USER SCIENCE HORIZONS

2016 APS/CNM USERS MEETING

GENERAL SESSION ABSTRACTS

Combined Plenary Session Keynote

Towards Complete and Comprehensive Fine Structural Mapping of Brains

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The Kasthuri lab is pioneering new techniques for large volume reconstructions of the fine structure of the nervous system. These developments include: large volume automated electron microscopy and synchrotron source x-ray microscopy to map the cellular composition of entire brains; improving sample preparation for serial electron microscopy in order to increase the efficiency of automated algorithmic tracing of these datasets; and combining electron microscopy with current techniques for interrogating the proteome and the genome. These tools will be applied in the service of answering the question: how do brains learn as they grow up? The lab focuses on the synaptic and cellular development of brains as a basis ultimately for understanding the cellular underpinnings of pathologies such as addiction and mental illness.

APS PLENARY

Development of “Color” X-ray Histology Using Multiple Metal Stains and Multi-energy Synchrotron CT

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In this talk, we will discuss a technique for performing three-dimensional, “color” x-ray histology using multiple heavy-metal stains and a multi-energy computed tomography (CT) acquisition technique. The technique employs biologically specific heavy-metal stains such as osmium tetroxide and uranyl acetate that have been widely used in electron microscopy. While such stains have previously been used in high-resolution x-ray imaging of biological samples, previous studies have focused on single-stained specimens. Using monochromatic synchrotron radiation, we demonstrate that it is possible to produce quantitatively accurate maps of the distribution of two distinct stains. We validate the quantification using both L-edge subtraction and single stain controls. We demonstrate using a juvenile zebrafish that the differential distribution of uranyl acetate and osmium tetroxide can be used to differentiate tissues in much the same way as hematoxylin and eosin are used in a conventional optical histology image. While the technique is demonstrated using zebrafish, it is expected to be applicable to other biological specimens, potentially including human pathology tissue, allowing for three-dimensional virtual histology without physical sectioning. We conclude with a brief discussion of the potential for translating the technique into lab-based benchtop CT systems.

APS PLENARY

Biological and Bio-inspired Multifunctional Structural Materials

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Our ability to incorporate and optimize additional properties into multiphase composites without compromising their mechanical integrity is currently limited due to the lack of a comprehensive understanding of the interplay between multiple distinct, potentially conflicting, properties and their underlying structures. Through million years of evolution, however, biological systems have evolved an encyclopedia of material designs for a variety of mechanical purposes with additional properties such as lightweight, transparency, photoreception, and flexibility. In this talk, I will discuss my research in the emerging field of biological and bio-inspired multifunctional structural materials. I will first introduce the structural basis for the highly transparent yet damage tolerant bioceramic material system from the shell of the windowpane oyster *Placuna placenta*. Combining quantitative indentation testing and synchrotron x-ray tomographic measurement, I show that the shell’s unique 3D integrated laminate structure leads to its remarkable resistance to damage at both microscopic and macroscopic level. Secondly, we will explore the dual-functional design of the biomineralized armor of the chiton *Acanthopleura granulata*, which incorporates an integrated sensory system based on hundreds of mineral lenses. We used optical experiments to demonstrate, for the first time, that these microscopic, mineralized lenses are able to form images, and the optical behavior is also systematically investigated through ray-trace simulations by incorporating the quantitative structural information obtained from tomography data. Lastly, we will discuss the flexible biological armor from the dorsal girdle scales of chitons, which consists of three main components: aragonite-based scales, a soft substrate, and an assembly of mineralized microrods underneath. A full 3D parametric model describes the geometry of scales, from which a new bio-inspired armor is developed to achieve simultaneous protection and flexibility.

APS PLENARY

Harnessing Metal-metal Bonds for Small-molecule Activation

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Our group studies metal-metal bonded complexes of first-row transition metals. Bonds between first-row metals are typically weaker than their heavier congeners, which presents a synthetic challenge to isolate and study them.

We are broadly interested in developing these bimetallic complexes for catalysis, where using non-precious metals is sensible from economical and sustainability standpoints.

Transition metal pairs can exhibit multi-electron redox capability, which is promising for reducing small-molecules. The synergistic combination of different metals could generate hybrid "metals" with original properties and/or unique reactivities. We have investigated diverse metal-metal pairings to understand: (1) how one transition metal influences another, and (2) how to tune chemical properties by simply varying the metals. We are currently using this approach to develop bimetallic catalysts for activating dinitrogen and dihydrogen.

APS PLENARY

Self-assembly of Nanoparticles: From Non-additivity to Chirality

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The intrinsic ability of nanoparticles (NPs) to self-organize can be seen virtually everywhere around us. Although omnipresent, the mechanisms of these processes are not well understood. A step toward adequate description of these mechanisms can be made by the juxtaposition of self-organization processes known for biological species and those for NPs. Analysis of comparative strengths of electrostatic, London dispersion, and coordination interactions across all types of chemical structures known to self-assemble can be instructive in understanding the special place occupied by inorganic NPs as well as other self-assembled molecular and nanoscale systems. Analysis of attractive and repulsive forces driving self-assembly phenomena using x-ray diffraction at the Advanced Photon Source and other methods indicate the need to transition from DLVO-based models of NP interactions to their descriptions based on non-additivity of the classical forces and their "entanglement." By other words, multiscale collective effects and non-orthogonality of classical equations for electrostatic and dispersion forces, make the NP-NP interactions no less complex than those found in biology for proteins.

These findings open several avenues for inquiry about the specificity of NP-protein interactions and the structural/functional versatility of their hybrid assemblies. The recent data on selective enzyme inhibition by NPs mimicking the lock-and-key mechanism will be presented. Another active research venue is represented by the chirality effects in individual NPs and their assemblies. Self-organization of chiral nanoparticles represent perhaps one of the best examples of biomimetic inorganic assemblies. The latest data on chirality transfer from (a) chiral surface layers to virus-like supraparticles, (b) circularly-polarized photons to NPs and their helical assemblies, and (c) twisted macroscale state to nanoscale will be presented.

Special effort will be placed on understanding the pathway for translation of the unique structural and optical properties of chiral nanoscale materials to technological applications. This will be exemplified by their bioanalytical application in the detection of DNA oligomers using CD spectroscopy, which enables improvements of one to three orders of magnitude in the detection of proteins, DNA oligomers, and small chiral molecules.

APS PLENARY

Ligand Substitution and Guest Exchange in a Metal-Organic Framework Monitored by *in situ* Dynamic X-ray Diffraction Techniques

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Metal-organic frameworks (MOFs) are a class of materials which have attracted much attention in recent years for their potential applications in separations, gas storage, and drug delivery. While single-crystal x-ray diffraction remains the premier method to obtain Angstrom resolution structural information for crystalline solids, the length of a typical data collection generally limits a routine experiment to probing thermodynamically stable structures. However, *in situ* x-ray diffraction techniques can be employed to allow scientists the opportunity to explore metastable and transient crystalline species, as well as the real time responses of crystalline materials to stimuli such as temperature, light, pressure, and local chemical environment.

We report the development of an improved environmental control cell for *in situ* x-ray diffraction applications, as well as the development of novel techniques for use with such a device. We have also employed this device to study a cobalt-based MOF, $[Co(aip)(bpy)_{0.5}(H_2O)]\cdot 2H_2O$ (aip = 5-aminoisophthalate, bpy = 4,4'-bipyridine), and the ethanol solvation/desolvation processes within the crystalline lattice. During the course of this study, a novel congener of this framework was determined which was effectively dehydrated by the application of ethanol, a process which was not observed in studies of crystals in bulk. An explanation for this process as well as the kinetic studies of the solvation/desolvation processes will be presented as well.

APS PLENARY KEYNOTE

Dynamics in Proteins Investigated by Time-resolved Serial (Femtosecond) Crystallography

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Serial Femtosecond Crystallography (SFX) is an emerging technique performed at ultra-brilliant and ultra-shortly pulsed x-ray sources. The Linac Coherent Light Source (LCLS) at SLAC in Stanford, Ca is a Free Electron Laser for Hard X-rays (X-ray FEL) which produces ultra-short (~40 fs, 40×10^{-15} s) x-ray pulses with 10^{12} x-ray photons in each pulse. The x-ray beam can be focused without loss to spots smaller than 1 µm which is exquisitely suited to investigate tiny specimen such as nano- and micro crystals down to the single molecule level. The tiny crystals are injected into the x-ray beam in a serial fashion, one by one, and in random orientation. When a crystal in flight is hit by the intense 40 fs x-ray pulse, it disintegrates. However, before it is destroyed, it scatters and a diffraction pattern with Bragg spots is recorded on a specially designed detector with fast readout times. This is called the diffraction-before-destruction principle and lies at the heart of SFX. From tens of thousands of these diffraction patterns complete crystallographic datasets with accurate intensities can be collected. If a reaction can be initiated in the crystal for example with an ultrashort optical laser pulse a time-delay Δt before it is probed by the x-ray pulse, the reaction can be structurally investigated. The time-resolution is essentially given by the 40 fs duration of the x-ray pulse. The tiny crystals are intercepted twice in flight, first by the optical pump laser, and then by the probe x-ray pulse. SFX becomes time-resolved (TR-SFX). Here, TR-SFX results are presented on a time-scale from 100 fs to 1 µs. We [1] show the earliest events of a photo-activated reaction in a protein and gain unprecedented insight into the chemistry and the mechanism of the reaction.

Serial crystallography is also feasible at synchrotron light sources. The Laue method has the advantage that the entire reflection range (all mosaic blocks) are optimally excited by the polychromatic radiation. This allows for short exposure times on the order of a few µs with 10 µm crystals. Since the crystals are small, reactions in enzyme crystals can be initiated swiftly by diffusion of active substrate. The catalytic reaction can then be followed on sub millisecond time scales. The time-resolution is given by the diffusion time or the mixing time, whichever is longer. This method allows for a convenient way to study reaction in enzymes with time-resolved crystallography.

[1] Collaboration of 45 scientists from 3 countries and 13 institutions led by the BioXFEL Science and Technology Center (NSF-1231306).

CNM PLENARY KEYNOTE

Materials by Design: 3-dimensional Architected Nanostructured Meta-materials

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Creation of extremely strong yet ultra-light materials can be achieved by capitalizing on the hierarchical design of 3-dimensional nano-architectures. Such structural meta-materials exhibit superior thermomechanical properties at extremely low mass densities (lighter than aerogels), making these solid foams ideal for many scientific and technological applications. The dominant deformation mechanisms in such “meta-materials,” where individual constituent size (nanometers to microns) is comparable to the characteristic microstructural length scale of the constituent solid, are essentially unknown. To harness the lucrative properties of 3-dimensional hierarchical nanostructures, it is critical to assess mechanical properties at each relevant scale while capturing the overall structural complexity.

We present the fabrication of 3-dimensional nano-lattices whose constituents vary in size from several nanometers to tens of microns to millimeters. We discuss the deformation and mechanical properties of a range of nano-sized solids with different microstructures deformed in an *in situ* nanomechanical instrument. Attention is focused on the interplay between the internal critical microstructural length scale of materials and their external limitations in revealing the physical mechanisms which govern the mechanical deformation, where competing material- and structure-induced size effects drive overall properties.

We focus on the deformation and failure in metallic, ceramic, and glassy nano structures and discuss size effects in nanomaterials in the framework of mechanics and physics of defects. Specific discussion topics include: fabrication and characterization of hierarchical 3-dimensional architected meta-materials for applications in biomedical devices, ultra lightweight batteries, and damage-tolerant cellular solids, nano-mechanical experiments, flaw sensitivity in fracture of nano structures.

CNM PLENARY

Molecular Engineering of Nano-optomechanical Transducers

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Quantum information presents an emerging area of research that prospects exciting new technologies, ranging from optical telecommunications, laser physics to quantum computing. Crystalline materials that behave as optical actuators and proceed via some for m of nano-optomechanical mechanism are of particular interest for optical data storage [1] or quantum computing [2]. Nonetheless, the field is facing a dearth of suitable functional materials for applications. One possible material option is a series of compounds based on the generic formula, $[Ru(SO_2)(NH_3)_4X]Y$, whose SO_2 group manifests solid- state linkage photo-isomerization (X is the *trans*-ligand to SO_2; Y is a counterion). This light-induced phenomenon causes these materials to act as photo-induced molecular switches [3–5] or molecular transducers [6,7] whose nano-optomechanical properties exist in the single-crystal state: a high-quality solid-state medium for single-photon control. This talk will present the development of this family of materials towards such applications, via a range of advanced materials characterization experiments conducted at the CNM, APS and MSD within Argonne National Laboratory. These are enabling our understanding of the light-induced molecular structure [8–10] and nano-optomechanical properties of these light-induced solid-state actuators. Establishing this knowledge-base of structure- to-function relationships leads to the ultimate goal of being able to molecularly engineer these materials for a given device application.

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CNM PLENARY

Designing Functional Oxide-based Optical Materials from Quantum Mechanics to the Laboratory

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Modern first-principles calculations based on density functional theory and related techniques enable the predictive modeling of the linear and nonlinear optical (NLO) properties of materials without adjustable or empirical parameters. Today, atomistic calculations are an indispensable tool by which to understand the interrelationship between the underlying structure and the measured optical properties and are particularly suited for the design of new materials with desirable optical responses and performance; for example, obtaining light sources with shorter wavelength means higher resolution. Thus for applications involving photolithography, laser surgery, and nanoscale imaging, short wavelength (below 250 nm) light is desirable. Unfortunately short wavelengths are challenging to achieve—the state-of-the-art deep-ultraviolet (DUV) materials rely on frequency doubling NLO borates, including β-BaB_2O_4 and $KBe_2BO_3F_2$ (KBBF). Owing to the scarcity of materials with DUV cutoff edges and the toxicity of Be, however, new chemically benign NLO compounds are highly sought. Here I describe predictive *ab initio* models for tailoring NLO activity, which relies on formulating an atomic structure-optical function relationship in terms of a response activated at a symmetry breaking transition due to correlated atomic displacements [1]. This methodology is then applied to Be-free DUV materials prior to and after synthesis: $Ba_4B_{11}O_{20}F$ [2], $Ba_3(ZnB_5O_{10})PO_4$ [3], and the $A_3B_3CD_2O_{14}$ (A = Sr, Ba or Pb; B = Mg or Zn; C = Te or W, and D = P or V) Dugganite family [4]. These families of materials combine multiple types of NLO building blocks that synergistically enhance their DUV capabilities, such as borate groups for inducing the effects through symmetry breaking, phosphate groups for a shorter absorption edge, and stereoactive lone pair cations for increased frequency doubling response and efficiency. I show how chemically intuitive guidelines based on realizing either static polarizations or increased dielectric polarizability by atomic scale control emerge in this process. Finally, I discuss the important role of "closing-the-loop" synchronously with experiment rather than iteratively to rapidly realize new functional optical materials.

This work was financially supported by the National Science Foundation (DMR-1454688) and performed in collaboration with the Poeppelmeier (Northwestern) and Halasyamani (Houston) research groups. Computational results were obtained on the CARBON cluster at the Center for Nanoscale Materials, an Office of Science user facility, was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

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CNM PLENARY

Underneath the Surface of Block Copolymer Thin Films

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Block copolymers are known to spontaneously self-assemble into periodic nanoscale morphologies with characteristic feature sizes of 5–50 nm, making them attractive materials for templating and scaffolding nanostructures in applications ranging from energy harvest and storage to nanomanufacturing. In particular, the use of block copolymers in lithography processes is considered an attractive strategy to enhance the capabilities of current tools in semiconductor patterning. Since block copolymer self-assembly is inherently a three-dimensional (3D) process, quantitative 3D characterization is necessary to fully understand the development of 3D structures and the relationship between the substrate's guiding patterns and the assembled block copolymer films.

In this talk I will discuss our work on developing methods for 3D characterization of block copolymer thin films using scanning transmission electron microscopy (STEM) tomography, and the insights obtained by this characterization in various systems. To enable high contrast STEM imaging of block-copolymers, selective inorganic growth using sequential infiltration synthesis was utilized as a new staining method in polymers. The SIS staining together with artifact-free sample preparation developed in the CNM, lead to high-quality tomography data which allowed us to decipher the 3D structure of self-assembled and directed self-assembled block copolymer films. STEM tomography characterization of lamellar and cylindrical block copolymer films revealed the through-film morphology, changes in feature's roughness with depth, and defects that were previously hidden underneath the surface. The knowledge obtained by this detailed 3D characterization will enable further development of materials and processes for next generation devices.

CNM PLENARY

Accelerating Nanomaterial Property Prediction Using Machine Learning

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The dramatic increase in computational power allows for the generation of large quantities of data from first principles and classical material simulations. Today, the size and speed of data production from these simulations do not allow manual categorization and mining tasks to reach meaningful scientific information. Instead, discoveries often rely on automation techniques using machine learning algorithms. Here, we will present the use of such techniques combining global optimization methods (evolutionary and particle swarm algorithms), local minimizers (gradient methods, simplex), first principles and classical atomistic models to parameterize force-fields for molecular dynamics/mechanics simulations of nanomaterials. The complexity of the force-field is determined according to the material and properties that are sought. In this talk we will focus on three systems: Transition metal dichalcogenides (TMDs), gold nanoclusters and IrO_2. We develop 3-body potentials to study thermal conductivity in 2-dimensional TMDs. To predict Au nanocluster structures and represent bulk properties at the same time, a bond-order/long range hybrid model is used. Finally, we parameterize a variable charge model to understand the catalytic activity in IrO_2 nanoclusters.

CNM PLENARY

Ultrafast All-optical Modulation of the Full-visible Spectrum with Indium-Tin-Oxide Nanorod Arrays

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Optical nonlinearity of metallic nanostructures induced by optical excitation of mobile electrons permits dynamic tuning of their electromagnetic response, and opens up opportunities for all-optical signal switching and processing. Here we report on the ultrafast, sub-picosecond optical response of indium-tin-oxide nanorod arrays (ITO-NRAs) induced by resonant, intraband optical pumping, which enables strong modulation of the entire visible spectrum from 360 nm to 710 nm with favorable spectral tunability and unique beam-steering capability. On the basis of a semi-quantitative model, we show that the large modulation amplitude and high switching rate stem from a significant electron redistribution due to the low electron density in ITO in comparison to noble metals. Furthermore, we show an ultraslow transient response in the microsecond regime associated with the lattice cooling of the long aspect-ratio nanorod structure. Our work shows that novel nanophotonic functionalities can be achieved by using alternative plasmonic materials such as heavily doped semiconductors.