zinc and manganese¹, stabilized with oleic acid/oleylamine in organic solvents, and transferred to the aqueous phase by an amphiphilic polymer coating (dodecyl-grafted-poly(isobutylene-alt-maleicanhydride, in the following referred to as PMA)². Modified-PMA confers colloidal stability to the NPs in high ionic strength media and provides several chemical groups (e.g., carboxyl, dibenzocyclooctyne, furfuryl, etc.) for further functionalization with other macromolecules, including homing antibodies, polyethylene glycol, and imaging agents as PET radiotracers and fluorescence markers.

COLL 638

Targeted delivery of supra-assembled nanocargoes *in vivo* to overcome the chemoresistance in colon cancer

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Chemotherapeutic drugs are often said to be more responsible for cancer patient's death than from cancers itself. Tumor cells develop resistance to chemotherapeutic drugs that lead to a failure or inefficient action of the drug on cancer cells and unregulated action on normal cells. Targeted intracellular drug delivery, enhancement of the drug payload and multimodal therapeutic actions within a short period of time have been proposed as means to overcome such chemiresistance. Nanomedicine approach using nanoscale drug delivery systems can offer an effective means of providing such therapy in tackling the drug resistance problem in cancer and is the focus of our study. Among the various nanomaterials/nanoparticles (NPs) used in nanomedicine, silica is one of the most employed and studied materials. Its structure allows tuning its surface chemical and physical properties with relative ease. The present investigation thus focuses on developing a single nanomedicine modality against colon cancer cells which have become resistant to chemotherapeutic drug doxorubicin (DOX). For this purpose, we have designed and synthesised a supra-assembly of cytochrome c (CytC), doxorubicin (DOX) and AS1411 aptamer loaded on ordered nanoporous structure of porous silica nanocargo (**Fig. 1.**). CytC is a multi-functional enzyme involved in life-sustaining energy production in one hand and cell apoptosis in the other. It thus act as a switching device between the life and the death of a cell. Nucleolin-binding aptamer AS1411 is a potential anticancer drug under phase II clinical trials. So, we hypothesise that cancer drug resistance can be successfully overcome by such nanocargos (SNCs) that synergistically combine the actions of CytC, AS1411 and DOX (triple action) in one supra-assembly on nano porous silica as the vehicle of the drug payload carrier.



COLL 639

Investigating tantalum nanoparticles for X-ray CT and therapeutic use

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Advancements in nanoparticle (NP) design can transform Computed Tomography (CT) into a robust molecular imaging platform. Various NPs based on Au, Bi, Ta, etc. have been investigated to substitute for iodine-based Contrast Agents (CAs) currently approved for clinical use. The drawback of CT is the low sensitivity of CT contrast agents; currently 10's mM is required for detection. As such, pre-amplified radiopaque contrast agents are necessary to realize the molecular imaging potential of CT. Nanocrystals (NCs) are such a pre-amplified system, with 1000's of radiopaque atoms per NC. The purpose of this work was to develop flexible and biocompatible, pre-amplified NCs and nanoparticles (NPs) for CT. Two different NP platforms were fabricated using Tantalum Oxide (TaO_x ; k-edge 67.4 keV) NCs as the X-ray dense component. TaO_x NCs with high Ta content (78%) were synthesized by a base-catalyzed sol-gel method. Encapsulation of bare NCs within mesoporous silica and PLGA was carried out to afford TaO_x @MSNPs and TaO_x @PLGA NPs, respectively. Both NP types were characterized for size, structure and composition using DLS, TEM, SEM, EDS and ICP-OES, and for biocompatibility in cell culture. The TaO_x NCs and NPs were also evaluated *in vivo*. Following IV injection in BALB/c mice, TaO_x NCs circulated in blood for ~3 hours, accumulating eventually in RES organs. Bolus IM injections of TaO_x @PLGA NPs and TaO_x @MSNPs produced significant contrast enhancement in BALB/c mice. We also report an intrinsic mesoporous structure for individual TaO_x NCs, similar to the intricate pore structure in MSNPs. Both TaO_x NCs and TaO_x @MSNPs displayed higher Doxorubicin Hydrochloride (DOX) loading as compared to empty MSNPs, with a programmable pH dependent DOX release over 72 h. This work shows considerable promise for TaO_x NCs/NPs in theranostics.

Synthesis, characterization, *in vivo* evaluation and drug loading/release for TaO_x NCs and NPs

COLL 640

Two-phase synthesis of gold-copper bimetallic nanoparticles of tunable composition

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Ultrasmall (3 nm or less) bimetallic nanoparticles with controllable compositions and structure are of great interest for their catalytic activity. Herein is reported a synthesis for bimetallic AuCu nanoparticles of tunable composition that takes advantage of complex-ion chemistry. These AuCu nanoparticles exhibit ultrasmall sizes (~ 2 nm) and the observed metal compositions are similar to the nominal metal ratios in the synthesis, roughly 3:1, 1:1, and 1:3 for Au:Cu. Oxidation state analysis of Cu was carried using XPS and showed that the 1:1 AuCu composition had greater percentages of Cu²⁺ than the other compositions as the particles aged but initially oxidation was not observed. This may suggest that the 1:1 Au:Cu composition forms a core-shell structure overtime with Cu in the shell while other compositions are suggested to be disordered alloys. The original capping agent for the nanoparticles, dodecanethiol, is complexed with sodium dodecyl sulfate to transfer the particles to the aqueous phase. Nanoparticles were synthesized for studies into catalytic and dissolution properties.

COLL 641

Tuning the frequency of localized surface plasmon resonances

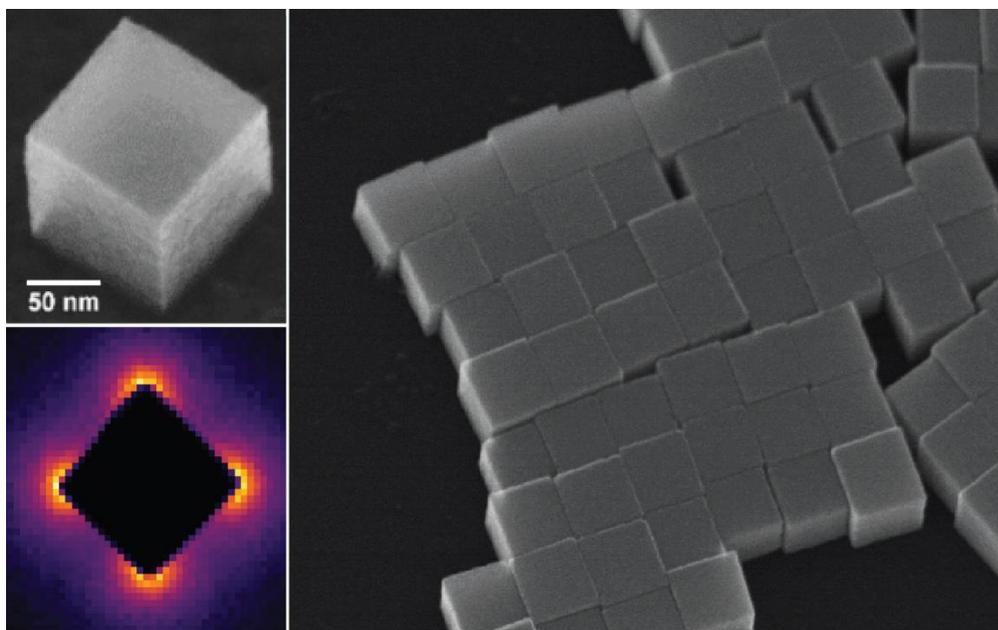
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Localized surface plasmon resonance research has been extended from noble metals to doped metal oxide nanoparticles. Unlike noble metal nanoparticles, the carrier density of metal oxide semiconductors can be tuned by doping. The ability to tune the plasmon frequency offers potential applications in optoelectronics and sensing. Here we present the tuning of the plasmon frequency of tin(IV) indium oxide nanoparticles through the near-IR by doping with gallium(III). Doping with gallium(III) results in fine-tuned control of the resonant frequency, as well as well-defined Vegard behavior in the nanoparticles. The LSPRs and optical band gaps are characterized by UV-Vis-NIR spectroscopy, while the crystal structure and Vegard behavior are studied via pXRD.

Syntheses of colloidal F:In₂O₃ cubes: Fluorine-induced faceting and infrared plasmonic response

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Cube-shaped nanocrystals (NCs) of conventional metals like gold and silver generally exhibit localized surface plasmon resonance (LSPR) in the visible region with spectral modes determined by their faceted shapes. However, faceted NCs exhibiting LSPR response in the infrared (IR) region are relatively rare. Here, we describe the colloidal synthesis of nanoscale fluorine-doped indium oxide (F:In₂O₃) cubes with LSPR response in the IR region, wherein fluorine was found to both direct the cubic morphology and act as an aliovalent dopant. Single crystalline 160 nm F:In₂O₃ cubes terminated by (100) facets and concave cubes were synthesized using a colloidal heat-up method. The presence of fluorine was found to impart higher stabilization to the (100) facets through density functional theory (DFT) calculations that evaluated the energetics of F-substitution at surface oxygen sites. These calculations suggest that the cubic morphology results from surface binding of F-atoms. In addition, fluorine acts as an anionic aliovalent dopant in the cubic bixbyite lattice of In₂O₃, introducing a high concentration of free electrons leading to LSPR. We confirmed the presence of lattice fluorine dopants in these cubes using solid-state ¹⁹F and ¹¹⁵In nuclear magnetic resonance (NMR) spectroscopy. The cubes exhibit narrow, shape-dependent multimodal LSPR extinction peaks due to corner- and edge-centered modes. The spatial origin of these different contributions to the spectral response are directly visualized by electron energy loss spectroscopy (EELS) in a scanning transmission electron microscope (STEM).



COLL 643

Electrochromic niobium oxide nanorods

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Niobium oxide (Nb_2O_5) is an interesting active material for diverse technologies ranging from catalysis and sensors to energy storage and electrochromic devices owing to its unique combination of optical, electronic, and electrochemical properties. These properties vary between different phases and morphology in the Nb_2O_5 system, but systematic studies that correlate properties to phase and morphology are limited by current synthetic methods, which require post-synthetic high temperature treatments and suffer from a lack of direct and precise control over morphology, crystal structure, and stoichiometry. Here, we report on a heat-up colloidal synthesis method that produces orthorhombic Nb_2O_5 nanorods with an aspect ratio of 1 nm in width by 31 nm in length that preferentially grow along the [001] direction. We found that the synthesis of nanorods does not proceed by aminolysis of niobium oleate, unlike conventional metal oxide nanocrystal synthesis, based on X-ray diffraction, Raman, and Fourier-transform infrared spectroscopy. Instead, the mechanism involves three distinct subsequent steps: formation of niobium oxo clusters by adding oleylamine into a niobium oleate solution, condensation into an amorphous Nb_2O_5 intermediate below the

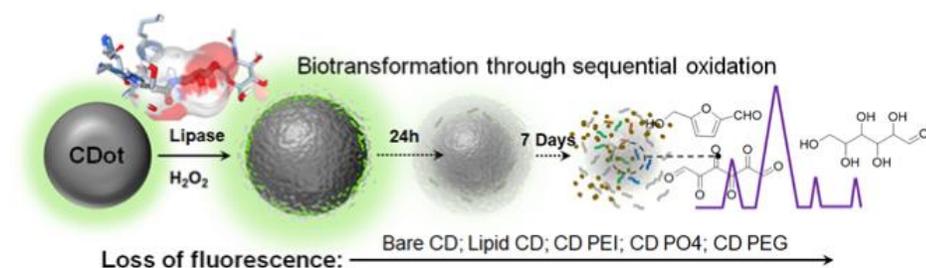
reaction temperature, and crystallization and growth of Nb₂O₅ nanorods. We investigated the electrochromic behavior of nanorod thin films upon Li⁺ intercalation and observed predominantly near-infrared plus modest visible modulation, fast switching kinetics, and durability for 500 charge-discharge cycles.

COLL 644

Lipase-catalyzed enzymatic biodegradation of carbon dots follows sequential oxidation pathways

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Carbon dots (CDs) have garnered significant recent attention owing to their excellent luminescence properties, thereby demonstrating a variety of applications for in vitro and in vivo imaging. Understanding the long-term metabolic fate of these agents in a biological environment is the focus of this work. Here we show that the CDs undergo peroxide catalyzed degradation in the presence of lipase. Our results indicate that differently charged CD species exhibit unique degradation kinetics upon being subjected to enzyme oxidation. Further, this decomposition correlates with the relative accessibility of the enzymatic molecule. Using multiple physicochemical characterizations and molecular modeling, we confirmed the interaction of passivating surface abundant molecules with the enzyme. Finally, we have identified hydroxymethyl furfural as a metabolic by-product of CDs used here. Our results indicate the possibility and a likely mechanism for complete CD degradation in living systems that can cover the way for a variety of biomedical applications.



Lipase Catalysed Biotransformation of Carbon Dots. Enzymatic biodegradation in the presence of H₂O₂ follows sequential oxidative pathway where intermediates are identified by MALDI-TOF Spectroscopy.

COLL 645

Green synthesis of palladium nanomaterials via biological templates using TMV and BSMV virus-like particles

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Naturally occurring biomolecules are used to generate monodisperse nanomaterials where, especially by the use of self-assembling biological structures are used to form for ordering inorganic materials into one-dimensional metal nano-structures (nanorods and nanowires)., biotemplating has become a promising mean in bottom-up nanofabrication. The self-assembly of virus-like particles (VLPs) as biotemplates are used to understand the underlying mechanisms governing bottom-up nanofabrication. Genetically engineered Tobacco Mosaic Virus (TMV) and Barley Stripe Mosaic Virus (BSMV) VLPs produced from *Escherichia Coli*. are served as biotemplates in the synthesis of metal nanorods. The recent work has focused on customizing the lengths of BSMV VLPs to meet the multiple applications ranging from electronics, sensing, optics, catalysis and cancer therapy. A hydrothermal solution process in the absence of external reducing agents is performed in the high yield synthesis of more monodisperse/uniform palladium nanomaterials with controllable shapes. The visualization of purified VLPs and the metal coated VLPs via biomineralization are monitored with characterization techniques such as UV-Vis spectroscopy, X-ray absorption spectroscopy and transmission electron spectroscopy. Overall, BSMV VLPs produced from the bacterial expression system is a promising biotemplating candidate with the enhanced stability and the malleability of genetic modification of novel functionalities.

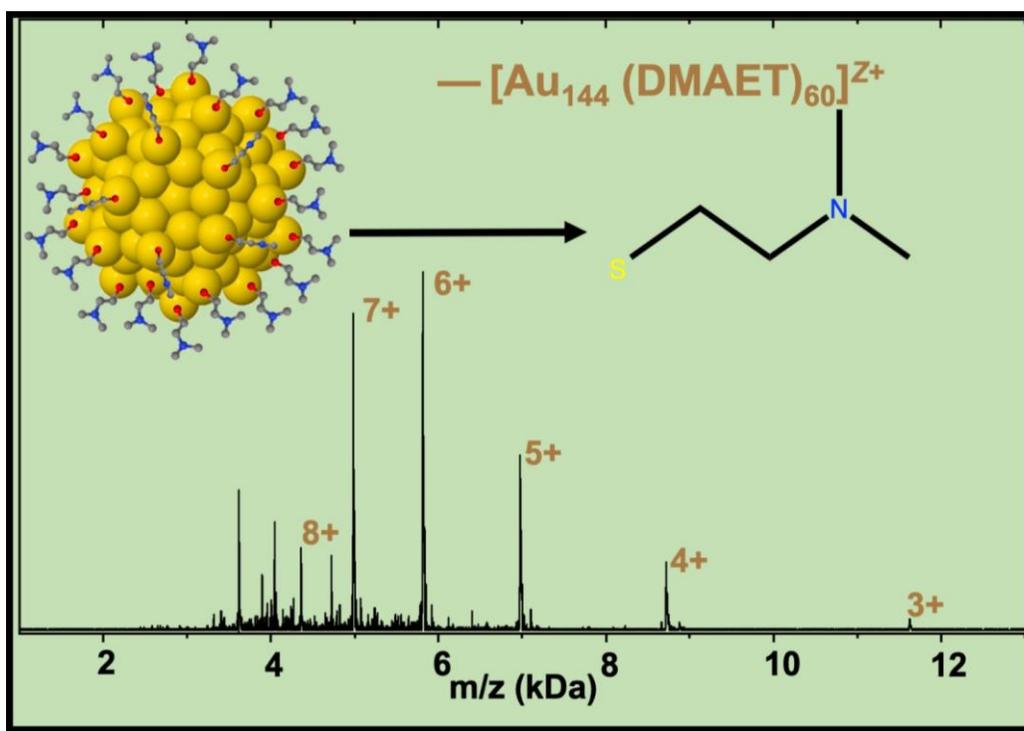
COLL 646

Precision thermal and reaction control leads to selective formation of amphiphilic cationic gold clusters in the critical size range, n = 130-146 Au atoms [1.6-nm core diameter]

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Ubiquitous Au₁₄₄(SR)₆₀(~ 29 kDa), where -SR represents thiolate, is the most studied clusters since its discovery in 1996. Now a days these MPCs are being used as a scaffold for various ways, ranging from fundamental study to applications in biology. These clusters are either water soluble, typically mercaptobenzoic acid/glutathione protected; or organic soluble, typically alkanethiol or 2-phenylethanethiol protected.

Organic soluble clusters are preferable for fundamental studies because they are easy to handle, and can be readily studied using analytical tools, whereas aqueous phase is required for biological applications. However, ionization of aqueous clusters for higher charge states is challenging, though there are some reports of highly charged clusters' evidence from ESI-MS analysis, either by ligand exchange or intrinsically charging the core. We report herein, the direct synthesis captamine, a tertiary amine, protected $\text{Au}_{144}(\text{SR})_{60}$ clusters that promises to overcome these challenges due to its amphiphilic nature and solubility in both aqueous and organic phase upon contact with acid or base in the solution. We report the ESI-MS analysis of ions up to 8+ charge state without any special ion-pairing agent, UV-Vis spectra for optical absorbance analysis, XRD and STEM HAADF characterization to show size distribution and morphology.

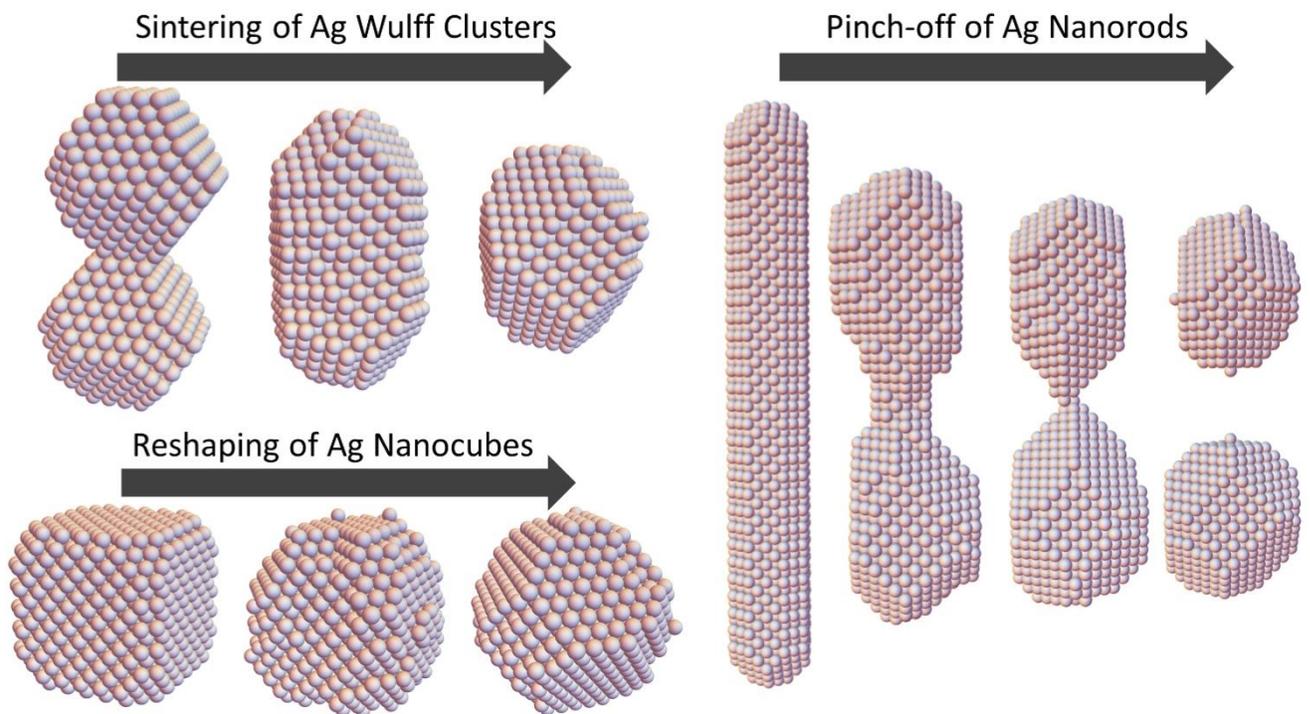


COLL 647

Reshaping and sintering of 3D fcc metal nanocrystals: Stochastic atomistic modeling with realistic surface diffusion kinetics

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Controlled synthesis of metallic nanocrystals allows tuning of shapes and thus properties for applications, e.g., to catalysis and plasmonics. However, these shapes are metastable. Far-from-equilibrium evolution back to equilibrium Wulff shapes is mediated by surface diffusion, and is highly sensitive to the numerous atomistic-level diffusion barriers for diverse local surface configurations. Thus, realistic description of surface diffusion kinetics is thus crucial to predict the stability of non-equilibrium nanocrystal shapes, a prerequisite for functionality in applications. A stochastic lattice-gas model was developed incorporating realistic values for the multiple barriers for terrace, edge, and interlayer diffusion (contrasting previous generic bond counting prescriptions) based upon insights from homoepitaxial film growth. [Phys. Rev. Materials **3** (2019), 026001] In this talk, we will describe the model, and apply kinetic Monte Carlo (KMC) simulations to assess: reshaping of Ag nanocubes to Wulff polyhedra mediated by nucleation of new {100} facets; the pinch-off of sufficiently elongated Ag nanorods; and key aspects of sintering for orientationally-aligned Ag or Au nanoclusters. The time scale for sintering of ~ 4 nm Au nanoclusters observed in HR-TEM studies was also recovered.



Snapshots from KMC simulations of Ag nanocrystal shape evolution

Site-selective carving and co-deposition: Transformation of Ag nanocubes into concave nanocrystals encased by Au-Ag alloy frames

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We report the seed-mediated transformation of the Ag nanocube into Ag@Au-Ag concave nanocrystals, a nanostructure with six concave side faces decorated by Au-Ag alloy frames at the edges and corners. The synthesis was performed by titrating aqueous H₂AuCl₄ into an aqueous mixture of Ag nanocubes, ascorbic acid (H₂Asc), NaOH, and cetyltrimethylammonium chloride (CTAC) at an initial pH of 11.6 under ambient conditions. The use of CTAC at sufficiently high concentration enabled the site-selective carving of the Ag atoms from the side faces through galvanic replacement. Specifically, the CTAC-derived Cl⁻ ions played three key roles: (1) they would preferentially bind to the side faces of Ag nanocubes and direct the galvanic replacement reaction to that site; (2) they would maintain the Au(III) species as AuCl₄⁻ to facilitate its galvanic replacement with the Ag atoms; and (3) they would complex with the released Ag⁺ ions into AgCl₂⁺ species that are soluble. Concurrently, both the AuCl₄⁻ and AgCl₂⁻ species would be reduced by the ascorbate monoanion, generated from the neutralization of H₂Asc by NaOH, to Au and Ag atoms for their preferential co-deposition onto the edges and corners of the Ag nanocubes. As the Ag atoms continue to be carved out from the side faces and the Au and Ag atoms continue to deposit on the edges and corners of the Ag nanocube, we could eventually obtain the Ag@Au-Ag concave nanocrystals. We evaluated that the Ag@Au-Ag concave nanocrystals exhibit stronger SERS activity compared with Ag nanocubes at an excitation of 785 nm, making it feasible to monitor the Au-catalyzed reduction of 4-nitrothiophenol by NaBH₄ *in-situ*. By removing the Ag cores from the concave nanocrystals, we could obtain Au-Ag nanoframes with controllable ridge thicknesses.

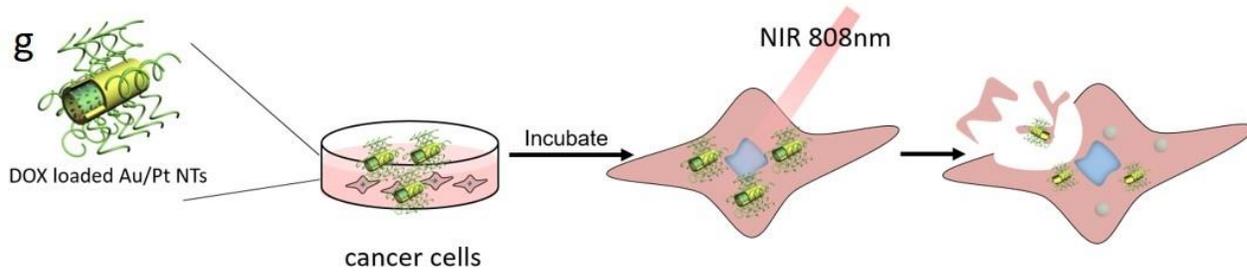
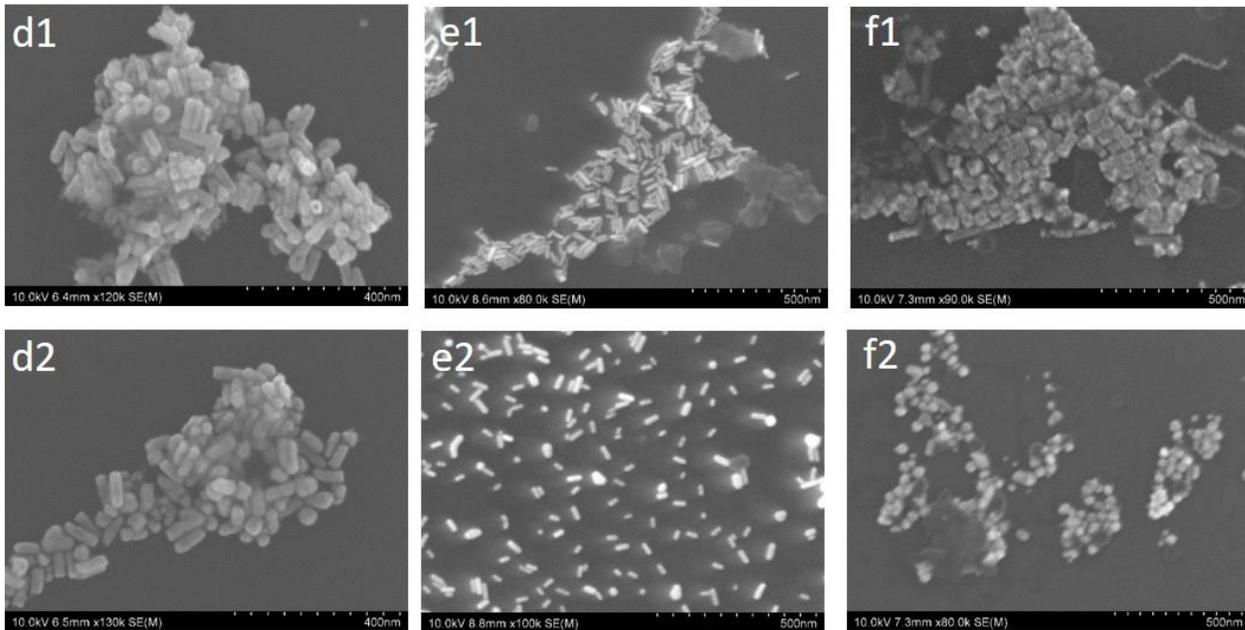
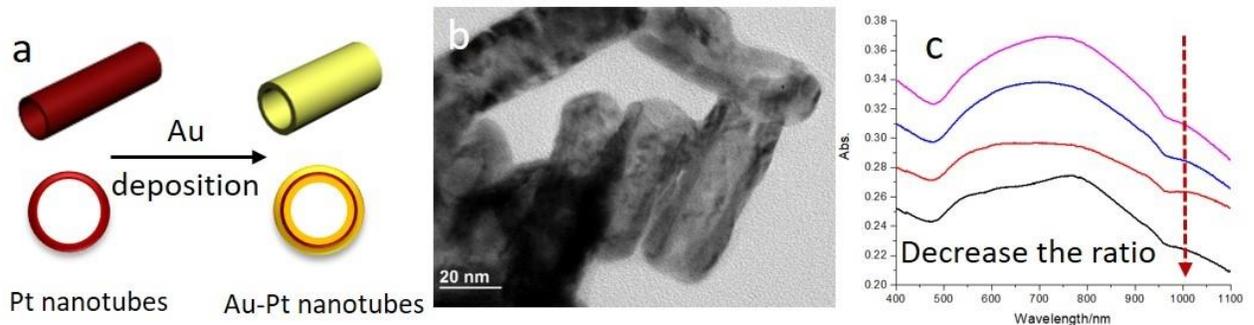
COLL 649

Synthesis of Au-Pt coaxial nanotubes with high photothermal stability for chemophotothermal therapy

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Cancer has been one of the most pervasive and malignant diseases nowadays. Laser photothermal therapy (PTT), which ablates tumor cells via laser-induced hyperthermia, has been proven as an effective and non-invasive therapeutic method. Various nanomaterials have been investigated as photothermal transduction agents (PTAs); however, the following prerequisites must be fulfilled: 1. High biocompatibility and low toxicity to the local tissue environment; 2. High photothermal conversion efficiency; 3. Absorption ranges that fall in the NIR window I (650nm-900 nm); 4. High photothermal stability, allowing PTAs to maintain their structural integrity and related absorption under

cycles of laser irradiation. Gold (Au) nano-materials are favored as PTAs for their well-known biocompatibility and low toxicity with the advantages of tunable NIR absorption and high photothermal conversion efficiency. However, its photothermal stability has been under questioned. Here, we developed a Au-based multifunctional chemo-photothermal PTA with improved photothermal stability and investigate its potential application in chemo-photothermal synergistic cancer treatment. A gold-platinum (Au-Pt) coaxial nanotube structure was synthesized by employing a template-guided method (Fig. a and b). The tunability of absorption was realized by adjusting ratio between the wall thickness and diameter of the inner cavity (Fig. c). The photothermal stability results showed that the Au-Pt nanotube can maintain their shape integrity after several laser irradiation cycles as shown in Fig. d1 and d2, comparing with pure Au nanorods and Au nanocages (Fig. e1 and e2, Fig. f1 and f2 respectively), which are popular PTAs in the field. Anticancer drug doxorubicin was loaded in the nanotube structure. The Au-Pt nanotube showed excellent synergistic photothermal-chemo therapeutic effect to cancer cells under laser irradiation (Fig. g).

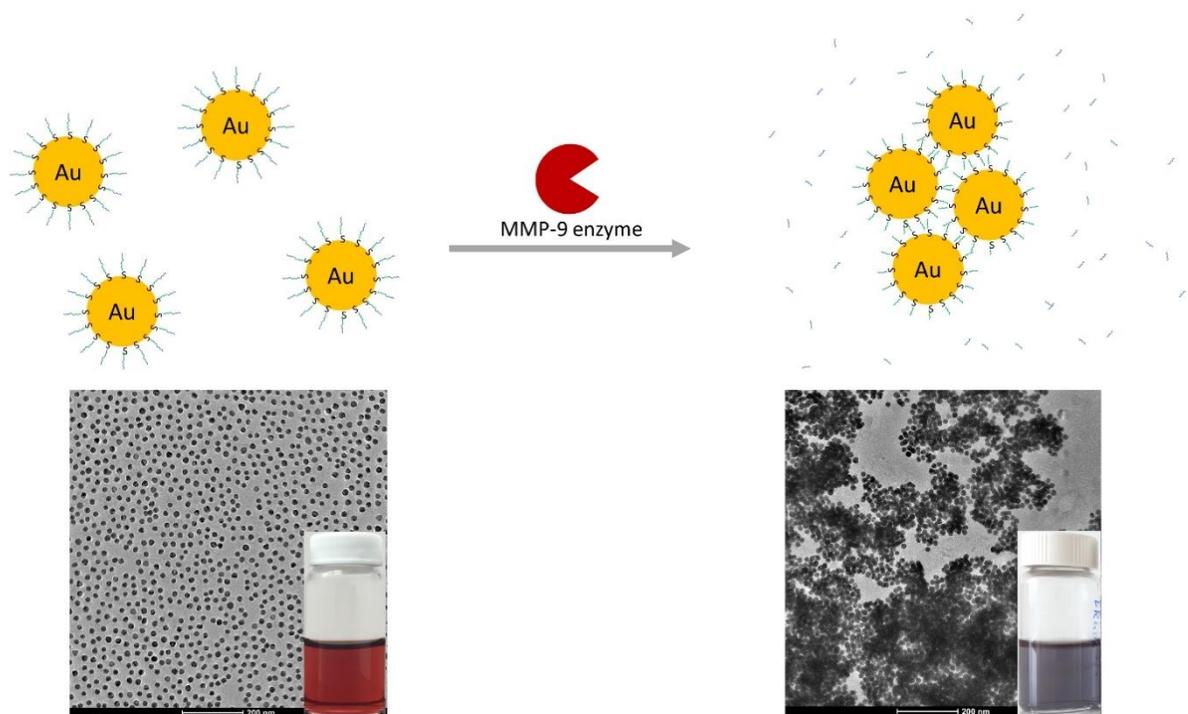


COLL 650

Enzymatically activated aggregation and cell-adhesion of peptide-nanoparticle conjugates selectively target tumor tissue with enhanced delivery efficiency

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The nanotechnology community has put tremendous efforts on developing new materials that can be engineered to selectively target tumor tissue. One critical challenge that researchers find is to ensure that the administered nanoparticles reach and accumulate at the tumor tissue, because organs in the mononuclear phagocytic system and renal clearance pathway compete with the tumor for nanoparticles. However, the delivery efficiency of these novel nanomaterials to targeted tumor sites has remained poor in the past decade. One of the key challenges to increase delivery efficiency is to prolong the blood circulation time of administered nanomaterials by avoiding interactions with competing organs. To achieve this, we developed a multifunctional nanoparticulate model that is only activated when reaching the tumor environment, while stays deactivated elsewhere in the bloodstream. Short peptides with an enzyme-responsive linker which incorporates a cryptic adhesive ligand are immobilized onto gold nanoparticles (GNP) and recognized and cleaved by collagenase MMP-9. MMP-9 is overexpressed by malignant tumor cells and plays a central role in metastatic cancer progression by degrading proteins in the extracellular matrix (ECM). The hydrophobic enzymatic product retained on the surface of GNP trigger nanoparticle self-assembly. Moreover, the RGD motif on the enzymatic product binds preferentially to $\alpha_v\beta_3$ integrins which are protein receptors overexpressed on tumoral endothelial cells primarily during angiogenesis. The advantage of this design is that the peptide-functionalized GNPs remain an inactive state through the blood circulation and become active once they enter the tumor ECM, hence exposing the RGD surface for cell binding. This active targeting mechanism can reduce the binding of RGD to non-tumoral integrins and increase the specific binding of the nanoparticles to tumor.



Schematic illustration of enzyme-triggered gold nanoparticle aggregation. TEM images show the states of gold nanoparticles before and after enzyme treatment.

COLL 651

Molecular layer deposition: Mechanisms of vapor-phase organic thin-film synthesis

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Molecular layer deposition (MLD) is an increasingly popular process for the growth of organic ultrathin films. This vapor-phase, layer-by-layer technique, which relies on the same principle of self-limiting surface reactions as atomic layer deposition, has shown promise for the development of many applications that require conformal organic-containing coatings, such as in diffusion barriers, photoresists, and porous catalysts. Despite recent developments in MLD, there is still a significant gap in our understanding

of the mechanisms behind MLD growth and the microscopic properties of MLD-grown films, such as the origin of the film growth rate or their molecular-level structure. In this presentation, we present results of our recent studies to understand such mechanisms, and discuss how that understanding can be used to better control the properties of these materials.

First, we discuss our exploration of the growth behavior of MLD films by examining trends in film properties as a function of backbone flexibility [1]. Our results suggest that changes in growth rate between the most rigid and most flexible backbones (4 Å/cycle vs 1 Å/cycle) are not caused by differences in length of molecular precursors, chain orientation, or film density, but are instead caused by an increased frequency of terminations in the more flexible chemistries. These terminations likely result from monomers reacting with more than one functional group on the underlying surface, which reduces the total number of available reactive sites. We further elaborate on the relationship between the number of reactive sites and the film growth rate by modeling growth behavior after an intentional reduction in the number of reactive sites [2]. We show that terminations caused by dual-reacting monomers reduce the film growth rate; however, the adsorption of monomers likely reintroduces reactive sites, preventing the complete cessation of film growth. Finally, we discuss the structure of films by examining crystal orientation and infrared absorption data, which suggest that films consist of a mixture of upward growing chains and horizontally aligned layers of paracrystalline polymer segments [1]. Combined, these results provide a clearer picture of MLD film growth and provide insight for the design of future ultrathin film synthesis chemistries.

COLL 652

Amphiphilic conjugated polymers for nanoparticle stabilization

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Solution-processable semiconducting materials in organic solar cells (OSCs) enable the roll-to-roll printing of functional devices. However, the dissolution of these materials commonly requires toxic solvents, thus hindering the translation to industry. To enable large scale printing in industry, they should be formulated as inks using a less toxic medium such as alcohol or even water.

Researchers have fabricated OSCs by dispersing semiconducting materials in water/alcohol with the help of surfactants. However, significant surfactants remained in the active layer even after extensive dialysis, reducing the device performance and solar cell life-time. Recently, devices were fabricated using a dispersion of poly-3-hexylthiophene (P3HT) with indene-C₆₀ bisadduct (ICBA) in methanol and showed a 3.8% device efficiency without the need of a surfactant. However, in this case, the performance was highly dependent on the batch of polymer used for dispersion. Hence,

there is a requirement of an appropriate surfactant which not only controls the size of nanoparticles but also increases nanoparticle stability whilst maintaining device efficiency.

To address this problem, we synthesized P3HT end-capped with pyridine. We expected this pyridine-P3HT to be protonated on addition of acid and act as a surfactant by making an electrical double layer around the nanoparticles, inducing a repulsive interaction and preventing aggregation, however under thermal annealing the pyridinium salt would decompose removing all trace of the acid. By using a combination of 3 wt% pyridine-P3HT and trifluoroacetic acid as additives, stable P3HT:ICBA nanoparticle dispersions of up to 30 mg/mL in methanol were achieved. The nanoparticles in these dispersions were 120 ± 5 nm, and the dispersions were stable up to 60 days. Inverted architecture OSC built using these nanoparticle dispersions exhibited 3.4% efficiency, a result that is comparable to the state-of-the-art P3HT:ICBA solar cells fabricated under optimized conditions using chlorinated solvents.

COLL 653

Multiscale analysis of the doping-driven wettability of two-dimensional materials

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Engineering molecular interactions at two-dimensional (2D) materials interfaces enables new technological opportunities in functional surfaces and molecular epitaxy. Understanding the wettability of 2D materials represents the crucial first step towards quantifying the interplay between the interfacial forces and electric potential of 2D materials interfaces. Here we develop the first theoretical framework to model the wettability of the doped 2D materials by properly bridging the multiscale physical phenomena at the 2D interfaces, including: (i) the change of 2D materials surface energy (atomistic scale, several Angstroms), (ii) the molecular reorientation of liquid molecules adjacent to the interface (molecular scale, $10^0 \sim 10^1$ nm), and (iii) the electrical double layer (EDL) formed in the liquid phase (mesoscopic scales, $10^0 \sim 10^4$ nm). The latter two effects are found to be the major mechanisms responsible for the contact angle change upon doping, while the surface energy change of a pure 2D material has no net effect on the wetting property. When the doping level is electrostatically tuned, we demonstrate that 2D materials with high quantum capacitances (e.g., transition metal dichalcogenides, TMDCs) possess a wider range of tunability in the interfacial tension, under the same applied gate voltage. Furthermore, practical considerations such as defects and airborne contamination are also quantitatively discussed. Our analysis implies that the doping level can be another variable to modulate the wettability at 2D materials interfaces, as well as the molecular

packing behavior on a 2D material- coated surface, essentially facilitating the interfacial engineering of 2D materials.

COLL 654

Investigating physico-chemical properties of dynamically crosslinked nanopatterned hydrogels

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Hydrogels are hydrophilic, porous, swollen polymers with properties (mechanical) that depend upon environmental and fabrication conditions. Devices with topographical nanostructures, such as arrays of nanopillars less than 1000 nm tall, have historically been difficult to fabricate on hydrogels. The relationship between shape and stability remains elusive and a point of research interest.

In this study, a biocompatible chitosan hydrogel was fabricated with nanopillar arrays having periodicities of 300 - 500 nm. Chitosan is a derivative of chitin, the second most abundant polysaccharide in nature. We studied the effect of crosslinking and nanopattern surface area to maintain geometric stability and mechanical integrity on chitosan films. We avoid using common harsh cytotoxic crosslinkers -- instead utilizing crosslinkers such as tripolyphosphate (TPP) and genipin. TPP is a physical, ionic crosslinker; while genipin is a chemical crosslinker derived from gardenia flower.

While dry, the nanopillars have a defined shape and are mechanically robust, but when wet become swollen, altering the characteristics of the films. We found the water content was strongly dependent on both the crosslinker and nanopillar geometry. Simply measuring the equilibrium swelling and changing nanopillar periodicity from 300 nm to 500 nm shows a 25% increase in water content. In this presentation, we report on results to determine whether this change is due to crosslink density, surface area, or crosslink type using mechanical testing, AFM, UV-Vis, and DSC.

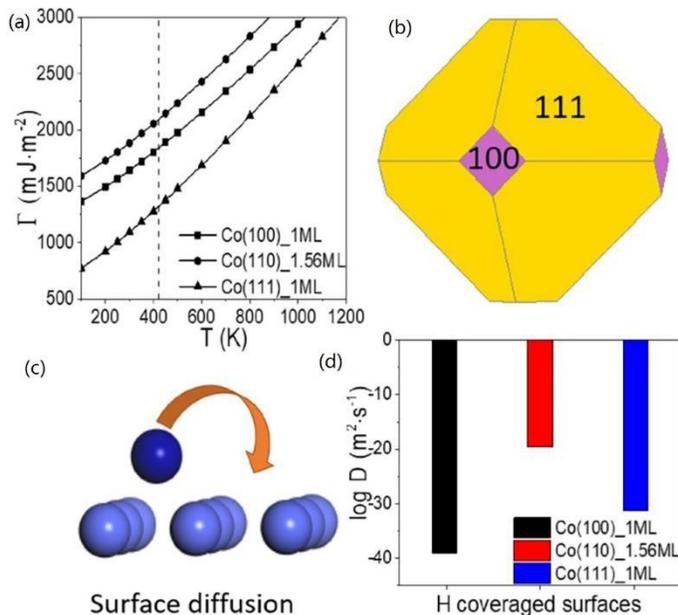
COLL 655

Thermodynamic and kinetic roles of H₂ on shape-controlled urchin-like Co: A DFT study

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Small gas molecules acting as structure-directing agents (SDAs) play important roles in controlling the morphologies and surface structures of metal nanocrystals. In present work, the thermodynamic and kinetic roles of H₂ played on the morphology of Co

nanocrystals were systematically investigated by density function of theory (DFT). The Gibbs surface free energies of Co(100), Co(110), and Co(111) at different hydrogen surface coverages (θ_H) and the phase diagram of stable θ_H on each surface were calculated, based on which the morphology evolutions of Co nanocrystals under various θ_H were obtained. It was found that the H_2 working as SDA could alter the facet stability. Thermodynamically, Co nucleus exhibited the most stable structure at θ_H of [1-1.5-1] ML for (100) / (110) / (111) facets, respectively. Kinetically, the addition of H_2 could influence the surface diffusions of the adatoms Co. The related diffusion energy barriers and diffusion coefficients were further calculated and compared with each other under different θ_H . Finally, much higher surface free energies of Co(100) associated with much lower Co adatom surface diffusion rate on Co(100) under $\theta_H = 1$ ML cooperatively lead to the atomic Co being preferably deposited on Co(100) and overgrowing along the [100] direction to produce the urchin-like structure.



(a) The lowest Gibbs surface energy of Co(100), Co(110) and Co(111) at 423 K, (b) Wulff shape of the most stable condition, (c) pathway of the surface diffusion of adatom and (d) the highest diffusion coefficients of Co(100), Co(110) and Co(111), respectively.

COLL 656

Development of next-generation materials for hybrid electro-optic systems

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Recent developments in hybrid electro-optic (EO) systems, in which an organic material with an ultra-large second-order susceptibility is combined with silicon (SOH) or gold (POH) waveguides at the nanoscale, have enabled breakthrough EO performance in systems that can be implemented on silicon-on-insulator (SOI) wafers. Tight confinement of the optical and RF fields in hybrid devices has enabled operating frequencies >300 GHz and voltage-length parameters ($U_{\pi}L$) < 40 V- μm with existing high-performance organic electro-optic (OEO) materials. However, achieving $U_{\pi}L$ values on the order of 1 V- μm will require a new generation of OEO materials. The short path lengths within hybrid devices greatly alleviate concerns about optical loss, enabling development of OEO chromophores with extraordinarily large hyperpolarizabilities and refractive indices at telecom wavelengths. However, as device dimensions shrink, chromophore-surface interactions, space-efficiency, and refractive index anisotropy become more critical. Addressing these challenges requires a combination of theory-aided molecular design to improve hyperpolarizability, chromophore order and thermal stability; development and evaluation of surface coatings to improve material compatibility and poling behavior; as well as spectroscopic and electro-optic characterization of new chromophores. We apply these techniques and experimental methods to develop a new generation of OEO materials intended to improve the performance of hybrid devices and enable chip-scale integration.

COLL 657

Monodisperse magnetic silica hexapods

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A simple yet versatile solution-based process to produce colloidal silica hexapods is developed in which various shapes of silica rods are grown on the faces of cubes in a controlled manner. In the presence of hematite cubic particles, water droplets nucleate on the surface of hematite by phase separation in pentanol. By adjusting the water concentration, six droplets can form on each face of the hematite cube. A silica precursor is then administered into the system, which gradually diffuses into the water droplets through the oil phase. Within the droplets, hydrolysis and condensation of the precursors take place, leading to formation of silica rods. As a result, silica hexapods on a magnetic hematite cubic seed are produced. Furthermore, when the emulsions are aged at 60 °C prior to the silica growth, the water content in the solution decreases gradually due to evaporation and spiky sharp hexapods are produced. On the other hand, when organosilane precursor is added, pancake-like hexapods are formed due to the reduction of interfacial tension. These colloidal hexapods can further be utilized as new building blocks for self-assembly to construct functional materials or as a model system to understand collective behaviors.

Additive-free processing of carbon nanotubes in cresols as dispersions, pastes, gels and dough

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Carbon nanotubes can now be produced in the ton scale as powders, but they need to be further processed, usually by solution-based routes, into disaggregated and more usable forms for applications. Extensive efforts have been made to search and design solvents that can disperse nanotubes, which can also be easily removed afterwards. Here we report that cresols, a group of naturally occurring and massively produced methylphenols with broad uses in the chemical industry, are surprisingly good solvents for processing carbon nanotubes. They can disperse carbon nanotubes of various types at unprecedentedly high concentrations of tens of weight percent, without the need for any dispersing agent or additive. Cresols interact with carbon nanotubes by charge-transfer through the phenolic hydroxyl proton, and can be removed after processing by evaporation or washing, without altering the surface of carbon nanotubes. Cresol solvents render carbon nanotubes polymer-like rheological and viscoelastic properties and processability. As the concentration of nanotubes increases, a continuous transition of four states can be observed, including dilute dispersion, thick paste, free-standing gel, and eventually a kneadable, playdough-like material. As demonstrated with a few proof-of-concepts, cresols make powders of agglomerated carbon nanotubes immediately usable by various material processing techniques to create desirable structures, form factors and for making their polymer composites.

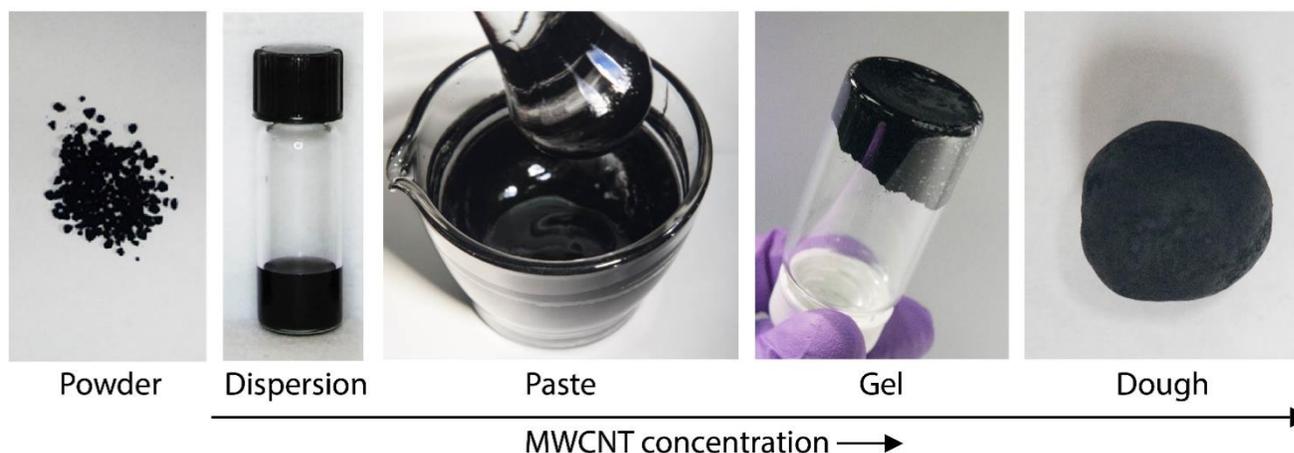


Figure 1: Four continuous states of MWCNT in *m*-cresol exhibiting polymer solution like rheological and viscoelastic properties. The nanotube powders can be processed in *m*-cresol to yield dilute dispersion, thick paste, self-standing gel, and finally kneadable dough.

COLL 659

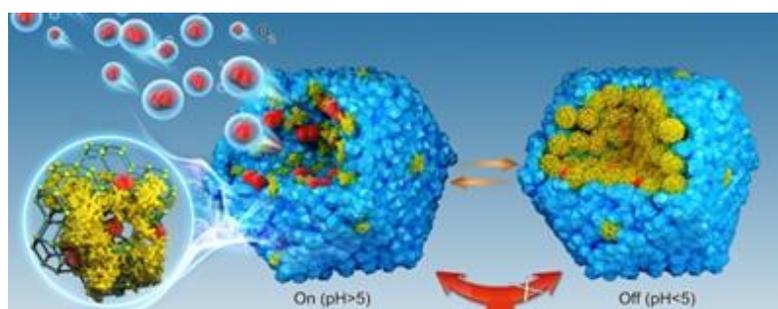
Biocatalytic porous frameworks with reversible pH-gated speed regulation for smart micromotors

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Abstract Summary: Synthetic nano/micromotors are a class of materials with vast promise for applications ranging from environmental remediation to nanomedicine. To our knowledge this study represents the first example of chemically driven metal-organic framework (MOF) micromotors with rapid, reversible pH-responsive motility.

Introduction: Chemically driven self-propelled nano/micromotors have been receiving increasing attention for drug delivery¹, biosensing² and medical imaging. However, it is difficult to tune the propulsive speed of synthetic chemically driven motors. Therefore, there is a growing effort to engineer stimulus-responsive speed control mechanisms into synthetic motors for various applications.

Results and discussion: In this work, we in-situ co-encapsulated the catalase and succinylated β -lactoglobulin into MOF, using peroxide as biofuels to generate oxygen bubbles to propel micromotors (Schematic). Here, we demonstrate the motion of MOF micromotors is precisely tuned by the pH-induced reversible protein conformational change within the frameworks that act as a gate keeper to control the access of chemical fuels. More importantly, the dual pH and H_2O_2 responsiveness in the micromotor system for programmed degradation and release of payload can offer more precise control to deliver drugs to the cells³.

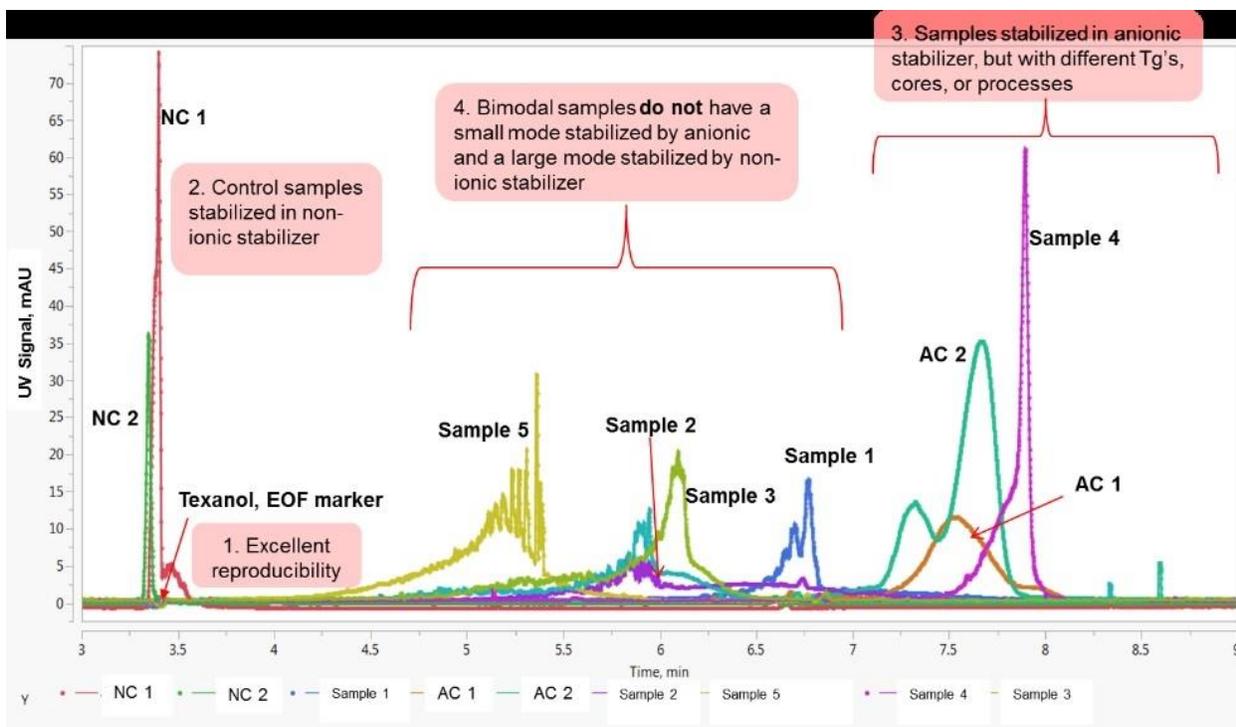


COLL 660

Characterization of core-shell latex particles by capillary electrophoresis

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Latex particles with core-shell structures are of great interest in industry as the design provides improved stability, better water-proofing, and enhanced adhesion properties. Three types of latexes, with (1) anionic stabilizer, (2) nonionic stabilizer, and (3) both anionic and nonionic stabilizers have been investigated in this study. Capillary zone electrophoresis (CZE) is an advanced separation technique with superior separation efficiency. Although most particle separation technologies focus on particle sizing, CZE has a unique advantage of separating particles based on both size and charge. The latter allows us to explore the surface composition and chemistry of latexes, which are of ultra-importance in understanding their behaviors in industrial products. In the current study, we first demonstrated that CZE was able to separate latexes with similar size, indicating their different surface chemistries. Moreover, CZE was successfully applied to study the interaction between nonionic stabilizer and latex particles. By analyzing latexes both chemically synthesized with the nonionic stabilizer and incubated with the nonionic stabilizer post-reaction, we found that the nonionic stabilizer interacted with the particle surface through both chemical grafting and physical adsorption. Lastly, CZE results showed that both the large and small modes of these latex particles had very similar electrophoretic mobility, indicating that the two modes either had significantly different surface charge densities or morphologies. AFFFF was then employed to obtain particle size and particle molar mass. The determined apparent densities of the two modes from AFFFF-MALS-RI measurement proved that the modes had different morphologies, which confirmed the finding of CZE.



COLL 661

CO₂-responsive polymer nanoparticles

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Poly(2-dimethylamino) ethyl methacrylate (PDMAEMA) with narrow molecular weight distributions were prepared by atom transfer radical polymerizations in this study and were investigated as a CO₂-triggered emulsifier for emulsion polymerizations of CO₂-responsive poly(methyl methacrylate)(PMMA) core-shell nanoparticles in water. PDMAEMA and PMMA nanoparticles were characterized by ¹H NMR, SEM, particle size, UV-vis, GPC, DSC, and Zeta potentials. The results found that the synthesized PMMA nanoparticles were coated with about 15 wt% PDMAEMA and had diameters of about 125 nm. These core-shell nanoparticles exhibited CO₂/N₂-responsive dispersion/aggregation behavior in aqueous solutions. The CO₂-responsive behavior was associated with the tertiary amine groups of PDMAEMA which was on surface of PMMA nanoparticles. Upon bubbling CO₂ in aqueous solution, the tertiary amine groups were protonated resulting in hydrophilic and water-soluble PDMAEMA and thus water-dispersible PMMA nanoparticles. Upon bubbling N₂ in aqueous solution, CO₂ could be removed and the PMMA nanoparticle dispersion reverted to aggregation. A higher molecular weight of PDMAEMA led to a faster CO₂-responsive dispersion but a

slower N₂-responsive aggregation of the PMMA nanoparticles. This newly developed synthetic system offers a highly efficient route for the fabrication of highly effective stimuli-responsive polymer nanoparticles that enable more precise control over the composition, physical properties, and environmentally responsive performance of nanoparticles in aqueous solution.

COLL 662

Soft nanocomposite hydrogel microspheres with defined nanostructures

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Hydrogel microspheres (microgels) are composed of cross-linked hydrophilic polymer chains, and due to their fascinating properties, they found variety of applications including sensors, catalysts, and coatings.¹ To realize and develop such applications, we developed a series of hydrogel/hydrophobic nanocomposite microgels synthesized by seeded emulsion polymerization in the presence of microgels (SEPM).²⁻⁶ We believe that the study of nanocomposite microgels will lead to understand the role of local micro-hydrogel environment, such as polarity and hydrophobicity. In this presentation, we will present the impact of charge distribution in seed microgels on the structure of resultant nanocomposite microgels. Different from microgels whose charged groups are localized at their center, polystyrene nanoparticles were formed inside the core microgels when microgels whose charged groups were localized on their surface were used as cores for SEPM (Figure(a)). The nanostructures are also dependent on monomer concentration during SEPM; water-swollen microgel was occupied by hydrophobic polystyrene (Figure(b)). Additionally, the size and morphology of the composites were tuned by surfactants (Figure (c)).³ From these results, we concluded that styrene monomer can penetrate into polyelectrolyte hydrogel layer, however, resultant polystyrene nanoparticles do not favor combination with polyelectrolyte hydrogels,⁴ which allows us to design the morphology of composite microgels.⁴⁻⁶

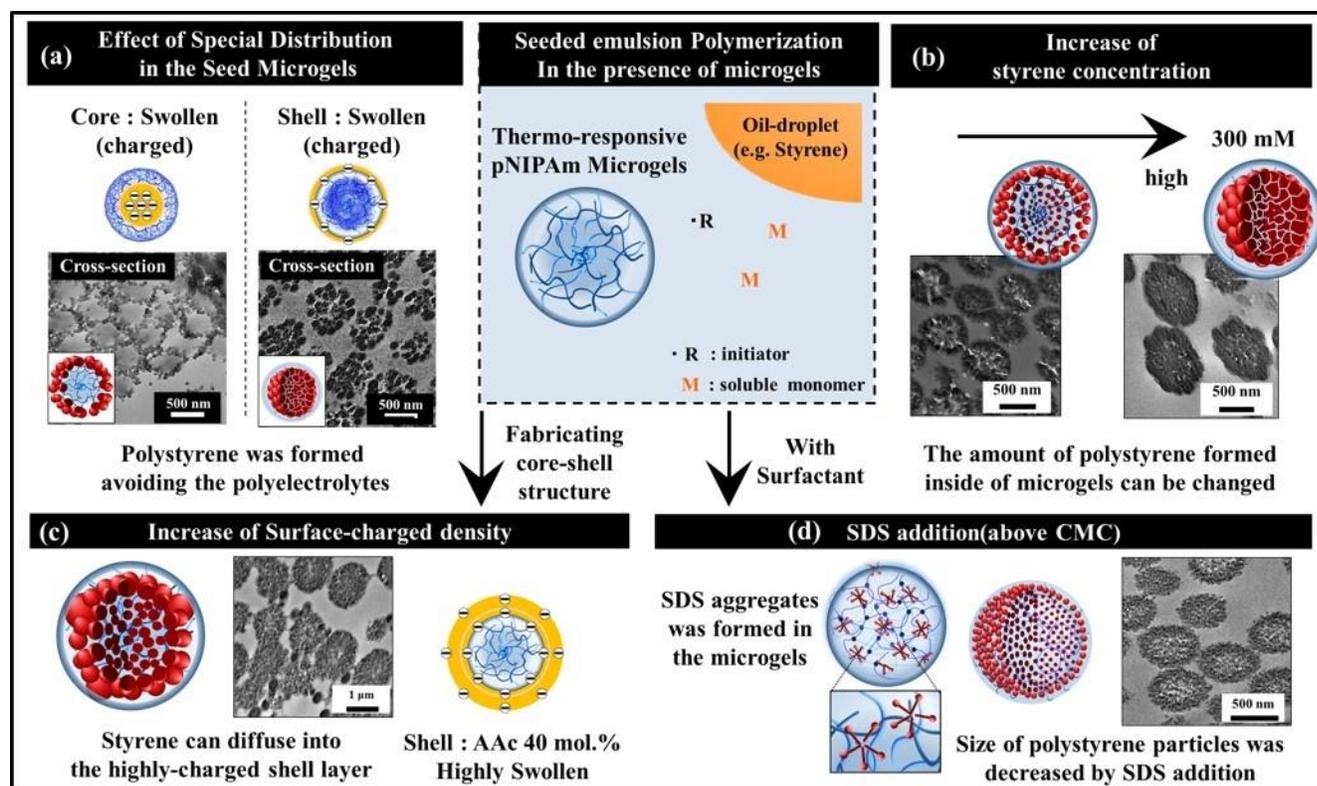


Figure. Summary of this study.

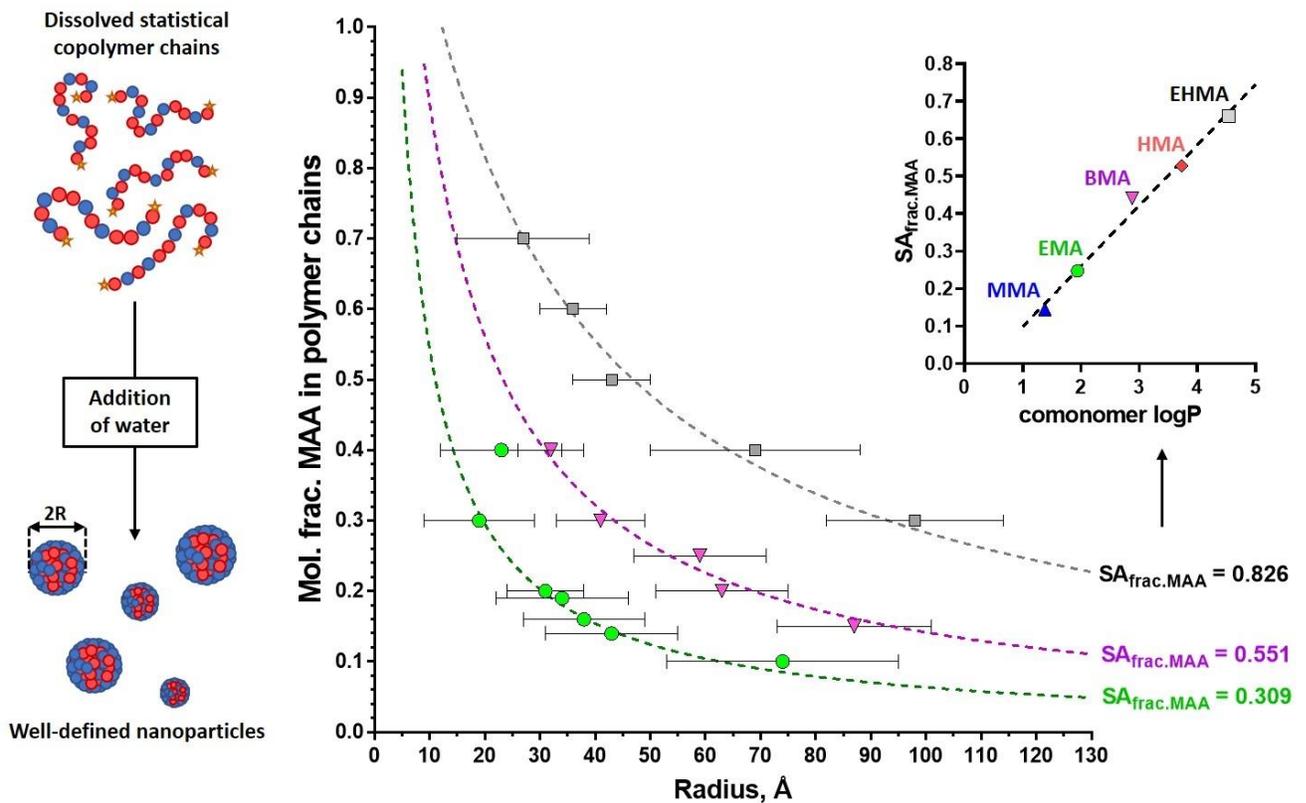
COLL 663

Tuning composition and hydrophobicity of ionic statistical amphiphilic copolymers to control and predict copolymer particle size

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A range of amphiphilic statistical copolymers was synthesized using reversible addition-fragmentation chain transfer (RAFT) solution polymerization where the hydrophilic component was methacrylic acid and the hydrophobic component was one of a variety of a hydrophobic methacrylic ester monomers with different carbon chain lengths and in turn different hydrophobicity and logP values. The hydrophobic monomers investigated were methyl, ethyl, butyl, hexyl, and 2-ethylhexyl, methacrylate where they increase in hydrophobicity respectively. Small-angle X-ray scattering (SAXS) studies showed that these copolymers aggregate into well-defined spherical particles on dilution with water where the size of the particle was highly composition dependant. Furthermore, varying the hydrophobic group also influenced the self-assembly where a more hydrophobic monomer induced a larger particle size. A contrast matching small-angle neutron

scattering (SANS) experiment was used to investigate the internal structure of these particles and found that the copolymers arrange within the particle to locate MAA onto the surface causing pseudo-phase separation and a BMA-rich core. Finally, a mathematical model based around surface charge density stabilization was used to describe the relationship between the copolymer composition and the particle size formed. The model fits well with the experimental data collected across all the investigated systems and showed a linear relationship between the surface charge density needed to achieve stabilization and the logP of the hydrophobic component in the copolymer. This finding allows the particle size of similar amphiphilic statistical copolymers to be predicted accurately based upon the copolymer composition and the hydrophobicity of the hydrophobic component, therefore, making these types of systems a cheaper and highly viable alternative to diblock copolymer nano-particles currently used in industrial applications.



Structure property correlations, gelation, mechanical, and thermal properties of molecular gels derived from *N*-phenyloctadecanamides and *N*-(phenylalkyl)octadecanamides as molecular gelators

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Molecular gels are semi-solid like viscoelastic materials consists of low concentration of a gelator (low molecular mass compound) and a liquid. This presentation will summarize the self-assembly, structure and properties of molecular gels derived from *N*-phenyloctadecanamides and *N*-(phenylalkyl)octadecanamides as molecular gelators. The nature of the self-assembly and gelation properties including critical gelator concentrations, gel-sol transition temperatures, thermodynamic, and mechanical properties will be presented. Many of these derivatives gelate water (hydrogel) and many organic liquids (organogels) as well as exhibit thixotropic properties. These results show that simple structural modifications of *N*-phenyloctadecanamides and *N*-(phenylalkyl)octadecanamides derivatives can cause very large changes in the properties of their gels.

We thank Prof. Richard Weiss (Georgetown University) for the use of rheometer and polarizing optical microscope.

COLL 665

Evaluation of thermoresponsive structural changes in hydrogel microspheres by high-speed atomic force microscopy

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Hydrogel microspheres (microgels) are hydrophilic polymeric particles that can respond rapidly to external stimulus owing to their colloidal size dimensions. Thus, microgels are expected to find numerous applications such as molecular separation, drug-delivery vehicles and sensors. Up to now, the stimulus-responsive behavior of the microgels has been mainly investigated by scattering techniques, calorimetry, sensors, and so forth. However, these techniques provide ensemble-averaged information for the entire system. In order to obtain deeper insight into the stimulus-responsive behavior of individual microgels, a combination of conventional techniques and real-time direct observation is important. In this study, we applied high-speed atomic force microscopy (HS-AFM) to visualize dynamic behavior of individual microgels at nanoscale in real time. Here, we investigated thermoresponsive behavior of poly(*N*-isopropyl acrylamide) (pNIPAm) based microgels prepared by precipitation polymerization by combining dynamic light scattering (DLS) and HS-AFM observation.

Figure (a) shows the temperature dependences of the normalized height of the microgels obtained from the HS-AFM images (nonequilibrium states) and the normalized hydrodynamic diameter (D_h) of the microgels determined by DLS (equilibrium states). The tendencies of the thermoresponsive behavior for the normalized height and D_h of the microgels were similar, indicating the rapid stimulus-responsiveness of microgels. Notably, domain structure (several tens of nanometer in size) was observed in the microgels even below the volume phase transition temperature (VPTT, $\sim 35^\circ\text{C}$) of the microgels (Figure (b)) and became clear with deswelling of the microgels. In this presentation, further investigations regarding the domain formation in the microgels synthesized under the different polymerization conditions will be discussed.

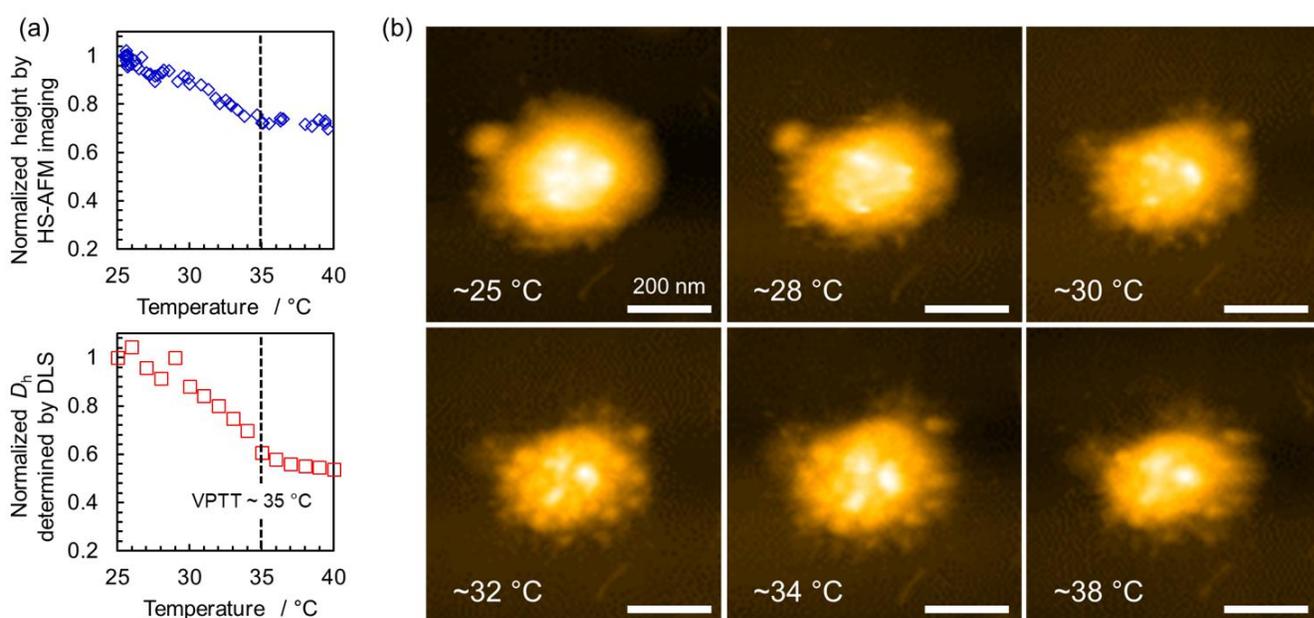


Figure. (a) Temperature dependence of normalized height (above) and normalized D_h (below). (b) HS-AFM images of pNIPAm based microgels during heating.

COLL 666

Formulation of new responsive and self-repairing magneto-capillary gels

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Reconfigurable materials have been a topic of intensive scientific interest recently due to their tunability in engineering the material response to stimuli and thus their potential applications in numerous fields such as coatings and catalysts. Magnetic-field-directed assembly of nanoparticles, for example, allows for the remote control of the particles' assembly and even structural self-repairing as well as the generation of anisotropic nanostructured materials. Polymer capillary suspension can transition from highly elastic to gel-like depending on the amount of immiscible secondary liquid. We will report how the control of the capillary forces and magnetic interactions can be used to form new smart gel systems. We will describe two types of such Magnetically Responsive Capillary Gels (MRCGs). In MRCG Type 1, the magnetic nanoparticles (MNPs) are dispersed in the liquid phase that forms capillary bridges between the polydimethylsiloxane microspheres. MRCG Type 2 is constituted of magnetically responsive elastomer microbeads with internally embedded MNPs. We will present the characterization of these gels in terms of rheology, magnetic response, and the ability to self-repair. This ongoing research demonstrates how capillary forces can be used as a basis for magnetically-directed assembly of magneto-capillary gels. We were able to show operational capillary bridging forces at a dense gel scale and demonstrated that an external magnetic field could direct the aggregation of the system through a magnetic response. We established that the formation of capillary bridges between PDMS microbeads via the addition of a secondary, immiscible fluid will lead to gel-like behavior. We proved that both MRCGs exhibit the property of magnetic-field-induced self-repair. We characterized the properties of the gels with respect to rheology, magnetic properties, and ability to re-assembly application. We will discuss how these gels can be used in the formulation and testing of new classes of soft, responsive, and multifunctional matter.

COLL 667

New cationic sterically-stabilized diblock copolymer nanoparticles exhibit exceptionally high salt tolerance in aqueous media

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For certain commercial applications such as enhanced oil recovery, sterically-stabilized colloidal dispersions that exhibit *extreme* salt tolerance are desirable. Herein we report a series of cationic nano-objects that display high colloidal stability in highly salty aqueous media. More specifically, various binary mixtures of poly(*N'**N'*-dimethylacrylamide) (PDMAC) and poly(2-(acryloyloxy)ethyl trimethylammonium chloride) (PATAC) chains were chain-extended with diacetone acrylamide (DAAM) *via* reversible addition-fragmentation chain transfer (RAFT) aqueous dispersion polymerization at 70 °C to produce (n PATACx + 1-n PDMACy) - PDAAMz diblock

copolymer nano-objects at 20 % w/w solids via polymerization-induced self-assembly (PISA). TEM analysis confirms that systematic variation of the mean degrees of polymerization (x, y and z) of each block and the mole fraction of the cationic PATAC (n) enables the formation of well-defined cationic spheres, worms or vesicles. The cationic character of the spheres can be tuned simply by varying the mole fraction of PATAC (n) for fixed x, y and z values, as indicated by aqueous electrophoresis. SAXS analysis indicates that the mean diameter can be adjusted by varying z (for fixed n, x and y). Remarkably, dynamic light scattering studies confirmed that highly cationic spheres prepared using PATAC as the sole steric stabilizer remained well-dispersed in the presence of 4 M KCl. Similarly, cationic worms and vesicles prepared using binary mixtures of PATAC and PDMAc remained stable up to 1 M KCl. Such systems are expected to be useful models for understanding the behavior of aqueous colloidal dispersions in the presence of high salt.

COLL 668

Preparation of fluorescent microspheres with conjugated polymers

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Fluorescent microspheres are greatly demanded in many applications based on suspension array technology, such as immune assay, disease diagnosis, drug screening and so on. In general, these microspheres are required to be uniform in size at micrometer scale, have strong and even emission as well as surface reactive sites for interacting with analytes. In addition, different sets of microspheres with different optical codes are also indispensable in the multiplex assay. Here we report our research about the preparation of fluorescent microspheres by introducing conjugated polymers onto the monodispersed substrate spheres. Two types of conjugated polymers were employed, poly(phenylene vinylene (PPV) and poly(arylene ethynylene) (PAE), synthesized via the Wessling method and Sonogashira coupling, respectively. The PPVs were coated onto the substrate microspheres by adsorption of the positively charged PPV polymer precursor (pre-PPV) onto the negatively charged substrate spheres via electrostatic interaction, followed by thermal elimination to convert pre-PPV into fluorescent PPV. The PAEs were introduced onto the spheres via chemical reaction. The tuning of emission color to give different optical codes and introduction of reactive sites were realized. Confocal microscopy and flow cytometry were used as the main characterizations for these spheres. The interaction and reaction between the polymers in solution and substrate spheres will also be discussed.

COLL 669

Synthesis of well-defined, pyrrolidone-based homopolymers and stimulus-responsive diblock copolymers via RAFT aqueous solution polymerization of 2-(N-acryloyloxy)ethylpyrrolidone

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Poly(*N*-vinylpyrrolidone) (PNVP) is a well-known, highly polar, nonionic water-soluble polymer. However, *N*-vinylpyrrolidone (NVP) usually exhibits strongly non-ideal behavior when copolymerized with methacrylic or styrenic monomers. Moreover, NVP is not particularly well-controlled under living radical polymerization conditions. For these reasons, alternative pyrrolidone-based monomers have been investigated. For example, the reversible addition–fragmentation chain transfer (RAFT) polymerization of 2-(*N*-methacryloyloxy)ethylpyrrolidone (NMEP) has been recently investigated using various polymerization formulations. However, PNMEP homopolymers are significantly less hydrophilic than PNVP and exhibit inverse temperature solubility in aqueous solution. In the present work, we studied the RAFT aqueous solution polymerization of 2-(*N*-acryloyloxy)ethylpyrrolidone (NAEP) using either AIBN at 70 °C or a low-temperature redox initiator at 30 °C. PNAEP homopolymers are obtained in high yield (>99%) with good control ($M_w/M_n < 1.20$) for target degrees of polymerization (DP) of up to 400 using the latter initiator, which produced relatively fast rates of polymerization. However, targeting DPs above 400 led to lower NAEP conversions and broader molecular weight distributions. 2-Hydroxyethyl acrylate (HEA) and oligo(ethylene glycol) methyl ether acrylate (OEGA) were chain-extended using a PNAEP_x macro-CTA via RAFT aqueous solution polymerization, yielding double-hydrophilic acrylic diblock copolymers with high conversions (>99%) and good control ($M_w/M_n < 1.31$). In addition, a PNAEP₉₅ macro-CTA was chain-extended via RAFT aqueous solution polymerization of *N*-isopropylacrylamide (NIPAM) at 22 °C. Dynamic light scattering (DLS) analysis indicated that heating above the lower critical solution temperature of PNIPAM led to so-called “anomalous micellization” at 35 °C and the formation of near-monodisperse spherical micelles at 40 °C. Finally, 2-(diethylamino)ethyl methacrylate (DEA) was polymerized using an *N*-morpholine-functionalized trithiocarbonate-based RAFT chain transfer agent and subsequently chain-extended using NAEP to form a novel pH-responsive diblock copolymer. Above the pK_a of PDEA (~7.3), DLS and ¹H NMR studies indicated the formation of well-defined PDEA-core spherical micelles.

COLL 670

Competitive interactions in confined environments

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Confinement manifests itself in a wide array of chemical systems, and can derive from both structural and chemical origins that introduce competitive interactions that alter dynamic behavior. In recent years, generalized features of confinement have emerged from multimodal spectroscopic characterization, as well as multiscale modeling and simulation. This includes trends in how different solvents respond to confinement, as well as hierarchically organized structural behavior and dynamic response at

characteristically different time scales. Herein, we will compare and contrast these trends and make comparisons of solvents adsorbed in porous materials to solvents trapped in highly structured fluids.

COLL 671

Modeling of the hydration of nanoporous materials by machine learning

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Nanoporous materials (e.g., zeolite, activated carbon, metal-organic framework, polymeric membranes, etc.) have various technological applications, including gas separation, gas storage, catalytic transformations, etc. The functionalities of nanoporous materials strongly depend on their pore size and shape distribution—which present virtually limitless degrees of freedom. Here, based on high-throughput simulations and machine-learning-based pattern recognition algorithms, we present a framework allowing us to predict the water sorption isotherm of hydrophilic and hydrophobic nanoporous materials. This framework allows us to conduct the inverse design of optimal porous microstructures featuring tailored sorption isotherms.

COLL 672

Computer modeling of water adsorption and water-mediated proton conduction in metal-organic frameworks

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Metal-organic frameworks have recently attracted much interest as promising materials for water generation and purification, proton conduction, and molecular sensing. Contrary to other porous materials like zeolites, MOFs are highly tunable, which implies that it is possible to rationally design the framework properties, including both pore size and shape, for specific applications. In this talk, I will present our results from advanced molecular dynamics simulations that are used to develop a microscopic picture of the mechanisms associated with water adsorption and water-mediated proton conduction in different MOFs. Particular focus will be on the analysis of both guest and framework properties as a function of temperature, guest loading, and pore size/shape, which are characterized in terms of specific spectroscopic signatures.

COLL 673

Out-of-the-box implicit solvation at dielectric interfaces

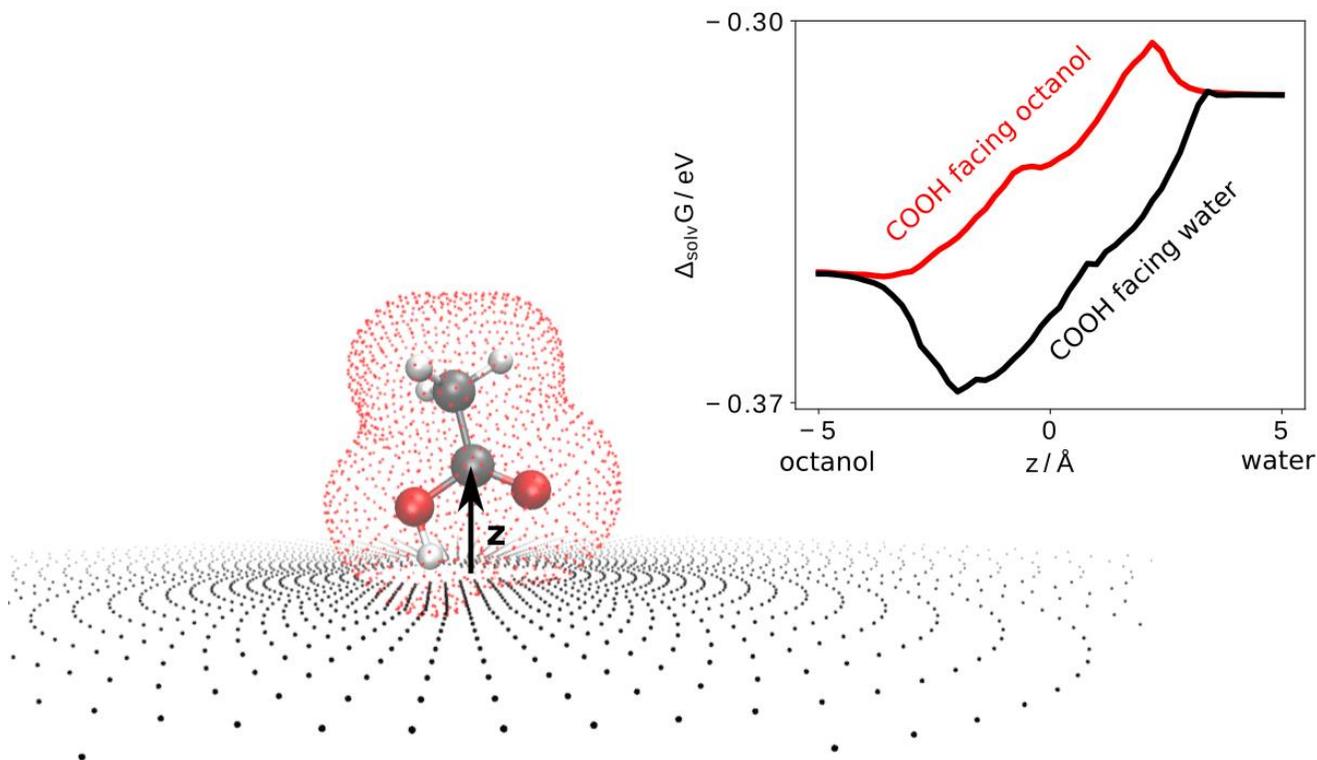
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Implicit solvation models are widely used to incorporate solvent effects in electronic structure theory. Treating the solvent as a structureless dielectric continuum, they lift the necessity to explicitly sample solvent degrees of freedom. Recently, various efforts have been made to extend such models to heterogeneous dielectric environments.

In our work we modify the multipole expansion (MPE) model to also account for dielectric interfaces, specifically focusing on the electrostatics of mutually interacting dielectric regions. The resulting method shows remarkable robustness and computational efficiency over a wide range of dielectric media and solute molecules, opening the way to include it in molecular simulations packages as an out-of-the-box functionality. The necessary input is restricted to a small set of experimentally accessible, macroscopic quantities and model parameters, which need to be determined only once for each solvent.

Non-electrostatic free energy contributions thereby are treated with a simple linear model, fitted to experimental free energies of solvation in the two liquids. We demonstrate the efficacy of this approach for small molecules at a water–1-octanol interface, which show the correct qualitative behaviour with respect to orientation and position at the interface.



Bottom left: Acetic acid molecule at an interface between water (bottom) and 1-octanol (top). The boundaries between the implicit solvent cavity and the continua, as well as between the two media are discretized into a finite set of points. Top right: Free energy of solvation plotted against distance of the C atom of the carboxylic group to the interface plane, with the polar group facing octanol (red) and water (black). Of the sampled positions, the one with the smallest free energy is shown in the bottom left.

COLL 674

Polarizable molecular simulations reveal how silicon-containing functional groups govern the desalination mechanism in nanoporous graphene

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A highly polarizable molecular mechanics force field model was developed for simulating reverse osmosis desalination by graphene nanopores passivated by SiH₂ and Si(OH)₂ functional groups of various sizes and geometries. The simulated water fluxes and ion rejection percentages are explained using detailed atomistic mechanisms derived from analysis of the simulation trajectories. Our main findings are: (1) The Si(OH)₂ pores possess superior ion rejection rates due to selective electrostatic repulsion of Cl⁻ ions, but Na⁺ ions are attracted to the pore and block water transfer. (2) By contrast, the SiH₂ pores operate via a steric mechanism that excludes ions based on the size and flexibility of their hydration layers. (3) In the absence of ions, water flux is directly proportional to the solvent accessible area within the pore; however, simulated fluxes are lower than those inferred from recent experimental work. We also provide some hypotheses that could resolve the differences between simulation and experiment.

COLL 675

Water at charged interfaces: Localized vs. delocalized charges

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Confined water, as well as water in contact with a solid surface may have properties substantially different from those of the bulk, strongly modulated by the surface charges and surface hydrophobicity/hydrophilicity. Both structural and dynamical properties can be strongly affected. As an example, I will discuss the structural and dynamical properties of water at the interface with calcium/fluorite over a wide range of pH conditions using Density functional theory (DFT) -based molecular dynamics

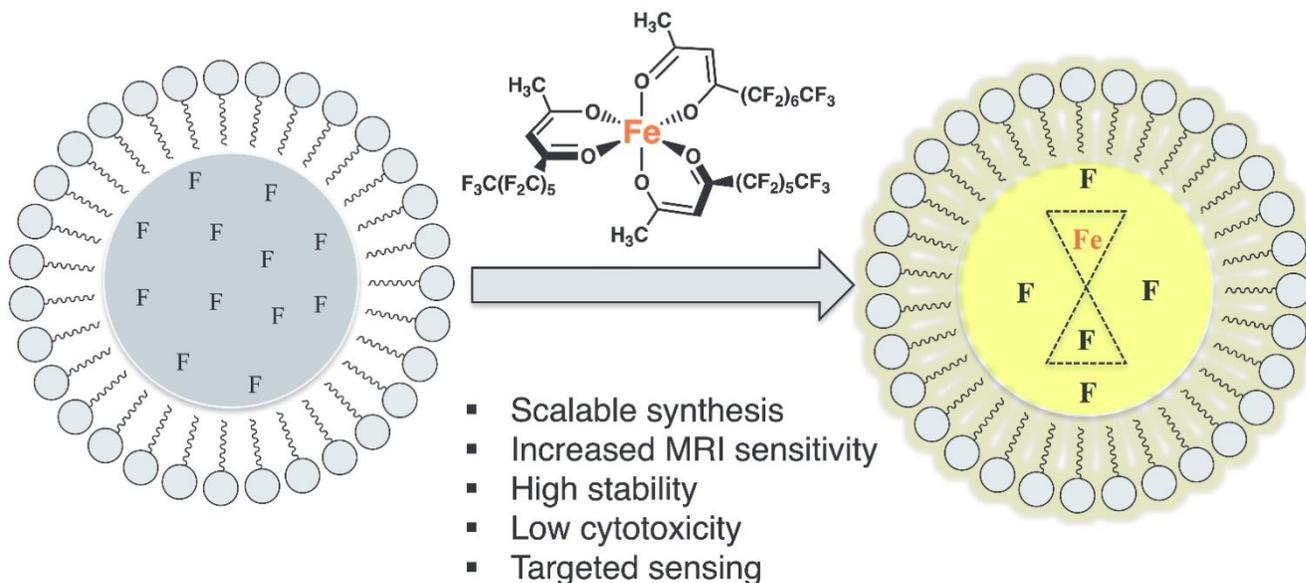
simulations as well as force field simulations. In the case of low pH, the presence of localized charges on the surface gives rise to a well-ordered water layer, where vibrational energy relaxation can occur on time-scale even faster than in bulk water. This situation is very different from that where charge is instead delocalized and properties become close to bulk-like.

COLL 676

β -Diketonate-iron(III) complex: Versatile fluorine-19 MRI signal enhancement agent

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Fluorine-19 magnetic resonance imaging (MRI) has gained considerable momentum as a promising imaging modality for *in vivo* tracking of cellular therapies and as a diagnostic for inflammatory disease. To further the utility of this technique, we increase imaging probe sensitivity by merging paramagnetic metal chelates with aqueous perfluorocarbon (PFC) nanoemulsions. We prepared a highly fluorinated ferric tris(β -diketonate) chelate (MW = 1265.2 g/mol) at high purity and at gram scale. This iron chelate is soluble in multiple PFC oils used for MRI and readily reduces the ¹⁹F longitudinal relaxation time (T_1) to <100 ms with modest line broadening and displays superior properties for ¹⁹F MRI applications. Additionally, ¹⁹F relaxivity of nanoemulsions incorporating other metal ions, including Gd, Er, Ho, Dy, Mn, Cr, and Ni, were evaluated. High-moment lanthanide ions, such as Gd(III), display severe line broadening, but induces pseudo-contact chemical shifts (up to 0.5 ppm) of ¹⁹F in nanoemulsion, which makes them potentially useful for multichromatic ¹⁹F imaging. The sensitivity enhancement by Fe(III) laden PFC nanoemulsion was confirmed in MRI phantom studies, where reduced T_1 speeds data acquisition thereby increasing the ¹⁹F image sensitivity per time via signal averaging. Paramagnetic nanoemulsion is stable when challenged with a competing chelate, ethylenediaminetetraacetic acid, added to the aqueous phase. Formulated nanoemulsions have a shelf-life >200 days. Free β -diketonate or its iron complex in formed PFC nanoemulsion did not induce cytotoxicity in intracellularly labeled macrophage. Overall, ferric tris(β -diketonate) chelate provides a scalable, generalizable approach for boosting sensitivity of PFC-based ¹⁹F MRI probes.



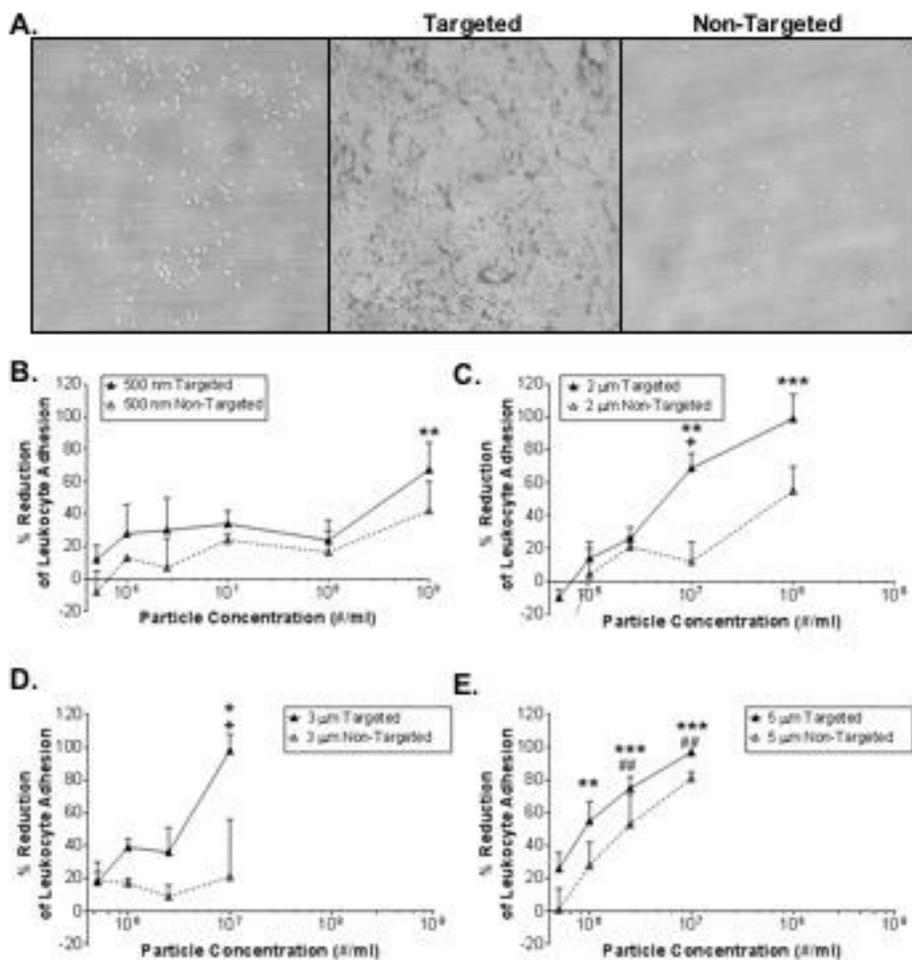
Use of a highly fluorinated ferric complex to increase the intrinsic sensitivity of fluorine-19 MRI

COLL 677

Inhibition of leukocyte adhesion in the presence of model particulate drug carriers

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Drug carriers have been widely explored as a method of improving the efficacy of therapeutic drugs for a variety of diseases, including those involving inflammation. However, very few of these formulations have advanced past clinical trials, and there are still major gaps in our understanding as to how drug carriers might impact leukocytes in blood, particularly in inflammatory conditions. In this work, we investigated how targeted and non-targeted drug carriers affect the function of leukocytes in blood flow through three primary mechanisms: (1) collisions in blood flow disrupting leukocyte adhesion, (2) specific binding to the endothelium competes with leukocytes for binding sites, and (3) particle phagocytosis alters leukocyte phenotype, resulting in reduced adhesion. We find for the first time that each of these mechanisms contributes to significantly reduced leukocyte adhesion to an inflamed endothelium, and that particle phagocytosis may be the most significant driver of this effect. These results are crucial for understanding the totality of the impact of drug carriers on leukocyte behavior and response to inflammation and should inform the future design of any such drug carriers.



Particle reduction of leukocyte adhesion in pulsatile blood flow. (a) Example images of leukocyte and particle adhesion on a HUVEC monolayer. Reduction of leukocyte adhesion observed following pulsatile flow with (b) 500 nm, (c) 2 μm, (d) 3 μm, and (e) 5 μm targeted (sLeA) or non-targeted particles. (*) indicates significant difference in leukocyte adhesion of targeted (sLeA) particles relative to particle-free blood, (#) indicates significant difference in leukocyte adhesion of non-targeted particles relative to particle-free blood, and (+) indicates significant difference between targeted and non-targeted groups ($p < 0.05$).

COLL 678

Interfacing enzymes with inorganic materials for semi-artificial photosynthesis

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Combining the catalytic strength of enzymes with inorganic conductors and light absorbers gives rise to a series of intriguing model systems that exhibit functionality not attainable with each system on its own. Within this context, the field of semi-artificial photosynthesis aims to carry out solar and electrical energy conversion to generate fuels from water and carbon dioxide. In this talk, I will discuss efforts in understanding the interface of enzymes and electro/photoactive materials through advanced analytical techniques and how such efforts lead to the development of next-generation functional systems. In particular, I will focus on developing and understanding the interface of electrode materials with Photosystem II, Photosystem I, and hydrogenase enzymes to carry out photoelectrochemical water oxidation and proton reduction using photoelectrochemistry, rotating ring disk electrode, and quartz crystal microbalance techniques. This work is instrumental in accelerating the development of bio-based renewable energy systems and in gaining a deeper fundamental understanding of the biological systems function.

COLL 679

Photoconjugating affibodies to their receptor prevents their proteolytic degradation and preserves their activity: Strategy for gene-free cell modification

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The ability to program cell function with biochemical tools has driven many recent breakthroughs in immunology, oncology, and medicine. Presently, the most effective method to change the behavior of a cell is to modify its genetic machinery, but this method requires cell purification and can change other off-target cell behaviors. Here, we instead show a method to photoconjugate protein fragments onto live cell receptors and show that covalent conjugation of these proteins results in their extended expression on the cell surface, thereby avoiding proteolysis.

First, we synthesized anti-EGFR affibodies, which when functionalized with benzophenone-maleimide can specifically conjugate to Epidermal Growth Factor Receptors (EGFR) under UV irradiation. Of the twelve cysteine mutants designed through site-specific mutagenesis, only one showed successful crosslinking to EGFR. This modified affibody demonstrated enhanced retention in EGFR-expressing 2D breast cancer cells and 3D tumor spheroids for up to 24 hours, when compared to non-crosslinkable affibodies.

Next, to monitor the structural fidelity of proteins attached to the EGFR, a fusion protein was designed that contains the anti-EGFR affibody and enzyme cytosine deaminase (CD), capable of converting the prodrug 5-Fluorocytosine (5FC) to an anticancer metabolite 5-Fluorouracil (5FU). The enzyme-affibody fusions were conjugated to a pH-sensitive dye (pHAb) and a pH-insensitive dye (AlexaFluor 488). The dye-conjugated fusions were incubated with EGFR positive breast cancer cells and their fluorescence was monitored using flow cytometry. The results revealed that the fusion proteins were endocytosed

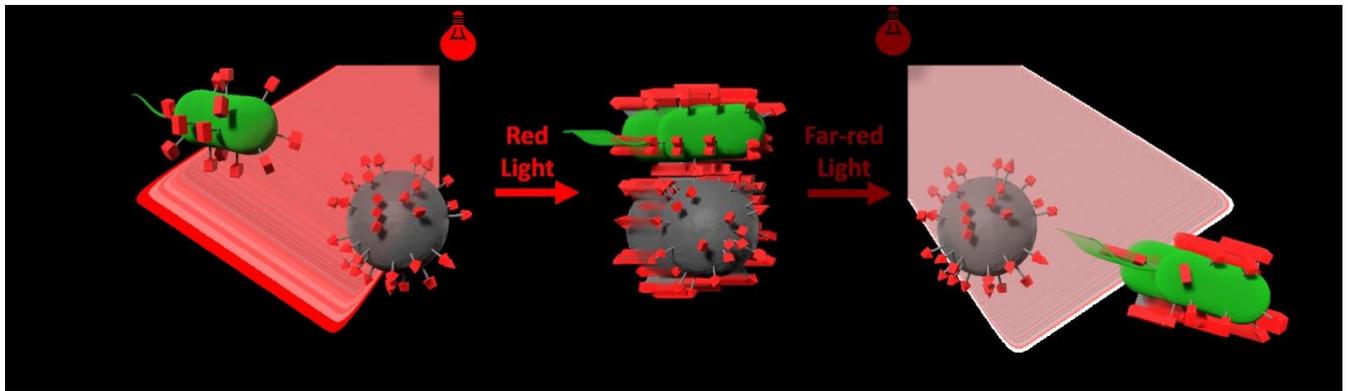
after binding to EGFR and the photocrosslinked proteins were ejected out of endosome, without degradation, and were therefore retained on the cell membrane. On the other hand, the non-crosslinked control proteins underwent proteolysis, evidenced by a reduction in both the pHAb and AF488 fluorescence after 24 h. These results were then confirmed by confocal microscopy. Finally, the fusions and the prodrug 5FC were incubated with EGFR-expressing MDA MB 468 cells, and it was observed that the fusions were capable in converting the prodrug into 5FU, even 48 hours post conjugation, without any apparent loss in activity. Therefore, this work not only demonstrate the therapeutic efficiencies of such moieties in cancer cell killing but also shows that their activity can be preserved by covalent conjugation to cell membrane proteins.

COLL 680

Red/far-red light controlled bacteria-driven microrobots for cargo delivery and release

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Biohybrid microrobots combine flagellated chemotactic bacteria with a synthetic cargo for the propulsion and steering. They are extensively studied for delivery of sensitive materials such as peptides, plasmid DNA proteins and other therapeutic agents to mammalian cells. In order to achieve maximum functionality, these two components have to be incorporated efficiently. Besides cargo integration, controlled release of the cargo is the key factor determining the efficiency for delivery applications. Controlling on-site release and active delivery of the cargo improves the bioavailability of the administration. However, very few numbers of studies so far reported demonstrating the release of cargo from a biohybrid system with respect to external stimuli. Therefore, we propose a method to spatially and temporally control the integration and the release of cargo by using visible light as the trigger. Upon red light illumination, a micro size polystyrene particle as cargo is integrated into the body of a bacteria cell (*E.coli*) and transported to the target site. Upon far-red light illumination, the cargo is release at the target site. For such, we exploit light dependent unique photoisomerization ability of the proteins phytochrome B (PhyB) with the phytochrome interaction factor 6 (PIF6). Upon red light treatment (650 nm) PhyB protein dimerizes with PIF6 and this interaction is reversed under far-red light. Our experimental results demonstrate a dynamic effective cargo integration and cargo release for the first time by using non-benign visible light as the stimuli as a proof-of-concept. This study paves the way towards improving the control of biosystems with a transforming impact in bioengineering, targeted drug delivery, and lab-on-a-chip devices.



The schematic representation of red light-induced cargo integration and far-red light induced cargo drop.

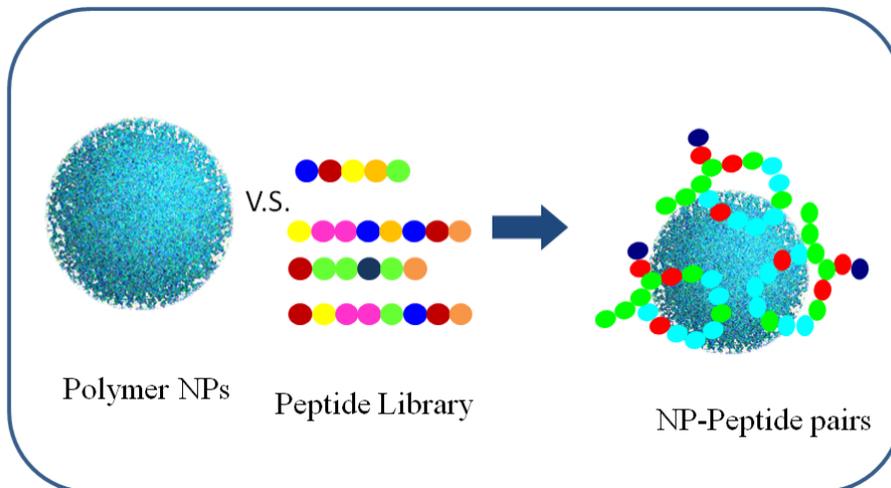
COLL 681

Mining for peptides with affinity for a synthetic copolymer hydrogel nanoparticle: Compositional and structural contributions to affinity

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Material-peptide pair interactions have found applications as interfaces and connectors to metal surfaces, as templates to control size and crystal phase of semiconductors and for synthesis of orientated assemblies of materials. These polymer-peptide interactions also have been exploited for cell-adhesion enhancement, non-fouling surfaces, the control of drug release and the desired protein collection. In this study, a general procedure for identifying matched affinity pairs of peptides and synthetic copolymer hydrogel nanoparticles (NPs) is described. A phage library was used to present a large ($> 10^{10}$) number of linear and cyclic peptides to NPs with discrete chemical compositions. Most peptide sequences had little or no affinity for the synthetic polymers. However, phage selection by the NP and sequencing provided a small number of peptides with high affinity for the synthetic copolymer hydrogel. The affinity was quantitatively evaluated by quartz crystal microbalance (QCM). A 12 amino acid cyclic peptide with approximately 23 nM affinity for a NIPAm based hydrogel nanoparticle copolymer was selected. Binding studies of the cyclic and linear forms of the peptide established that NP affinity was significantly influenced by peptide conformation. The cyclic form, that which was presented in the selection process, had >3 times higher affinity for the NP compared to the linear form. Affinity studies of series of single and multiple point mutations of the peptide established NP affinity for the peptide was based not only upon peptide conformation but also the specific sequence of amino acids in the peptide chain with both hydrophobic and electrostatic interactions contributing to binding. The results establish a general method for discovery of high affinity selective synthetic hydrogel copolymer-peptide affinity pairs, insight into the molecular details of

these interactions and the potential for utilizing these affinity pairs in applications that range from biomacromolecule purification to therapeutics.



Discovery of nanoparticle-peptide pairs.

COLL 682

In situ surface modification of 3D printed emulsion inks

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Our lab has developed a new solid freeform fabrication technology capable of printing curable emulsion inks to fabricate complex materials with hierarchical porosity. Briefly, an emulsion ink based on a high internal phase emulsion (HIPE) is deposited layer-by-layer using an open source 3D printer equipped with a syringe and motor-actuated plunger. Emulsions inks are rapidly cured after deposition by constant UV irradiation to form rigid constructs with interconnected porosity in a method we term Cure-on-Dispense (CoD) printing, **Figure 1**. 3D printed polyHIPE constructs benefit from the tunable pore structure of emulsion templated materials and the fine control over complex geometries of 3D printing that is not possible with traditional manufacturing techniques. In this study, we report on the *in situ* surface modification of these 3D printed grafts by incorporating bioactive hydrogel precursors into the aqueous phase of the emulsion inks prior to cure. Hydrogel precursor solutions containing 2.5 wt% of polyethylene glycol diacrylate (PEGDA) with or without 2.5 wt% extracellular matrix protein (gelatin or collagen) were investigated. During the HIPE cure, a hydrogel coating

of the pore surface was formed as radical initiation of the precursor solution occurred at the droplet interface. After printing, PEGDA coating was confirmed with ATR-FTIR spectroscopy and PicoSirius Red staining was used to verify successful incorporation of the protein, **Figure 1**. Standard cell culture methodology established in our lab was used to investigate integrin-mediated osteogenic differentiation of human mesenchymal stem cell cultured on polyHIPE grafts. Overall, these studies demonstrate our ability to print porous materials using emulsion inks and improve cell-material interactions via incorporation of ECM proteins. These scaffolds have a great potential to improve clinical outcomes for treatment of critical size bone defects due to their composite, biomimetic nature.

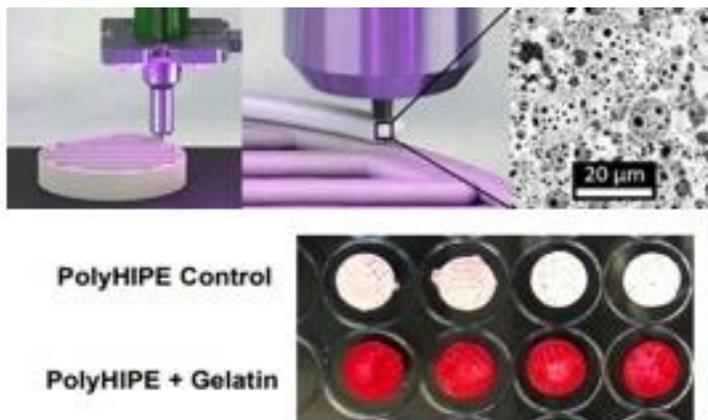


Figure 1. Schematic of UV Cure-on-Dispense (CoD) HIPE printing system and successful surface modification with bioactive hydrogel.

COLL 683

Extracellular DNA provides structural integrity to a *Micrococcus luteus* biofilm

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Force spectroscopy was used to show that extracellular DNA (eDNA) has the pre-eminent structural role in a *Micrococcus luteus* (*M. luteus*) biofilm. The adhesive

behavior of extracellular polymeric substances to a model hydrophobic surface was measured in response to their degradation by hydrolytic enzymes known for their biofilm-dispersion potential: DNaseI, protease, cellulase, and mannanase.

This method of using force spectroscopy to investigate biofilm structure involved growing biofilms on a tipless cantilever and probing it against a poly(ethylene terephthalate) surface, a known favourable substrate for *M. luteus* binding. Force retraction curves were analysed for the magnitude and number of force events occurring after treatment with each enzyme to characterise the roles that target molecules in the biofilm structure. eDNA and proteins were shown to play structural roles while polysaccharides are responsible for adhesion. Confocal microscopy was also used to measure biovolume changes of *M. luteus* biofilms when exposed to the various enzymes to further understand the observed effects of enzymes. DNaseI was found to be the only treatment that significantly decreased the amount of biovolume present.

Only treatment with DNaseI significantly decreased the adhesive force of the model bacterium *M. luteus* with the surface, and furthermore this treatment almost completely eliminated any components of the biofilm maintaining the adhesion, establishing a key structural role for eDNA.

COLL 684

Chirality engineering of supraparticles for controllable nanomedicine

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Chirality is ubiquitous in nature that is hard-wired into every living biological system. Despite of the critical role, the nexus of chirality engineering on biomaterials has not been explored. Here we designed chiral supraparticles (SPs) that react distinctively to cells and proteins depending on their handedness. SPs coordinated with *D*-chirality showed at least three times more efficient cell membrane penetrations and anti-cancer properties. We carried out quartz crystal microbalance with dissipation (QCM-D) and isothermal titration calorimetry (ITC) measurements to understand the mechanism, which confirmed that *D*-SPs had more effective adhesion on lipid layers where most of phospholipids in nature has *D*-chirality. The stronger affinity of *D*-SPs over *L*-SPs to lipids was because interactions between *D*- to *D*- are thermodynamically more stable than that of *D*- to *L*-. When it comes to *in vivo* environments that contains a large, heterogeneous population of proteins, *D*-SPs showed superior stability and longer biological half-lives due to the incompatible chirality with endogenous proteins including proteases. This study shows that incorporating *D*-chirality into nanosystems enhances cellular uptake and *in vivo* stability in blood providing support for the importance of chirality in biomaterials. Chirality engineering will provide “smart” platforms for drug

delivery systems, tumor detection markers, biosensors, and many other biomaterial devices.

COLL 685

Preparation of fluorinated aliphatic diol/phosphonic acids/magnetite composites: Application to separation of mixture of oil and water

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Phosphonic acid unit [-P(=O)(OH)₂] is one of the most important functional groups to modify metal oxide surfaces because it can easily form strong P-O-metal bonds. In fact, we have already reported that the colloidal suspensions of fluoroalkyl end-capped vinylphosphonic acid - *N,N*-dimethylacrylamide cooligomers - encapsulated magnetite nanocomposites are stable in water and traditional organic solvents without separation over 12 hr at room temperature.

From the developmental viewpoint of new fluorinated magnetic composite materials, it is of particular interest to develop the novel magnetite composites by using the phosphonic acid derivative as a key intermediate. Here we report on the preparation of fluorinated aliphatic diol/phosphonic acid derivatives/magnetite composites by the reactions of the corresponding fluorinated diol, phosphonic acid derivatives and magnetic nanoparticles. Interestingly, we have also found that that these obtained composites can exhibit a highly oleophobic/superhydrophilic characteristic to separate not only the mixture of oil/water but also the O/W emulsion. These findings will be demonstrated in this conference.

COLL 686

Synthesis of thermoresponsive block copolymer vesicles via polymerisation-induced self-assembly for oil thickening applications

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Recently, it has been shown that poly(stearyl methacrylate)-poly(benzyl methacrylate) diblock copolymer vesicles can be prepared via RAFT dispersion polymerization of benzyl methacrylate in mineral oil at 90 °C. This is an example of polymerization-induced self-assembly (PISA). Such vesicles undergo a vesicle-to-worm transition when heated up to 150 °C. This morphological transition leads to a significant increase in oil viscosity and can be explained in terms of surface plasticization of the oil-insoluble PBzMA block by hot solvent, which causes a subtle reduction in the fractional packing parameter for the diblock copolymer. In principle, this PISA formulation offers a new

high-temperature oil-thickening mechanism for automotive engine oils. Herein we revisit this system with the aim of reducing the critical temperature at which the vesicle-to-worm transition occurs. A series of poly(stearyl methacrylate)-poly(benzyl methacrylate-*stat*-*n*-butyl methacrylate) diblock copolymer vesicles were prepared by RAFT dispersion copolymerisation in mineral oil. Oscillatory rheology studies confirmed that increasing the mole fraction of *n*-butyl methacrylate in the membrane-forming block significantly lowers the onset temperature required for the vesicle-to-worm transition. More specifically, introducing 47 mol % *n*-butyl methacrylate lowered the critical temperature required for the vesicle-to-worm transition by nearly 60 °C compared to the equivalent diblock copolymer prepared using solely benzyl methacrylate for the membrane-forming block. Moreover, an unexpected reduction in viscosity was observed above 125 °C, suggesting that a worm-to-sphere transition occurred. TEM studies confirm that worms are no longer observed at 140 °C. Preliminary variable temperature small-angle x-ray scattering (SAXS) experiments suggest rich thermoresponsive behavior, with spheres being formed at 180 °C and molecularly dissolved copolymer chains at 200 °C.

COLL 687

Fabrication of Janus nanocups and selective loading with cargo

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Amongst all the shape- and surface-anisotropic colloids, cup-shaped particles have special advantages in uptake and release of cargo due to the combination of anisotropic shape with an open cavity, which may have potential application in drug delivery. In order to load cargo to only the interior of the cup when facing different environments, it would be desirable to give cups a Janus character. However, the synthesis of Janus nanocups (JNCs) with control of the Janus character, and opening/closing of the cup cavity has been very challenging.

In a recent publication, we demonstrate the fabrication of JNCs through evaporation-induced confinement assembly (EICA) of ABC triblock terpolymers (**Figure 1**). The interaction between all blocks and the surfactant creates unusually shaped “tulip-bulb” microparticles. Cross-linking and disassembly of the microparticles resulted in two types of JNCs with attoliter volume, nanoscale wall thickness, and different chemistry on the in- and outside. The mechanical stability of JNCs which controls the opening/closing cavity can be synthetically tuned by block lengths. Moreover, model cargo including polymer or nanoparticles can be selectively loaded to the in- or outside according to the chemistry of JNCs.

The presented concept provides a template- and additive-free route towards JNCs which inspire applications in locomotion, oil spill recovery, storage & release, and as nanoreactors.

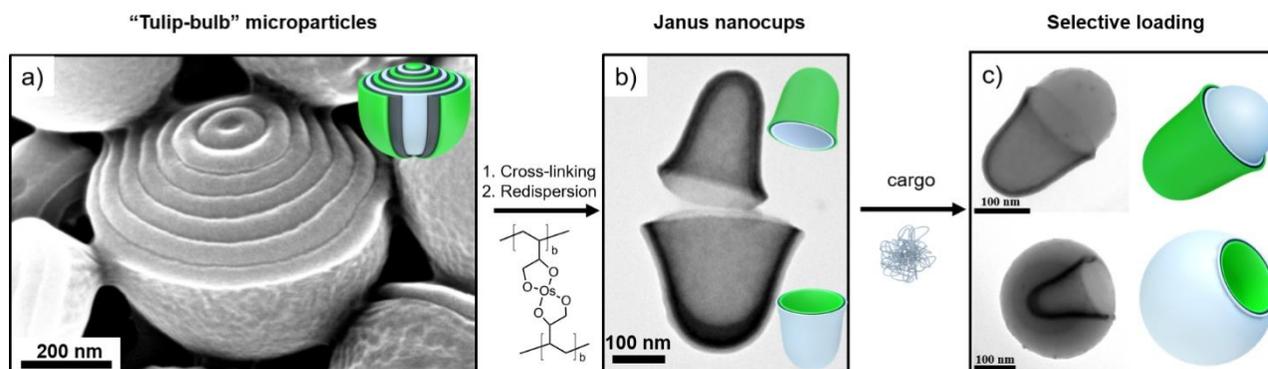


Figure 1. a) SEM image of “tulip-bulb” microparticles; TEM images of b) JNCs and c) Selective loading with JNCs.

COLL 688

Synthesis and performance of nanoreactors from mesoporous silica

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In this talk, we will discuss several interesting properties of nanoreactors made of mesoporous silica. The size range spans over a few hundred nanometers, and the shapes range from cubic to cylindrical. These nanoreactors support unique properties as well. Transport of molecules through the pores are also studied and results are presented.

COLL 689

One-pot hydrothermal synthesis of benzalkonium-templated mesostructured silica antibacterial agents

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Quaternary ammonium compounds (QACs) have a number of applications as antimicrobial agents, pharmaceutical active ingredients (APIs) and catalysts. However,

the widespread use of these materials worldwide can lead to detrimental effects such as bacterial resistance. In this work, we not only synthesized an advanced functional material by utilizing a quaternary ammonium antibacterial drug as a template for preparation of mesoporous silica nanoparticles (MSNs), but also demonstrated that benzalkonium chloride (BAC) exhibits enhanced antimicrobial efficacy in the silica host as compared to the pure compound. Additionally, these studies have shown a pH-responsive controlled release of BAC without additional surface modification of the materials. The findings will help in widening the use of BAC as a disinfectant and bactericidal agent, especially in pharmaceutical and food industries where Gram-positive and Gram-negative bacterial contamination is common.

COLL 690

Kinetic modeling of simple organophosphates hydrolysis using mixed metal nanofibers

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The exact mechanism where metal oxides such as TiO₂ facilitate the decomposition of various organophosphates (OPCs) in aqueous environments is still understood poorly at the atomistic level. We determined reaction rates and propose mechanisms of OPC degradation from uv-vis spectroscopy and chromatography-mass spectrometry measurements. Degradation mechanisms of OPCs in addition to hydrolysis steps, include complex semi-irreversible interactions with the solid substrate. This has made developing comprehensive kinetic models elusive. We used computational chemistry to model hydrolysis paths and to calculate activation free-energies to rationalize observed experimental kinetics. From this, we propose a surface-mediated OP degradation model.

COLL 691

Photothermal killing of *Escherichia coli* using gold nanorods and gold nanobipyramids

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Antimicrobial resistance remains growing and constitutes a serious risk to public health. Among different solutions to overcome the concern, new development of antimicrobial is critically needed. Gold-based nanomaterials have revealed great potential in the field of photothermal killing of bacteria. The photothermal properties of gold-based nanomaterials can be tuned by their different size and shape. In this work, gold

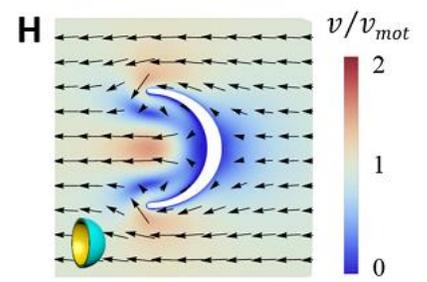
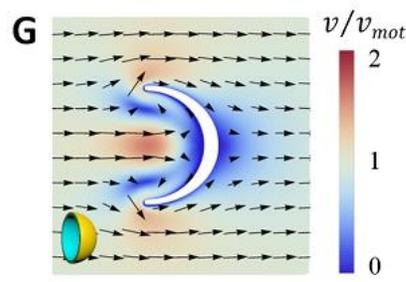
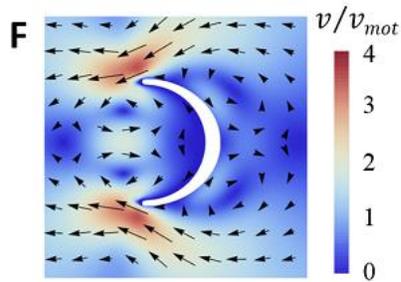
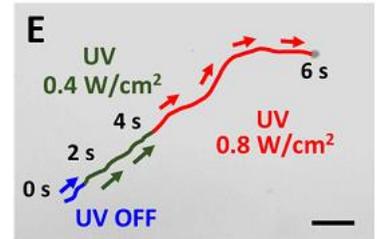
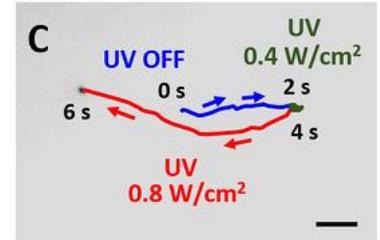
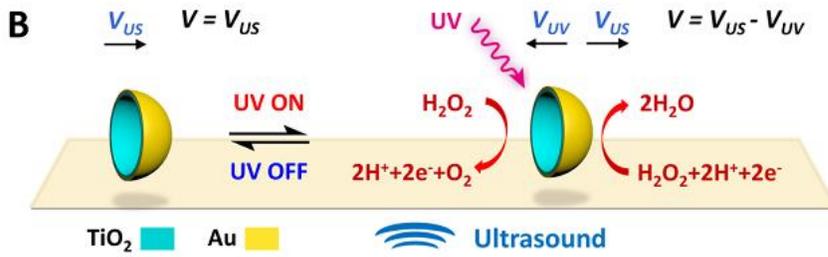
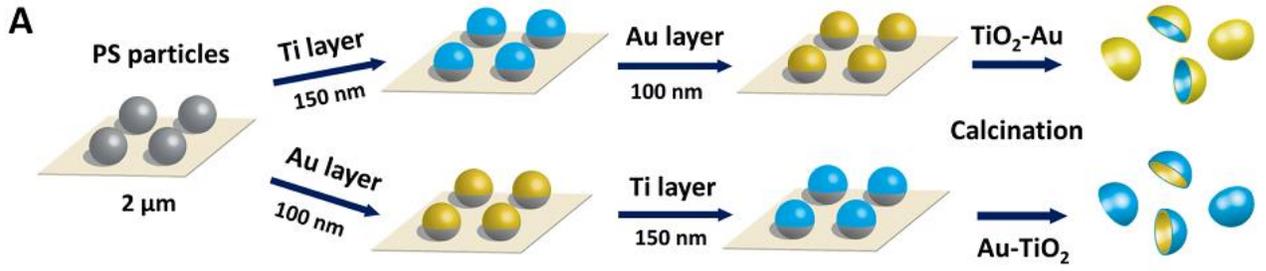
nanorods and gold nanobipyramids were prepared by seed-mediated growth method with surface plasma absorption bands at ~ 520 nm and ~ 808 nm, corresponding to their transverse and longitudinal surface plasma bands, respectively. The as-prepared gold nanorods and gold nanobipyramids were characterized by UV-Visible absorption spectroscopy and transmission electron microscopy. With the similar surface plasma absorption bands at 808 nm, gold nanorods and gold nanobipyramids were respectively applied as photothermal reagents to examine their killing efficiencies of *Escherichia coli* by near-infrared 808 nm laser irradiations. We hope that our photothermal system can be further applied for the application in noninvasive photothermal therapy to treat disease in the near future.

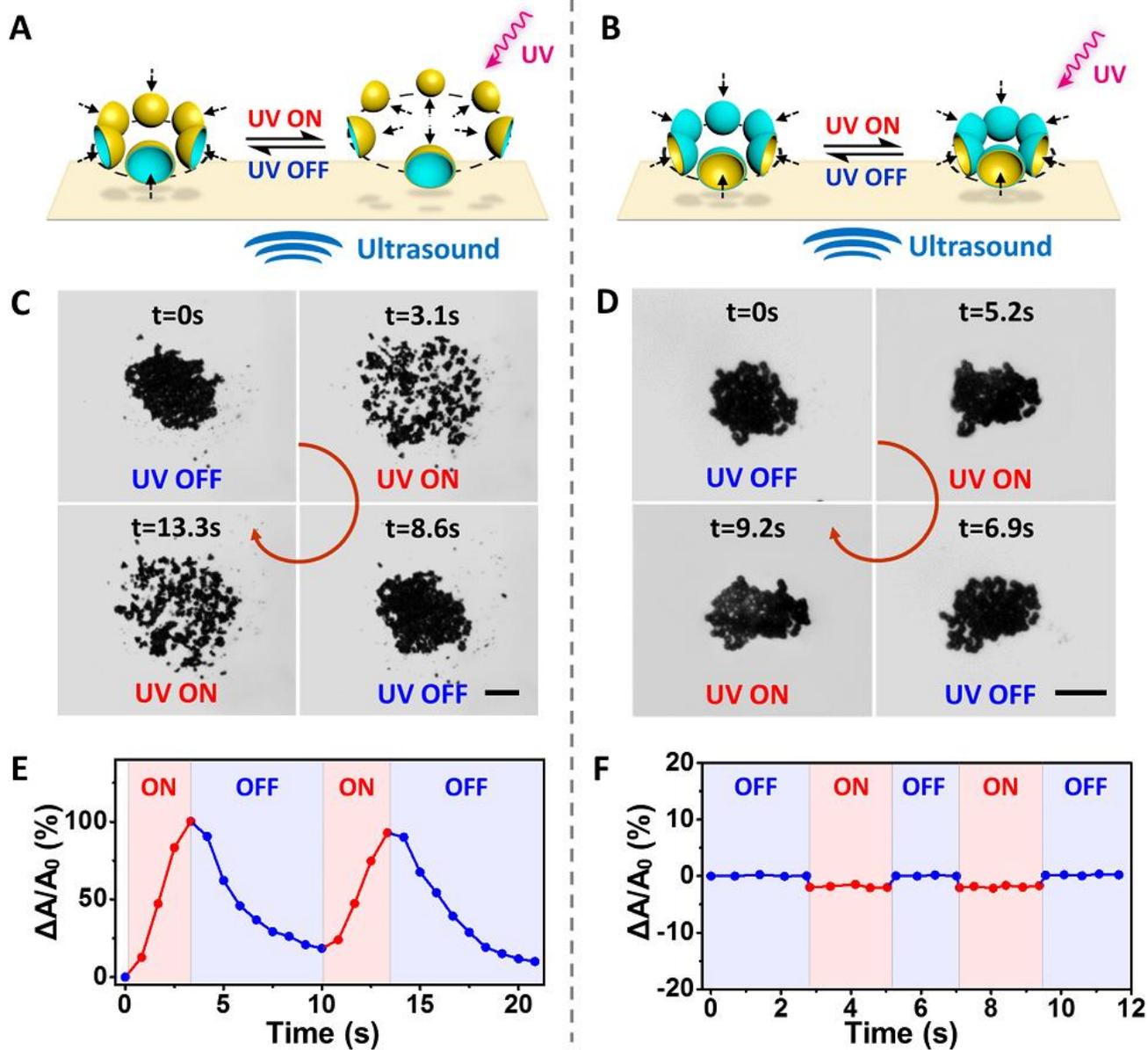
COLL 692

Structure-dependent optical modulation of propulsion and collective behavior of acoustic/light-driven hybrid microbowls

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We report on hybrid light/acoustic-powered microbowl motors, composed of gold (Au) and titanium dioxide (TiO₂), with a structure-dependent optical modulation of both their movement and collective behavior. The microbowl propels in an acoustic field toward its exterior side. UV light activates the photochemical reaction on the TiO₂ surface in the presence of hydrogen peroxide and the Au/TiO₂ system moves towards its TiO₂ side by self-electrophoresis. Reversing the inner and outer positions of Au and TiO₂ in the microbowl structure changes the structure-dependent optical modulation behavior of the acoustic propulsion. Controlling the light intensity allows switching of the dominant propulsion mode and provides braking or reversal of motion direction when TiO₂ is in the interior microbowl side, or accelerated motion when the TiO₂ is on its exterior side. Tuning the geometry and light intensity thus offer a dramatically modulated swimming behavior. Theoretical simulations offer understanding of the acoustic streaming flow and self-electrophoretic fluid flow induced by the asymmetric distribution of ions around the microbowl. The light-modulation behavior along with the tunable structure lead also to control of the swarm behaviors under the acoustic field, including expansion or compaction of ensembles of microbowls with interior and exterior TiO₂, respectively.





COLL 693

Photochemically patterned metal nanoparticle strontium barium niobate surfaces with tunable wettability, enhanced raman scattering and fluorescence emission

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Photochemically patterned Strontium Barium Niobate (SBN) surfaces are shown to exhibit tunable surface wettability which depends on the UV irradiation time and the type of deposited metal nanoparticle, namely silver or gold. SBN surfaces decorated with silver nanoparticles undergo a transition from hydrophilic to hydrophobic with increasing UV photodeposition time. The water contact angle of gold nanoparticle patterned SBN surfaces also increases with increasing photodeposition time but the surfaces remain hydrophilic regardless of photodeposition time. Local morphological studies of the patterned surfaces reveal a gradual increase in surface roughness and surface area coverage by particles with increasing photodeposition time. Taking advantage of the surface chemistry (surface charge) and favorable interaction of metal nanoparticles with electromagnetic waves, we further demonstrate enhanced Raman scattering and fluorescence emission of probe molecules of interest from metal nanoparticle patterned SBN surfaces. Our probe molecules are cationic Rhodamin 6G, and anionic Methyl Orange. To aid attachment of anionic MO onto the metal particles, the substrates were coated with Poly-L-Lysine prior to experimental investigations. Further, by employing simple ferroelectric lithography, we created nested “box inside a box” ferroelectric domains with spatially distinct metal particle deposition and patterned Raman scattering responses. Coupling ferroelectric and pyroelectric properties of the SBN substrates can enable the realization of future microfluidic sensors with enhanced detection capabilities.

COLL 694

Chemical, physical, and superstructural driving forces of aqueous interfacial phosphate recognition

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The development of effective phosphate receptors is an important remediation tool to mitigate the damaging environmental effects of phosphate eutrophication. However, our understanding of recognition at the aqueous interface is underexplored, which has hindered the rational design of surface receptors. The unique environment present at the air/water interface has remarkable advantages over recognition in bulk solution. It is also technologically-relevant, as interfaces are prevalent in remediation membranes. In this study, we explored a homologous series of synthetic receptors differing in functional group, charge, and number of alkyl chains to characterize the driving forces of aqueous interfacial recognition. We have found that the functional group at the binding site using guanidinium and thiuronium receptors and organization of the receptors using two alkyl anchoring groups were important design features for phosphate binding. The

guanidinium and thiuronium receptors were 1000 and 10 fold more selective for phosphate over chloride respectively, at chloride concentrations mimicking natural waters. Charge screening at high chloride concentrations led to a decrease in the binding affinity due to significant weakening of the electrostatic potential of the receptors. This study helps merge the physical and organic communities in their understanding of receptor design for phosphate remediation and provides some of the first understanding of phosphate recognition at the air/water interface.

COLL 695

Heterogeneity in urban environmental films

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Mixtures of heterogeneous particles, individual molecules, and small aggregates suspended in the atmosphere ultimately deposit onto all of Earth's solid surfaces. The resulting surface films act as environmental sinks, sources, and reaction centers, impacting fate and transport pathways. We present physical and chemical analyses of passively collected environmental films, aimed at understanding how a film's morphology, spatial chemical profile, and maturation behavior can affect participation in fate and transport. We examine the surfaces' physical morphology from millimeter to nanometer dimensions using bright-field, scanning electron, and atomic force microscopies. Chemical analysis maps are provided by energy dispersive x-ray spectroscopy and secondary ion mass spectrometry. Surface feature sizes span six orders of magnitude, indicative of super- and sub-micrometer PM as well as conformal films of nanoscale PM and semi volatile molecules. Our sampling sites and timeframe allow preliminary insights to characterize seasonal variations in film chemistry and anthropogenic influence of point sources such as biomass fired power plants.

COLL 696

Viscosity increases in the core of phase separated particles after IEPOX uptake

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In atmospheric particles, organic species become mixed with inorganic species via gas-phase oxidation of volatile organic compounds (VOCs) with subsequent condensation of the low-volatility products, such as isoprene epoxydiols (IEPOX), key products of

isoprene photo-oxidation. This process leads to the formation of secondary organic aerosol (SOA), a ubiquitous component of submicron aerosols. Chamber and field studies have observed complex physicochemical properties of SOA, such as liquid-liquid phase separations (LLPS) and viscous or glassy organic phases that inhibit reactive uptake of gaseous species, lower partitioning of chemical species from particle to gas phase, and lower the relative humidity (RH) at which particles undergo efflorescence and deliquescence. To determine the impact these complex morphologies have on the formation of IEPOX-derived SOA, laboratory experiments were conducted by exposing gaseous IEPOX to acidic ammonium sulfate particles coated with α -pinene and toluene SOA over a range of RH (15-50%). To determine individual particle morphology and viscosity, single-particle microscopic and spectroscopic techniques including scanning electron microscopy coupled with energy dispersive x-ray spectroscopy (SEM-EDX), Raman microspectroscopy, and atomic force microscopy (AFM) were used. After IEPOX uptake, changes to particle morphology and an increase in particle viscosity were observed, which decreased additional IEPOX uptake and limited subsequent particle growth. These results indicate that particle phase and viscosity determination is necessary to more accurately predict atmospheric fate of ambient aerosols, and the effect aerosols have on heterogeneous (multi-phase) chemistry, climate, and air quality.

COLL 697

***In situ* molecular imaging of the air-liquid and liquid-liquid interface in the environment**

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We invented a vacuum compatible microfluidic interface, System for Analysis at the Liquid Vacuum Interface (SALVI), to enable direct observations of liquid surfaces, air-liquid, liquid-liquid, and solid-liquid interactions using time-of-flight secondary ion mass spectrometry (ToF-SIMS) and a variety of spectroscopy and microscopy characterization techniques. In this talk, I will show three examples of how ToF-SIMS and in situ liquid SIMS are used in studying the air-liquid and liquid-liquid interfaces of importance in the environment. First, ToF-SIMS is applied to study if photochemistry plays a role in the photolysis of pyruvic acid in water. Depth profiling results coupled with spectral and multivariate analysis illustrate strong influence of the air-water interfacial photochemistry in pyruvic acid oxidation. Second, the effect of time on photochemical aging in glyoxal and hydrogen peroxide photochemical aging is studied using in situ liquid SIMS. Our results offer new insights into the evolution of the air-liquid interface and formation of aqueous secondary organic aerosol (aqSOA) over time. Third, the oil-in-water bilgewater emulsion is studied using in situ liquid SIMS. The evolving liquid-liquid interface is mapped showing hydrophobicity and hydrophilicity changes at the microscale.

COLL 698

Reflection-absorption infrared spectroscopy is not only a vibrational spectroscopy: Case of thin amorphous solid water (ASW) films

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Reflection-absorption infrared spectroscopy (RAIRS) displays complex features arising from the interplay between refraction, absorption within the sample, and interference effects between the multiple reflections at the film-substrate and film-vacuum interfaces. The interpretation of the infrared spectra of amorphous solid water (ASW) film is therefore made all the more challenging as spectral features resulting from trivial optical effects are difficult to distinguish from chemically relevant absorption. These difficulties are compounded by the fact that optical, physical and chemical properties can all be greatly impacted by subtle details in sample preparation protocols and experimental conditions. Efforts towards providing a quantitative interpretation of experimental RAIRS spectra, along with a critical review of the numerous optical parameters that have been reported for nanoporous ASW, will be presented. RAIRS spectra from vapour deposited nanoscopic ASW films in the 650-4000 cm^{-1} range are compared and contrasted with theoretical infrared spectra calculated using a classical optics model based on Fresnel equations using published optical constants [i.e., $n(\omega)$ and $k(\omega)$][1–3]. On the one hand, selected optical constants from the literature afford a satisfactory description of most experimental spectral band shapes and intensities affording contributions from optical effects to be distinguished from features arising from excitations of molecular vibrations. However, discrepancies with other published optical constants enables the influence of ASW growth conditions on the reported optical parameters to be inferred paving the way for rigorous study of the impact of deposition parameters on morphological properties of vapour deposited ASW films.

COLL 699

Mineralogy dependent atmospheric processing of mineral dust aerosols and their impact on the growth of marine diatoms

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A large part of oceanic biological production is limited by the scarcity of dissolved iron. Mineral dust aerosols, processed under acidic atmospheric conditions, are the primary

natural source of bioavailable iron to oceanic life. However, the mineralogical impact on atmospheric processing of Fe-containing mineral dusts as well as that on the phytoplankton growth is poorly understood. The current study focuses on the mineralogical influence on Fe solubility under atmospherically relevant conditions using natural dust samples collected from the Kalahari Desert and selected proxies for Fe-containing minerals, i.e. ilmenite (FeTiO_3), hematite (Fe_2O_3), and hematite mixed with TiO_2 . Further, the growth of a marine diatom, *Cyclotella meneghiniana*, was evaluated with respect to these different Fe sources. The solubility experiments were conducted over 48 hours, with a daytime: nighttime ratio of 16h/8h, where the daytime was simulated with a Sol1 ABB solar simulator. At the end of the 48th hour, Ti-bearing mineral dust showed comparatively higher Fe solubility in aerated nitric acid solutions (pH 2) maintained at 25 °C. Ilmenite and hematite mixed with TiO_2 produced $2037 \pm 123 \mu\text{M/g}$ and $2338 \pm 30 \mu\text{M/g}$ total dissolved Fe respectively whereas hematite alone produced only $1799 \pm 56 \mu\text{M/g}$. In a different setup, fresh dust samples were allowed to interact with water vapor and gaseous nitric acid for 48 hours to simulate the atmospheric-acidic processing and the formation of deliquescence layer. Both fresh and processed dust were then added to Fe starved seawater inoculums of *C. meneghiniana* and allowed to grow under simulated light. The periodic chlorophyll absorbance measurements and the cell counts indicate higher diatom growth in the inoculums containing processed dusts compared to their respective fresh dust containing counterparts. Further, the diatom growth is relatively higher in inoculums containing higher Ti:Fe ratio compared to others without such a significant amount of Ti, indicating the mineralogy dependency of ocean Fe fertilization.

COLL 700

Phenol-water vapor deposition in long-term exposure: Different interfaces, similar sigmoid kinetics, and enhanced water retention

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Environmental fate of multiple organic compounds, both natural and anthropogenic ones, is affected by their sorption and reactions at diverse interfaces present on soils, sediments, aerosols and, specifically, associated with natural organic matter (NOM) and clay minerals. In environment of variable humidity, water plays its own important role, by suppressing or cooperating in uptake and reactions of organic chemicals at interfaces. These processes are often monitored during relatively short time periods, which may not cover slow processes eventually leading to thermodynamically controlled endpoint. The current contribution presents a long-term study of interactions of mixed phenol-water vapors with model sorbents such as humic acid salt, leonardite and NOM- and clay-rich soils. Phenol is a representative of multiple organic compounds capable of polymerization at environmental interfaces, reactions with soil components, covalent binding to NOM and strong H-bond interactions. Gravimetric monitoring of phenol-water vapor uptake kinetics was performed during 4000 hrs by the sorbent materials

prehydrated at different levels of water activity. Differences between mixed vapor uptake kinetics and those observed for control sorbent samples exposed to phenol-free humid atmospheres (at the same water activities) allowed to demonstrate that phenol-induced vapor deposition follows sigmoid kinetics typical for second-order autocatalytic reactions. Interestingly, long-term kinetics on interfaces of some essentially different sorbents, such as NOM-rich and clay-rich soils, were associated with significant rise in hydration thus suggesting that organic vapor deposition created new sorption sites for water. Abiotic oxidative coupling of phenol associated with its polymerization at surfaces was considered to control phenol-water deposition such that large portion of sorbed phenol became resisting to extraction. Since sigmoid uptake kinetics were developed with the significant delay, limited-time observations would not allow detecting the processes finally leading to significant changes in the system composition. The apparent rate constants were not influenced by sorbent nature, water activity or phenol concentrations, thus suggesting "universal" phenol deposition mechanisms and opportunity to predict long-term uptakes on various materials.

COLL 701

Photochemical reaction dynamics and absorption spectroscopy of environmentally important species

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Sea surface microlayer and sea spray aerosols are enriched with many light absorbing organic species. The systems are very complex and a wide range of reactions and photochemical reactions occur simultaneously. In order to better understand photochemical reactions in this complex environment, model systems are needed. Pyruvic acid is an important chemical compound involved in many metabolic pathways in cells of living organisms and also serves as a model system for α -dicarbonyls. Four different species of pyruvic acid are known to exist in water solution.

Presented here is a combined experimental and theoretical study of the mechanism behind the photoabsorption spectrum of pyruvic acid and the influence of parameters such as pH and ionic strength. The theoretical part of the work is directed towards establishing the molecular mechanism of the photoabsorption spectrum. Theoretical spectra were obtained using two different approaches: (1) Calculation of vertical excitation energies using the ADC(2) method and (2) Molecular dynamics simulations using MP2 ground state potentials followed by calculations of vertical excitation energy on selected structures from the simulation.

Different theoretical models were used for the simulation of the spectrum. The absorption spectra for each individual isolated species of pyruvic acid were not sufficient for explaining the main features of the experimental spectra. Therefore a water cluster environment with and without H_3O^+ was used as a model system for the experimental spectra. Ionic strengths were modeled by explicitly adding particular ions to the cluster.

The theoretical calculations carried out for small finite clusters yield a good agreement with the experimental data and provide a microscopic picture of the steps and the interactions involved in the photoabsorption. Insights to the experimental spectrum obtained from this theoretical approach will be discussed.

COLL 702

Design and formulation of an iodine-based antimicrobial coating for sporicidal and bactericidal activities

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Among the numerous technologies employed to remove microorganisms from indoor environments, the use of filters in air circulation units is considered to be most efficient. High efficiency particulate air (HEPA) filter remove by trapping airborne microorganisms, but this presents a risk as microorganisms can remain viable on the filter and proliferate under ideal environmental conditions. They can become source of recontamination and gaseous emissions. This can lead to filter degradation, lowering its efficiency and also paving the way for microbial penetration. In this work, a coating material was developed based on iodine containing polymers assembled into a colloidal shell that can rapidly inhibit the growth of microorganisms on the filter material. Direct inoculation of select test organisms shows that these filters exhibit contact-killing and release-killing properties, that inactivate a broad spectrum of microorganisms at a short contact time. The coated filters can achieve more than 2 log ($\geq 99\%$) reduction in viable bacteria (*Escherichia coli*, *Staphylococcus aureus*, and *Pseudomonas aeruginosa*) and spores (*Aspergillus niger* and *Penicillium chrysogenum*) compared to uncoated filters.

COLL 703

Surface chemistry of cerium oxide nanoparticles in an engineered UV/persulfate process with dissolved organic matter

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The wide industrial applications of cerium oxide nanoparticles (CeO₂ NPs) have increased their release into water treatment processes. After secondary water treatment, CeO₂ NPs can persist and undergo tertiary treatment. However, we do not fully understand how their behavior in tertiary treatments, such as advanced oxidation

processes (AOPs), will change. In recent years, ultraviolet/persulfate (UV/PS) treatment has emerged as a promising engineered AOP to treat micropollutants such as pharmaceutical organic compounds. To improve our understanding of the effects of a UV/PS process on the fate and transport of CeO₂ NPs, this study investigated the surface chemical property changes of CeO₂ NPs at pH 5.4 during a UV/PS process in the presence of three model dissolved organic matters (DOM: alginate, polyaspartic acid, and citrate). Without UV, PS itself decreased the colloidal stability of CeO₂ NPs by decreasing the electrostatic repulsive interactions between NPs. Under UV irradiation, the electrostatic interactions between CeO₂ NPs and sulfate anions, which were generated from the activation of PS by UV, neutralized the surface charge of NPs and accelerated their sedimentation. Alginate, polyaspartic acid, and citrate all increased CeO₂ NPs' colloidal stability in the presence of PS, both with and without UV, via surface complexation, and reversed the surface charge of CeO₂ NPs from positive to negative. S2p peak changes in XPS revealed that three DOM molecules could replace adsorbed PS on the surface of CeO₂ NPs. Furthermore, under UV irradiation, CeO₂ NPs' sedimentation was promoted when DOMs were present. The degradation of DOMs on CeO₂ surface through the ligand-to-metal charge transfer (LMCT) mechanism reduced the absolute value of the zeta potential, accelerating CeO₂ sedimentation. The new findings provide a better mechanistic understanding of the chemical reactions on the surface of CeO₂ NPs in a UV/PS process where DOM such as proteins and polysaccharides are also present.

COLL 704

NiAu single-atom alloys for selective C-C coupling

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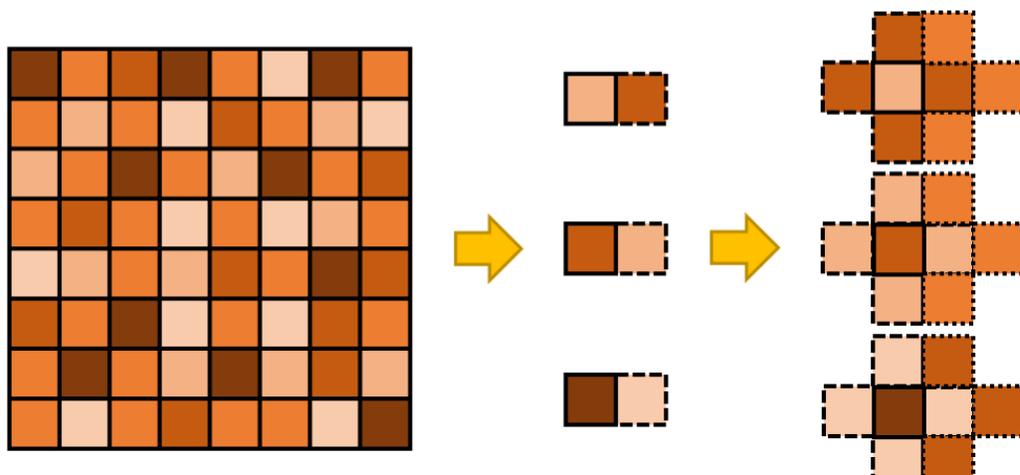
Carbon-carbon coupling is a key step in the formation of larger hydrocarbons. Currently the most common method employs homogenous Pd catalysts. The selectivity towards the desired coupling product is often controlled using expensive ligands and metals that are costly and suffer from deactivation via aggregation and leaching. A heterogenous method could aid in recovery of precious active metals for C-C coupling. Gold provides facile coupling of adsorbed alkyl fragments, but is poor at activating the carbon-halogen bond that starts the reaction by forming alkyl species on the surface. Ni based catalysts provide low barriers for dehalogenation, but will decompose adsorbed alkyl fragments and deactivate the Ni itself. By alloying Ni into Au at the single-atom limit, it is possible to activate key steps on the Ni site while retaining the selectivity of Au. This bifunctionality offers unique chemistry not available on either metal. We report selective C-C coupling of methyl groups on NiAu single-atom alloys using Temperature Programmed Reaction studies and Scanning Tunneling Microscopy to build structure-activity relationships of NiAu single-atom alloys (SAAs). These fundamental studies will further the understanding SAAs and allow for the rational design of NiAu alloy catalysts at the single-atom limit for more economical and efficient C-C coupling.

COLL 705

Pair approximation of heterogeneous reaction networks

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We present an extension of the pair approximation to model reaction networks whose rate constants are heterogeneous. Taking a pair of impurity sites, we reconstruct the probable nearest neighbor interactions based on the pairwise correlation. Comparison with kinetic Monte Carlo and the mean field approximation reveals that explicit treatment of impurity pairs recovers the effects of dynamic correlation in addition to the effects of static disorder. Moreover, implicit treatment of static disorder in the second impurity site leads to considerable reduction of computational costs without loss of accuracy. The heterogeneous pair approximation is an inexpensive method to obtain qualitative improvements when the mean field counterpart exhibits discrepancies with kinetic Monte Carlo.



Graphical representation of the heterogeneous pair approximation.

COLL 706

Atomic-scale characterization and reactivity of PtAg surface alloys

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Catalytic hydrogenation reactions are important in many industrial applications. While Pt is catalytically active towards hydrogenation, it is very costly, and can suffer from poisoning by CO, and coke. Previously, Ag based catalysts have been modified by alloying Pt or Pd for applications in highly selective heterogeneous catalysis, promising for catalyst design since Ag is cheaper than Pt and more resilient to poisoning. By analogy to our single-atom alloy approach in other systems such as PtCu and PdCu, alloying Pt into Ag has the potential to greatly enhance Pt's catalytic selectivity while reducing the cost of precious metal required to catalyze industrially relevant reactions and reduce poisoning, due to weaker binding on Ag. The atomic-scale surface structure of dilute PtAg alloys has not been reported to date. Using scanning tunneling microscopy (STM) and STM-based spectroscopies, we characterized the surface structure and local geometry of Pt deposited on Ag(111) as a function of temperature. At low temperatures, intermixing of PtAg is driven by a negative mixing enthalpy, resulting in different metastable states such as isolated Pt atoms in, and islands on, Ag terraces, as well as Pt rich brims located along Ag step edges. Increasing the alloying temperature results in an increased concentration of Pt atoms along Ag steps edges as well as direct exchange of Pt atoms into Ag terraces. At higher temperatures, there is sufficient thermal energy for Pt atoms to fully disperse in the Ag(111) surface layer as isolated atoms, forming single-atom alloys. This characterization of PtAg surface alloys will enable us to correlate reaction activity and selectivity to the atomic-scale structure of the alloy and potentially tune catalytic selectivity and resilience to poisoning.

COLL 707

Triaqua surface coordination complex on Co₃O₄(111)

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Understanding the interaction between water and metal oxide surfaces is crucial in heterogeneous catalysis and electrocatalysis. Fe₃O₄, Co₃O₄ and their transition metal-substituted derivatives are often used in water-gas shift and water splitting.^{1,2} Water impurities in the gas

atmosphere poisons Co₃O₄'s reactivity in CO oxidation and perturbs the interaction between Fe₃O₄ and supported Au atoms.^{3,4} Previously, it was observed that exposing Co₃O₄(111) surface to 3x10⁻⁸ mbar D₂O generates water ad-layers below 300 K, isolated hydroxyls above 500 K, and a complex array of hydroxyl groups between 300 K and 500 K.^{5,6} In this work, we combined density functional theory (DFT) calculations, infrared reflective absorbance spectroscopy (IRAS), and ¹⁶O-¹⁸O isotope-switching to

identify the principle motifs observed in water adsorption on $\text{Co}_3\text{O}_4(111)$. We found that surface Co^{2+} ions covered with three molecular D_2O ligands, perturbed by surface hydroxyls in its proximity make up many components of the complex spectrum observed between 300 K and 400 K. The surface $\text{Co}(\text{D}_2\text{O})_3$ complexes, to our knowledge, has not been reported previously. This peculiar structure is stable on $\text{Co}_3\text{O}_4(111)$ but not $\text{Fe}_3\text{O}_4(111)$ due to both a more covalent bonding picture on the $\text{Co}_3\text{O}_4(111)$ surface and more favorable ligand field splitting of octahedral Co^{2+} compared to Fe^{3+} . With these reasons, we believe that this local hydration phenomenon can be extended to other d^6 , d^7 , and d^8 ion-substituted $\text{Co}_3\text{O}_4(111)$ and $\text{Fe}_3\text{O}_4(111)$ surfaces as well.

COLL 708

Role of functional groups for the synthesis of nanomaterials within metal organic frameworks materials

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Incorporation of nanomaterials such as nanoparticles into nanoporous materials such as metal organic frameworks (MOFs) is attractive to broaden their applications. However, it is challenging to control the synthesis in this nanoconfined environment without fundamental understanding of molecular local chemistry, in particular the role of functional groups. This work illustrates how functional groups can both catalyze the initial nucleation reactions and control the size of nanoparticles by combining *in situ* spectroscopic, physical, and imaging measurements, with *ab initio* calculations for two distinct conditions, vapor and liquid phase processing. Firstly, the synthesis of Al_2O_3 by atomic layer deposition (ALD) is considered. For this vapor phase method, the reactivity of ALD precursors in Zr-based MOFs is shown to critically depend on the presence of internal functional groups such as $-\text{NH}_2$, which act as catalyst to foster hydrolysis. First principles calculations reveal that the $-\text{NH}_2$ group anchors the precursor molecule in close proximity to the MOF bridge OH. In the absence of $-\text{NH}_2$, the precursor resides in the middle of the pore too far from the $\mu_3\text{-OH}$ to react. The understanding derived from this work explains previous experimental observations of nanoclusters growth in UiO-66- NH_2 template [ACS Catal., 2014, 4, 1340]. Secondly, we demonstrate that isolated, ligand-free Au NPs (~1nm) can be synthesized by photo-reduction of HAuCl_4 inside thiol-functionalized MOFs, including MOF-808-SH and MIL-101 (Cr) in an alcoholic MOF suspension without the need for additional reducing or stabilizing agents. A combination of physical, imaging, spectroscopic measurements, and *ab initio* calculations confirms that the Au NPs are dispersed inside the bulk of the MOFs and demonstrate that the thiol group is critical to stabilize the Au NPs inside *individual* pores. The thiol-functionalized MOFs thus fulfill a dual purpose: they

foster the nucleation of the Au NP and also provide confinement and a framework that keeps the NPs separate.

COLL 709

Challenges in surface chemical analysis in nanomaterial systems

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X-ray photoelectron spectroscopy (XPS) is a widely-utilized tool in surface chemical analysis for semi-quantitative elemental and chemical characterization. However, challenges can occur when trying to characterize poorly conducting surfaces and those that react when exposed to X-rays and low energy electrons. While these concerns are evident in materials of all two-dimensional size scales, this talk will focus on studies involving nano-silver and other nanomaterials (time permitting) where X-ray induced chemical transformations, low energy electron induced transformations, aging, peak fitting and/or charging issues have been observed. In the case of silver, we will discuss the impact of charge neutralization on reduction of silver oxide nanomaterials and photolysis of nanoscale silver chloride transformation products. Lastly, the information that can and cannot be obtained from these materials, the controls necessary to run, and whether the information obtained should be considered semi-quantitative or qualitative will be discussed.

COLL 710

Hydrophobic CeO₂ nanoparticles coating using polymer binder for enhanced adhesion capability

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An effective and facile strategy to regulate surface characteristics of hydrophobic CeO₂ nanoparticle (NPs) coating, and drastically improving interfacial adhesion of NPs with substrate is developed. In this work, CeO₂ NPs are synthesized using a simple, low temperature solution process and coated using spin coating and spray coating approaches. Spin coating is an easy and quick way to produce uniform thin films over flat surfaces while spray coating is more appropriate for coating complex 3D structures. Interestingly, coating technique didn't influenced the hydrophobic characteristics. Although the surfaces coated by CeO₂ NPs had excellent hydrophobicity, they showed poor adhesion properties with the substrate, probably due to the low surface polarity of CeO₂ NPs with substrates. Polyacrylic acid (PAA) is introduced as adhesion promotor to improve surface characteristics and obtain a firm coating. Slight polarity tuning and binder inclusion displayed significantly enhanced binding capability during peel-off measurement. Superior mechanical properties of PAA binder attributed to the polymeric

network resulting in more active interaction sites between the binder and CeO₂ NPs, ultimately aiding NPs to anchor more firmly over Si substrate. Since film adhesion to the substrate is a key issue in the fabrication of hydrophobic coatings, this simple and efficient binder coating approach could be effectively applicable for coatings with enhanced adhesion strength. CeO₂ NPs coating showed stable hydrophobicity at high temperature with excellent adhesion, can be successfully applied to cooking wares since its non-toxic and harmless to the human body. We believe that such robust hydrophobic coatings can find potential in many other technological applications.

COLL 711

Formation of tough latex films of polymeric microspheres crosslinked with rotaxane

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Soft and deformable elastomer microsphere dispersions can be formed into latex films by evaporating the water from dispersions. In order to obtain tough polymer latex films, a post-polymerization reaction for chemical crosslink between the elastomer microspheres is usually necessary, which requires extra additives during the drying process. This restriction renders the latex film formation technology complex and rather unsuitable for applications in which impurities are undesirable. The latex films, in which the microspheres are crosslinked only physically, are brittle because the chain entanglement between the microspheres can slip easily upon elongation. However, in the present study, it has been demonstrated that tough elastomer microspheres crosslinked with rotaxanes can form tough bulk films by evaporating water from microsphere dispersions, so that post-polymerization reactions are not required (**Figure (a)**). The latex film showed higher fracture stress and fracture strain, compared to the latex films of the microspheres crosslinked with a conventional crosslinker or non-crosslinked (**Figure (b)**). It suggested that the stress relaxation in each elastomer microsphere originating from the flexibility of the crosslinking points affected on the mechanical properties of the latex film of microspheres crosslinked with rotaxanes, even though the post-crosslinking reaction between the microspheres was not performed. These results should find the advanced applications in the areas of medicine and cosmetics, in which the minimization of impurities is desirable. Furthermore, the annealing effect of latex films will also be discussed.

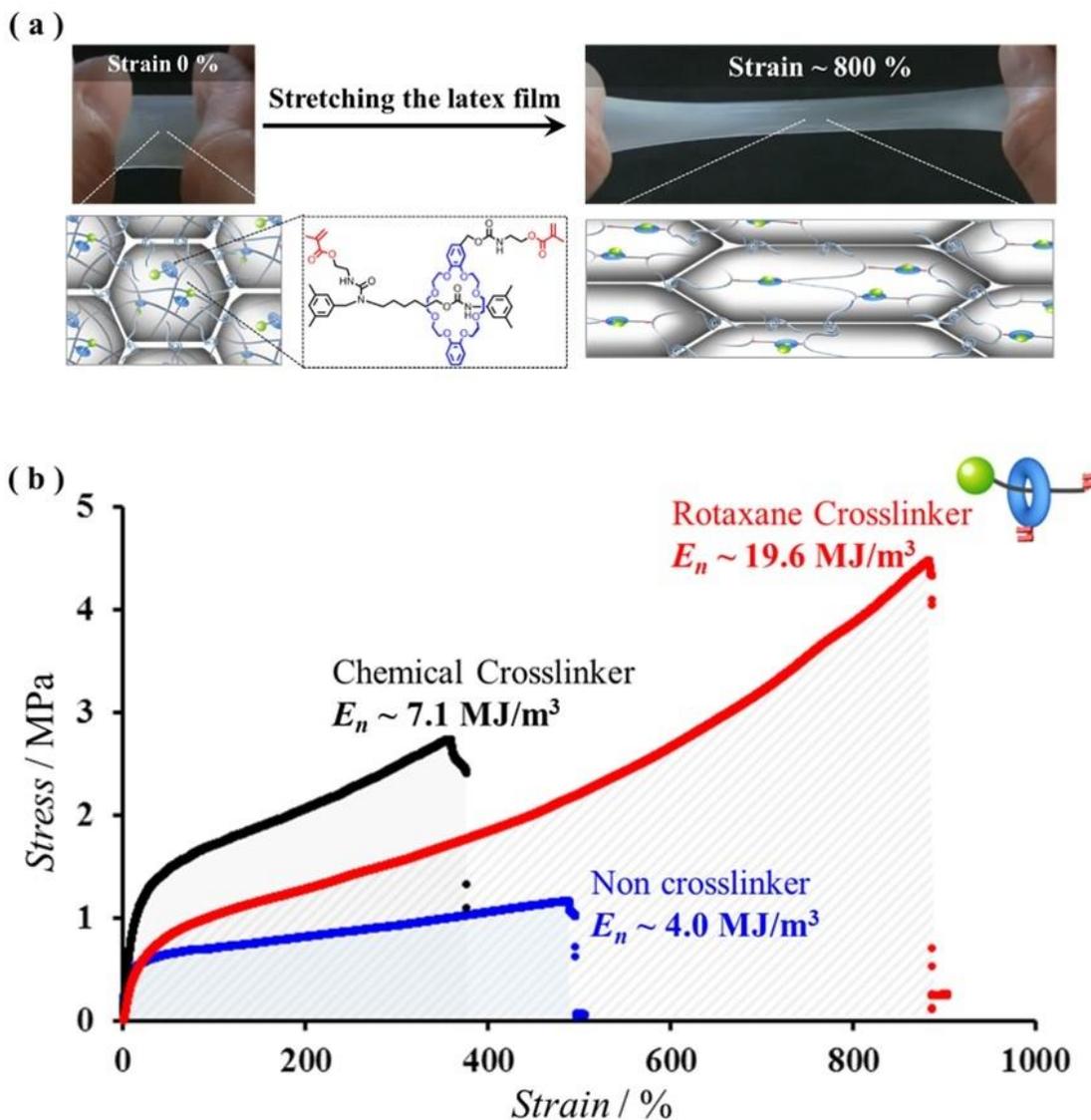


Figure (a) Tough latex film containing microspheres crosslinked with RC.
(b) Stress-Strain curves for films prepared from different microspheres.

COLL 712

Molecular insights into surface ligand-dynamics and their impact on functionality of self-assembled nanoparticle superlattices

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Advances in colloidal chemistry techniques have enabled self-assembly of ligand-stabilized nanoparticles (NPs) into highly ordered arrays (termed superlattices) with exotic collective properties that are entirely different from those of bulk phase crystals, isolated nanocrystals and even disordered nanocrystal assemblies. The exceptional thermal, mechanical, electronic, and optical properties of these superlattices (SLs) make them promising for numerous optoelectronics, energy harvesting, and sensing applications. However, precise engineering of SLs to realize their full potential remains challenging due to lack of fundamental understanding of the molecular mechanisms controlling their collective properties. Here, we integrate coarse-grained molecular dynamics simulations with small/wide angle X-ray spectroscopy, and electron microscopy experiments to identify the crucial role played by ligand coverage density, and surface dynamics of ligands on the structure, thermo-mechanical, and high-pressure behavior of SLs. We find that ligand coverage density dictates (a) the extent of diffusion of ligands over NP surfaces, (b) spatial distribution of the ligands in the interstitial spaces between neighboring NPs, and (c) the fraction of ligands that interdigitate across different nanoparticles. These inter-dependent processes lead to a critical ligand coverage density (1.8 nm^{-2} for 7 nm PbS NPs capped with oleic acid) below which, the SLs collapse via sintering of individual NPs. Above the critical coverage, the SLs can preserve their crystallinity crystalline order even under high applied pressures ($\sim 40\text{--}55 \text{ GPa}$), and show a completely reversible pressure behavior.¹ Such coverage-dependent processes also govern exceptional thermo-mechanical properties of 2D SLs. These results will be discussed in the context of designing superlattices with prescribed functionality for various energy applications.

COLL 713

Applications of SERS encoded particles

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Plasmonic nanostructures present unique optical properties due to the generation of strong electric fields caused by the excitation of the localized surface plasmon resonances (LSPRs). One of the main applications of such LSPRs are the so-called surface enhanced spectroscopies, mainly the surface enhanced Raman scattering (SERS). These spectroscopies have potential for the detection of single molecules under the natural environmental conditions of the analyte and thus, present a broad potential application in different (bio)fields including medicine, the development of new diagnostic tools, multiplex detection and bioimaging and high-throughput screening applications for drug discovery. Herein we will discuss about the fabrication of SERS

encoded particles and their application to the high-throughput screening multiplex identification and recounting of microorganism in biological samples in real time.

COLL 714

“Smart” DNA-based materials for controlled release

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Stimuli-responsive hydrogels undergoing trigger-controlled stiffness changes have attracted substantial interest as functional matrices for different applications. The base sequence of nucleic acids encodes structural and functional information into the DNA biopolymer. External stimuli such as metals ions, pH or light can be used as triggers to reversible switch nucleic acid structures. These features suggest that crosslinking of polymers matrices by means of stimuli-responsive DNA units could provide versatile means to design signal-triggered DNA-based hydrogels materials.

We want report in an approach to create stimuli-responsive DNA-based hydrogel coated materials for controlled release of loads and drugs. The method involves activation of the hybridization chain-reaction (HCR) by a surface-confined promoter strand, in the presence of polymers chains modified with two DNA hairpin structures and appropriated stimuli-responsive tethers. Specifically, we will focus on:

- 1) Stimuli-responsive DNA-based hydrogel coated metal-organic framework nanoparticles (NMOFs).
- 2) Bi-layer DNA-based hydrogel coated CaCO₃ microcapsules. The unique features of this system include: i) The spatial separation of two aqueous compartments that contain two different loads. ii) The triggered release of the loads by the selective unlocking of the outer/inner hydrogel layers or both. iii) Controlling chemical reactivity within the microcapsules confined volume.
- 3) Thermoresponsive plasmonic DNA-based hydrogel coated microcapsules as light responsive microcarriers. The irradiation of the plasmons associated with Au nanoparticles or nanorods are known to induce local heating. These thermoplasmonic effect will be used to dissociate the duplex nucleic acids, acting as temporary crosslinking elements in the hydrogels, leading to the selective ON/OFF release of the loads.

COLL 715

Triple-labelling of polymer-coated quantum dots and adsorbed proteins for tracing their fate

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Colloidal CdSe/ZnS quantum dots were water-solubilized by overcoating with an amphiphilic polymer. Human serum albumin (HSA) as model protein was either adsorbed or chemically linked to the surface of the polymer coated quantum dots. As the quantum dots are intrinsically fluorescent, and as the polymer coating and the HSA were fluorescently labelled, the final nanoparticle had three differently fluorescent components: the quantum dot core, the polymer shell, and the human serum albumin corona. Cells were incubated with these hybrid nanoparticles and after removal of non-internalized nanoparticles exocytosis of the three components of the nanoparticles was observed individually by flow cytometry and confocal microscopy. The data indicate that HSA is partly transported with the underlying polymer coated quantum dots into cells. Upon desorption of proteins, those initially adsorbed to the quantum dots remain longer inside cells compared to free proteins. Part of the polymer shell is released from the quantum dots by enzymatic degradation, which is on a slower time scale than protein desorption. Data are quantitatively analyzed and experimental pitfalls, such as the impact of cell proliferation and fluorescence quenching are discussed.

COLL 716

Accessing intracellular targets using designed nanoplatforms

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Neurodegenerative disorders and intracranial tumors touch many lives. Therapeutic interventions of brain diseases are limited due to the difficulty in reaching the disease site by crossing the impermeable blood brain barrier. The success of in vivo delivery of therapeutics to the brain requires a delivery vehicle which can reproducibly and efficiently transport through the brain capillary endothelium to deliver therapeutics at the target site/cells. In this presentation, I will discuss the optimization of a biodegradable nanoparticle for efficient brain accumulation and protection of astrocytes from oxidative damage and mitochondrial dysfunctions to enhance the neuroprotection ability and also explore the ability of this nanoparticle to attack glioma stem cells/secondary brain tumor cells for therapeutic outcome in glioblastoma or brain metastasis.

COLL 717

Assessing the effect of surface chemistry on targeted delivery and cellular uptake of silica nanoparticle

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Nanoparticles have been attracting tremendous attention for drug delivery and bioimaging up to date. However, the nanoparticles for live cell monitoring and tracking of cytoplasmic processes still remain limited due to inefficient delivery methods, altered state or function of cells during the delivery process and the requirement of surface-

functionalized nanoparticles for specific labeling of subcellular structures. In addition, current understanding and connection between the physicochemical characteristics of a nanomaterial and its interactions with a physiological system are unclear. Here, we investigate the role of surface chemistry in mediating serum protein adsorption to the nanoparticles and their cellular uptake. To suppress protein adsorption or nonspecific bindings, researchers often functionalize the nanoparticle surface with the antifouling polyethylene glycol (PEG). The relative density of the serum proteins depends on the nanoparticle size and the PEG grafting density, and variations in serum protein adsorption is further correlated with the uptake mechanism and efficiency of nanoparticle. Thus, PEG density and nanoparticle size together determine the mechanism and efficiency of cellular binding and uptake, probably by controlling either the identity or accessibility of adsorbed serum proteins. Although PEG can facilitate the reduction of nonspecific binding to cells, this process is not as simple as just putting PEG on the surface, since the chain length of the PEG has to be less than that of the ligand linker in order to not interfere with the binding of the targeting moiety (e.g. peptide) to its target receptor. Our study provides controllable manner of nanoparticle uptake by changing nanoparticle size and surface chemistry, and ultimately establishes principles for the rational design of clinically useful nanoparticle for translational uses of nanomedicine.

COLL 718

Micromotors as targeted payload delivery platforms

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Currently, drugs, imaging agents and other payloads are administered through the mouth are delivered in a static function. Thus, a large portion of the active components are not absorbed necessitating larger doses which induce undesirable side effects. Chemically powered micromotors are autonomously propelled small-scale structures which can increase retention time in the gastrointestinal tract (GI) to promote higher absorption. Micromotors utilize the robust reaction of magnesium with biofluids to propel, lodge into and retain on tissues while pH-sensitive coatings endow them the ability to localize within different areas of the GI tract. Our results have shown that active micromotor delivery strategies prove much more effective than static particle or even free drug analogs opening the door towards more efficient targeted therapies.

COLL 719

Stable J-aggregation of an aza-BODIPY lipid in a liposome for multimodal cancer imaging

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The organic building block is the center piece of “one-for-all” nanoparticle development, whereby the self-assembly into a nanostructure can induce novel nanoscale properties and provide advancement to the design of multimodal nanoparticles for cancer imaging. These beneficial properties have led to the development of a liposome with the phospholipid serving as the key building block for various drug delivery applications.[1,2] Near-infrared (NIR) dyes provide desirable photophysical characteristics for in vivo cancer imaging and the development of new dye-lipids can introduce novel nanoscale properties and broaden the purview of “one-for-all” lipid nanoparticles. However, there are significant difficulties associated with synthesis of new dye subunits that are capable of self-assembly into nanoparticles and therefore hindering the development of a new “one-for-all” nanoparticle. Herein, we report the synthesis of a novel aza-BODIPY lipid building block and discovered that its self-assembly into a liposome-like BODIPY nanoparticles (BODIPYsome) to produce a stable near infrared (NIR) J-aggregate. Tuning the molar ratio of aza-BODIPY lipid from 5% to 95% in the BODIPYsome consistently formed J-aggregates that are optically stable against external stimuli such as serum, time, temperature and pH, is likely attributed by an intermolecular J-dimer effect. BODIPYsomes exhibit enhanced extinction coefficients and high fluorescence quenching in comparison to monomeric aza-BODIPY lipid, which enabled photothermal and photoacoustic properties in its intact form, while retaining NIR fluorescence properties when disrupted in cancer cells. We demonstrate that BODIPYsomes have favorable pharmacokinetics and high tumor accumulation in an orthotopic prostate mouse model. This enabled spectrally distinct photoacoustic imaging (intact nanostructure) and fluorescence imaging (disrupted nanostructure) of its behavior (accumulation and disruption) in tumors over 24 hours after intravenous injection. The successful demonstration of stable J-aggregate BODIPYsomes opens the door for engineering of new building blocks for the design of novel nano-theranostics.

COLL 720

Study on surface interfacial regulation and properties of nanocomposites based on grafting of nano-Al

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As an important metal additive, nano-Al powder has an important prospect in the field of energetic materials. However, nano-Al powder has not been widely used at present due to a large specific surface area and easily reacting with water, which reduces the content of active aluminum (only about 50%). In this word, the one of the -NCO acted as bridged functional groups have been connected with -OH on the surface of nano-Al powder, and the other one will be reacted the energetic molecule GAP by covalently

grafting. After surface modifying, the surface moisture resistance and antioxidant ability of nano-Al powder have been improved, realizing the functional regulation of nano-Al powder. Through the change of surface energy, the compatibility between nano-Al powder and fluoropolymer was enhanced, and the practical application value of nano-Al in composites is improved. At the same time, based on the surface treatment, the core-shell nanocomposites of energetic-crystal HMX@Al was constructed. Nano-Al powder is evenly distributed on the crystal surface, increasing the contact area of two phases, and promoting the combustion properties and mechanical properties of nanocomposites.

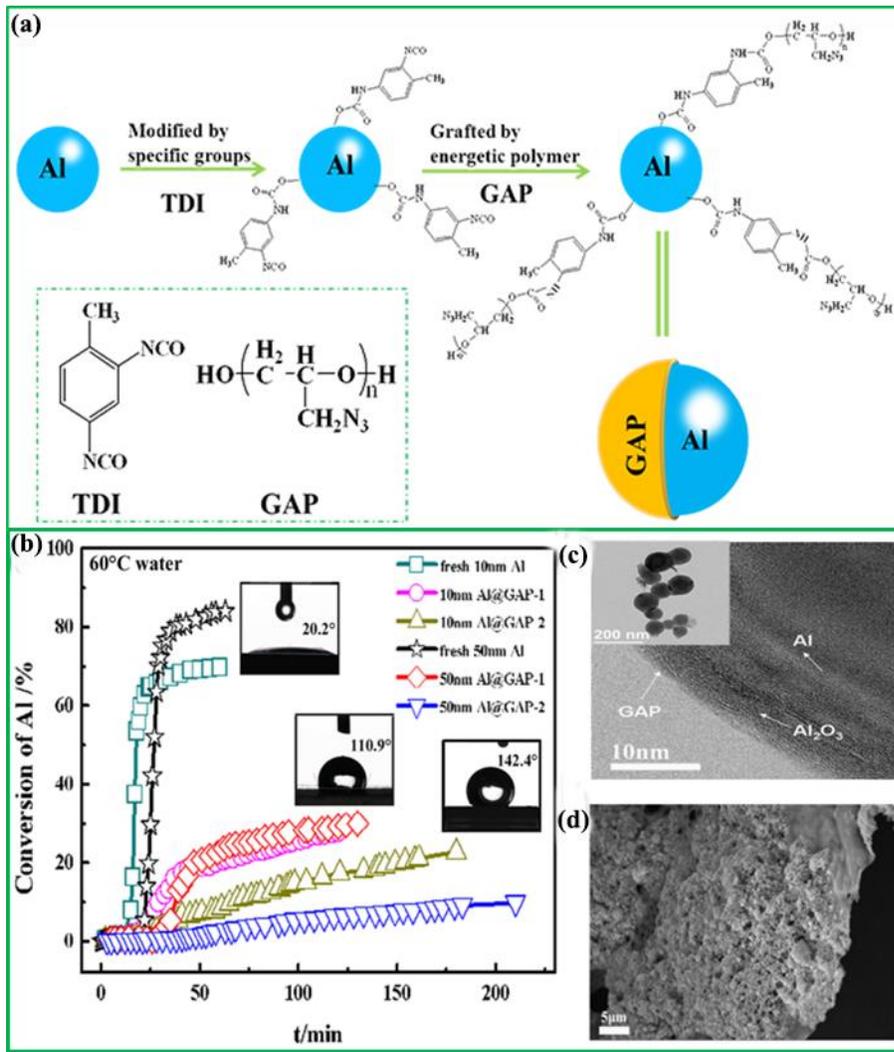


Figure 1 (a) Preparation diagram, (b) accelerated aging test, (c) TEM picture and (d) compatibility with fluoropolymer for modified nano-Al particles.

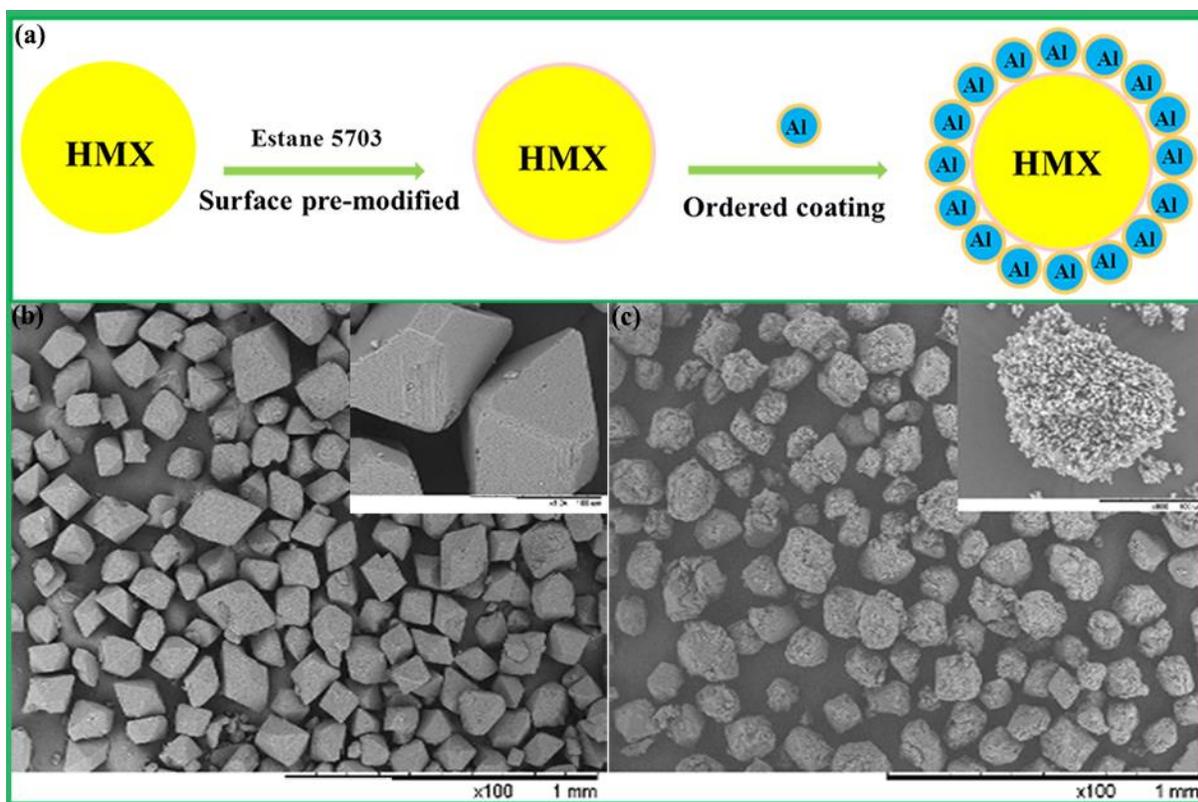


Figure 4 (a) Schematic diagram of preparation and (b) SEM pictures for core-shell nanocomposites.

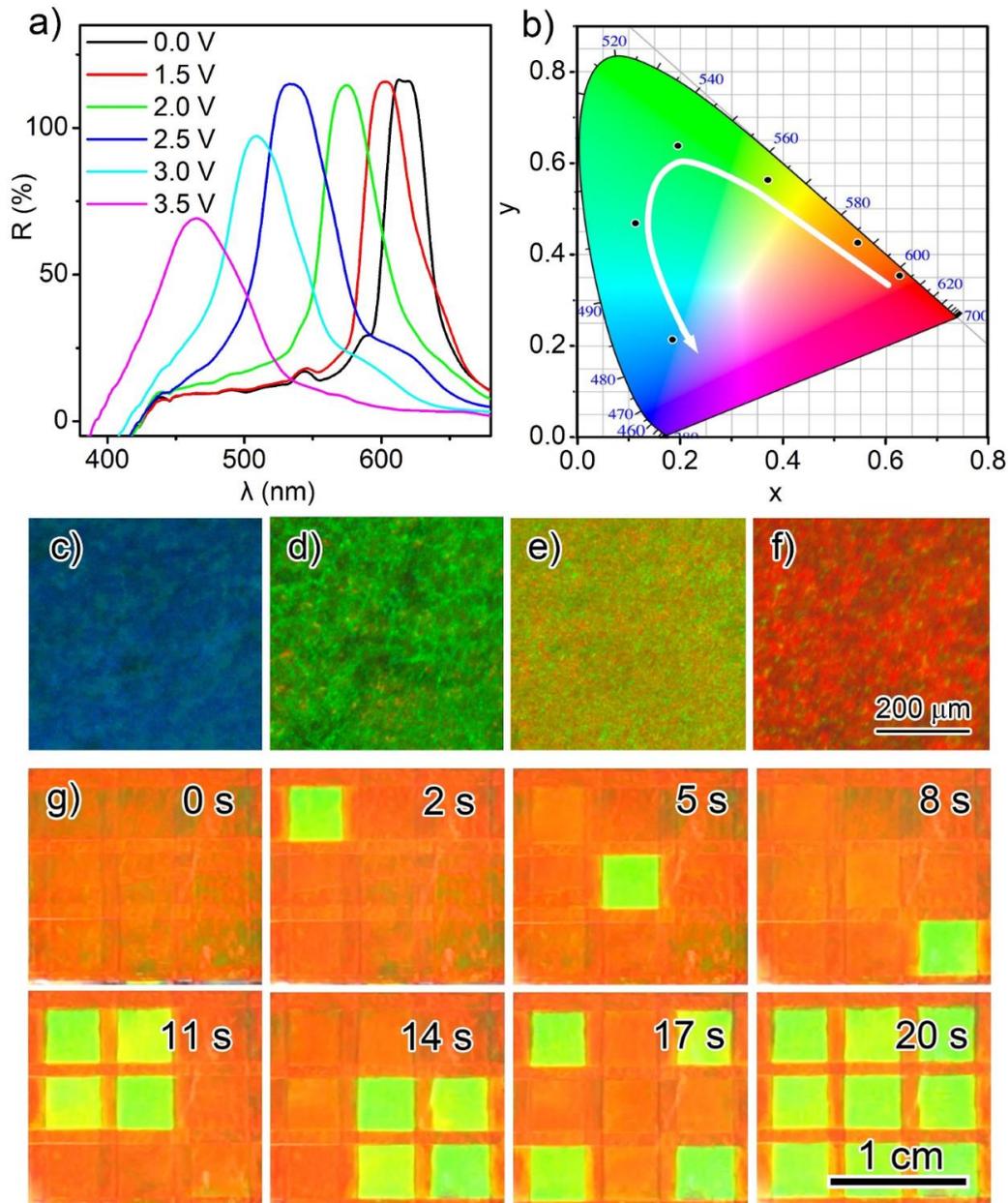
COLL 721

Electrically tunable liquid photonic crystals with highly saturated structural colors for display unit

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New display technology with good visibility, energy-saving features and high safety levels is highly desired due to their applications in wearable products and portable electronics. Herein, $\text{CeO}_2@SiO_2$ colloidal particles are synthesized on large scale and the electrically tunable liquid photonic crystals (PCs) are prepared from the propylene carbonate solution of these particles. It is found that the large dielectric contrast between CeO_2 or $\text{CeO}_2@SiO_2$ particles and propylene carbonate will render the liquid PC a wide photonic bandgap and highly saturated colors with little fading of reflection intensities in electric field, which address the problem of color fading for previous PCs with small dielectric contrast. The $\text{CeO}_2@SiO_2$ based liquid PC simultaneously possesses broad tuning range and highly saturated colors in electric and angular tuning.

Meanwhile, the highly dielectric particles also bring this liquid PC faster electrical response, more reproducible signals in on–off switching, and better stability for long-time working. By combining programmable voltage designing and photonic crystal display units, continuous and program controllable display arrays were obtained, which makes them ideal materials for electronic display devices.



a) Reflection spectra of $\text{CeO}_2/\text{SiO}_2$ /propylene-carbonate liquid PC in different electric fields. b) CIE chromaticity diagram showing the color changes in different electric field. c–f) Optical microscope images for liquid PC at 3.5, 2.5, 2.0, and 0 V. g) Digital photos of PC display unit at

denoted times.

COLL 722

Self-aligned anisotropic plasmonic nanostructures

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Control over localized surface plasmon resonance frequency of metal nanoparticles by shaping the geometry of the nanostructure has attracted continued attention. Herein, we report a stepwise seeded growth method for the synthesis of rod-shaped plasmon nanostructures which are vertically self-aligned with respect to the surface of colloidal substrates. Anisotropic growth of metal nanostructure is achieved by depositing metal seeds onto the surface of colloidal substrates and then selectively passivating the seed surface to induce symmetry breaking in the subsequent seed-mediated growth process. The versatility of this method has been demonstrated by producing nanoparticle dimers and linear trimers of Au, Au-Ag, Au-Pd, and Au-Cu₂O. Further, this unique method enables the automatic vertical alignment of the resulting plasmonic nanostructures to the surface of the colloidal substrate, thereby making it possible to design magnetic/plasmonic nanocomposites that allow for dynamic tuning of the plasmon excitation by controlling their orientation using an external magnetic field. The controlled anisotropic growth of colloidal plasmonic nanostructures and their dynamic modulation of plasmon excitation further allow them to be conveniently fixed in a thin polymer film with a well-controlled orientation to display polarization-dependent patterns that may find important applications in information encryption.

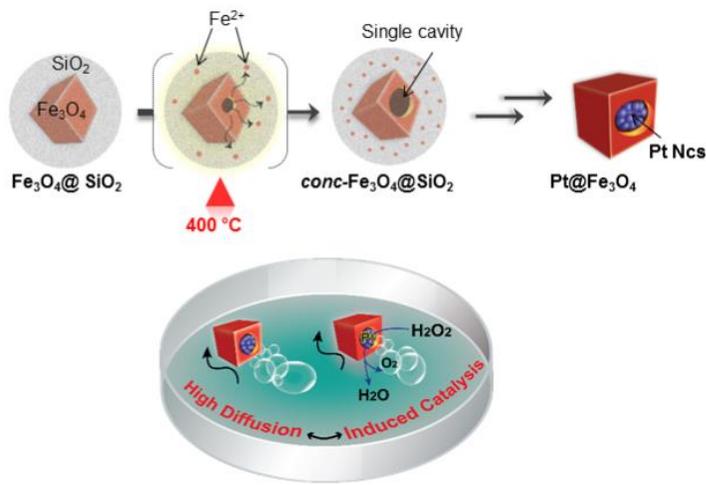
COLL 723

Monofacet-selective cavitation within solid-state silica-nanoconfinement towards Janus iron oxide nanocube

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Post-synthetic strategies for site-selective engineering and functionalization of nanocrystal-surfaces are important for tuning and maximizing the nanoscale-properties, useful in various applications, mainly in catalysis. In spite of the tremendous application potential, the synthesis of the 3-dimensional nanocrystals with anisotropic high-energy negative surface-curvature composed of densely populated low-coordinated atoms is still elusive. The existing strategies towards concave-surface-nanocrystals can only generate negative curvatures indiscriminately, all around the nanocrystal's chemically equivalent facets, resulting a symmetrical structure. Before our work, there was no

method for controllable and facet-selective fabrication of single concave-cavity in a symmetrical 3-dimensional nanocrystal, leaving other parts of the nanostructure unaffected. We developed a highly selective solid-state nanocrystal conversion strategy under thermal reductive conditions towards concave iron oxide (Fe_3O_4) nanocube with an open-mouthed cavity engraved exclusively on a single face of the nanocube. The systematic mechanistic studies based on the investigation of time-course reaction snapshots and various control experiments on the facet-selective cavitation process revealed a novel heat-induced nanospace-confined domino-type migration of Fe^{2+} ions from the SiO_2 - Fe_3O_4 interface towards the surrounding silica shell and simultaneous self-limiting nanoscale phase-transition to the Fe-silicate form. Installed with the mono-directional single cavity, the produced Janus-type concave iron oxide nanocube was further functionalized with controllable density of catalytic Pt-nanocrystals exclusively on concave sites; and such nanostructure was utilized as H_2O_2 -fueled highly diffusive catalytic Janus nanoswimmer for the efficient degradation of pollutant-dyes in water.



COLL 724

Block copolymers in 3D confinement: Janus structures with complex topology

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Block copolymer nanoparticles with unusual morphologies and complex surface are currently in high demand due to their unique physical properties as non-trivial soft matter. Compared to topologies such as spheres, cylinders and vesicles, the precise formation of patchy polymeric rings (toroids) or discs with defined surface structure are still rare.

This presentation discusses new directions for the self-assembly of block copolymers in the spherical confinement of o/w nanoemulsion droplets (**Figure 1**). Upon solvent evaporation the polymer concentrates within the droplet leading to its self-assembly, in which the interfacial energy at the water interface controls microphase separation behaviour. As a result multicompartiment microparticles with complex inner lamellar morphology are produced, consisting of two strictly separated polymer brushes of different chemistry. Subsequent cross-linking of the inner polymeric domain (core) fixes the geometry and generates symmetric Janus nanostructures after re-dispersion of the microparticles in organic solvents. Depending on experimental conditions and the polymers' composition, we either obtain nanorings, -grated, -perforated as well as filled disks, all inheriting Janus character.

The presented process opens the way to novel polymeric nanoparticles and thus gives the opportunity to systematically test the influence on the nanoparticles' shape, inner structure and surface in the field of drug delivery and catalysis.

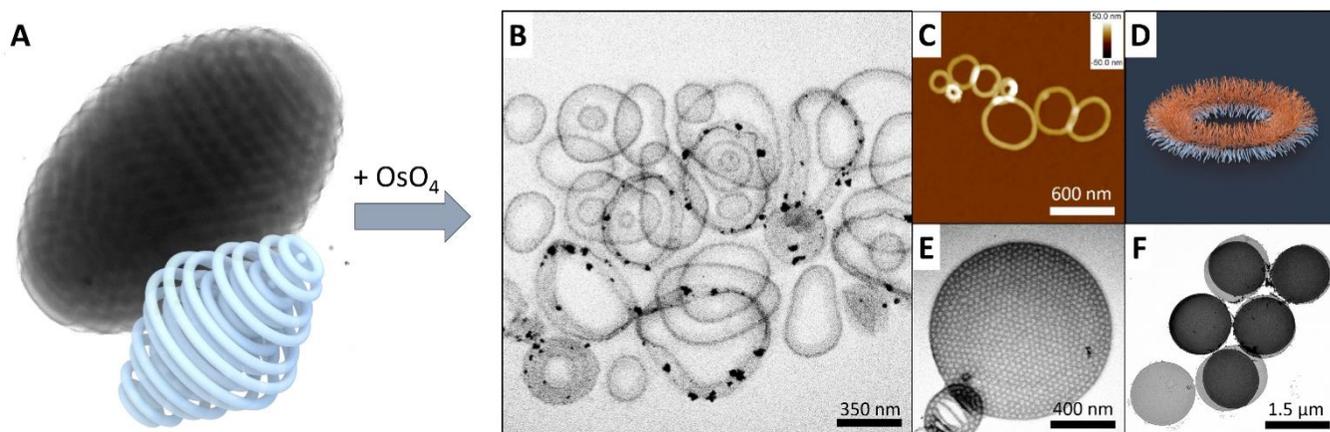


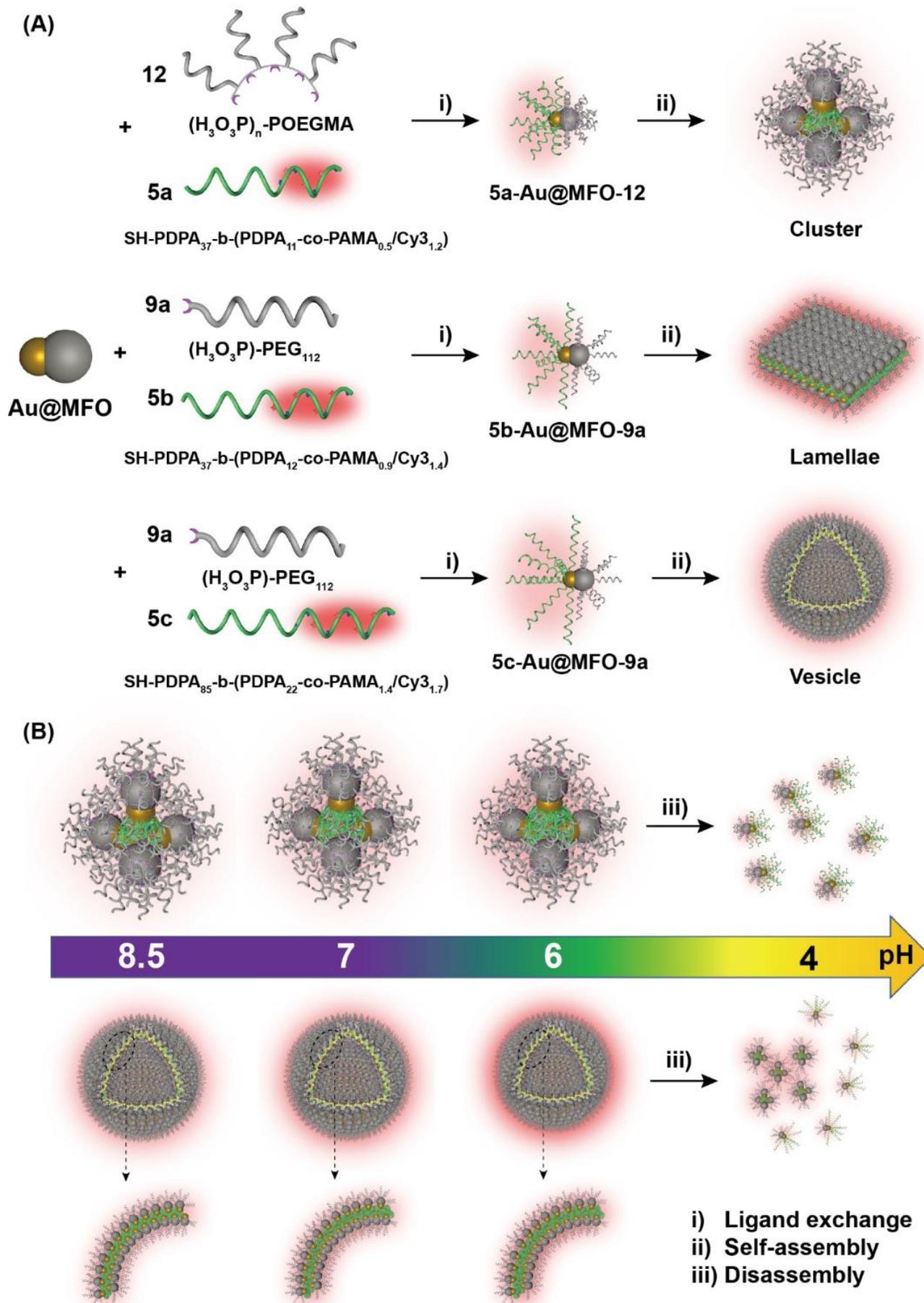
Figure 1: A) TEM of a triblock terpolymer microparticle with lamellar-ring morphology. B-D) TEM, schematic and AFM of Janus nanorings after cross-linking and redispersion of (A). E-F) TEM image of cross-linked Janus-grates (E) and filled disks (F).

COLL 725

Fluorescent dye-encoded assemblies of amphiphilic Janus magnetoplasmonic nanoparticles: Cluster, lamellae, and vesicles

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We report the morphological transition of plasmonic assemblies from cluster-to lamellae-to-vesicle assembled from magnetoplasmonic Janus nanoparticles decorated with pH-responsive dye-conjugated copolymer. The polymer grafts provide the driving force for self-assembly and serve as modulator to tuning dye-plasmonic nanoparticles distance and control the disassembly of resulting assemblies, stimulated by the dimensional changing of copolymer spacing layer. The dye-encoded assemblies exhibit pH-dependent variation in terms of fluorescence emission intensity owing to the swelling and the hydrophobic/hydrophilic transition of copolymer grafts. The incorporation of size tunable spacer allows for the experimentally investigate the influence of quenching efficiency and scattering intensity on over all quantum yield of dye by excluding the impact of excitation enhancement arising from the enhanced electric field. The simulation was also utilized to reveal the dominant contribution on apparent fluorescence emission intensity depending on the relative position of dye and the physical extinction cross sections of assemblies.

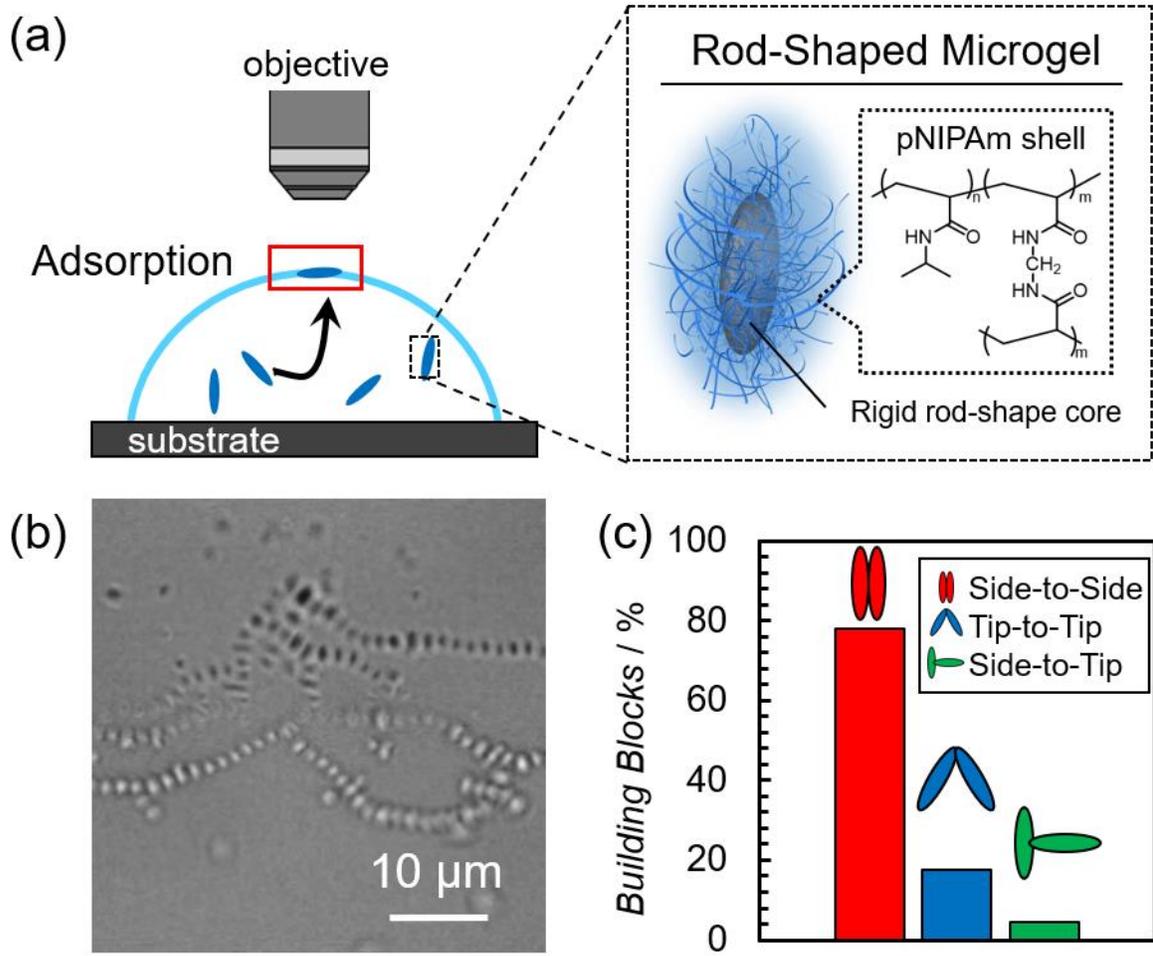


Assembly of rod-shaped hydrogel microspheres at the air/water interface

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Self-organization of colloidal microspheres upon water evaporating is desirable, because it provides ordered structures on the microscale, which allows controlling the optical, wetting, and mechanical properties. Given such background, our group has been investigating drying mechanism of droplets containing poly(*N*-isopropyl acrylamide), pNIPAm-based hydrogel microspheres (microgels). The pNIPAm microgels spontaneously adsorbed at the air/water interface of the droplets, provide the thin films of microscopically ordered microgels from simple drying on a solid substrate. Moreover, such assemble structure and adsorption kinetics can be tuned by changing the properties of microgels such as size and softness.

Here, we have prepared the rod-shaped microgels and investigated the self-organization of rod-shaped microgels at the air/water interface (**Figure a**). The real-time assembly of the rod-shaped hydrogel microspheres was directly visualized by optical microscopy. During the water evaporation, the adsorbed rod-shaped microgels were attracted to each other due to capillary interactions, resulting in the formation of chain-like structure (**Figure b**). Moreover, unlike the case of rod-shaped solid microspheres, the high percentage of side-side structure was maintained during the water evaporation in the case of the rod-shaped microgels due to the interpenetration of the hydrogel layer at the air/water interface (**Figure c**). Therefore, we believe that both softness and anisotropic shape of colloidal microspheres are crucial factors for design the self-organization of microgels at the air/water interface.



COLL 727

Complex inorganic nanomaterials by block terpolymer templating

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Hybrid materials based on polymer and inorganic components are of increasing importance because of their potential in catalysis, micro-electronics or biomedical applications. For instance, helical architectures may have stronger visible-light absorption capability and a higher catalytic performance as compared to spherical nanoparticles. The great advantage of polymer-templated hybrid materials is the access

to complex three-dimensional morphologies on the nanoscale, which are very difficult to achieve through common wet chemical processes.

This presentation discusses a synthetic route for nanometer-sized platinum double helices based on ABC triblock terpolymers with a helix-on-cylinder bulk morphology.

After film formation of polystyrene-*block*-polybutadiene-*block*-poly(*tert*-butyl methacrylate) (SBT) and cross-linking of the helical B microdomain, the bulk film is re-dispersed into high aspect ratio nanofibers in THF. Selective loading of these multicompartament templates with platinum precursor yields rigid and functional hybrid nanohelices (Figure 1). We follow carbonization *in-situ* in TEM, analyze the three-dimensional nanostructure by electron tomography, and verify the catalytic performance in model catalytic reactions.

The synthesis of multicompartament nano-templates opens up new opportunities to create well-defined, uniform and highly ordered materials for electrical energy storage or nanophotonics with special tailored properties. The multicompartament character further inspires the synthesis of magnetic or bimetallic hybrid materials to extend the range of applications.

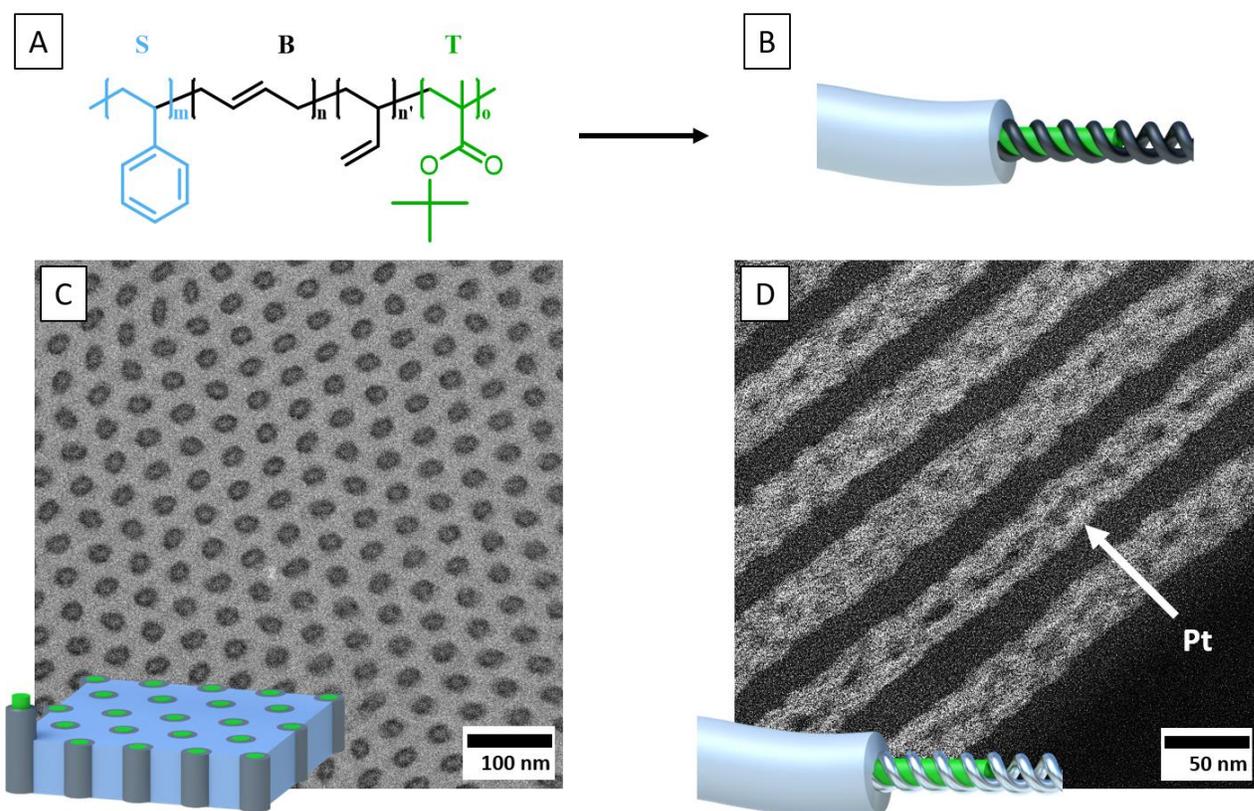


Figure 1: From core-shell cylinder morphology to double helices. A) Chemical structure of SBT. B) Schematic of cross-linked and unloaded cylinder. C) SBT bulk film. D) Platinum loaded

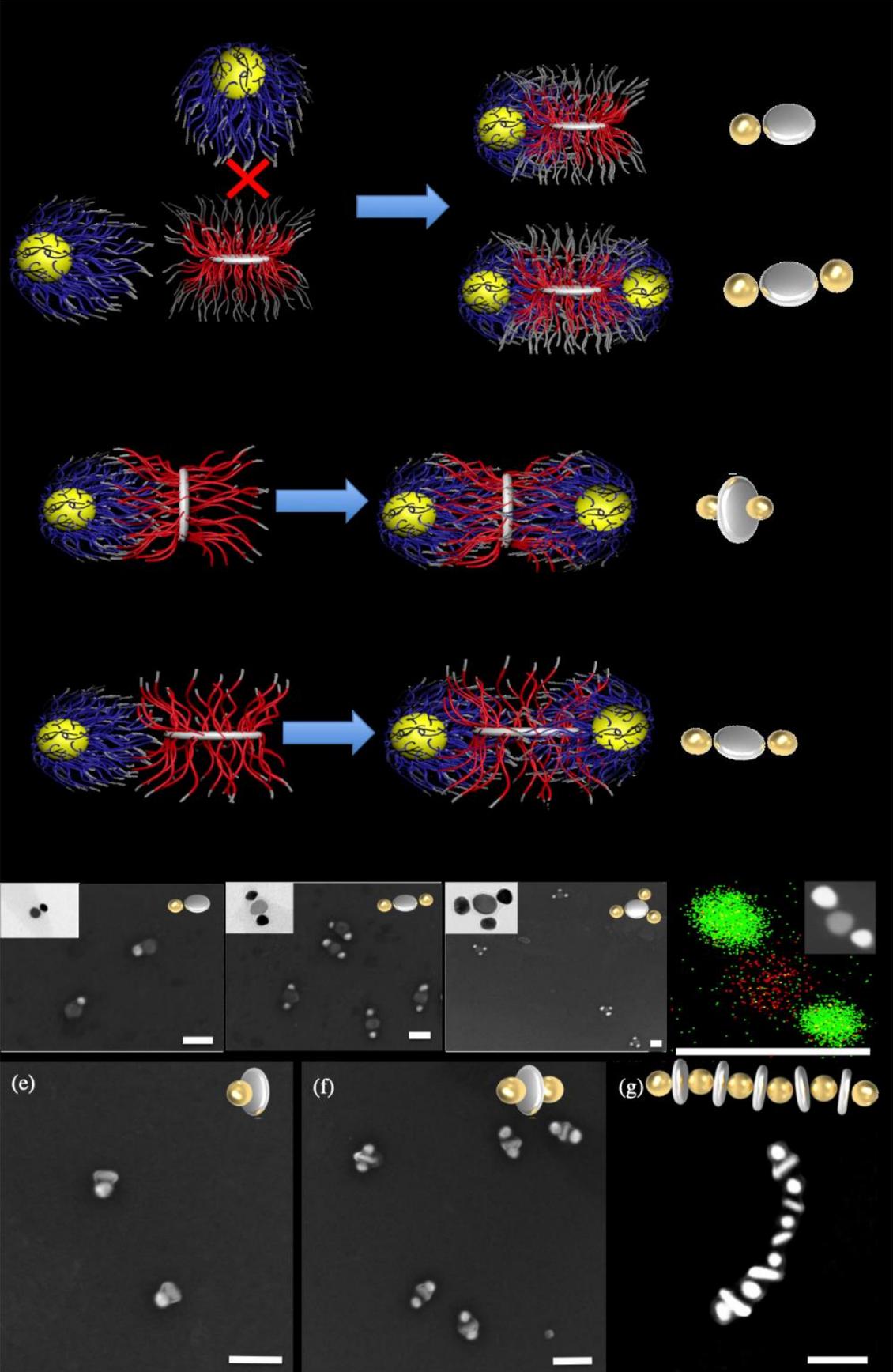
cylinder.

COLL 728

Regioselective self-assembly of gold nanospheres and silver nanodiscs modulated by block copolymers with steric hindrance

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In the designing of nanoparticle assemblies, directional interactions play a crucial role in controlling the spatial arrangement and orientation of the building blocks. Sophisticated surface ligands facilitate the formation of directional bindings via specific interactions and encoding of surface. Anisotropic building blocks also attracted much attention with their unique geometries and shape constraints. In this article, we combine the steric hindrance of polymeric ligands and the anisotropy of nanoparticles to develop a self-assembly system with precise control of the relative orientation of gold nanospheres on silver nanodiscs. The simple yet versatile strategy produces assemblies with ultrahigh regioselectivity and high yields of each assembly. This study may provide new insights for designing supracolloids with increased complexity and functionality. Studying the optical properties of the bimetallic assemblies with different orientations of plasmonic building blocks may contribute to the understanding of complex plasmonic coupling phenomena.

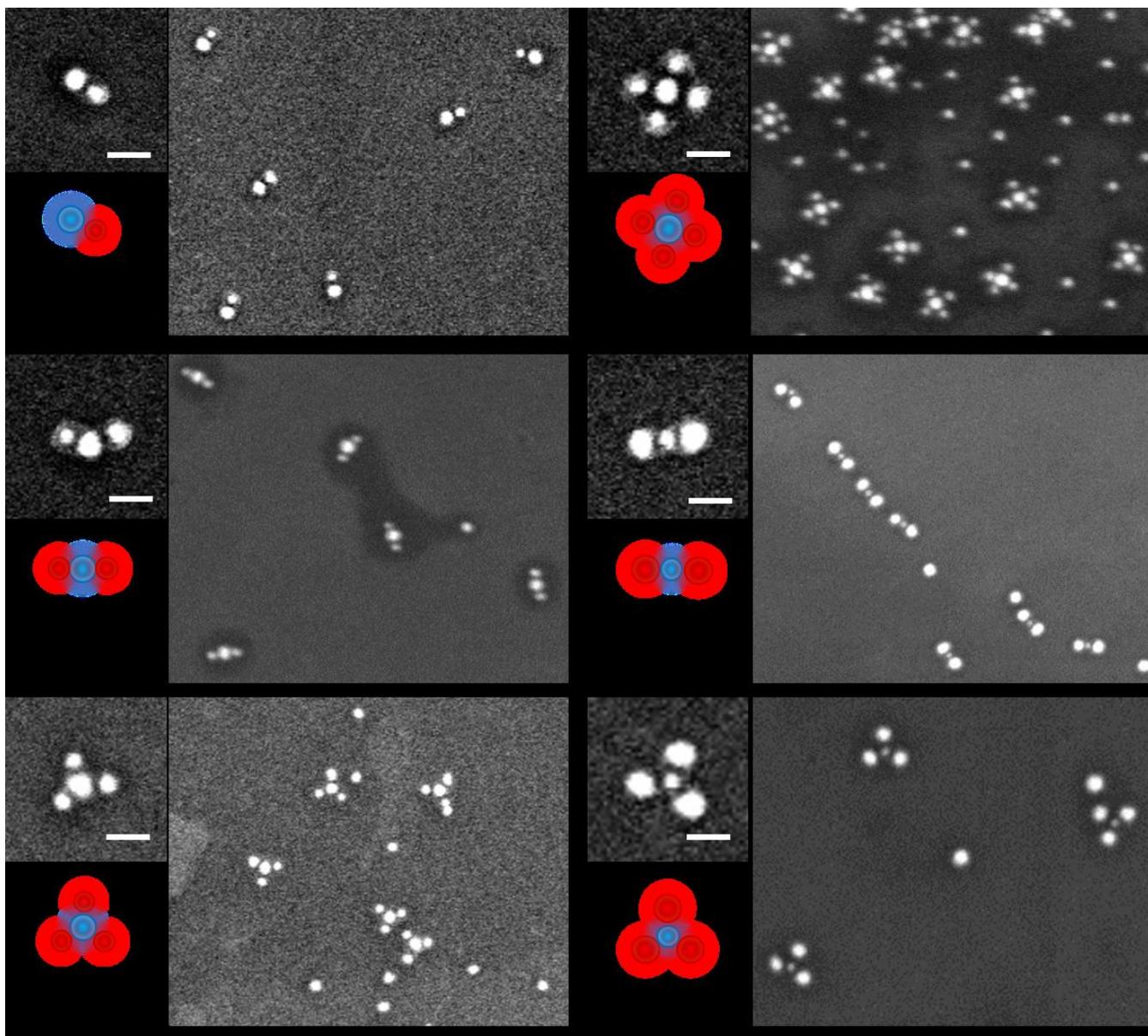


COLL 729

Controlled self-assembly of water-soluble, “hairy,” inorganic nanoparticles (HINPs) into supracolloids with defined valence

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Nature has developed clever and intricate strategies to assemble simple building blocks into complex architectures, ranging from stacking in tubulin to complex twisting and folding in DNA. Drawing inspiration, much research has been done to mimic this molecular programming to develop well-defined nanoscale structures via nanoparticle (NP) self-assembly. However, architectures remain largely simplistic due to the isotropic nature of established assembly protocols. Consequently, we have developed a new self-assembly technique that utilizes favorable Lewis acid/base interactions or Cu(I)-catalyzed azide-alkyne cycloaddition between block-co-polymers (BCPs) tethered to the surface of AuNPs. AuNPs are synthesized via reduction of a gold precursor, using sodium citrate as both a reducing and capping agent. Concurrently, thiol-terminated BCPs are synthesized via Reversible Addition-Fragmentation Chain-Transfer (RAFT) polymerization, with desired functionalities incorporated into the polymer backbone. Subsequently, these BCPs are tethered to the NP surface through ligand exchange, achieving hairy inorganic NPs (HINPs). We demonstrate, that through careful tuning of the BCP length and particle concentrations, we can control the interactions between particles, yielding structures (ie. dimers, trimers, tetramers, etc.) with high yields. Particularly intriguing is the ability to then transfer these structures into aqueous media without loss of structural integrity. We will show that by selecting a hydrophilic outer BCP block of sufficient length, we can form water stable, HINPs, which can be assembled into water soluble supracolloids. Additionally, AuNPs possess a strong localized surface plasmon resonance (LSPR) band that can be easily shifted by changing the size, shape, and interparticle distance of the NPs. This, coupled with their water stability, makes them strong candidates for use in biomedical applications.



Assembled Supracolloidal Structures

COLL 730

Complex behavior of metal surface corrosion and passivity in cellular automata-based simulations

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We present simulation results for our cellular automata based studies of the passivity and corrosion processes on metal surface immersed in aggressive electrolyte solution both in 2D and 3D. We obtain a qualitatively correct description of three groups of phenomena that may occur on such surfaces: spontaneous microcell structure (MCSF) formation at a corrosion potential [1,2], nanopore formation (NPF) on anodized alumina [3,4], electric potential (V) or electric current (I) oscillations (VIO) in passivating systems [5,6]. These phenomena emerge from simple and well understood phenomenology that we code as a mesoscopic-level cellular-automaton model. The inherent nonlinearity of the problems becomes apparent in that the simulation results display a symmetry breaking behaviour. We argue that the common feature of these systems is a characteristic length at which the surface structures appear both in the transient and stationary regimes. This is best understood for the MCSF in terms of the competition between pair creation and pair annihilation processes that take place at the corroding surface for acidic anodic and basic cathodic solutions appearing at the corroding surface. However, our recent study in a 2D system reveals a somewhat more complex mechanism occurring at different length scales for stationary regime [2]. The appearance of the length scales in NPF and VIO is less clear but still some tentative propositions can be formulated. Future developments in this type of modelling for the three phenomena MCSF, NPF and VIO are also outlined.

COLL 731

***Xylopi*a *aethi*o*pica* extract as green and eco-friendly corrosion inhibitor and its quantum chemical analysis**

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This work examines the corrosion inhibitory behavior of *Xylopi*a *aethi*o*pica* stem bark and root bark extracts respectively on corrosion of mild steel in 2M HCl solution and their quantum chemical analysis using gravimetric technique and quantum computational modeling. The corrosion rates of the mild steel coupons in blank HCl solutions were found to increase with increase in concentration of the corrodent, period of immersion and rise in temperature. On the other hand, the corrosion rate decreased in the acid solution containing the test extracts and the decrease became more pronounced on increase in the concentrations of *Xylopi*a *aethi*o*pica* stem bark and root bark extracts respectively. The decrease in corrosion rate indicates that the extracts inhibited corrosion of mild steel in the acid solution and inhibition efficiency increased with increase in extract concentrations. The inhibition is attributed to adsorption of the test extract constituent molecules on the mild steel surface, forming a film layer that protects the metal surface from the corrodent. Results of quantum chemical computational analysis proved that, 3-dimethyl-1-vinylcyclohexene among the constituent compounds of *Xylopi*a *aethi*o*pica* bark extract would be the most likely organic compound to share electrons with the metal surface for possible adsorption bond. The adsorption of the extract molecules on the mild steel surface fitted into Langmuir adsorption isotherm with slope values of 0.86 and 0.98 for *Xylopi*a

aethiopica root bark and stem bark extracts respectively, and regression correlation (R^2) values of 1.0 and 0.99 for root and stem extracts respectively.

COLL 732

Dynamics of 2D materials with nanometer-scale thickness at fluid-fluid interfaces

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Molybdenum disulfide (MoS_2), graphene, and hexagonal boron nitride (h-BN) are 2D materials that can form nanometer-thick films with high optical transparency along with either high conductivity, high resistivity, or high reactivity. A potentially low-cost, high-volume method to produce such films is to trap and assembling them at a fluid-fluid interface and subsequently deposit the assembled film onto a solid substrate. This method has been employed using spherical particles, and it has recently been utilized with 2D particles. In the formation of films with desirable properties it is critical to control the morphology of the film, and the morphology depends on the dynamics of self-assembly. That assembly depends on the relevant forces between the particles, and in nanometer-thick 2D particles pinned to a fluid-fluid interface there are important unknowns about the nature of the relevant forces, especially capillary interactions. We have investigated the self-assembly behavior of CVD-grown MoS_2 platelets, h-BN, and graphene at air-water and oil-water interfaces. This presentation will include results of this ongoing study and a discussion of how the observations here may have consequences for all 2D particle systems of nanometer-scale thickness at fluid-fluid interfaces.

COLL 733

On the temperature dependence of interfacial structure in liquid-liquid interface

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Recent work has demonstrated that significant heterogeneity exists in water interfaces with organic solvents, a feature that can be incredibly sensitive to the nature of the organic solvent and presence of surface active solutes. In the ternary system consisting of water/hexane/tri-butyl-phosphate prior work has demonstrated that interfacially mediated water protrusions are the primary mechanism by which water gets transferred into the organic phase. Herein we investigate the temperature dependence of protrusion formation, including how the temperature affects surfactant adsorption, hydrogen bond structure, protrusion formation and water extraction. A new geometric measure-theory based algorithm is defined that quantifies these characteristics and reveals the balance of forces (thermodynamic vs. entropic) that contribute to protrusion formation. This work is contrasted to other water/organic systems so as to elucidate the generality of water protrusion formation and its underlying mechanistic features.

COLL 734

Water condensation on ionic liquid infused nanostructured surfaces

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Ionic liquids (ILs) have gained more attention of researchers to explore potential applications in different areas because of their unique physical and chemical properties, such as low vapor pressure, high electrochemical and thermal stability, hydrophobicity and water immiscibility. One of the possible applications is infusing a nanostructured superhydrophobic surface with ILs to make a slippery lubricant-infused porous surface (SLIPS) for enhancing heat transfer performance during dropwise condensation. It was previously reported that ionic liquid does not cloak condensate water droplets due to the partial miscibility between the two liquids. In this work, we show that the lubricating ionic liquid cloaks around water droplets immediately upon condensation. Using environmental scanning electron microscopy (ESEM), we conduct water condensation experiments on nanostructured superhydrophobic surface infused with 1-Butyl-3-methylimidazolium hexafluorophosphate (BMIm-PF₆), one of the most widely studied ILs. The ESEM images show multiple satellite droplets sitting on the primary water droplets, indicating presence of a cloaking lubricant layer around the primary water droplets. By using a semi-empirical method, the polar and nonpolar surface tension components of BMIm are predicted and used to calculate its spreading coefficient on water. The resulting positive spreading coefficient further validates our experimental finding. Same experimental and theoretical methods are applied to a non-cloaking lubricant, i.e., dodecane, which is essentially nonpolar. The overall findings indicate that polarity of the lubricant plays important role in the spreading or cloaking on condensate droplets. Further studies will be conducted to investigate the heat transfer performance of surfaces infused with different lubricants, considering cloaking/non-cloaking and various thickness of the infusing lubricant layer.

COLL 735

Adsorption of aqueous inorganic fluoride ions by bauxite: Natural composite mineral ore

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To address the global health crisis caused by fluoride-contaminated groundwater, inexpensive and scalable remediation technologies are necessary. Although many adsorbents (e.g., activated alumina, bone char, hydroxyapatite) have been tested for fluoride removal, few are readily accessible or locally affordable. Bauxite is a globally abundant and naturally occurring mineral assemblage comprising oxides of Al, Fe, Si,

and Ti. Despite its lower surface area and fluoride adsorption density, bauxite (\$30/tonne) appears to be a cost-competitive alternative to refined activated alumina (\$2000/tonne). To determine intrinsic features governing fluoride removal by bauxite, diverse ores from Guinea, Ghana, USA, and India were characterized using analytical techniques including XRF, XRD, PZC, TGA-MS, SEM, FTIR, and BET. Ionic strength and spectroscopic studies confirmed that fluoride formed specific inner-sphere complexes with bauxite through ion exchange with surface hydroxyl groups. Weaker electrostatic interactions did not play a major role in fluoride adsorption. Material characterization data concluded that bauxite's chemical composition, and therefore its geographical origin, substantially impacts fluoride removal. Specifically, bauxite from India required twice the dose (22 g/L) of other bauxite ores to reduce 10 ppm F⁻ down to the permissible drinking water standard (1.5 ppm F⁻). Indian bauxite's reduced affinity for fluoride uptake could not be explained by its differences in PZC, dominant crystalline mineral phase, aluminum content, surface area, or intrinsic affinity and capacity for fluoride sorption. Rather, the presence and dissolution of the trace mineral CaCO₃ in Indian bauxite increased solution pH above the optimal pH (5.5-6.5) for fluoride adsorption.

Studying material characteristics and removal mechanisms of diverse bauxite ores informed subsequent work on enhancement of Indian bauxite's performance. Heating Indian bauxite to 300°C increased available surface area by over 15 times (to 170 m²/g) through gibbsite

dehydroxylation. The loss of structural water and transformation of crystalline gibbsite to a more amorphous phase reduced the bauxite dose for remediating 10 ppm F⁻ by 93%. Lowering the alkaline pH of groundwater from pH 8.7 to 6.0 through HCl addition and CO₂ bubbling also

improved fluoride removal. Ongoing research is on the regenerative capacity of bauxite as a granular filtration media and on the potential leaching of trace metals.

COLL 736

Effect of rigid red blood cells on platelet adhesion in flow

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Thrombocytes, more often referred to as platelets, are a key component of blood whose primary function is to maintain hemostasis by rapidly plugging any interruptions in the vasculature, a process known as clotting. Clotting begins with damage to the endothelium, causing platelets to activate and bind to the endothelial cells or underlying exposed extracellular matrix proteins. Platelet margination and binding to the vascular wall is promoted through hemodynamic, heterogenous collisions between cellular components, including deformable red blood cells (RBCs) in the RBC core. However, RBCs can undergo membrane rigidity in blood-related diseases, such as sickle cell disease (SCD). Experimental research has shown that artificially rigidified RBCs lead to

an expanded RBC core and significantly impact white blood cell (WBC) adhesion to the endothelium. However, little experimental work exists to fully elucidate the effect of rigid RBCs on platelet margination and binding in vessels.

We utilized an *in vitro* flow-based system to examine how the extent of rigidification and rigid RBC concentration affect platelet margination and binding to a damaged endothelium model mimicking acute vascular damage. RBCs were removed from the whole blood and artificially rigidified using a peroxide solution. The RBCs were then reconstituted into blood and perfused over the damaged endothelium. Platelet adhesion was quantified and compared to a healthy control.

The presence of rigid RBCs in flow drastically increases platelet adhesion under specific rigidities and concentrations. This finding suggests that rigid RBCs may play a major role in disrupting normal hemodynamics and contributing to the pervasive vaso-occlusive crises that occur in many SCD patients. Overall, we will elucidate how rigid RBC-platelet interactions affect platelet binding, a critical step in hemostasis. This study can help determine the mechanism causing vaso-occlusive events in SCD patients and can form the basis of the study of platelet-cell dynamics in the future.

COLL 737

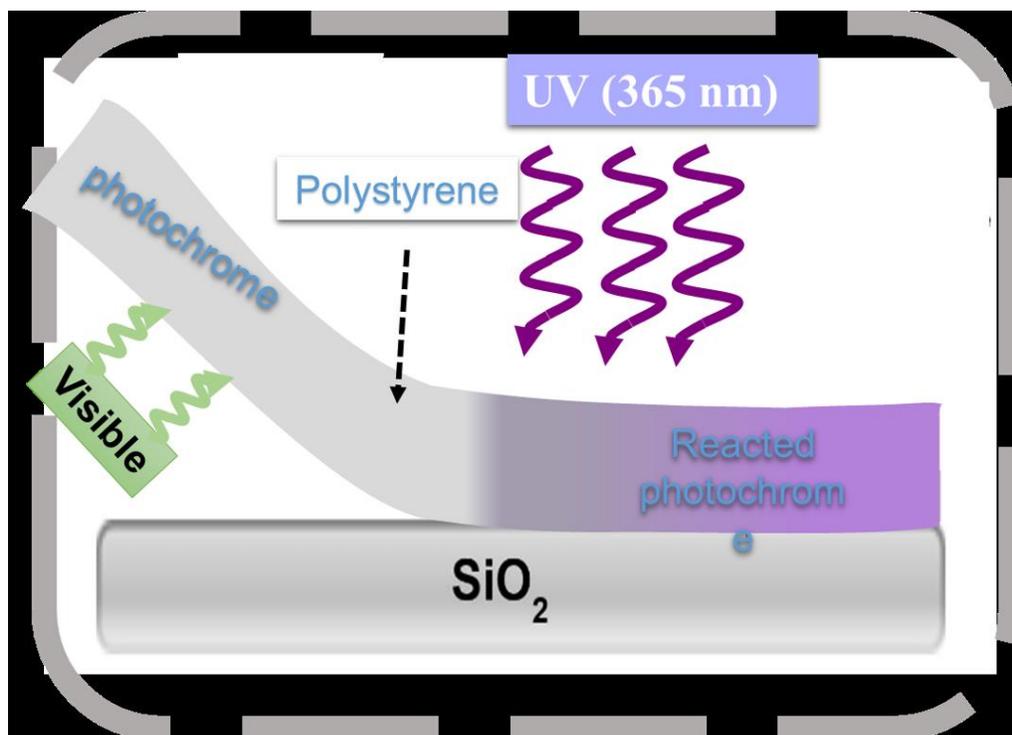
Photoinduced changes in polymer-glass adhesion

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Developing smart materials that respond to external stimuli is a central goal of materials science. Adhesion is a material property that is important in many areas of industry and medicine. Light is a stimulus that is easy to tune and convenient to use in both biological tissues and industry.

Scientists in many fields have demonstrated light induced adhesion based on cross-linking for various applications, however reversible adhesives have not been fully developed. Our strategy was to use photochromic molecules dissolved in a polymer to change chemical interactions and consequently modulate adhesion. Photochromic molecules are molecules that undergo structural change upon light irradiation. In our previous studies we demonstrated that we could significantly increase adhesion of a polystyrene polymer film to a glass surface using nitro spiropyran as the photochromic molecule. We have recently developed a way to switch adhesion off using light and a different photochrome. As a final goal we want to increase and decrease adhesion based on our needs in one sample. In the current studies we have tried to use both molecules with an optimized concentration. We found out that shining UV light will

increase adhesion of thin films of polystyrene (PS) to the substrate and irradiating laser light will decrease adhesion. This will help us to engineer a controlled release device which enable us to release encapsulated chemicals from wells or capsules whenever needed. As a proof-of-principle, we encapsulated a food dye in a small well of microscopic slide and covered it with small cover glass and glued them together using a polystyrene/photochrome mixture. Upon UV irradiation the adhesion of our glue increased and after visible irradiation the glass cover detached, and the encapsulated dye released. We are working on different substrate and polymers to maximizing the control of adhesion by light.



COLL 738

Quantifying the exposure time-dependent wetting properties of plasma-treated polymer surfaces

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Precise control and characterization of surface wettability is critical when applying coatings, inks, adhesives, and other materials to solid surfaces. This is particularly true of plastics which generally exhibit poor wettability due to low surface free energy (SFE). A number of surface modification techniques, such as flame treatment, chemical adhesion promoters, and plasma treatment, can improve wettability, but thorough characterization of the treated surface is needed to demonstrate efficacy as well as optimize the process to reduce costs. In this presentation we demonstrate how contact angle (CA) measurements incorporated into SFE calculations can both optimize the process and provide physical insight into complex surface reactions. We will discuss how this approach is superior to qualitative techniques such as dyne pens while not requiring significant costs associated with rigorous analytical techniques such as FTIR. To illustrate this point we treated polypropylene (PP) samples with air-plasma for between 1-120 s. Subsequently, CA's of water, diiodomethane and ethylene glycol were measured with an Attention Theta optical tensiometer and SFE calculations, including polar and dispersive components, were made automatically with OneAttention software. While untreated PP exhibited CA >100°, surprisingly only a 3 s treatment reduced the CA to 64°. In that time, SFE increased from 24.2 to 46.8 mJ/m² during which a rapid increase in surface polarity indicated efficient surface oxidation. Interestingly, treatment times from 5-15 s reduced polarity and SFE, indicating competition between oxidation and destruction of the surface species. Beyond 15 s, SFE gradually increased again. The effect of storage time on the degradation of SFE was also monitored. Thus, we demonstrate the ability to precisely determine optimum surface treatment protocols using CA and SFE measurements, and gain physical insight into the underlying process.

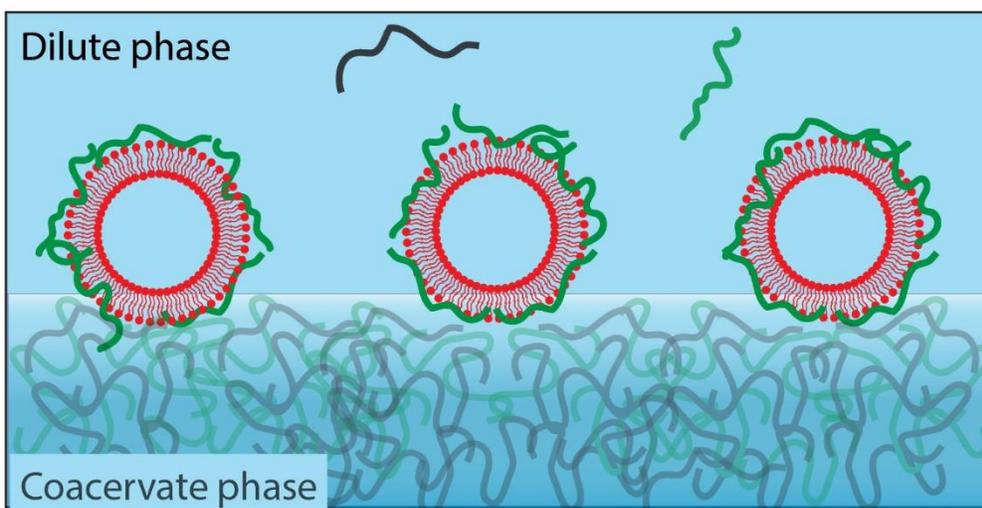
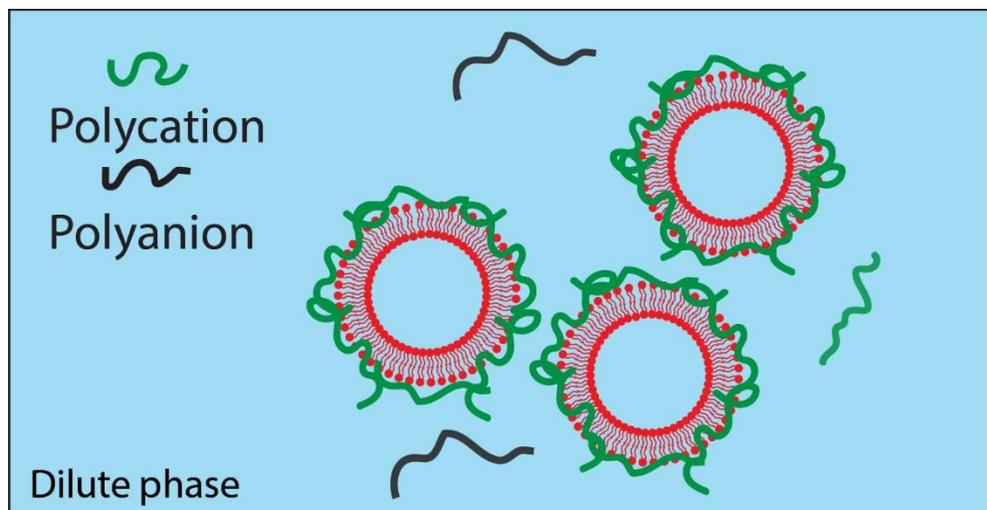
COLL 739

Lipid and complex coacervates interactions

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Phase separated systems attracted more attention due to recent discovery of cellular condensates. Compartmentalization by complex coacervation is important across a range of different fields including subcellular and prebiotic organization, colloidal science, biomedicine, food science, and personal care products. Often, lipid self-assemblies such as vesicles are also present intracellularly or in commercial formulations. A systematic understanding of how phospholipid vesicles interact with different complex coacervates could provide insight and improve control over these systems. We used anionic phospholipid vesicles in a series of different complex coacervate samples in which coacervates were formed by mixing one of five polycations with one of three (poly)anions that varied in chemical structure and length. Vesicles were found to assemble at the coacervate/continuous phase interface and/or form aggregates. We studied how factors such as the length and identity of the

polyelectrolytes and the charge ratio of cationic to anionic moieties impacts vesicle distribution in coacervate samples. Our findings emphasize the importance of interactions between vesicles and polycations in the dilute supernatant phase for determining whether the vesicles aggregate prior to assembly at the liquid-liquid interface. Uptake of an RNA oligonucleotide was also investigated to understand the effect of these liposome coatings on diffusion into coacervate droplets. Systems in which uniform vesicle coronas assemble around coacervate droplets without restricting entry of biomolecules such as RNAs could be of interest as bioreactors.

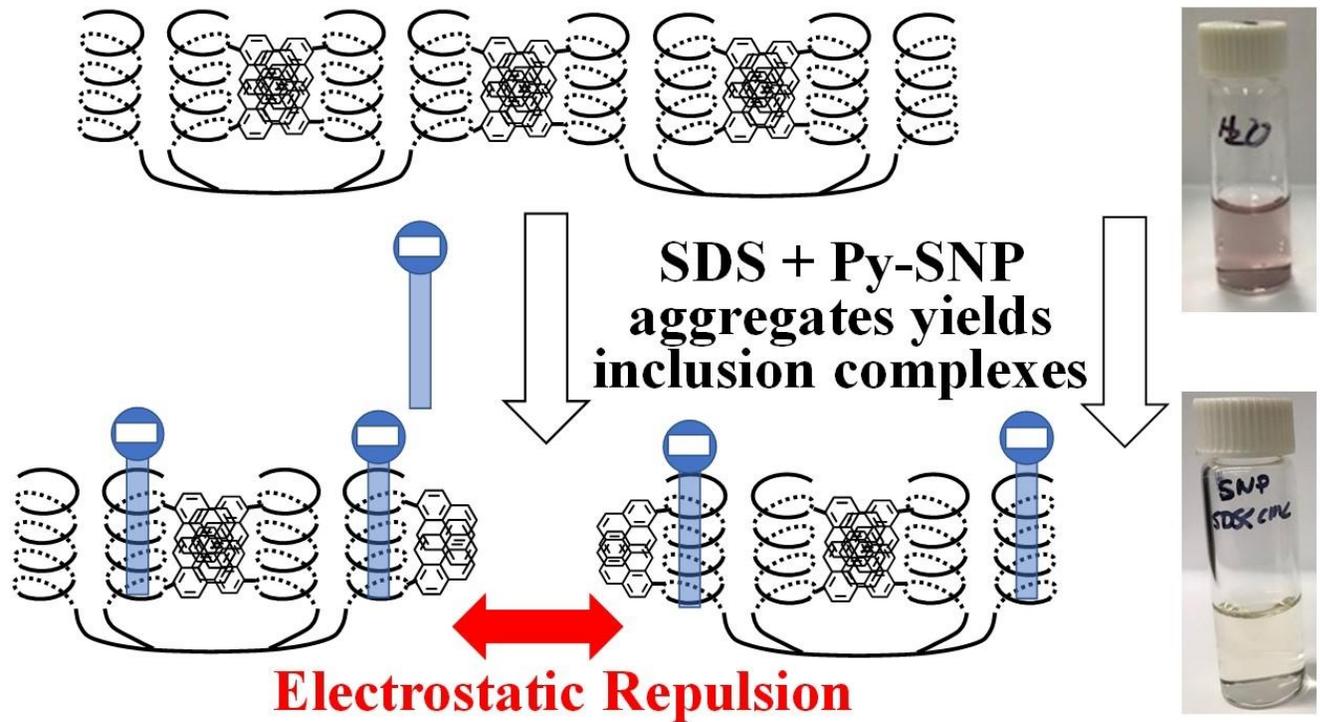


COLL 740

Probing interactions between surfactants and hydrophobically modified starch nanoparticles by fluorescence

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With its large number of hydroxyl groups, starch can be chemically reacted with hydrophobes to yield hydrophobically modified starch (HMS). Due to its interesting colloidal properties, HMS has been the focus of intense research. Since an HMS prepared with a large amount of hydrophobic material is insoluble in water, HMS can be stabilized with surfactants. Yet little is known on how surfactants interact with HMS. To this end, starch nanoparticles were fluorescently labeled with the hydrophobic dyes pyrene (Py-SNPs) or naphthalene (Np-SNPs) and their behavior was monitored as sodium dodecyl sulfate (SDS) and sodium dioctyl sulfosuccinate (AOT) were added to the aqueous dispersions of Py-SNPs and Np-SNPs. In water, Py-SNPs and Np-SNPs aggregated resulting in enhanced pyrene excimer fluorescence (PEF) for the Py-SNPs and fluorescence resonance energy transfer (FRET) between Np-SNPs and Py-SNPs. Addition of surfactants to the aqueous dispersions of the fluorescent SNPs uncovered a number of surprises. First, SDS interacted with the fluorescent SNPs at concentrations that were much lower than expected for typical hydrophobically modified water-soluble polymers. Second, AOT did not interact with the fluorescent SNPs up to the CMC, above which PEF increased and FRET decreased. Third, the fluorescence data indicated that at the low concentrations where SDS interacted with the Py-SNPs, SDS did not seem to target the hydrophobic pyrene labels. These findings could be rationalized by noting that SDS with its linear alkyl tail formed inclusion complexes with starch in a process that stabilized the HMSNPs with apparently little interactions with the hydrophobes. By contrast, the branched nature of AOT prevented the formation of inclusion complexes with starch which explained the absence of interactions at low AOT concentrations. These conclusions were supported by colorimetric assays with potassium triiodide. The formation of inclusion complexes between SDS and HMSNP is expected to provide a simple means for their stabilization in water.



Stabilization of Hydrophobically Modified Starch Nanoparticles through the Formation of Inclusion Complexes with Surfactants

COLL 741

Small molecule segregation from poly(vinyl alcohol) films

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Molecular migration concerns a huge number of industrial systems containing mobile components in polymer matrices. The behavior of surfactants at polymer interfaces is relevant to a wide range of systems in which polymer films encounter surfactant-rich environments. Although the surface and bulk properties of large polymers in solution is well studied and the adsorption of surfactants onto liquid surfaces has been extensively characterized, the case where the solution is replaced by a solid polymer has received little attention. Predicting the behavior of surfactants in polymer films therefore remains a fundamental scientific challenge. In this work, attempts are made to isolate parameters responsible for the blooming of additives from poly(vinyl alcohol) (PVA) in order to ultimately predict and control segregation

The segregation of surfactants from PVA films has been explored using neutron reflectivity to depth profile additives and a rich and diverse range of behaviors has been identified. When PVA contains the anionic surfactant sodium dodecyl sulfate, a wetting

layer of surfactant on the film surface is formed. In the presence of an additional plasticizer (glycerol) this SDS surface excess is greatly enhanced, and smectic nanostructures are formed on the surface, consisting of surfactant lamellae separated by interstitial glycerol layers. In contrast, the segregation of a zwitterionic surfactant from PVA reflects behavior commonly observed in solution, where a monolayer of surfactant covers the surface but the remaining additive is distributed evenly throughout the bulk polymer.

Studies of the polymer and additives in aqueous solution enable identification of driving forces for this behavior. Surface energy arguments can be used to rationalize segregation to a great extent, but cannot alone explain the plasticizer enhancement of the surface excess of SDS or wide range of segregation behaviours observed. We therefore utilize the phase behavior of model systems to determine the compatibility of film components, assessing this a likely driving force for segregation from the polymer.

COLL 742

Morphology, texture and stability of spin dewetted 5CB nematic liquid crystal droplets

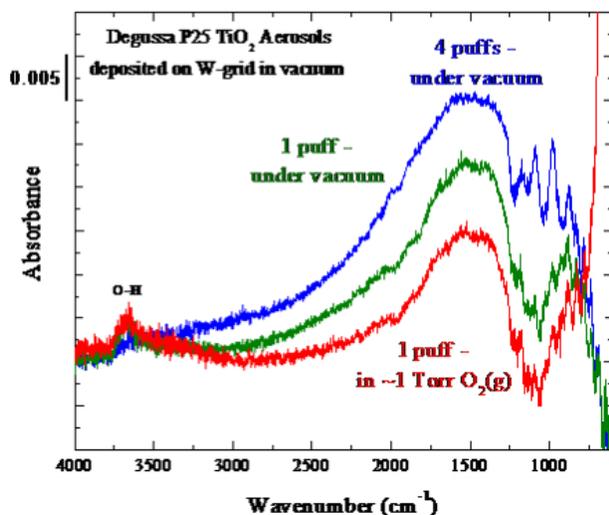
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Ultra-thin film (< 100 nm) of soft materials has a tendency to rupture and form holes at the surface due to attractive Van der Waals interaction active between surface and interface. This phenomena is called dewetting. Dewetting is not desirable for thin film coating applications but it can be used as an effective alternate lithography technique to create meso or nano structures. A thin film under go through the dewetting process when it is annealed above its glass transition temperature (T_g) or exposed to solvent vapor. But dewetting with the help of external stimuli takes long time. Here, we have reported a rapid and ultrafast dewetting process during the spin coating. Spin coating with very dilute solution of casting material fails to form a continuous film but the solution layer rupture and form isolated droplets during the spin coating process. This process is termed as spin dewetting. Here, we have reported spin dewetting of 5CB liquid crystal (LC) at room temperature at its nematic state on a Poly(methylmethacrylate) (PMMA) substrates. The hemispherical spin dewetted droplets of 5CB show radial texture under the polarized microscope as two different kind of molecular anchoring are observed at LC-PMMA interface (planar) and LC-air surface (homeotropic). Interestingly, the diameter (d_D) and periodicity (λ_D) of the droplets decrease with increasing the concentration (C_n) of 5CB within the spin dewetting regime. This is an opposite trend than the conventional dewetting process. Transition of texture from radial hemispherical droplets to schlieren texture continuous film is observed by changing C_n above the spin dewetting region. The droplets spread on the polar PMMA surface with time as the end group of 5CB (-CN) gets absorbed on polar surface. Further, array of aligned spin dewetted droplets are obtained by guiding the spin dewetting process on topographically patterned substrates.

Characterization of particle charge from aerosol generation process: Impact on infrared signatures and material reactivity

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Aerosols are one of the most important and significant surfaces in the atmosphere. They can influence weather, absorption and reflection of light, and reactivity of atmospheric constituents. A notable feature of aerosol particles is the presence of surface charge, a characteristic imparted via the aerosolization process. The existence of charge can complicate the interrogation of aerosol particles, so many researchers remove or neutralize aerosol particles before characterization. However, the charge is present in real world samples, and likely has an effect on the physical and chemical properties of an aerosolized material. In our studies, we aerosolized different materials in an attempt to characterize the charge imparted via the aerosolization process and determine what impact it has on the aerosolized materials' properties. The metal oxides, TiO₂ and SiO₂, were aerosolized expulsively and then characterized, using several different techniques, in an effort to determine the surface charge imparted upon the particles via the aerosolization process. Particle charge distribution measurements were conducted via the employment of a custom scanning mobility particle sizer. The results of the charge distribution measurements indicated that expulsive generation of 0.2 μm SiO₂ particles produced aerosols with upwards of 30+ charges on the surface of the particle. Determination of the degree of surface charging led to the use of non-traditional techniques to explore the impact of additional surface charge on the overall reactivity of the metal oxides, specifically TiO₂. TiO₂ was aerosolized, again expulsively, onto a gold-coated tungsten mesh, which was then evaluated with transmission infrared spectroscopy in an ultra-high vacuum environment. The TiO₂ aerosols were exposed to O₂, H₂ and CO, respectively. The results observed during exposure suggest that the additional charge imparted via aerosolization does impact the interaction with each probe gas.



COLL 744

Interfacial behavior of amino acid residues on gold surfaces studied with electrical spectroscopy and atomistic reaxFF simulations

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Understanding of the interfacial behavior of biomolecules has critical applications in biodetection. In this study, the interface of amino acid residues are studied with in-situ electrical spectroscopy and atomistic reactive force field (ReaxFF) simulations. Electrical spectroscopy measures the electrical properties of materials through relaxation phenomena of different types of amino acid residues on gold electrode surfaces to validate the simulations results. Electrochemical impedance spectroscopy (EIS) is performed during specific adsorption of amino acids on gold-plated electrodes. From EIS measurements, the capacitance associated with adsorption is extracted to determine the surface coverage of the amino acid along with its rate of adsorption. ReaxFF simulations, which utilize a polarizable charge model based on the bond order, provide insights into both the physical interactions and chemical reactions (such as protonation/deprotonation and thio-interactions) of amino acid residues and peptides on flat plain gold electrode surfaces and gold nanoparticle surfaces. The effect of the surface's curvature on amino acid residues' adsorption behavior is investigated. Moreover, simulations also elucidate the surface's polarization upon the adsorption of

polarizable oxygen, nitrogen and sulfur atoms from amino acid residues. In the meantime, simulations provide in-depth understanding of the experimental signals.

COLL 745

Tuning the interaction energies between lipid head groups and planar substrates

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Phosphatidylinositol 4,5-bisphosphate (PI(4,5)P₂) lipids in supported bilayers show a relatively low mobile fraction on planar glass supports compared to other membrane components. Moreover, it can be shown that the mobile fraction decreases with time. Using the fluorescence recovery after photobleaching (FRAP) technique, we have explored the limited mobility and slow diffusion coefficients as a function of temperature, pH, water isotope, and lipid headgroup structure. Such systematic studies allow us to obtain direct information on the exact conditions that lead to inositol lipid immobilization on the substrate surface. Specifically, the question concerns the interactions of the phosphate moieties on the ring as well as the bulky size of the ring itself. Based on our experimental results, in this talk, we will provide insight into the structural basis and the physical chemistry behind the low mobility for an entire class of lipids in typical planar supported bilayer systems.

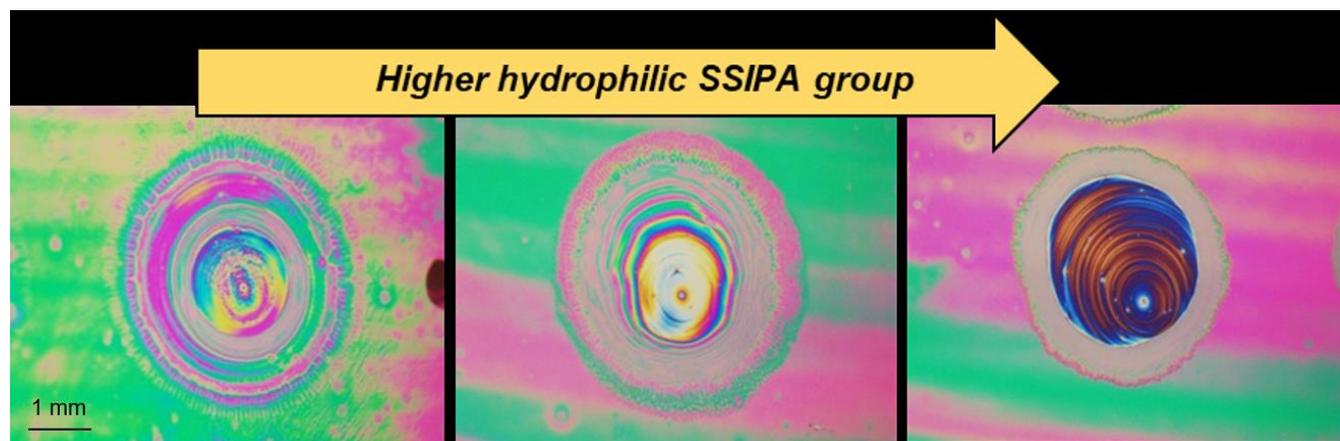
COLL 746

Revisiting the colloidal fundamentals and exploring nanofilm formation of water-dispersible polyesters

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Waterborne polymers have enormous potential as an environment-friendly substitute of organic solvent-borne polymers. Driven by environmental and legislative pressures, the specialty aromatic polyesters were rendered water-dispersible by functionalizing the polymer backbone with ionic monomers. Since these polyesters are designed to be used as waterborne dispersions, understanding their colloidal interactions in dispersions is critical for their application. By using a range of commercially available sulfopolyesters as a model system, we investigated the relationship between their molecular composition, colloidal interactions, and phase equilibria. As a result of being partially water-soluble, these polyesters form self-assembled nanoaggregates (20 ~ 50 nm) in water without the need for additional stabilizer(s). These nanoaggregates are composed of hundreds of polymer molecules, where their aggregation number is

determined by the composition, ionic groups and molecular weight of the polymers. By using static, dynamic, and electrophoretic light scattering, we present a model for nanoaggregate formation in water based on the critical surface charge density of these nanoparticles. Since the ultimate goal of developing such waterborne system is to apply them in films and coatings, we also explored how these films interact with water by forming nanofilms of brilliant structural colors. To test the structure and properties of the dried films, we deposited sessile water drops on the films which lead to partial dispersion and evaporation-induced “coffee ring” formation. We further characterized this new class of coffee ring phenomena as “coffee ring erosion” and demonstrated that such water-damage property is governed by the ionic composition of the polyesters. Additionally, we showed that the water-resistivity and integrity of the coatings can be significantly improved by incorporating rapid thermal-curing. Such fundamental understanding of colloidal interactions could be used to efficiently control and improve the colloidal stability and film-formation ability of these polyesters. Therefore, this study may enable the design of novel high-performance volatile solvents-free and surfactant-free waterborne dispersion systems.



COLL 747

Water interactions with striped phases of amphiphiles on 2D materials

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Nanostructured water environments are frequently examined in the context of porous materials such as zeolites. However, noncovalent functionalization approaches commonly applied to 2D materials such as graphene can also create nanostructured

interactions with water — such interactions are critical to issues including processability and integration into composites. On 2D materials, long-chain functional alkanes (e.g. fatty acids, phospholipids) assemble into lamellar phases, with alkyl chains oriented parallel to the surface and polar headgroups forming ordered rows. These phases resemble a repeating cross-section of a lipid bilayer, with 1-nm-wide hydrophilic stripes alternating with ~5-nm-wide hydrophobic stripes (tunable based on alkyl chain length). Although the stripes of amphiphiles are noncovalently adsorbed at the interface, use of amphiphiles containing an internal diyne allows the monolayer to be photopolymerized, increasing robustness. The molecular-scale polar/nonpolar boundaries have important consequences for the behavior of functional groups, including substantial pK_a shifts that impact bulk wetting; just as in the cell membrane, exact details of both headgroup and chain structure are important in this regard. Recently, we have also found that water adsorbed on striped phases from the lab environment can be retained in certain nonpolar solvent environments, forming nanometer-wide hydrated channels with surprising impacts on interactions with the environment. We will discuss experimental approaches including contact angle, scanning probe, and PM-IRRAS measurements, as well as molecular dynamics simulations, aimed at understanding the relationship between surface chemistry and the behavior of water at these interfaces.

COLL 748

Understanding an active role for water in zeolite-hydrocarbon reactions

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Water is present at some level in almost all existing solid-acid catalyzed chemistries, even gas phase reactions, due to its affinity for zeolite and zeotype catalysts. In the emerging areas of emulsion catalysis involving solid acids for biomass conversions, water is a major component in the reaction mixture. Some recent literature reports indicate that water can increase hydrocarbon reactivity in a few acidic zeolite systems, but the mechanistic origins of this unexpected water effect have not been discussed. Many mechanistic possibilities exist, including enhanced proton transfer through Vehicle-Hopping or Grotthuss mechanisms, transition state solvation, or synergistic proton-affinities afforded by water-reagent clusters. Combining catalyst synthesis, spectroscopic, and reactor experiments with computational investigations should reveal the origin of and potential for water's active role in solid-acid catalysis. More importantly, mechanistic information can be exploited to potentially increase activity, selectivity, and/or catalyst lifetimes in solid-acid catalysis. Recent experimental data implicating

small populations of catalytically active sites as those most responsive to the presence of water will be discussed.

COLL 749

Water adsorption in zeolites: Insight from multiscale modeling

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Zeolites are aluminum-silicate minerals with sub-nanometer pores, widely used as support for heterogeneous catalysis and as gas traps. Their capability of trapping water makes these porous minerals appealing also as desiccants in food drying technology. Understanding the processes of water adsorption and desorption at the molecular scale would be essential to design desiccants with specific temperature range, higher efficiency and stability. Here we investigate the process of water adsorption and desorption in Faujasite - a natural zeolite - as a function of the aluminum content, by combining molecular modeling techniques at different scales, including first-principle total energy calculations, classical and *ab initio* molecular dynamics and grand canonical Montecarlo (GCMC) simulations. GCMC simulations are predictive as for the thermodynamics and kinetics of water adsorption, providing an estimate of the water uptake at various thermodynamic conditions. First principles calculations shed light on the preferred adsorption sites, which are characterized by computing NMR shifts. Equilibrium and non equilibrium MD simulations unravel the mechanisms of water dynamics and desorption.

COLL 750

Understanding material and component level properties on the performance of MOF-based atmospheric water harvesting systems

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Water scarcity is a particularly severe challenge in arid and desert climates. While a substantial amount of water is present in the form of vapor in the atmosphere, harvesting this water by state-of-the-art dewing technology can be extremely energy intensive and impractical, particularly when the relative humidity (RH) and/or temperature are low. In contrast, atmospheric water harvesters (AWHs) that utilize sorbents enable capture of vapor at low RH conditions and can be driven by the abundant source of solar-thermal energy, and consequently exhibit higher efficiency even at low RH conditions. Metal organic frameworks (MOFs) are particularly attractive

as an adsorbent for this application because they can capture more water and require lower regeneration temperatures for its release compared to conventional sorbents (zeolites, silica gels, etc.). Much of the recent materials development has focused on a single material metric, equilibrium vapor uptake in the material (kg of water uptake/kg of dry adsorbent), as found from the adsorption isotherm. This equilibrium property, however, is not alone a good indicator of the actual performance of the AWH system. Understanding material properties which affect heat and mass transport are equally important in the development of materials and components for AWH, because resistances associated with heat and mass transport in the bulk material dramatically change the system performance. This talk will first outline the detailed experimental measurements required to understand the transport properties at the material level and a theoretical framework which can connect mass transport all the way to the system scale. The framework considers diffusion both inside a single crystal as well as macro-scale geometric parameters, such as the thickness of the adsorbent layer. System level design implications will also be discussed.

COLL 751

Interplay between specific-ion effects and confinement in the aqueous electric double layer

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Understanding the electric double layer (EDL) of aqueous electrolytes near the carbon interface is critical for optimizing device performance in a wide variety of emerging technologies, including water desalination and supercapacitors for energy storage. However, despite considerable theoretical and experimental efforts, a final consensus has not been reached on the behavior of simple ions, such as alkali cations, at the graphitic interface. This key knowledge gap becomes even more significant for solutions in carbon nanopores, where the paramount important effects of confinement must be taken into account. Here, we integrate high-level first-principles simulations with electrochemical measurements to unravel the key features of the EDL of several aqueous solutions at the interface with graphene and under confinement within carbon slit-pores. We find that large, strongly polarized cations with weak hydration energy exhibit a stronger affinity to the graphene interface. In addition, space charge transfer (SCT) effect was found to have substantial impact on the electrochemical interface, which was often neglected in conventional force field simulations, and essential to reproduce the capacitive behavior of the interface observed experimentally. These effects are dramatically enhanced by nanoconfinement, which can be ultimately related to the intrinsic properties of the ions and the nature of their solvation. Our study points to the complex interplay between confinement and specific ion effects on the interfacial capacitance and ion accessibility, suggesting general improvement strategies for

optimizing carbon-based materials for energy storage and water desalination technologies.

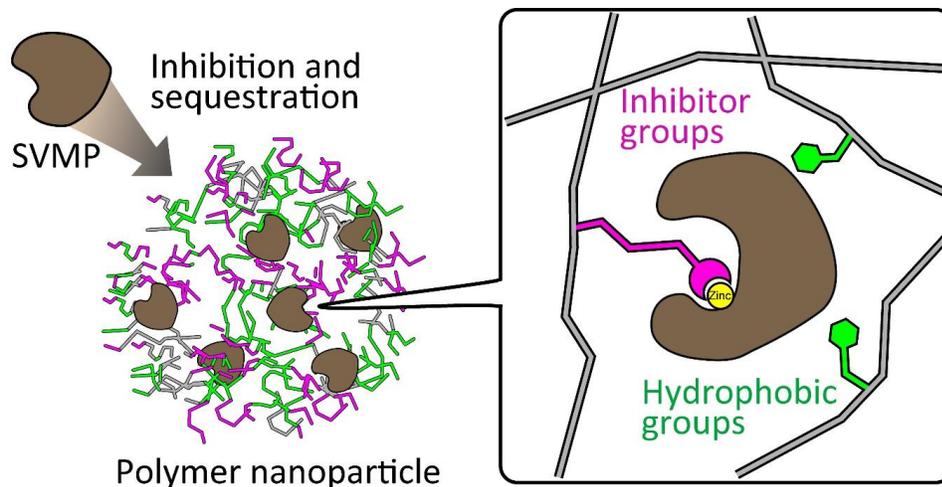
COLL 752

Design of synthetic polymer nanoparticles for metallo proteinase inhibition

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Enzyme inhibition is a therapeutically important approach to regulate many biological processes. Enzyme inhibitors may be based on small molecules, biomacromolecules and/or synthetic polymers. In this study, we hypothesized that synthetic polymer nanoparticles (NPs) displaying both inhibitor-bearing groups and hydrophobic functional groups can achieve high inhibition for a target enzyme. We describe efforts to synthesize polymer NP inhibitors against snake venom metalloproteinases (SVMPs), one of the major families of toxic proteins found in venomous snakes. Traditional antivenom, comprised of antibodies isolated from the blood of large mammals inoculated with venom, is utilized as an antidote for snake bite. However, SVMPs, major contributors to tissue necrosis, are fast acting and even in the event that traditional immunological therapy can be administered in a timely manor, it does little to mitigate morbid injuries at the site of envenomation. Further complicating an effective therapeutic intervention is the fact that SVMPs are not pure substances, they consist of many isoforms, which can moderate the therapeutic efficacy. Our goal is to develop a stable and inexpensive abiotic NP therapeutic intervention with broad spectrum efficacy against SVMPs.

We selected whole venom from *Crotalus atrox*, a typical SVMP rich venom as a target for our studies. SVMPs are zinc ion dependent enzymes and their catalytic domains are highly conserved. Lead NP candidates were identified by directed chemical evolution, a process involving synthesizing and screening synthetic polymer libraries of poly-*N*-isopropylacrylamide based NPs with various functional groups. Promising candidates were found to require both inhibitor and hydrophobic groups. The talk will describe progress towards developing an effective, broad-spectrum abiotic inhibitor for SVMP.



Inhibition of snake venom metalloproteinases by polymer nanoparticle

COLL 753

New polymer formulations for cryostorage of biologics

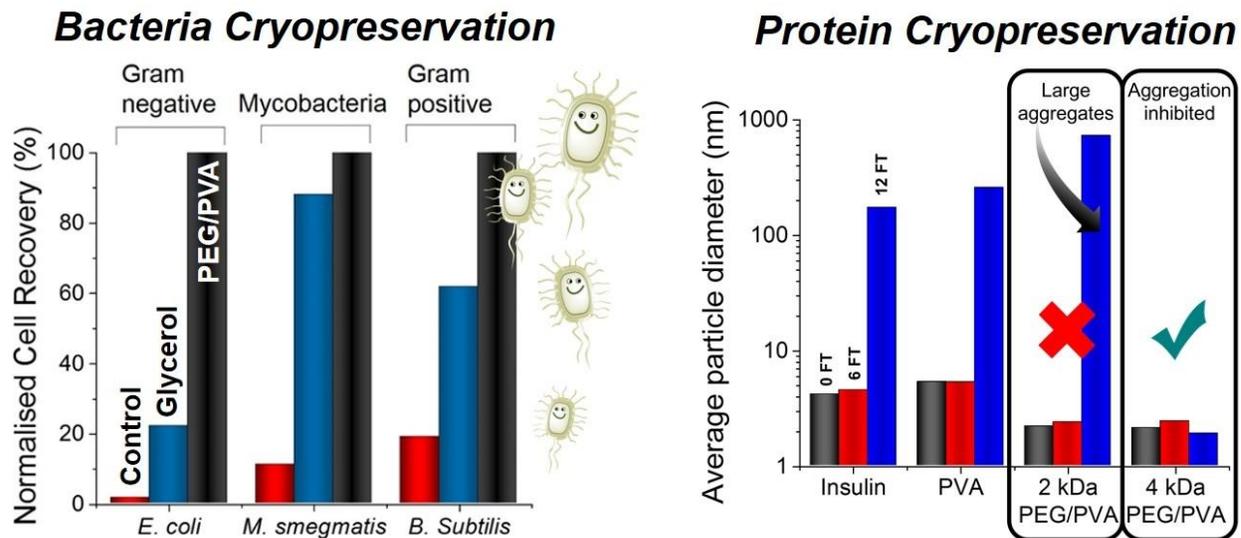
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A key challenge with any biotechnology or cell-based process is logistics – the storage, transport, distribution and recovery of intact and viable cells suitable for purpose, with no pheno/genotype alterations with minimal risk of contamination. Proteins and antibodies are often used as therapeutics, however limited storage lifetime and degradation are major issues. Lyophilisation and cryopreservation are commonly used in academic and industrial settings to store biologics. Traditionally the addition of organic solvents mitigates the damage caused by ice formation and growth. These can be DMSO, glycerol or trehalose. However, they can be intrinsically toxic and often can impact down-stream applications and assays.

By employing physical, biological and chemical principles, this work explores extremophile survival by examining the effect of different compounds including antifreeze proteins (AFPs), polymer mimics and small molecules, on ice morphology and growth, with the aim of elucidating mechanisms of action and enabling the production of more active, less toxic polymer mimics of biomacromolecular antifreezes. Extremophile organisms survive repeated freeze/thaw cycles by producing antifreeze proteins that are potent ice recrystallization inhibitors. Here we introduce a new concept for the storage/transport of biologics by using ice recrystallization inhibiting poly(vinyl alcohol) in tandem with a bulky hydrophilic polymer, poly(ethylene glycol). Our results expose the versatile nature of this polymer formulation, as the method is appropriate for

a panel of Gram negative, Gram positive and Mycobacteria strains as well as a range of proteins.

The ice growth process and the mechanism of action of ice recrystallization inhibition (IRI) active compounds are investigated, with the goal of characterising ice structures and how they are affected by these compounds. The mechanism of biologic protection is demonstrated to be linked to inhibiting ice recrystallization (by comparison to a recombinant antifreeze protein) but also to the significantly lower toxicity of the polymers compared to glycerol.



COLL 754

Electron mediators shuttling between erythrocytes and liposomes encapsulating hemoglobin (artificial red cells) to reduce methemoglobin by using abundant glycolytic electron energies

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Our previous studies have clarified that NADH and NADPH, re-energized repeatedly by erythrocyte glycolysis, can be utilized for extracellular chemical reactions, where electron energies are extracted by electron mediators, such as methylene blue (MB) (Ref.1&2). The electron mediators, which are reduced by NAD(P)H, permeate both the biomembrane of erythrocytes and the phospholipid bilayer of liposomes encapsulating

hemoglobin (Hb-vesicles; HbV, known as artificial oxygen carriers) and reduce autoxidized ferric methemoglobin (metHb) in HbV to ferrous Hb. In vitro screening study clarified some other potential electron mediators with comparable capacity to reduce metHb. Given this background, eight of these compounds: MB, 1,9-dimethyl MB, azure A, azure B (AB), azure, toluidine blue, brilliant cresyl blue and toluylene blue, were evaluated in both in vitro and in vivo studies in this work. Compared with MB as a reference, in vitro experiments demonstrated that most compounds caused effective metHb reduction of HbV in the presence of erythrocytes (Ref.3). However, in vivo experiments of bolus injection of autoxidized HbV to rats (10mL HbV/kg body weight) followed by injection of the dye (1.53 mL/kg body weight, 2.6mM) led to some differences from in vitro results. Effective metHb reduction was found for the combination of AB. To evaluate AB effectiveness further, a haemorrhagic shock and resuscitation model was used, where the rats were resuscitated with HbV injection. When the level of metHb increased to 50%, a dye solution was injected. Again, AB caused sufficient reduction of metHb. Through these in vivo experiments, this study clarified that AB is a suitable electron mediator to prolong the functional lifetime of HbV as a transfusion alternative.

COLL 755

pH-Response tunable mixed-charged polymers for reversible adsorption and desorption of proteins

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Smart polymers, whose characteristics undergo appropriate changes in response to surrounding environmental conditions, enable control over properties as the transport of molecules, changes in wettability, and the adhesion of different species among others. pH-Responsive mixed charge polymer provide a new avenue to achieve reversible switching between non-fouling and fouling properties. When carboxylic acid is used as the anionic group of mixed-charge polymer, pH-responsive behavior from mixed charge to positive charge with decreasing pH based on the protonation state of the carboxylic acid group can be switched between fouling and non-fouling properties. Anionic carboxylic acid groups used in mixed-charge polymer has relatively lower $pK_a \sim 5$, which is inadequate physiological pH. Therefore, we aimed to shift the $pK_a \sim 5$ value of the anionic group to neutral by changing the pH-responsive anionic monomer and introduction of spacer moiety. We prepared three type of carboxylic acid monomers with different hydrophobicity of side groups, and synthesized pH-responsive mixed-charged polymers (Fig. 1). The pK_a values of polymers were determined by pH titration. As the hydrophobicity of carboxylic acid monomers, and neutral monomers increased, the pK_a values shifted to higher values. In addition, Increasing the composition ratio of neutral monomers, the pK_a values shifted to higher values. Finally, the pK_a value of polymers shifted from 4.6 to 5.8. Switching pH between mixed-charge and positive

charge was successfully tuned by changing the anionic monomers, and composition ratio. In addition, we confirmed pH-responsive protein adsorption with using heparin, which is a well-known anionic protein by dynamic light scattering (Fig. 2). These results indicated that pH-responsive characteristic of mixed-charge polymer was successfully tuned by changing the pH-responsive carboxylic acid group and introduction of spacer moiety.

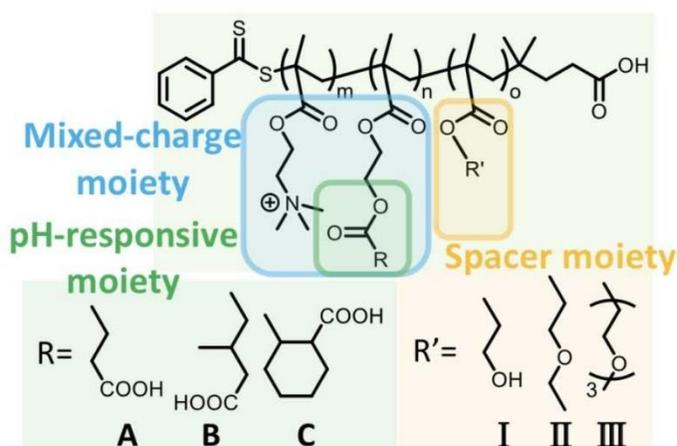


Fig. 1 Chemical structures of pH-responsive mixed-charge polymers

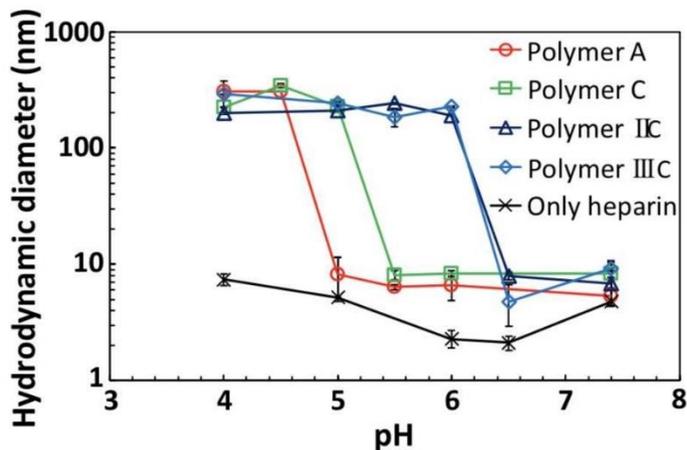


Fig. 2 pH-dependent heparin adsorption

Determination of the adsorption orientation of amyloid beta 1-40 monomer over nano-gold colloidal particles' surfaces

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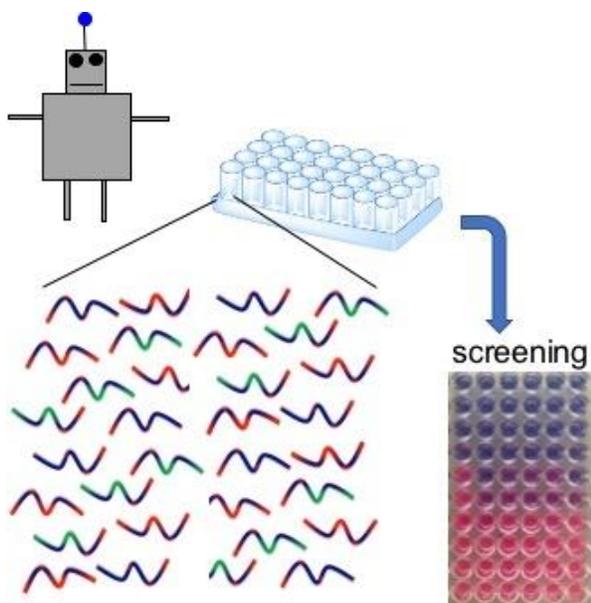
The adsorption orientation of amyloid beta 1-40 ($A\beta_{1-40}$) was investigated over the surface of nano-gold colloidal particles, ranging from $d = 10$ nm and 100 nm in diameter (d). The color change of the $A\beta_{1-40}$ coated nano-gold colloids occurred due to aggregation of the nano-gold colloids. This color change was interpreted to be the change surface property (*i.e.*, coverage of $A\beta_{1-40}$, Θ). Based on this idea, values of Θ were extracted as a function of d . It showed non-monotonic and complex nano-size dependence. A monomer of $A\beta_{1-40}$ was approximated as a prolate, and geometric simulation to reproduce Θ was conducted. While the "lie-down" orientation was highly expected due to an availability of interaction with the surface, the "spike-out" orientation enabled to reproduce the Θ values.

COLL 757

Discovery of anti-mycobacterial copolymers using a photo-chemical combinatorial platform

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The emergence and spread of antimicrobial resistance is a rapidly growing, global, healthcare threat. To counter this, new and innovative approaches to drug design are required. Cationic antimicrobial peptides and polymers have shown promise as non-traditional antimicrobial agents, killing microbes by mechanisms postulated to include membrane disruption/channel formation, DNA intercalation and as immunomodulators. Copolymerization is an established strategy to tune activity, but traditional synthetic methods do not explore this broad chemical space due to the need for the exclusion of air and sealed vials creating a bottleneck in the discovery process. Here a photo-chemical synthetic platform was used to synthesize 648 polymers in 96-well plate format covering wide chemical diversity. High-throughput screening against model organisms and red blood cells showed significant enhancements in activity compared to cationic homopolymers. This was translated to study the polymers against *Mycobacterium tuberculosis*; the pathogen which causes tuberculosis. Homopolymers were poor antimicrobials, requiring > 1 mg.mL⁻¹ concentration in some cases, but copolymerization enabled identification of lead polymers capable of killing this particularly robust pathogen. This methodology, shows that polymer libraries of 100's rather than traditional iterative studies on < 10 polymers is feasible and enables acceleration of the discovery of biomedical polymers.



'Robotic' high-throughput antimicrobial polymer discovery approach

COLL 758

Probing the nano-bio interface of hydroxyapatite with solid-state MAS NMR

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Hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, HAP), is the predominant inorganic material in bio-hard tissue such as bone and teeth. Nano-sized HAP crystallites are the building blocks taking on platelet or rod-like shapes which stack together with structural proteins in a highly-oriented assembly to form rigid nanocomposites of hard tissue. Although the chemical composition and the mineralogical features of bone apatite have been abundantly investigated by numerous research groups, the mechanisms of its formation, especially the molecular interactions at the bio-inorganic interface are not fully established. The surface reactivity of HAP nanoparticles depends on their crystallinity, morphology and crystal orientation. Atoms are ordered and exposed in different fashions on the planes that grow along different crystallographic axes. In the *c*-plane, hydroxyl groups and phosphate with negative charges are exposed, while in the *ab*-plane it is positively charged with Ca^{2+} ions present. In this study, amino acids are applied as probes to characterize the bioactivity of different types of nanocrystalline HAP. HAP with preferred orientation and different degrees of crystallinity were synthesized and structurally characterized with a combination of X-ray diffraction (XRD), ^{31}P solid-state nuclear magnetic resonance (NMR), infrared spectroscopy (IR) and transmission electron microscopy (TEM). The molecular interactions between amino acids and the HAP mineral phase are being probed with a combination of

advanced solid-state magic angle spinning (MAS) NMR spectroscopic techniques. Amino acids with charged side chains such as arginine and aspartic acid are adsorbed and immobilized on these HAP nanocrystals. The physio-chemical interaction between these two phases is determined by ^{13}C , ^{15}N and ^1H solid-state MAS chemical shift and relaxation measurements and $^1\text{H}/^{13}\text{C}/^{31}\text{P}$ triple resonance techniques are applied to interrogate the nano-bio interaction directly.

COLL 759

Collagen thin film adhesion mediated by mussel-inspired catecholamine surface primers

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Improving adhesives for use in aqueous ionic solutions is an important challenge relevant to dental and surgical adhesives. Prospective adhesives for biologically relevant environments face reduced van der Waals interactions under water, charge screening by dissolved ions, and hydration layers on hydrophilic surfaces. Many existing biomedical adhesives including cyanoacrylates and fibrin sealants have been brittle or poorly biocompatible, motivating the development of a robust, biocompatible adhesive. Marine mussels adhere to a wide variety of surfaces under water, making them attractive inspirations for synthetic adhesives. Here, we explore interactions between synthetic mussel-inspired catecholamine surface primers and films of collagen type-1 (Col-1), a major component of animal connective tissues. Using a surface forces apparatus (SFA), we show that these primers mediate persistent adhesion between Col-1 films in acidic and neutral aqueous solutions. We complement these force measurements with atomic force microscopy (AFM) and isothermal scanning calorimetry (ITC). Our findings suggest that the mussel-inspired catecholamine surface primers may be a promising candidate for biomedical adhesives.

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Targeting *S. aureus* in osteoblast infection employing antibody linked metallic nanoparticles

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Metallic alloy nanoparticles (NPs) of Silver-Copper (Ag-Cu) are known to exhibit potent

antimicrobial activity by releasing Ag⁺ and Cu⁺ ions, but their toxicity may also extend to the host cells. However, targeting the NPs to the causative agent can decrease their toxicity to host cells. This study focusses on the synthesis and functionalization of Ag-Cu with biomolecules that can target the causative agent in osteoblast infection. *Staphylococcus aureus* (*S. aureus*) is the most prominent causative agent of intracellular osteoblast infection in osteomyelitis and have developed mechanisms to evade antibiotic treatment and immune response. The effect of antibiotics in intracellular infection may become ineffective due to low intake and diffusion of antibiotics into host cells as well as the development of bacterial antibiotic resistance. However, the ions released from the NPs can penetrate into the host cells. Therefore, our treatment strategy involves the release of ions at the site of infection where the concentration of *S. aureus* is high. In our work, *S. aureus* is targeted by the functionalization of the NPs with anti-*S. aureus* antibodies that have high affinity and specificity to *S. aureus*. The *in vitro* antimicrobial studies have shown that the NPs conjugated with anti-*S. aureus* antibodies have higher antimicrobial activity against *S. aureus* than non-antibody conjugated NPs or antibodies alone, after 7 hours of incubation. Furthermore, the targeting NPs were also efficient in clearing a major percentage of infection in *S. aureus*-infected osteoblasts after 24 hours of incubation. Moreover, the strategy of targeting *S. aureus* reduces the dose of NPs for treatment and proportionally lower NP toxicity to host cells which can contribute to clinical osteomyelitis management and needs to be further studied employing *in vivo* animal models.