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at the University of Pennsylvania

*June 26-28, 2023
Singh Center for Nanotechnology*

Organized by
The Laboratory for Research on the Structure of Matter &
Center for Soft and Living Matter,
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and
Division of Colloid and Molecular Assembly,
Polymer Society of Korea

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Jin Woong Kim (SKKU)

Zahra Fakhraai (Penn)

Daeyeon Lee (Penn)

Discussion Leaders:

Etienne Ducrot, CNRS Bordeaux

Yufeng Wang, Hong Kong University

Scientific Program

Monday, June 26, 2023

8:00 AM	Registration/Breakfast
8:45 AM	Welcome message & opening remarks
9:00 AM	David Pine, New York University Electrokinetic Characterization of Colloids with and without Polymer Brushes
9:30 AM	Jiheong Kang, KAIST Supramolecular chemistry in polymer networks
10:00 AM	Zhihong Nie, Fudan University Functional Optical Materials and Devices of Nanoscale Colloidal Molecules
10:30 AM	Coffee break
11:00 AM	Dong-June Ahn, Korea University Ice-Active Assemblies
11:30 AM	Jerelle A. Joseph, Princeton University Accurate models for interrogating and engineering biomolecular condensates
12:00 PM	Lunch & Poster
1:15 PM	Jiho Shin (substituting for Jeehwan Kim), MIT Wafer-free Heterogeneous Integration for next generation electronics: advanced display, 3D integration, and bioelectronics
1:45 PM	Vinothan Manoharan, Harvard University Micromanipulation using capillary forces
2:15 PM	Dohyung Kim, University of Pennsylvania BEYOND SURFACE Facilitates Electrocatalytic Reactions of Renewable Carbons
2:45 PM	Poster
4:00 PM	Moon-Sung Kang, Sogang University Photopatterning Colloidal Quantum Dots via Ligand Crosslinking
4:30 PM	Cécile Monteux, ESPCI & CNRS Leaching foams
5:00 PM	Break
6:00 PM	Banquet

Tuesday, June 27, 2023

8:00 AM	Breakfast
9:00 AM	Arnold Mathijssen, University of Pennsylvania Transport and delivery by active materials
9:30 AM	Su-Mi Hur, Chonnam National University Effect of Soft Confinement Boundaries on Self-Assembly
10:00 AM	Jinkon Kim, POSTECH Unconventional Microdomains of Block Copolymers
10:30 AM	Coffee break
11:00 AM	So-Jung Park, Ewha Womans' University Dynamic Nanostructures from Self-Assembly of Functional Polymers and Nanoparticles
11:30 AM	Oleg Gang, Columbia Programming Nanoscale Assembly and Transformations
12:00 PM	Lunch & Poster
1:30 PM	Julia Dshemuchadse, Cornell Simulating complex crystal structures and their assembly with simple, soft-matter models
2:00 PM	Theodore Hueckel, MIT Template-Guided Nanoparticle Superlattice Assembly: Controlling Nucleation & Growth
2:30 PM	Jin Woong Kim, SKKU Bioadhesion of Bacterial Cellulose Nanofibers to Promote Topical Wound Healing
3:00 PM	Poster
3:30 PM	Anderson Shum, Hong Kong University Dynamic assembly in aqueous phase separating systems
4:00 PM	Lauren Zarzar, Penn State Chemically programmable active oil droplets
4:30 PM	Hyomin Lee, POSTECH Microfluidic design of polymersomes for spatiotemporal control of biochemical reactions
5:00 PM	Closing remarks

Wednesday, June 28, 2023

9:00AM-10:00 AM	Executive Committee Meeting
10:00AM-12:00 AM	Group Discussions

ORAL PRESENTATIONS

[001]

Electrokinetic characterization of colloids with and without polymer brushes

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The electrophoretic motion of colloidal particles is exquisitely sensitive to the density, conformation, charge, and length of grafted polymer brushes. We use measurements of the electrophoretic mobility together with dielectric relaxation to characterize a bare charged colloid, colloids coated with PEO brushes, and colloids coated with DNA coupled to PEO brushes. Using the latest numerical solutions to the governing electrokinetic equations, we are able to quantitatively characterize ~10-nm polymer brushes grafted to micron-sized colloidal particles.

[002]

Supramolecular chemistry in polymer networks

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Polymeric materials in nature regularly employ ordered, hierarchical structures in order to perform unique and precise functions. Importantly, these structures are often formed and stabilized by the cooperative summation of many weak interactions as opposed to the independent association of a few strong bonds. Here, I will discuss our approach to realize the polymer networks having supramolecular nanostructures. This was achieved by incorporating supramolecular stickers periodically in the controlled length of polymer chains. The detailed design strategy and their unique dynamic mechanical properties will be discussed in my presentation. Next, I will share our two assembly methods of conducting materials, including PEDOT:PSS conductive polymer and liquid metal particles in a dynamic polymer network for soft electronics.

References

- [1] **Kang, J.**; Miyajima, D.; Mori, T.; Inoue, Y.; Itoh, Y.; Aida, T. "A rational strategy for the realization of chain-growth supramolecular polymerization," *Science* **2015**, 347 (6222), 646 (**Highlighted in Nature chemistry News and view, Science Perspective, and Angewandte chemie Highlight**)
- [2] **Kang, J.**[†]; Son, D.[†]; Wang, G.J.N; Liu, Y.; Lopez, J.; Kim, Y.; Oh, J.H.; Kasumata, T.; Mun, J.; Lee, Y.; Jin, L.; Tok, J.B.; Bao, Z. "Tough and Water-Insensitive Self-Healing Elastomer for Robust Electronic Skin," *Advanced Materials* **2018**, 30 (13), 1706846 (**Highlighted in Advanced Science News**)
- [3] **Kang, J.**[†]; Son, D.[†]; Wang, G.J.N; Liu, Y.; Lopez, J.; Kim, Y.; Oh, J.H.; Kasumata, T.; Mun, J.; Lee, Y.; Jin, L.; Tok, J.B.; Bao, Z. "Tough and Water-Insensitive Self-Healing Elastomer for Robust Electronic Skin," *Advanced Materials* **2018**, 30 (13), 1706846 (**Highlighted in Advanced Science News**)
- [4] **Chong, J.**[†]; Sung, C.[†]; Nam, K.; **Kang, T.**; **Park, H.**; **Kim, H.**; Park, S.*; **Kang, J.*** "Highly conductive tissue-like hydrogel interface through template-directed assembly" *Nature Communication*, **2023**, 13 (1), 2206
- [5] **Lee, W.**[†]; **Kim, H.**[†]; Kang, I.; Park, H.; **Jung, J**; **Lee, H**; **Park, H.**; Ryu, S.; Jeong, J-W.; **Kang, J.*** "Universal assembly of liquid metal particles in polymers enables elastic printed circuit board" *Science*, **2022**, 378, 637 (**Highlighted by Science 'Perspective'**)

[003]

Functional optical materials and devices of nanoscale colloidal molecules

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The past decades have witnessed remarkable success in the synthesis of inorganic nanoparticles with interesting optical, electronic, or magnetic properties. Realizing the enormous potential of nanoparticles in such as energy, biomedical, and optoelectronic fields requires the organization of these particles into precisely controlled, hierarchically ordered structures with defined macroscopic properties [1]. Inspired by the covalent bonding of atoms into molecules and the molecular self-assembly into structures with astonishing complexities and functions, we and others are striving to achieve programmable self-assembly of nanoparticles as “atom or molecule equivalents” [2]. The ability to do so holds great promises to manipulate matter at nanoscale scale and to exploit the emergent properties of next generation hybrid materials. The anchoring of polymers onto nanoparticle surfaces offers a powerful route to direct the self-assembly of nanoparticles into precisely defined structures. In this talk, I will present our efforts to the design of functional nanoscale colloidal molecules and polymers through directional assembly of nanoparticles as atoms or organic molecules, as well as the development of new materials and devices (e.g., metasurfaces and metamaterials) from these nano-molecules.

[004]

Ice-active assemblies

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Water freezing is a commonly observed natural phenomenon; however, ice growth and recrystallization can critically damage living organisms. Nature has evolved to produce antifreeze proteins (AFPs) to survive this freezing threat. Their specific amino acid sequence has been widely accepted to play a critical role in binding to ice, which can result in antifreeze activity when the Kelvin effect is dominant at the ice interface. On the contrary, ice-binding surfaces can also lead to heterogeneous ice nucleation when the appropriate chemical and dimensional aspects are satisfied. Ice nucleation proteins and their mimics possess a large ice-binding surface, which facilitates the organization of surrounding water molecules in an ice-like lattice that could promote ice nucleation. Both phenomena, which require ice-binding characteristics in common, demand distinct design protocols, and thus active materials have been developed by tailoring them for respective purposes. In this presentation, mimicking the unique ice-activity of proteins, we will address recent achievements based on tailored designs of the hydrogen-bonding nature at the water-ice interface enabled by assemblies with topological engineering [1-3].

References

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[005]

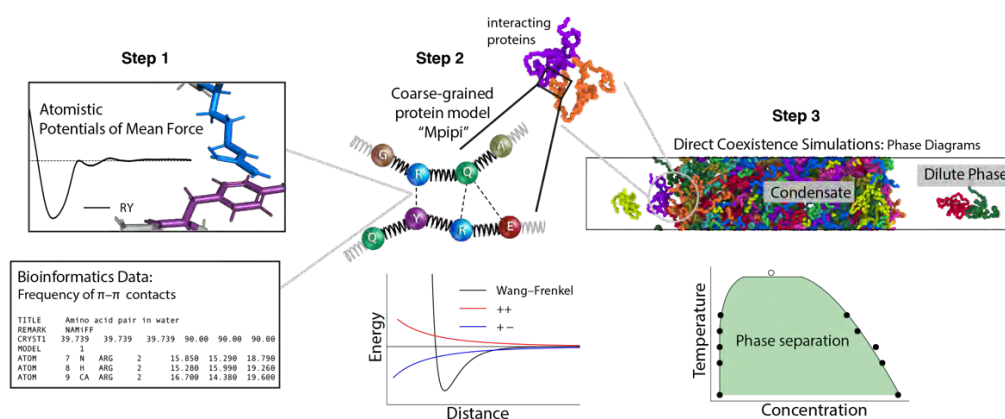
Accurate models for interrogating and engineering biomolecular condensates

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The interior of cells contains numerous components that need to be carefully organized in space to fulfil a wide range of biological functions. The most widespread form of intracellular compartments completely lack membranes. In the place of membranes, these compartments—so called biomolecular condensates—are sustained and segregated in space via liquid–liquid phase separation. Molecular modelling and simulations complement experiments by providing close-up views that elucidate the physicochemical principles shaping biomolecular condensates. Within the paradigm of phase separation, I will discuss our efforts at developing quantitatively accurate submolecular-resolution computer models for studying biomolecular condensates. Additionally, I will demonstrate how these approaches can be leveraged for engineering intracellular compartments.



References

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[006]

Wafer-free heterogeneous integration for next generation electronics: advanced display, 3D integration, and bioelectronics

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For future of electronics such as bioelectronics, 3D integrated electronics, and bendable electronics, needs for flexibility and stackability of electronic products have substantially grown up. However, conventional wafer-based single-crystalline semiconductors cannot catch up with such trends because they are bound to the thick rigid wafers such that they are neither flexible nor stackable. For the past decade, my research group has focused on mitigating such performance-mechanical compliance dilemma by developing methods to peel and transfer chips from a wafer. In today's talk, I will discuss about our strategies to realize such a dream electronic system [1-5] and how these strategies unlock new ways of manufacturing advanced electronic systems [6-10]. I will highlight our remote epitaxy technique that can produce single-crystalline freestanding membranes from any semiconducting materials with their excellent performances. In addition, I will present unprecedented artificial heterostructures enabled by stacking of those freestanding membranes, e.g., world's smallest vertically-stacked full color micro-LEDs [10], world's best multiferroic devices [7], battery-less wireless e-skin [9,11], and reconfigurable hetero-integrated chips with AI accelerators [8,12].

References: [1] *Nature* 544, 340 (2017), [2] *Nature Materials* 17, 999 (2018), [3] *Nature Materials* 18, 550 (2019), [4] *Nature Nanotechnology* 15, 272-276 (2020), [5] *Science* 362, 665 (2018), [6] *Nature Electronics*, 2, 439 (2019), [7] *Nature*, 578, 75 (2020), [8] *Nature Nanotechnology* 15, 574 (2020), [9] *Science Advances*, 7, 27 (2021) [10] *Nature* 614 (2023), [11] *Science* 377, 859 (2022), [12] *Nature Electronics*, 5, 386 (2022)



[007]

Micromanipulation using capillary forces

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Capillary forces arise when objects deform a liquid interface. These forces can be attractive or repulsive, depending on the contact angles at the surfaces of the objects. We harness both types of capillary forces to move microscopic objects in prescribed patterns. To do this, we 3D-print a device with hollow millimeter-scale channels, place it in a water bath, put floating objects inside the channels, and move the device up and down. We call these devices “capillary machines” because moving the device vertically causes the floating objects to move laterally. By designing machines with interconnected channels, we can manipulate multiple objects in complex patterns. I will explain the fluid-statics and mathematical design principles, and I will show how the machines can be used to braid microscopic wires and move micrometer-scale colloidal particles.

[008]

BEYOND SURFACE facilitates electrocatalytic reactions of renewable carbons

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There has been growing interest to drive chemical reactions via the direct use of renewable electricity to address sustainability challenges. To efficiently catalyze electrochemical reactions, catalyst materials are engineered to contain the desired active sites. Despite the success, there is still much room for improvement. It is because of how we typically view catalytic reactions at the solid-liquid interface that often lacks consideration of the liquid phase (e.g., solvent molecules, double-layer ions). The BEYOND SURFACE approach not only recognizes the presence and role of liquid phase components but alters their characteristics to facilitate chemical reactions and progress beyond the performance levels achieved to date. In this talk, examples of the BEYOND SURFACE approach are presented for electrocatalytic reactions of renewable carbons, CO₂ and biomass. The first example concerns the discovery of a unique interfacial configuration on the surface of colloidal nanoparticles, that is the Nanoparticle/Ordered-Ligand Interlayer (NOLI). Its operation by the synergistic act of the nanoparticle surface and surface ligands hovering above suggests a new route to promote reactions by tuning the electric double layer. The other example presents the need for a better understanding of solvent molecule behavior at electrochemically active interfaces. During electrooxidation of biomass-derived polyols, it is shown that the interaction between the Pt surface and surrounding water eventually leads to its surface oxidation limiting catalytic activity at fixed potential conditions. Thus, a method so-called electrochemical potential cycling is devised to exploit the short-lived high-activity state of Pt nanoparticles otherwise difficult to maintain under typical conditions. These studies highlight the complexity of electrochemical interfaces and the potential of thinking beyond the surface for electrocatalytic reactions.

[009]

Photopatterning colloidal quantum dots via ligand crosslinking

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Electroluminescence from quantum dots (QDs) is a suitable photon source for futuristic displays offering hyper-realistic images with free-form factors. Accordingly, a nondestructive and scalable process capable of rendering multicolored QD patterns on a scale of several micrometers needs to be established. In this talk, two different nondestructive direct photopatterning methods for QDs are introduced, both of which exploit crosslinking reaction between the ligands of neighboring QDs. The first method exploits an additive that can crosslink with native aliphatic QD ligands. This additive is referred to as light-driven ligand crosslinker (LiXers) [1]. Specifically, we employ LiXers in branched structure containing multiple azide units [2]. The branched LiXers effectively interlock heavy-metal-free QD films via photocrosslinking native aliphatic QD surface ligands without compromising the intrinsic optoelectronic properties of QDs. Using branched LiXers with six sterically engineered azide units, we achieved RGB QD patterns on the micrometer scale. The photocrosslinking process did not affect the photoluminescence and electroluminescence characteristics of QDs and extended the device lifetime. Alternatively, QD ligands by themselves containing a photocrosslinkable moiety can be anchored onto QD surface [3]. Specifically, photocrosslinkable ligands (PXLs) based on benzophenone derivative are exploited. The use of PXL permits employing a secondary ligand system (which is referred to as dispersing ligand, DL) that is devised to control the solubility of QDs to solvent. Based on a dual-ligand passivation system comprising PXL and DLs, we demonstrate that QDs can be direct patterned on various substrates using commercialized photolithography (i-line) or inkjet printing systems without compromising the optical properties of the QDs or the optoelectronic performance of the device.

[O10]

Leaching foams

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The recovery of metals from WEEE, Waste from Electrical and Electronic Equipment, is a major challenge to preserve natural resources. Hydrometallurgy, which consists in leaching metals is a promising method but generates large amounts of polluting effluents. In this study we design aqueous leaching foams, composed of 90% v/v of gas and 10% v/v of HCl solution to oxidize and dissolve copper. We take advantage of the oxidizing power of the dioxygen (O₂) present in the air bubbles whose fast transfer through the foams enables an efficient oxidation of copper. Using a forced drainage set up we show that the liquid fraction in the foam controls the transfer of O₂ from bubble to bubble as well as the transfer of the H⁺ ions in the continuous phase. Finally we show that it is possible to extend the concept of leaching foams to other metals such as silver (Ag) and to other surfactants that complex cupric ions and help improving the dissolution of the metal. These promising results open new recycling routes for metals contained in WEEE, with a lower environmental footprint.

Keywords: foams, oxidation, drainage

References

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[O11]

Transport and delivery by active materials

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One of the major challenges in robotics is controlling micromanipulation by active and adaptive materials. Existing delivery technologies often suffer from limited navigation control, low speeds, and proneness to environmental disturbances. Biology often solves these problems by collectively organizing actuation at the microscale. For example, pathogens are removed from our lungs by an active carpet of cilia [1]. Inside these cilia, in turn, microtubules form highways for molecular motors. In this talk, I will present developments in the microfabrication of “artificial cilia” [2] and “artificial microtubules” [3]. We designed amphibious cilia that can transport both liquids and dry objects. These carpets can sort particles by size and by shape using a crowd-surfing effect. We also designed magnetic microtubules, structured microfibers that rapidly guide particles through flow networks such as the cardiovascular system. These works offer unique strategies for robust microscale delivery, but equally shed light on non-equilibrium diffusion [4] in biological transport processes.

References

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[O12]

Effect of soft confinement boundaries on self-assembly

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Theoretical and numerical models have proven to be invaluable tools for understanding and controlling the self-assembly of polymeric systems, providing guidelines for experimentalists. However, in polymeric systems with deformable spontaneous organization, the kinetic route and the resulting self-assembled structures can be complicated. The intrinsic non-equilibrium nature of these systems, coupled with the limitations of simulation models to capture soft boundary effects, has made theoretical and numerical analyses of morphology formation mostly challenging. In this talk, I will discuss our efforts to extend the scope of numerical approaches based on coarse-grained models to describe soft confinement-induced self-assembly in either melt or solution. Our model accounts for the specific conditions and the interaction between the polymer and the surrounding environment, providing insights into the kinetic routes of self-assembly. We apply the model to predict the evolution of non-uniform surfaces and their effects on the final self-assembly in block copolymer thin films and emulsion droplets in solutions. Our diffusive particle-based simulations, in combination with the sampling technique named string method, have enabled us to provide a detailed mechanism behind boundary-directed epitaxy, in which vertical lamellae of PPC-PS-PPC are formed on low-resolution graphene (PS preferential) stripes on Germanium (PPC preferential) substrate, parallel to the boundaries. Furthermore, we use our approach to simulate structure and shape evolution in emulsified block copolymer droplets, where the concentration and domain shape change continuously during the process. We also investigate the effect of chain architectures in soft confinement-induced self-assembly.

[O13]

Unconventional microdomains of block copolymers

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The microdomains obtained by block copolymer (BCP) self-assembly are mainly decided by the volume fraction (f) of one block. Lamellar microdomains have been found at symmetric volume fraction of A block (f_A) in an AB diblock copolymer. Then, can we obtain lamellar microdomains at highly asymmetric f_A (say 0.8)?

A-cylinders in an AB diblock copolymer have been observed at $0.2 < f_A < 0.35$. How can one obtain inverted cylinders containing A-cylinders even at $f_A = 0.7$ (or even larger)? If one can fabricate this kind inverted cylinders, the inter-distance between two neighboring cylinders is significantly reduced. This allows one to fabricate an ultrahigh density array of contact holes which is very important to develop next-generation of semiconducting nanolithography.

The double gyroids with A channel have been found in an AB diblock copolymer at a narrow range of f_A (~ 0.35). However, various channel width in the gyroids is needed to design novel optical materials such as metamaterials, because bandgap and effective plasma wavelength are easily adjusted by the channel width of the gyroids. In addition, the spherical packing is unique and important because this structure could be regarded as artificial atoms, and thus it is helpful for understanding the emergence of different crystalline orders. Conventionally, A-spheres in an AB diblock copolymer are found at $f_A < 0.18$. Is it possible to obtain inverted spheres containing more than 50% volume?

In this talk, I tackle the above problems by modulating the chain architecture as well as the blending of different block copolymers. For example, we obtained “inverted cylinders” with a volume fraction of the cylinder as large as 0.71 by blending of a six-arm star shaped block copolymer [(AB)₆] and a linear AB block copolymer.

[O14]

Dynamic nanostructures from self-assembly of functional polymers and nanoparticles

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Here, we present two distinct approaches for the fabrication of dynamic nanostructures. Firstly, we have fabricated dynamic metamolecules composed of thermo-responsive poly(N-isopropylacrylamide) (PNIPAM) hydrogel core and plasmonic metal nanoparticles. The ability to dynamically control the assembly structure allowed us to investigate distinct optical magnetism in plasmonic nanoparticle assemblies. Secondly, responsive free standing films of nanoparticles were fabricated by the programmable DNA-directed self-assembly and the layer-by-layer (LbL) thin film fabrication technique. We demonstrate that the new approach combined with unique properties of nanoparticle building blocks provides a powerful means to generate dynamic nanostructures that can undergo complex and programmable shape transformation.

[015]

Programming nanoscale assembly and transformations

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There is an increasing need to organize functional nanoscale components into designed static and dynamic architectures for enabling diverse nanotechnological applications, from engineered biomaterials to photonic devices and chemically active media. However, we are currently lacking a broadly applicable approach for a formation of prescribed nanostructures via self-assembly, integrate different functional nanocomponents and control reconfigurations of such materials. The talk will present our progress in establishing a self-assembly platform for the fabrication of designed large-scale and finite-size nano-architectures from diverse inorganic and biomolecular nanocomponents through the DNA-programmable assembly. The considerations on inter-component interactions, an information required for encoding of assembly instructions, and a pathway control will be discussed. Building on our advances in assembly of designed architectures, a recent progress in creating reconfigurable nano-systems with defined transformation states will be presented. The use of the developed assembly approaches for generating functional nanomaterials with optical, electrical, biological and mechanical functions will be demonstrated.

[O16]

Simulating complex crystal structures and their assembly with simple, soft-matter models

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The emergence and transformation of ordered structures are ubiquitous processes that remain mysterious due to the short time and length scales on which they occur. We study crystal growth and solid–solid phase transformations with coarse-grained self-assembly simulations, modeling the spontaneous formation of various crystal structure types from systems of simple particles that interact via short-range forces to form long-range ordered structures. We explore model systems that can self-assemble a large variety of crystal structures—from simple to highly complex. In particular, we observe the transitions between liquid and solid states, as well as between different crystal structures—distinguishing reconstructive and displacive transformations. We uncover microscopic behaviors both of the development of order and how it can fail, on a particle-by-particle basis. Our goal is the elucidation of the pathway variety of these mechanisms on a fundamental level, with implications that allow us to understand and control real systems and physical processes for materials design in the future.

[O17]

Template-guided nanoparticle superlattice assembly: controlling nucleation & growth

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DNA's ability to direct nanoparticle interactions paves the way for the self-assembly of functional devices, including the potential development of advanced optical systems. For instance, faceted crystals formed on substrates can act as micromirrors and other essential components in optical systems due to their consistent shape. While there have been significant advancements in broadening the structural diversity of DNA-coated colloids, their applications have been limited due to an incomplete understanding and control over crystallization dynamics. This presentation delves into the role of templates in controlling crystal size, positioning, dispersity, and orientation. Photolithographic patterning is employed to create wafer-scale templates with a wide range of features that differ in size, shape, and spacing, enabling the investigation of surface-assisted crystallization mechanisms. We establish template design guidelines for accurately positioning large single crystals and analyzing the interplay between template geometry and crystal orientation. Our findings offer valuable insights into the principles needed to control — and ultimately incorporate — superlattices into devices.

[O18]

Bioadhesion of bacterial cellulose nanofibers to promote topical wound healing

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Bioadhesives are natural or synthetic materials that can adhere to biological surfaces under wet conditions, thereby allowing their use as tissue sealants and patches for tissue regeneration, drug delivery systems, and biosensors. Owing to their excellent biocompatibility as well as adhesion performance under wet conditions, they are of special interest in the field of tissue regeneration. In this study, we present a new type of skin adhesion system in which bacterial cellulose nanofibers (BCNFs) are employed for wound dressing. Since the BCNFs, known as bacterial-derived celluloses, have been regarded as safe biomaterials according to Generally Recognized as Safe (GRAS) by Food and Drug Administrator (FDA), outstanding potential in wound healing is expected due to their valuable properties such as high crystallinity, water holding and absorption capacity, and high mechanical strength. The essence of our approach is to fabricate skin adhesive sites-conjugated BCNFs as a bioadhesive for the skin tissue, in which peptide-receptor interaction, antigen-antibody interaction, and boronic acid-mediated covalent bonding in the stratum corneum and epidermal layer occur. After characterizing the adhesion performance of BCNFs, finally, we show that that our BCNF bioadhesive system is indeed effective for improving skin wound healing.

[O19]

Dynamic assembly in aqueous phase separating systems

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Fascinating structures and orders emerge from liquid systems as simple as aqueous solutions. New liquid phases can form through phase separation, which can be induced by repulsive or attractive interactions of the constituent components. The consequent phase separation can be classified as segregative or associative. Besides inducing phase separation, the constituent molecules, such as polyelectrolytes, polymers, nucleic acids and peptides, can also assemble dynamically within the background solution. The combined effect of phase separation and dynamic assembly may play a role in a myriad of systems, including biological systems, such as liquid organelles in cells. The strategy can also be employed to form new materials structures that may find applications in biomedical areas. In this talk, I will share some of our works in understanding dynamic assembly in phase separating systems. In particular, we will discuss how biomimicking networks with stimulus-responsiveness can be formed, and how properties of the assembled structures depend on the inherent molecular structures of the constituent units.

[O20]

Chemically programmable active oil droplets

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Understanding the chemo-mechanical mechanisms that direct the motion and interactions of self-propulsive colloids is a growing interest area in the field of active matter. An important consideration when designing chemotactic active colloids, such as self-propelled droplets, is the mechanism by which asymmetric forces will be generated and applied to direct the colloid motion. In the case of active droplets, motion is often driven by interfacial tension gradients and Marangoni flows induced by micelle-mediated solubilization, a process wherein the droplet contents are transferred into the continuous micellar phase. However, it is still not well understood how the chemical compositions and dynamics of these gradients can be harnessed to influence droplet activity. In this presentation, I will discuss chemomechanical frameworks for generating oil-in-water droplet behaviors like self-propulsion, attraction/repulsion, and non-reciprocal interactions (e.g. chasing) of tunable strength and directionality with a special focus on chemical composition of the emulsions. The interfaces present in the emulsion, and the structure of complex droplets, is observed to be critical to active behaviors, and I will propose ideas for how the non-equilibrium transport at liquid interfaces may play a role in governing the active behaviors of solubilizing droplets.

[O21]

Microfluidic design of polymersomes for spatiotemporal control of biochemical reactions

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Droplet microfluidics has emerged as a powerful tool in the field of artificial cells, enabling the synthesis of artificial cell-like vesicles that mimic the structure and function of natural cells. In this work, we utilize droplet microfluidics to synthesize polymersomes with a semi-permeable membrane which allow small molecules with molecular weight below the cut-off value to selectively permeate through to induce biochemical reactions. Depending on the composition of the bilayer membrane, we show that the molecular permeability can be fine-tuned without any use of biopores that are often difficult to purify and controllably insert into the membrane. Moreover, we demonstrate that the signal-driven enzymatic reaction can be further extended to induce complex coacervation as well as cascade reactions, and even reconstitute cytoskeleton in polymersomes. We envision that the spatiotemporal control offered by these microfluidically synthesized polymersomes provide insights into the complex interplay between cellular components and the surrounding environment and offer the means to design responsive and programmable protocell systems.

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[P01]

Self-assembled clusters of ultra-smooth gold nanospheres

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The use of polyDADMAC as a stabilizer and the top-down etching process can be helped to make perfectly spherical gold nanoparticles with a very smooth surface, unlike the results that is followed common synthesis method. These ultra-smooth shapes can form more ideal point contact structures instead surface contact and lead to reliable experimental results. However, due to the presence of the polyDADMAC, it is difficult to use the common methods in gold nanoparticle research area. Because of the high entanglement effect of polyDADMAC and very strong positive charge property, there are restrictions on its use and application. Long-chain polystyrene polymers are introduced to the particle surface through Au-S chemistry, giving the gold nanoparticles hydrophobic properties. Hydrophobic gold nanoparticles form clusters with various coordination numbers through oil-in-water emulsification. Due to their perfect shape, it is possible to produce repeatable and reliable repeatable results and fine-tune optical properties.

[P02]

Self-assembly of atomically aligned nanoparticle superlattices from Pt-Fe₃O₄ heterodimer nanoparticles

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Multicomponent nanoparticle superlattices (SLs) promise the integration of nanoparticles (NPs) with remarkable electronic, magnetic, and optical properties into a single structure. Here, we demonstrate that colloidal heterodimer NPs consisting of two conjoined nanocrystals can self-assemble into novel multicomponent SLs with a high degree of alignment between the atomic lattices of individual NCs, which has been theorized to lead to a wide variety of remarkable properties. Specifically, by using simulations and experiments, we show that heterodimers composed of larger Fe₃O₄ domains decorated with a Pt domain at one vertex can self-assemble into an SL with long-range atomic alignment between the Fe₃O₄ domains of different NPs across the SL. In situ scattering of the self-assembly reveals a two-stage mechanism of self-assembly: translational ordering between NPs develops before atomic alignment. Our experiments and simulation indicate that atomic alignment requires selective epitaxial growth of the smaller domain during heterodimer synthesis and specific size ratios of the heterodimer domains as opposed to specific chemical composition. This composition independence makes the self-assembly principles elucidated here applicable to the future preparation of multicomponent materials with fine structural control.

[P03]

Ultra-sensitive SERS platform based on nanoarchitecturing of plasmonic 3D porous metal materials and colloidal Au nanoparticles

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The soft-templating method using block copolymer micelles was used to fabricate plasmonic nanoporous Au films by electrochemical deposition technique for surface-enhanced Raman scattering (SERS) substrates. SERS is a fast, simple and powerful spectroscopic technique for molecular detection by plasmonic metals. Although SERS is a very useful and powerful technique, there are some problems in the fabrication of high performance SERS substrates. To solve these kinds of problems, the use of gold nanoparticles to surface enhanced Raman spectroscopy (SERS) effect is useful to solve the low signal problem. We designed a process to assemble mesoporous gold film internalized with AuNPs, which can then be monitored by surface enhanced Raman scattering (SERS). Precise nanogaps are generated by regular internalization of AuNPs into the cavities of the mesoporous gold film by thiol. The SERS intensity of mesoporous gold film internalized with AuNPs was identified with R6G as Raman chemical. Electromagnetic enhancement effects due to localized surface plasmon resonance significantly enhance the intensity of incident light when molecules are positioned near tiny nanogaps. The E-field at the gaps was enhanced and the NPs showed a strong Raman signal.

Keywords: SERS, mesoporous Au films, Au nanoparticles, micelle, nanogap

[P04]

Design of dendritic promesogenic ligands for liquid crystal-nanoparticle hybrid systems

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Liquid crystal-nanoparticle (LC-NP) hybrid systems allow synergistic interactions between LC matrixes with anisotropic alignment and NP dopants with versatile functionalities. A uniform, well-dispersed, and highly stable thermotropic LC-NP mixture paves the way for further applications. In this work, a linear promesogenic ligand and two types of dendritic promesogenic ligands with alkyl or oligo ethylene glycol (OEG) chains are designed and synthesized to facilitate incorporating NPs into the thermotropic 4-cyano-4'-pentylbiphenyl (5CB) LC matrix. A comparison study between the linear and the dendritic ligands on the capability to promote miscibility and stability of NPs in LCs is conducted. Miscibility test results show that the linear ligand and the OEG-chained dendrimer both perform well in uniformly dispersing NPs in LCs. Dynamic assemblies of NPs assisted by dendritic ligands and driven by aligning and equilibrating of mesogens are captured, showing the potential of manipulating the assembly of NPs through external thermal stimuli. The stability test shows that both types of dendrimers can significantly enhance the shelf-life time and thermal stability of NPs compared to the linear ligand. In particular, Au NPs capped with OEG-chained dendrimers are stable in 5CB for six months at room temperature and over ten hours at 50 °C. The synthesis of dendritic ligands is highly modulated and can be generalized onto NPs with different dimensions and properties. Tied by the dendritic promesogenic ligands, this LC-NP hybrid system with good uniformity and stability could be further applied to tunable optical displays, responsive materials, etc.

[P05]

Bacterial cellulose nanofibril-based high internal phase emulsion stabilization through restricted interdrop fusion across water drainage channels

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This study introduces a promising approach to stabilize high internal phase emulsions (HIPEs) in which droplets are enveloped by octadecane (C18)-grafted bacterial cellulose nanofibers (BCNF_{diC18}), which are mainly surrounded by carboxylate anions and hydrophobically modified with C18 alkyl chains. For this purpose, BCNF_{diC18}, in which two octadecyl chains were grafted onto each of several cellulose unit rings on 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated oxidized BCNFs, was fabricated using the Schiff base reaction. The wettability of BCNF_{diC18} was adjusted by controlling the amount of the grafted C18 alkyl chain. Interfacial rheological analysis revealed that BCNF_{diC18} enhanced the membrane modulus at the oil-water interface. We figured out that such a resilient interfacial membrane substantially prevented interdrop fusion across the water drainage channel formed between the jammed oil droplets, which was confirmed theoretically using the modified Stefan-Reynolds equation. These findings highlight that the use of surfactants in the form of nanofibers to form a rigid interfacial film plays a key role in hindering the interfusion of the internal phase and the collapse of the emulsion, which is essential for HIPE stabilization.

[P06]

Nanoparticle encapsulation and organization within ouzo effect fabricated nanocomposite colloids (Nanocolloids)

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The encapsulation and organization of nanoparticles within suprastructures can imbue added functionality to colloidal materials such as enabling heterogeneous catalysis, controlled release of encapsulants, and optical phenomena. While nanoparticle encapsulation is more commonly documented in macroscopic polymer matrices or micrometer-scale suprastructures, less efforts have been devoted to their assembly into submicrometer assemblies with control over their internal structures. In this work we study the encapsulation and organization of silica nanoparticles within solid oil/polymer nanocomposite colloids (nanocolloids) fabricated via co-precipitation of the oil and the polymer. Control over the number of nanoparticles encapsulated per capsule is demonstrated by varying the concentration of nanoparticles suspended in the precursor solution. Additionally, by using SiO₂ nanoparticles of varying surface chemistry/hydrophobicity we demonstrate a range of nanoparticle organization within the nanocolloids from distributing themselves throughout the oil core, a morphology akin to the distribution of seeds in a pomegranate, an intermediate morphology where particles are positioned throughout the shell and core, to positioning themselves along the shell of the nanocolloids resembling a raspberry-like morphology. This work aims to establish the design rules for control over the number density and spatial distribution of nanoparticles encased in nanocolloids for various applications.

[P07]

Formation of liquid cratering from the impact of liquid marbles on rough solid substrates

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The fluid dynamic phenomena of bare droplets impact on solid substrates have been studied for more than one century. However, studies on the impact of particle-armored droplets are rarely conducted. In this study, we report the formation of liquid cratering from the impact of liquid marbles, which are colloidal particle-stabilized droplets, on rough solid substrates. Using high-speed imaging, we reveal liquid marbles with size D_0 impact solid substrates vertically and mirror closely that of bare droplets at the spreading stage in a short timescale. By characterizing the spreading of the marble on the rough solid substrate, a power-law scaling is observed for the normalized maximum spread D_{max} in terms of the impact Weber number, $D_{max}/D_0 \sim We^\alpha$, with $\alpha \approx 1/3$. A thin layer of air is entrapped beneath the impact marble, which is later compressed into a bubble. Other than forming lenticular sessile droplets with the bubble entrapped, a toroidal-shaped liquid cratering is formed when the liquid marble hits the substrate above a critical height. The liquid cratering forms when the advancing liquid film starts to retract. Capillary waves converge at the center and lead the entrapped bubble to burst and form a dry patch. Extensive experiments show that, with sufficient inertia, the liquid cratering formation is a material constant and does not depend on the impact velocity. The Ohnesorge number, $Oh = \eta / \sqrt{\rho \gamma D_0}$, is the dimensionless parameter to forecast its formation.

[P08]

Recyclable 2D colloid surfactants with high catalytic activities at pickering emulsion interfaces

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This study introduces a novel 2D colloid surfactant system that exhibits catalytic activity at the interface of a reactant-containing water-in-oil Pickering emulsion microreactor. To this end, amphiphilic nanoplatelets (ANPLs) are fabricated by electron transfer atom transfer radical polymerization (SI-ARGET ATRP) on zirconium hydrogen phosphate (ZrHP) nanoplatelets. Subsequently, in situ reduction of metal precursors on the primary amine reaction sites on the hydrophilic face of ANPLs is conducted, thus enabling the production of ANPL catalysts (ANPLcat). Owing to the platelet geometry and catalytic functionalization, the ANPLcat demonstrates excellent ability to stabilize the Pickering emulsion reactant drops, while exhibiting its own catalytic activity at the interface. These results highlight that the ANPLcat-based emulsion microreactor system is expected to be widely applied as a high-performance catalyst for various organic chemical reactions.

[P09]

Synthesis of magnetic Janus superparticles through seeded growth of gold on pickering emulsions

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Multifunctional materials are an emerging class of materials with the ability to perform multiple functions within a single system. One promising approach to creating these materials is through the use of superparticles, which are nanoscale assemblies of smaller particles with unique properties that arise from their collective behavior. Among these, Janus particles are of particular interest due to their asymmetric structure, which can result in different properties on each side of the colloid. The ability to tailor the shape, size, and composition of Janus particles allows for precise control over their properties, making them a promising avenue for the design of multifunctional materials with enhanced functionality for a wide range of applications, such as targeted drug delivery, emulsion stabilization and tandem catalysis. This work explores synthesis strategies for the fabrication of magnetic Janus superparticles using Pickering emulsions of paraffin wax in water, stabilized by iron oxide superparticles manufactured by spray drying. The surface hydrophobicity of iron oxide superparticles can be controlled by the amount of surfactants added in a previous incubation step, and consequently this alters their degree of embedding into the paraffin wax and the stability of the formed emulsions. Their surface is then asymmetrically modified with gold nanoparticles upon seed-mediated growth and visualized through SEM/EDS.

[P10]

Understanding rheology of particulate suspensions via mesoscale simulation techniques

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Particulate suspensions are encountered in a multitude of industrially relevant products, for example, semiconductors, and secondary batteries, to list a few. Understanding what affects the rheology of particulate suspensions, and how this can be manipulated is important to improve the quality of products. Despite many studies to understand the flow behavior of suspension, they are lacking yet. For instance, the influences of interactions, shape, and size distributions of components on the rheology of particulate suspension are not fully understood. Our interest is to understand the flow behavior of complex fluids in a wide range of lengths and time scales. To aim that, we adopt “mesoscales simulation” techniques. In this presentation, we demonstrate several simulation results regards the rheological behavior of particulate suspensions. Firstly, we handle the “strain stiffening” phenomenon of hard-sphere suspensions in liquid and crystal coexistence regions. We study the rheology and microstructure of suspensions in oscillatory shear flow to explore the origin of strain stiffening in hard-sphere suspensions. Next, we shift to a more complicated and challenging topic, for example, the rheology of non-spherical particle suspensions. We explore the shear viscosity of rounded cubes, namely “superball” in a wide range of shear rates. While Newtonian behavior at a low shear rate regime, "shear thickening" begins to appear with an increase in applied shear rate. It proves that the superball system has a lower critical volume fraction and shear rate than the spherical particle system to reach the shear thickened state.

[P11]

Model complex fluids reveal rheological fingerprints of debris flows

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Climate change has exacerbated the frequency of landslide events causing huge loss to human life and infrastructure. The onset and dynamics of landslides are dictated by the rearrangement dynamics of the constituent materials and the magnitude of external shear forces. Here, we use a minimum ingredient model earth suspension mixture, containing two components: (1) silica sand ($\sim 100 \mu\text{m}$; frictional interactions) and (2) kaolin clay ($\sim 10\mu\text{m}$; attractive interactions), to study the effects of material properties on the yielding and flow properties in model earth suspensions. We find that addition of sand to pure clay mixtures, macroscopically anneals the suspension mixture by shifting the yielding towards higher shear rates. In doing so, the suspension fails more like a brittle material. Here, we developed a rheological framework to explore the effects of frictional interactions in model earth suspension mixtures.

[P12]

Stochastic thermodynamics with internal variables

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Far-from-equilibrium phenomena are essential to all natural and engineered systems, from geological to biological, chemical to electrical or mechanical. For over a century and a half, since Carnot, Clausius, Maxwell, Boltzmann, and Gibbs, among many others, laid the foundation for our understanding of equilibrium processes, scientists and engineers have dreamed of an analogous treatment of non-equilibrium systems. But despite tremendous efforts a universal theory of non-equilibrium behavior akin to equilibrium statistical mechanics and thermodynamics has evaded description. Several methods, including rational thermodynamics, thermodynamics with internal variables (TIV), the GENERIC framework, and Onsager's variational principle, have proved their ability to describe systems at the macroscopic scale. Yet, a key challenge remains in efficiently deriving models within these frameworks from microscopic physics. In our work, we utilize a variational technique for approximating non-equilibrium probability distributions to provide this microscopic foundation for TIV in systems well described by Langevin dynamics at the microscopic scale. The variational parameters of the method become the internal variables of the macroscopic system, and once the variational approximation is applied within stochastic thermodynamics the kinetic equations for the internal variables as well as standard TIV emerges naturally. We refer to this framework as stochastic thermodynamics with internal variables (STIV). We highlight STIV's effectiveness by deriving analytical approximations for evolving mechanical and thermodynamic quantities in a model of coiled-coil proteins and double stranded DNA, including, to the authors' knowledge, the first derivation of equations for a traveling phase front without appeal to phenomenology. Moreover, in this example, we find that the dynamics of the internal variables takes the form of a gradient flow with respect to the non-equilibrium free energy. As mentioned, the generality of our treatment allows for applications of STIV to any system described by Langevin dynamics at the microscopic scale, including colloidal macromolecules, hydrogels, and biopolymers.

[P13]

Detecting and identifying free fatty acid with holographic particle characterization

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In this work, we demonstrate that holographic particle characterization can yield quantitative information on different types of free fatty acids. In this approach, in-line holograms of colloidal particles are analyzed using the Lorenz–Mie theory of light scattering to determine individual particle diameter and refractive index. This method is effective for measuring individual sub-visible particles ranging in diameter from 0.5 μm to 10 μm . The measured refractive index of individual particles can also be used to distinguish particles of different composition. In addition, the symmetry of individual holograms provides information about particle morphology. We have successfully measured and identified various free fatty acids, including oleic acid, linoleic acid, and palmitic acid, using their sizes, composition, and morphology based on the analysis of their holograms.

[P14]

Imaging peptide surfactants for rare earth element recovery at the air-water interface via confocal laser scanning microscopy

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Rare earth elements (REEs), crucial to modern and green technologies, are notoriously difficult to purify owing to their recovery as mixtures of REEs, the similar diameters of REE cations and the fact that they are typically present in the (+3) oxidation state. We are developing an environmentally friendly REE separation process, inspired by biology, which exploits peptide surfactants (PEPS) that bind selectively to REEs and brings them to the air-water interface for recovery via a froth flotation process. We study PEPS that have been designed to bind specifically to a given REE. The PEPS bind to REE cations in bulk solution to form PEPS:REE complexes in which the REE is wrapped in a binding loop designed to sequester the cation. In this work, we study PEPS that have been modified to contain the unnatural amino acid, acridon-2-ylalanine (Acd), which can be excited at 405 nm and its emission can be measured at 420 nm. Using confocal laser scanning microscopy (CLSM), we can image the air-water interface using the Acd fluorescence signal to measure surface concentrations of peptides by relating interfacial excess fluorescence intensity to bulk fluorescence intensity. These measurements can have time resolutions on the order of seconds which allows for detailed study of the kinetics of the PEPS adsorbing at the interface for different PEPS:REE complexes. Additionally, the Acd fluorophore can undergo LRET with Eu^{3+} in the binding loop which diminishes the Acd emission at 420 nm and gives an emission signal for Eu^{3+} at 615 nm. Other lanthanides (Ln^{3+}), when present in the binding loop, do not reduce the Acd emission at 420 nm thus mixtures of Ln^{3+} with Eu^{3+} show intermediate Acd fluorescence intensity. We exploit the recovery of Acd emission at 420 nm in the presence of mixtures of Ln^{3+} with Eu^{3+} to study the kinetics of ion exchange in the binding pocket and to gain insight into ion selectivity at the air-water interface.

[P15]

Giant decrease in interfacial energy by native oxides

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Most metals and semiconductors react with air to form surface oxides. These oxides have tremendous technological importance. For example, they protect stainless steel and aluminum from rusting and serve as dielectric layers in computer chips. Here, we show that native oxides also significantly lower the interfacial tension of the materials they encase, as demonstrated using liquid metals. Using a variety of interfacial measurements, we show that the tension of liquid gallium lowers from 724 mN/m as a bare metal to 10 mN/m after reacting spontaneously with oxygen to form a conformal native oxide. In contrast, conventional surfactants such as soap lower the tension of water modestly from 72 mN/m to ≈ 30 mN/m and must be externally added to the water. The unprecedented surface activity of native oxides enables unique interfacial behavior and the creation of small, yet stable non-spherical liquid metal structures. Furthermore, this low interfacial tension can be harnessed to induce instabilities in thin liquid films, thereby providing a simple route to deposit thin (≈ 3 nm thick) oxide films on surfaces or create air bubbles encased only by a thin oxide membrane.

[P16]

Bubble-driven entrainment of yeast colonies in complex environments

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Despite the extensive role yeast plays across disciplines, our understanding of its growth and pathogenesis has been constrained to studies of yeast cultivated in bulk liquid media, typically on two-dimensional plates, or chemostat cultures. Such settings do not reflect the complex three-dimensional environments yeast inhabit in nature. The natural habitat for yeast, such as eukaryotic cells, tissues, soil, and biological gels, has porous microstructure and complex mechanical properties. Through direct imaging of yeast colonies in transparent three-dimensional viscoplastic microgels with tunable mechanical properties, we elucidate the adaptive response of dense yeast colonies to spatial confinement. We found that yeast colonies produce carbon dioxide bubbles in their environment via fermentation, and then leverage the bubble entrainment to break out of the nutrient-depleted core. We show that the motion of a bubble leaves a memory within the environment, serving as both a nucleation site and a guide for the subsequent rising trajectories of future carbon dioxide bubbles. Remarkably, this coupling between the bubbles and the viscoplastic matrix determines the final morphology of the colony. This study sheds light on the role of fermentation in the proliferation and transport of microorganisms within complex environments.

[P17]

Emergent behavior of growing bacterial communities in polymeric environments

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Many bacteria live in polymeric environments, such as mucus in the body, exopolymers in the ocean, and cell-secreted extracellular polymeric substances (EPS) that encapsulate biofilms. However, most studies of bacteria focus on cells in polymer-free fluids. How do interactions with polymers influence the behavior of bacterial communities? To address this question, we experimentally probe the growth of non-motile *Escherichia coli* in solutions of inert polymers. We find that, when the polymer is sufficiently concentrated, the cells grow in striking “cable-like” morphologies—in stark contrast to the compact morphologies that arise in the conventionally-studied polymer-free case. Experiments and agent-based simulations show that these unusual community morphologies arise from an interplay between polymer-induced entropic attraction between pairs of cells and their hindered ability to diffusely separate from each other in a viscous solution. These results suggest a pivotal role of polymers in regulating microbe-host interactions, by promoting bacterial exposure to external biochemical groups that protect the host against pathogens. More broadly, this work helps to uncover quantitative principles governing the morphogenesis of diverse forms of growing active matter in polymeric environments.

[P18]

Robotic motions from assemblies of asymmetric magnetic microcapsules

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Assemblies of particles have unique properties that differ from those of individual particles, making them suitable for various applications. Partially modifying the surface of particles with a magnetic material is a powerful approach to facilitate particle motion through increased magnetic torque under a rotating field. However, the conventional approaches to asymmetrically functionalizing particles with magnetic materials have limitations. In this study, we investigate the assembly and robotic control of asymmetric microcapsules made of magnetic and non-magnetic nanoparticles. We show that the asymmetric distribution of magnetic nanoparticles in the shell, induced by magnetizing and jamming magnetic nanoparticles in the emulsion state, significantly enhances the local magnetic response between microcapsules under magnetic fields, enabling them to perform various types of motion such as rolling, spinning, walking, incline walking, grouping, and repelling. Dynamic robotic microcapsule assemblies demonstrate enhanced mobility and directionality in their walking motions, enabling the assemblies to adaptively overcome physical and biological barriers to reach targeted areas, whereas such obstacles impede the motion of individual microcapsules. Our microcapsule-based robotic platform provides fundamental insights into fabricating and manipulating magnetic robots, leading to more complex and synergistic functions through collaboration among robots.

[P19]

Emergent bacterial dynamics in self-generated oxygen gradients

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In many biological and environmental settings, e.g. mucus in the lungs and subsurface porous media, bacterial populations are strongly confined in tight spots where oxygen availability is spatially variable. How do such variations in oxygen supply influence the collective behavior of a population of motile bacteria? To address this question, here, we experimentally study how bacterial suspensions react to self-generated oxygen gradients in micro-confinement. We find that the coupling between cellular motility and the local oxygen concentration gives rise to the formation of a dense, immotile phase that coexists with a less dense, highly motile phase in a manner reminiscent of Motility-Induced Phase Separation (MIPS). Furthermore, we show how the active turbulence generated by the motile phase can result in large-scale fluctuations at the interface between both phases, enhancing oxygen influx and thus subsequent propagation of this interface. Finally, we show how these collective dynamics are markedly altered in a complex fluid akin to airway mucus. Altogether, our work reveals the rich collective dynamics that can emerge for bacterial populations in environments with physicochemical complexity.

[P20]

Subnanometer heterojunction interfaces confined in 10 nm-scale nanocubes elevating photovoltaic alkaline water electrolysis

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Alkaline water splitting electrocatalysts have been widely studied for several decades; however, sluggish hydrogen evolution reaction (HER) kinetics and poor stability hinders the commercialization of electrocatalytic green hydrogen production.¹⁻³ Among the various kinds of electrocatalytic materials, transition metal phosphide (TMP) is known as an earth abundant and highly active material.⁴⁻⁶ To develop TMP-based electrocatalysts, some strategies have been proposed, such as interface modification from heterojunction, doping elements, and multimetallic phases⁷⁻¹⁰. Herein, we brought brand-new single nanoparticle (~10 nm) that is comprised with a bunch of heterojunction interfaces between two different cobalt phosphide and cobalt oxide phases. Our phosphidated cobalt oxide with a nanoscale heterointerface (hereafter PCO-nHI) showed outstanding electrocatalytic hydrogen evolution performance in alkaline condition where the novel property of PCO-nHI is originated from the convergence of both highly active cobalt phosphide and highly stable cobalt oxide. Experimental investigations revealed the excellent water splitting activity of PCO-nHI requires overpotentials of only 162 and 171 mV to reach 100 mA cm⁻², each for acidic and alkaline HER, respectively, implying capability of pH independent HER. The novel alkaline HER activity of PCO-nHI either showed excellent stability over 100 hours under various working conditions, which was superior to the single cobalt phosphide phase. In addition, owing to our spray-coating method, the scalability and applicability of the electrocatalyst was demonstrated where a large scale (~6.6 × 5.6 cm²) catalyst foam was uniformly fabricated, and a high solar-to-hydrogen (STH) efficiency of 11.5% over 100 hours was achieved with the help of Si solar cells. We believe our rationally designed hetero-interfacial electrocatalyst can outperform previously established electrocatalysts via its high efficiency, versatility, and scalability.

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[P21]

Stable and efficient Ir nanoshells for OER and ORR

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We report the characterization and applications of core-shell Cu-Ir nanocatalysts for fuel cells. Core-shell Cu-Ir particles with tunable thickness of Ir can be oxidized to remove the Cu core and obtain Ir shells. The thickness of the Ir shells determines the stability and optimization of the precious metals. We showed within situ scanning transmission electron microscopy the remarkable stability of the Ir shells at elevated temperatures under oxidative and reductive environments. In situ scanning transmission electron microscopy and in situ X-ray absorption spectroscopy showed that traces of remaining copper could be detected in the Ir shells. Electrochemical measurements for oxygen reduction reaction and oxygen evolution reactions show promising activity and stability compared to a commercial catalyst. Thin Ir shells, with high surface area per gram of Ir, were more active but less stable than thicker shells. In contrast, thicker Ir shells were more stable and had excellent electrochemical properties in both aqueous and alkaline environments. Hence, Ir nanoshells appear as interesting candidates to reduce the cost of catalysis while improving chemical performance in fuel cells.

[P22]

Self-healable solid-state electrolytes of polymer-grafted silica nanoparticles

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Solid-state polymer electrolytes have been identified as a promising option for improving the longevity of lithium-ion batteries. However, the addition of plasticizers to enhance ion conductivity at room temperature can have negative consequences such as reduced mechanical strength which leads to thicker electrolyte membranes. These drawbacks can compromise the safety and energy density of the batteries. In this research, we have developed electrolyte network materials that incorporate SiO₂ and schiff-based cross linker, which impart durability and self-healing capabilities to repair internal or external damages. This approach effectively mitigates the degradation of lithium-based batteries. Our material demonstrates improved self-healing abilities and mechanical properties, attributed to robust property of SiO₂ and an increase in cross-linked sites in the polymer matrix.

[P23]

Biodegradable polymer nanoparticles as biomedical adhesive

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Biocompatible adhesives to close wounds have been needed in medical area. Here, we prepare polymer nanoparticles using polyhydroxyalkanoate (PHA) which is biodegradable and evaluate their biocompatibility and the suitability as a medical adhesive. First, PHA nanoparticles are generated by emulsification and solvent evaporation process. Monodisperse oil-in-water droplets with PHA solution are formed using membrane emulsification and PHA nanoparticles are obtained via evaporation of oil phase. Then those PHA nanoparticles are applied as an adhesive between porcine skins to measure adhesive energy and on wounds of rats' skin to check ability for wound healing. Enzyme-linked immunosorbent assay was conducted to check the cytokine expression by PHA.

[P24]

Quantification of size-compatible host-guest interaction using a surface forces apparatus

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The supramolecular host-guest (H-G) interaction has been widely used to the biomedical areas such as hydrogel, bio-glue, and drug delivery. Especially, the H-G complex of cyclodextrin (CD) with adamantane (Ad) are emerging due to their inertness and compatibility in biological system. Despite the considerable interests, the relation of forces to thermodynamic energy of H-G complexes still remain ambiguous. Herein, we directly measured the interaction between CD surface and ditopic Ad (di-Ad) molecule in aqueous solution using a surface forces apparatus (SFA) depending on the cavity size of CD and the concentration of di-Ad. The adhesion forces were measured only between the β -CD surface in presence of di-Ad, which showed a drastic increase with increasing the concentration of di-Ad and gradually decreased after reaching complete H-G complex. Moreover, the molecular adhesion energy of a single host-guest inclusion complex was evaluated to be ~ 9.69 kT. This approach has potential for quantifying fundamental information toward furthering the understanding of supramolecular chemistry and its applications, such as molecular actuators, underwater adhesives, and biosensors, which require precise tuning of specific host-guest interactions.

[P25]

Solvent vapor annealing of a highly confined molecular glass

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Polymer nanocomposite films (PNCFs) with high loading of nanoparticles are desirable for a wide range of NPs and polymer-tailored applications. Capillary rise infiltration (CaRI) enables extreme nanoconfinement conditions with the production of polymer nanocomposites with high nanoparticle loading (>50%). In this study, we focused on fabricating CaRI with a molecular glass system using N,N'-bis(3-methylphenyl)-N,N'-diphenylbenzidine (TPD). We employed an indirect method to study the kinetic and thermodynamic stability of these CaRI films using in situ solvent vapor annealing (SVA). And utilized in situ spectroscopic ellipsometry to determine the diffusion coefficient of the solvent moving through the confined molecular glass. The speed of the moving front was measured by controlling the solvent vapor pressure. We observed that the diffusion of solvent through CaRI with variable nanoparticle pore sizes followed different diffusion processes. The results provide evidence for the slower dynamics of the solvent through the film with enhanced confinement. This solvent dynamics over the confined molecular glasses could be used to prepare effective barrier materials for applicative purposes. Our future work would probe the altering effect of temperature on the mechanism and dynamics of this solvent front with varying confinement.

[P26]

Engineering of surface shape morphing for function transformation in polymeric films

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A function is intricately linked to shape. For instance, transparent materials can exhibit vibrant colors when shaped as submicron grating patterns and hydrophilic materials can showcase superhydrophobicity when possessing doubly re-entrant shapes. In this study, we propose a scheme for function transformation through surface shape manipulation in films. Initially, we fabricate two-dimensional (2D) shapes such as lines or rectangles on a substrate, which are subsequently morphed into laterally buckled or inversely tapered forms. These alterations in surface shape trigger remarkable functional changes. The film can dissipate applied stress or repel low surface energy liquids, such as oil. To achieve shape transformations, we employ a swelling method using hydrogel shapes bonded to the substrate. Subsequently, we replicate the desired shape using functional materials by photopolymerizing liquid prepolymers filled within the cavities of the swollen hydrogel shapes. During photopolymerization, we explore techniques to retain water molecules within the hydrogel networks by controlling the surface energy of the photocurable liquid prepolymers and ensuring the removal of air between the liquid prepolymer and the cavities, facilitating easy infiltration into the inversely tapered shapes. The proposed scheme of function transformation through surface shape morphing serves as a versatile platform technology capable of developing unprecedented functions highly dependent on the specific shapes employed.

[P27]

Effects of film thickness on surface wetting of grafted nanoparticles in polymer nanocomposites

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Polymer nanocomposites (PNCs) allow for a broad range of applications owing to their versatile properties, which are directly correlated to the spatial arrangement of the nanoparticles in the polymer matrix. For instance, surface properties such as wettability, friction, and durability depend on the wetting behavior of nanoparticles in PNCs. Previously, we determined the diffusion coefficient of poly(methyl methacrylate) grafted silica nanoparticles (PMMA-NPs) in a poly(styrene-ran-acrylonitrile) (SAN) matrix using time-of-flight secondary ion mass spectrometry (ToF-SIMS). In this work, we continue to study the effect of film thickness on the PNC structure using ToF-SIMS, along with techniques such as atomic force microscopy and transmission electron microscopy. To decouple the surface and thermodynamic contributions, we investigate the effect of confinement on PNC structure using films with a thickness from 100 to 5000 nm. The results allow for greater control over NP dispersions and PNC morphologies, which are crucial in tailoring PNC properties.

[P28]

Counterplotting the mechanosensing-based fouling mechanism of mussels against fouling

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Marine organisms react to various factors when building colonies for survival; however, severe accumulation of diverse organisms on artificial structures located close to water causes large industrial losses. Herein, we identify a concept in the development of antifouling surfaces based on understanding the surface stiffness recognition procedure of mussel adhesion at the genetic level. It was found that on a soft surface the combination of decreased adhesive plaque size, adhesion force, and plaque protein downregulation synergistically weakens mussel wet adhesion and sometimes prevents mussels from anchoring, mainly due to transcriptional changes within the mechanosensing pathway and the adhesive proteins in secretory glands. In addition, the use of soft substrates or antagonists of surface mechanosensing behavior suppresses mussel fouling significantly.

[P29]

Hydrophobic alcohols as a potential nonsolvent for polysaccharide xerogels via a simple evaporation process

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Polysaccharide nanoporous structures are suitable for various applications ranging from biomedical scaffolding to adsorption materials, due to their biocompatibility and large surface areas. Pectin, in particular, can create 3D nanoporous structures in aqueous solutions by binding with calcium cations and by creating nanopores by phase separation, which includes hydrogen bonding hydrophobic alcohols with pectin chains in water and alcohol mixtures, and resulting penetration of alcohols into calcium-bound pectin gels. However, due to the hydration and condensation of polysaccharide chains during drying, it has proven challenging to maintain the 3D porous structure without aggregation and collapse in order to produce aerogels or xerogels. Herein, we outline a facile method for creating polysaccharide-based xerogels that involves co-evaporating water with a non-solvent, such as a low molecular weight hydrophobic alcohol like isopropyl alcohol or n-propyl alcohol. We present that the nanoporous morphology can be preserved upon evaporation of both alcohol and water when boiling points of two solvents are similar. It turns out that the mixing ratio of water and alcohol are maintained and that hydrophobic alcohol molecules hydrogen-bonded with pectin chains prevent the hydration and aggregation of the hydrophilic pectin chains during the drying process. We also show that the principle found in this study can be applied to produce 3D xerogels of other polysaccharides including hyaluronic acid, chitin and alginic acid, suggesting a general approach to produce 3D polysaccharide xerogels by a simple, convenient evaporation process.

Keywords: Xerogels, Porous structures, polysaccharides, pectin, and evaporation

[P30]

Ceramide-based nanovesicles with 1-O-acylceramide for improved skin barrier function

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Stratum corneum (SC) lipids have intensively been applied as a component of nanovesicles for enhancing skin barrier function, but the structure of nanovesicles composed of SC lipids is unstable due to high packing parameter of ceramide. Herein, we propose an extremely stable SC mimetic-nanovesicle system in which 1-O-acylceramide (1OA) facilitates tight interaction between the multi-layers of SC lipid vesicle containing ceramide NP, stearic acid, and cholesterol, thus showing an improved long-term stability. Regardless of presence of 1OA in the nanovesicles, they maintained their multi-lamellar structure. However, the addition of 1OA in the nanovesicles affects the inter-spacing distance and ceramide crystallinity, attributed to the acyl chain conformation of 1OA. Also, we confirmed the ability of 1OA to strengthen skin barrier by analyzing western blot. These findings indicate that 1OA is important for stabilizing the structure of nanovesicles containing SC lipids.

[P31]

Removal of microplastics *via* natural phenolics-mediated coagulation

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Phenolics are common moieties existed in bioadhesives such as marine mussel, tea, wine – playing role in robust wet-adhesion and universal adhesion on diverse substrates [1–3]. Microplastics are distributed in oceans worldwide, and the negative effects of microplastics on the environment and human health are increasing. Generally, three methods are employed to remove microplastics: filtration, biological degradation, and coagulation. Of these methods, filtration is the most commonly used but depends on the filter size or degree of microplastic coagulation. Although Fe- or Al-salts are generally used for coagulation via electrostatic interactions, their microplastic removal efficiency is less than 40 %, and the smaller the size, the lower is the removal efficiency.

In this presentation, microplastic coagulation using metal-phenolic coordinate bonds was used to improve microplastic removal efficiency. Plant-derived tannic acid contributed to interfacial bridging between the microplastics and Fe³⁺. Tannic acid–chitosan conjugates were synthesized as a single coagulant – phenolic-modified cationic polymer. The polymers were effectively modified on the surface of 0.5 μm polystyrene beads, and they demonstrated dramatic coagulation behavior within 5 min following the introduction of FeCl₃ additive. The removal efficiency of the beads exceeded 80% for all tested polymer types. Moreover, on-going projects in my research group will be introduced related to polyphenolic surface treatment and functionalization on biomaterials.

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[P32]

Surfactant-modified anionic silica nanoparticles (SANPs) for rare earth element separation via froth flotation

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Rare earth elements (REEs) are essential for clean energy technologies. Efficient methods for their recovery and separation are urgently needed to meet the growing demands of a rapidly evolving green economy worldwide. However, current separation technologies suffer from low selectivity, difficulty in recycling, and harmful environmental impacts due to the similar physiochemical properties of REEs and the use of organic solvents. To address these challenges, we are developing a froth flotation-based REE separation process that uses surfactant-modified anionic silica nanoparticles (SANPs) as vehicles to separate REEs in aqueous mixtures. We hypothesize that REEs can interact with SANPs via two different mechanisms: electrostatic interactions and pH-induced precipitation. As the solution pH is raised, REEs are known to form hydroxide precipitates at different pHs depending on their identity; SANPs could function as the nuclei for precipitation of hydrolyzed REEs. Under pH conditions that do not induce hydroxide formation, REEs can interact with SANPs via electrostatic interactions. The surfactant modification renders SiO₂ NPs hydrophobic, facilitating froth formation and its adsorption at air-aqueous interfaces. We explore the interactions of SANP with REEs at different pHs' using inductively coupled plasma-optical emission spectroscopy (ICP-OES), zeta potential and surface tension measurements. We also show that the REE cations in the complex can be recovered by changing the pH, allowing for SANP recycling. Our results imply that the envisioned process is a promising alternative to the existing REE recovery and separation methods.

[P33]

Super-adhesive biomimetic dust filter using liquid thin films

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Dry dust filters with small pores have been worldwide used to clean air and now are everywhere in our daily life. Dust, also called particulate matter (PM), are captured at the pore of the filters, therefore smaller pores result in higher PM capturing efficiency. However, air becomes more difficult to pass through the filter as the pores get smaller, which decreases the air permeability and increases the air pressure drop across the filter. This dilemma, caused by the low adhesion of solid PMs to the dry solid surface of the filters, has been one of the most important issue to be overcome on dry dust filter for several decades. Here, inspired by human nose filtering system with thin mucus coated nasal hairs, we create a dry dust filter having a thin non-volatile liquid layer at the surface of the pores. The strong adhesion of PM on liquid thin film improves the PM capturing efficiency without affecting the air permeability of the filter. The liquid thin film coated filter particularly exhibits outstanding dust filtering capability at fast speed filtering system with no re-dispersion of captured PMs. In addition, the suppressed PMs re-dispersion allows a new bi-directional dust filtering. The adhesion-enhanced liquid film (AeLF) filter proposes a new paradigm of dust filtering and opens a new door for fast and efficient air cleaning.

[P34]

pH-mediated size-selective adsorption of gold nanoparticles on diblock copolymer brushes

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Precise control of nanoparticles at interfaces can be achieved by designing stimuli-response surfaces that have tunable interactions with nanoparticles. In this study, we demonstrate that a polymer brush can selectively adsorb nanoparticles according to size by tuning the pH of the buffer solution. Specifically, we developed a facile polymer brush preparation method using a symmetric polystyrene-*b*-poly(2-vinylpyridine) (PS-*b*-P2VP) block copolymer deposited on a grafted polystyrene layer. This method is based on the assembly of a PS-*b*-P2VP thin film oriented with parallel lamellar that remains after exfoliation of the top PS-*b*-P2VP layer. We characterized the P2VP brush using X-ray reflectivity and atomic force microscopy. The buffer pH is used to tailor interactions between citrate-coated gold nanoparticles (AuNPs) and the top P2VP block that behaves like a polymer brush. At low pH (~4.0) P2VP brushes are strongly stretched and display a high density of attractive sites, whereas at neutral pH (~6.5) the P2VP brushes are only slightly stretched and have fewer attractive sites. Quartz crystal microbalance with dissipation monitored the adsorption thermodynamics as a function of AuNP diameter (11 and 21 nm) and pH of the buffer. Neutral pH provides limited penetration depth for nanoparticles and promotes size selectivity for 11-nm AuNP adsorption. As proof of concept, the P2VP brushes were exposed to various mixtures of large and small AuNPs to demonstrate selective capture of the smaller AuNPs. This study shows the potential of creating devices for nanoparticle size separations using pH-sensitive polymer brushes.

[P35]

Solvent effects on molecule adsorption and charge injection on TiO₂ nanoparticle surface

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The selection of solvent for preparing a working electrode (and as the electrolyte) is known to influence the efficiency of dye-sensitized solar cells. In this work, I present results on how protic and aprotic solvents, as well as solvent polarity, affect adsorption of dyes on the TiO₂ nanoparticle surface and electron injection from the dye to the semiconductor. Adsorption of dye molecules on nanoparticle surfaces was measured through second harmonic light scattering and electron injection through ultrafast transient mid-IR absorption. Results show that protic solvents do not allow direct adsorption of the dye onto the semiconductor surface, due to hydrogen bonding with the dye and competitive binding to the semiconductor surface. Aprotic solvents, on the other hand, support solvation of the dye molecules but also facilitate dye adsorption on the semiconductor nanoparticle. Among aprotic solvents, it was found that solvents with higher polarity result in larger adsorption free energy for the dye and faster electron injection. Overall, these studies reveal that aprotic solvents with high solvent polarity, such as acetonitrile, yield more efficient dye-sensitized solar cells.

[P36]

The efflux inhibitor PA β N crosses bacterial membranes into periplasm and cytosol

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Efflux pump inhibitors (EPIs) have been developed to suppress bacterial resistance to externally harmful molecules such as antibiotics. EPIs reduce the effectiveness of efflux pumps, whose functions are to eject the undesirable molecules out of the bacterial cell. The inhibitor molecule phenylalanine-arginine beta-naphthylamide (PA β N) has been shown over the last two decades to suppress bacterial efflux pumps in gram-negative bacteria broadly. However, the uptake of PA β N across the bacterial membrane is unclear, which could be an important piece of information to show the mechanism of action of PA β N to the efflux pumps. Herein, we reported the application of the second harmonic scattering (SHS) to measure competitive adsorption between polycationic PA β N (+2 charge) and the cationic triphenylmethane dye, malachite green (MG, +1 charge) as both molecules are taken up by the *P. Aeruginous* membrane. MG is a quaternary ammonium form cation that is SH active while the PA β N cation is SH inactive, making it possible to trace the PA β N within the cell membrane based on its competitive adsorption on the cell membrane. Indeed, the PA β N-induced perturbations in the MG SHS signal revealed a reduction in both the outer membrane and cytoplasmic membrane transport peak, showing that the PA β N cation is able to cross the outer membrane and reach the outer leaflet of the cytoplasmic membrane.

The effect of preequilibrium of the PA β N with the cell membrane, which is expected to result in asymmetric distribution of MG on the two leaflets of the cytoplasmic membrane if PA β N cannot cross the cytoplasmic membrane, was also examined. Indeed, when giving *P. Aeruginous* a head start dosing of PA β N, the SHS signal attributing to the cytoplasmic membrane transport peak shows invariant in the residual signal, indicating that PA β N can cross the cytoplasmic membrane.

Remarkably, when the transport of PA β N across the cell membrane is clear, we are able to propose the potential mechanisms of action of the PA β N. Furthermore, we note that when the mechanism of action of a chemical to the efflux pump is clear, its effect on the MG uptake across the cell membrane can be used as a reference to screen other inhibiting molecules.

[P37]

Harnessing MOF for colloidal assembly

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Assembling metal-organic framework (MOF) particles is an emerging approach for creating colloidal superstructures and hierarchical functional materials, due to their size-tunability, polyhedral shapes, rich molecular features, and multifunctionality. We developed several strategies for harnessing those features, designing new building blocks, and assembling MOF-based colloidal particles into ordered superstructures. First, we showcase the self-assembly of polyhedral MOF particles by depletion interaction, which enables a wide range of low-dimensional assemblies with anisotropic colloidal bonds. Second, we introduce low-symmetry, MOF-based patchy particles, which self-assemble into supra-colloidal structures with unprecedented precision. Third, we selectively modified the facets of polyhedral colloids and introduced patchy polyhedral particles (PPP). The self-assembly of these new building blocks have led to a much-expanded scope of colloidal superstructures that are programmable, including low-dimensional and open colloidal crystals. These strategies offer new opportunities for creating advanced materials for sensing, optics, and photonics.

[P38]

Unrefined coconut oil for hydrophobic anti-scaling coatings

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Many commercial hydrophobic coatings are composed of perfluorinated compounds that are toxic to humans and to aquatic life. Thus, environmentally-derived fatty acids, oils, and waxes have recently been increasingly investigated as alternatives to traditional hydrophobic coatings. Here we investigate the possibility of using unrefined coconut oil directly in a hydrophobic modification process. The direct use of coconut oil simultaneously avoids ethical/environmental concerns associated with other sources of naturally derived oils (especially palm oil) and reduces CO₂ emissions associated with refining oils into their constituent components. We demonstrate that coatings deposited from coconut oil and ethanol mixtures are able to hydrophobically modify a variety of materials including glass and polymeric membranes. We compare the coatings formed from coconut oil to coatings deposited from single-component fatty acids and to a perfluorinated coating. We also present on the potential sustainability benefits that can be realized from cutting chemical refining out of the life-cycle for naturally-derived hydrophobic modification.

[P39]

Plasmonic metamolecules: from synthetic approach to dynamic self-assembly

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We developed a templated surfactant-assisted seed-growth method to synthesize well defined gold nanoparticle assemblies, termed raspberry-like metamolecules (raspberry- MMs). This synthetic approach allows one-step synthesis, assembly of gold nanoparticles and yield raspberry-like nanoshell structures where gold nanoparticles are closely packed with only a few nanometer separations. The resulting raspberry-MMs show unique optical properties such as enhanced near-field scattering, strong magnetic resonances, and broad band extinction spectra in the visible and near-IR region. We also demonstrated that these properties can be controlled experimentally by using surfactant with different length or changing synthetic condition and that the experimental results are consistent with theoretical predictions. Secondly, we studied the optical properties of a stimuli-responsive three-dimensional plasmonic metamolecules composed of spherical plasmonic metal nanoparticles and thermoresponsive poly(N-isopropylacrylamide) (PNIPAM) hydrogels. PNIPAM can be used to control the interparticle distance and coupling of plasmonic metal nanoparticles in response to temperature cycling, resulting in reversibly tunable optical properties. In the presentation, we will discuss the factors affecting the optical properties of nanostructures, focusing on magnetic resonance.

[P40]

Understanding polymer transport properties in nanoporous media

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Understanding the transport properties of polymers in nanoporous materials is extremely important for heterogeneous catalytic polymer reactions. The polymers need to readily infiltrate into the nanopores, and the products should easily diffuse out of the pores to ensure high efficacy of the catalyst. A lot of factors can affect the transport properties of polymers inside these nanopores – the surface chemistry of the pore walls, the geometry of the pores, the level of confinement the polymer molecules experience inside the nanopores, etc. Literature shows that extreme confinement of polymers can drastically alter its diffusivity due to changes in confined entanglement molecular weight of the polymers. However, not much research has been done to study the effect of pore surface chemistry on polymer transport as well as the interdiffusion of two different polymers at high temperatures in nanopores. For polymer reactions using heterogeneous catalyst, these factors are important. We observe that polystyrene has stronger interactions with CaCO_3 as compared to SiO_2 based on polymer-solid contact angle measurements as well as heat of adsorption measurements. This information could be very useful for designing nanoporous supports for heterogeneous catalysts which polystyrene can easily infiltrate into.

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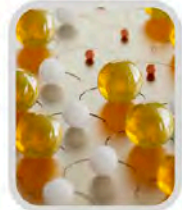


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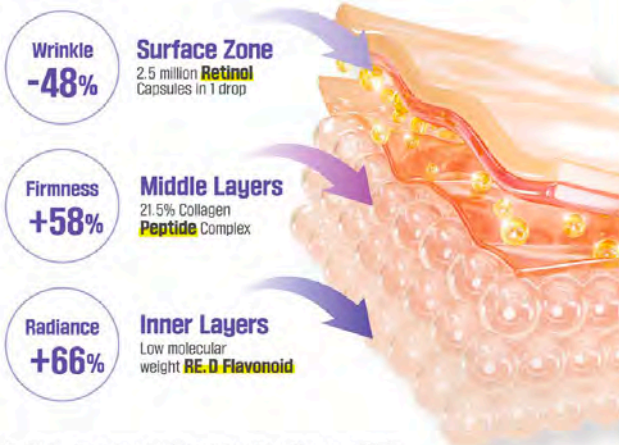


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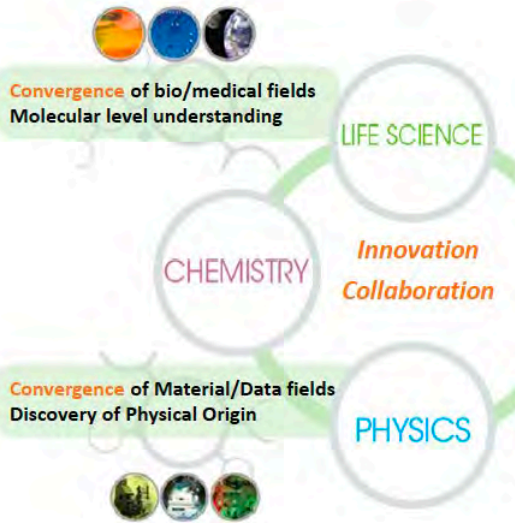




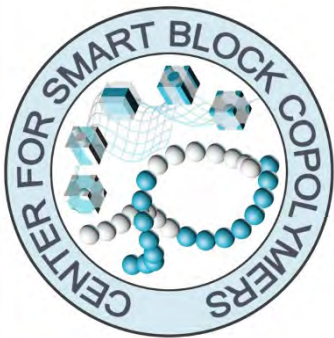
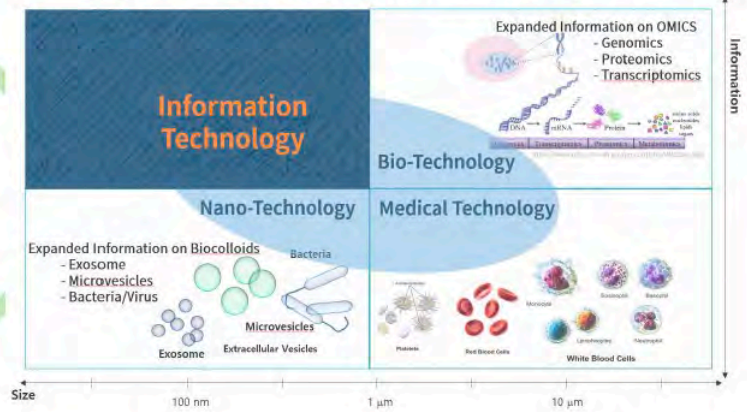
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