

# DRIVING DISCOVERY

## 2017 APS/CNM USERS MEETING

GENERAL SESSION ABSTRACTS



## COMBINED PLENARY SESSION KEYNOTE The Scientific Challenge of Replacing the Transistor with a Lower Voltage Device

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The NSF Center for Energy Efficient Electronics Science (E<sup>3</sup>S) is searching for an ultralow-voltage switching device to replace the current transistor. A lower operating voltage would permit more than four orders of magnitude reduction in electronics power consumption, triggering a new form of Moore's Law. E<sup>3</sup>S applies a multi-disciplinary approach, invoking the research themes: nanoelectronics, nanomechanics, nanophotonics, and nanomagnetism.

This talk will try to answer: What's standing in the way?

## APS PLENARY

### Microstructural Evolution in Materials

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Understanding the role of materials processing is central to the materials science engineering paradigm of linking the composition of a material with its properties.

Unfortunately, establishing this link has been hampered by the inability to follow the evolution of the microstructure of a material in three dimensions and as a function of time (4D). Synchrotron x-ray sources now provide this capability at both the micro and nanoscales. Not surprisingly, this has radically changed our understanding of the mechanisms responsible for microstructural evolution, such as eutectic solidification that occurs during the processing of all Al casting alloys that are used commercially today.

Through 4D x-ray tomography, we find eutectic growth mechanisms in these materials that are distinct from classical isotropic eutectics and from those proposed in the literature. In addition, the ability to track the evolution of a 3D microstructure in time provides new opportunities to link experiment and simulation. Examples will be given where this is used both as a test of simulation and to determine difficult-to-measure materials parameters. Finally, a major challenge with 4D experiments is the resulting large datasets. This demands new techniques to extract relevant information from these datasets. To address this big-data challenge, a computationally efficient method to extract important length scales from 4D datasets using two-point statistics will be discussed.

## APS PLENARY

### Beyond Crystallography: Coherent X-ray Diffractive Imaging and Atomic Electron Tomography

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Crystallography has been fundamental to the development of many fields of science over the past century. It has now matured to a point that as long as good quality crystals are available, their atomic structure can be routinely determined in three dimensions. However, many samples in nature are non-crystalline and their three-dimensional (3D) structures are not accessible by crystallography. Overcoming this hurdle has required the development of new structure determination methods. In this talk, I will present two methods that can go beyond crystallography: coherent diffractive imaging (CDI) and atomic electron tomography (AET). In CDI, the diffraction pattern of a non-crystalline sample or a nanocrystal is first measured and then directly phased to obtain an image. The well-known phase problem is solved by combining the oversampling method with iterative algorithms. In the first part of the talk, I will illustrate several important CDI methods and highlight some important applications using 3<sup>rd</sup> generation synchrotron radiation and x-ray free electron lasers. In the second part of the talk, I will present a general tomographic method, termed AET, for 3D structure determination of crystal defects and disordered materials at the individual atomic level. By combining advanced electron microscopes with novel data analysis and tomographic reconstruction algorithms, AET has been used to reveal the 3D atomic structure of crystal defects and chemical order/disorder such as grain boundaries, anti-phase boundaries, stacking faults, dislocations and point defects, and to precisely localize the 3D coordinates of individual atoms in materials without assuming crystallinity. As coherent x-ray sources and powerful electron microscopes are under rapid development in the world, it is anticipated that CDI and AET will find broad applications in both the physical and biological sciences.

J. Miao, T. Ishikawa, I.K. Robinson, and M.M. Murnane (2015). "Beyond crystallography: Diffractive imaging using coherent x-ray light sources," *Science* **348**: 530–535.

J. Miao, P. Ercius, and S.J.L. Billinge (2016). "Atomic electron tomography: 3D structures without crystals," *Science* **353**: aaf2157.

Y. Yang, C.-C. Chen, M.C. Scott, C. Ophus, R. Xu, A. Pryor Jr., L. Wu, F. Sun, W. Theis, J. Zhou, M. Eisenbach, P.R.C. Kent, R.F. Sabirianov, H. Zeng, P. Ercius, and J. Miao (2017). "Deciphering chemical order/disorder and material properties at the single-atom level," *Nature* **542**: 75–79.

**APS PLENARY****Synthetic-method Development for the Preparation of Robust and Functionalized MOFs (Metal-Organic Frameworks)**

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Metal-Organic Frameworks (MOFs) are an emerging class of porous materials constructed from metal-containing nodes and organic linkers. Due to their structural and functional tunability as well as their ever-expanding application scope, MOFs have become one of the most fascinating class of materials for both scientists and engineers.

Many early MOFs made from divalent metals showed exceptional porosity and promise for a wide variety of applications, but ultimately proved unsuitable for use under harsh conditions because of their lack of stability. To improve the robustness, we have been focusing on the development of stable MOFs based on trivalent and tetravalent metals [M (III) and M (IV)], which tend to possess much greater stability due to the increased strength and kinetic inertness of the M–O bonds. The exceptional stability of M (III) and M (IV) based carboxylate MOFs have made them feasible for use in a wide-range of practical applications.

However, on the other hand, the inertness of the metal-carboxylate bonds has posed a synthetic challenge for the preparation of the M (III) and M (IV) MOFs. By judicious kinetic control, we have developed multiple synthetic strategies, which have led to the “total synthesis” approach, through which a target MOF can be retro-synthetically designed and synthesized.

Prior to our work, MOFs were almost exclusively formed via “one-pot” approaches. We use labile metal-carboxylate bonds to “layer-on” molecular elaborations to preformed coordination assemblies, including clusters, metal-organic polyhedrons (MOPs) and other MOFs. This bridging ligand exchange reaction can make some new macromolecular coordination complexes readily accessible whereas previously they were difficult or impossible to obtain.

For instance, to form MOFs from M (III) and M (IV), we developed the following synthetic strategies:

- First, we explored a method of kinetically-tuned dimensional augmentation of robust clusters with terminal carboxylate groups by tuning the kinetics of the synthetic procedure.
- Second, we developed post-synthetic metathesis and oxidation reactions, where redox chemistry is applied to mediate bridging ligand exchange.

- Third, we used sequential installation of up to three different linkers to give mixed linker MOFs with crystallographically ordered structures.

Most recently, we enriched the MOF synthetic tool box by introducing linker labilization, in which selective linkers were exchanged, cleaved, and removed to create MOFs with hierarchical pore structures controllably. These MOFs are critical for a variety of applications including gas storage and separation, chemical sensing, energy harvesting and storage, catalysis, as well as biomedicine.

**APS PLENARY STUDENT INVITED TALK****Synthesis of High-temperature Materials from Amorphous Precursors at Ambient Conditions**Michael L. Whittaker<sup>1</sup>, Wenhao Sun<sup>2</sup>, Gerbrand Ceder<sup>2</sup>, and Derk Joester<sup>1</sup><sup>1</sup> Northwestern University, Department of Materials Science and Engineering, Evanston, IL 60208<sup>2</sup> Lawrence Berkeley National Laboratory, Berkeley, CA 94720

Solid solution strengthening is a classical method for enhancing the mechanical properties of materials through lattice distortion from disparate ionic radii. This mechanism is also active in carbonate minerals, out of which many organisms form their skeletons, teeth, and/or shells. Unlike most engineering materials, however, organisms are able to achieve enhanced properties by synthesizing and maintaining highly metastable compositions under ambient conditions. In this study, I demonstrate a bioinspired method for generating a highly metastable  $\text{Ca}_{1-x}\text{Ba}_x\text{CO}_3$  structure with hardness equivalent to that found in biogenic calcite. Barium-substituted disordered calcite (balcite) contained up to 50× more barium than the solubility limit of barium in calcite [1], and is thermodynamically stable only above 525°C, yet was formed under ambient conditions using amorphous precursors. Its structure was confirmed for the first time from high-resolution powder x-ray diffraction. Local structure in the amorphous precursor, investigated with vibrational spectroscopy, x-ray absorption spectroscopy, pair distance distribution function analysis, and a combined molecular dynamics/density functional theory approach, resembled that of balcite. Using microfluidically produced water-in-oil drops as microreactors, this structural similarity was shown to selectively reduce the barrier to balcite formation through a non-classical crystallization mechanism. This synthesis pathway improves our understanding of biomineral synthesis, which often proceeds through metastable, amorphous intermediates and introduces new mechanisms to generate persistent non-equilibrium compounds.

This work was supported in part by the International Institute for Nanotechnology, NSF (DMR-1508399), and ARO (W911NF-16-1-0262). In situ-WAXS, EXAFS, and hr-PXRD were performed at the DuPont-Northwestern-Dow Collaborative Access Team (DND-CAT) located at Sector 5 of the Advanced Photon Source (APS) a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. The authors thank Drs. Steven Weigand, Qing Ma, and Denis Keane.

[1] Tesoriero, A. and Pankow, J. (1996). Solid solution partitioning of Sr<sup>2+</sup>, Ba<sup>2+</sup>, and Cd<sup>2+</sup> to calcite. *Geochimica et Cosmochimica Acta* **60**: 1053–1063.

## APS PLENARY APS-U Feature Beamlines and Beamline Enhancements

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In the period since the last APS/CNM Users Meeting, Feature Beamlines for the APS-U have been selected, and the roadmapping process for the locations of these beamlines has been completed. Recent workshops that focused on the Feature Beamlines helped solidify the scientific case for each and gave the user community an opportunity to provide input on their Preliminary Designs. Highlights from the workshops will be presented. A description of the APS-U Beamline Enhancement process and status update will also be presented.

## APS PLENARY Breakthroughs in Biology Driven by Quantitative Subcellular X-ray Fluorescence Imaging

Thomas V. O'Halloran<sup>1,2</sup>, Amanda Bayer<sup>1,2</sup>, Haimei Chen<sup>1</sup>, Seth Garwin<sup>1,2</sup>, Adelita Mendoza<sup>1,3</sup>, Andrew Nowakowski<sup>1</sup>, Suning Wang<sup>1</sup>, Junjing Deng<sup>5</sup>, Chris Jacobsen<sup>1,4,6</sup>, Nan Zhang<sup>5</sup>, Teresa Woodruff<sup>1,5</sup>, Si Chen<sup>5</sup>, and Stefan Vogt<sup>6</sup>

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Recent applications of synchrotron based x-ray fluorescence microscopy (XFM) are at the heart of a number of breakthroughs in our understanding of the most fundamental aspects of biology. In conjunction with label-free, high-resolution ptychographic imaging, XFM is greatly enhancing the ability of chemists and biologists to interrogate chemical changes in subcellular compartments during developmental processes. The synchrotron

upgrades underway around the world will greatly expand the access of the biology community to entirely new domains in our understanding how cells work.

Several examples of quantitative subcellular inorganic flux mechanisms will be discussed, with particular focus on the zinc fluxes that regulate sperm activation, egg maturation and fertilization. Quantitative single cell x-ray fluorescence microscopy at APS beam lines and the Bionanoprobe at Argonne National Laboratory reveals a critical regulatory role changes in zinc content and subcellular localization (*Nature Chemistry*, 2015 PMID: PMC4315321). Coupled with live cell studies in confocal fluorescence experiments, zinc fluxes have been shown to involve the movement of zinc ions between subcellular compartments depending upon the cell type: millions of zinc ion must be taken up by sperm, whereas billions of zinc ions must first be taken up and then ejected in the egg. These movements of zinc must occur in a tightly regulated time over minutes to hours and cells use these events to control key physiological developmental decisions. This work reveals that fluctuations in the concentration and binding sites of zinc, like calcium and phosphorous, act as conductors of information in biological signaling networks. As sensitivity and resolution of XFM methods increase, we anticipate that quantitative imaging of the fluxes of other abundant inorganic cofactors, such as copper, potassium, sodium, iron and manganese will likewise reveal new mechanisms in biology.

## APS PLENARY KEYNOTE X-ray Diffraction on Mars: Scientific Discoveries Made by the CheMin Instrument

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The Mars Science Laboratory *Curiosity* landed in Gale crater in August 2012 with the goal to identify and characterize habitable environments on Mars. *Curiosity* has been studying a series of sedimentary rocks primarily deposited in fluvio-lacustrine environments ~3.5 Ga. Minerals in the rocks and soils on Mars can help place further constraints on these ancient aqueous environments, including pH, salinity, and relative duration of liquid water. The Chemistry and Mineralogy (CheMin) x-ray diffraction and x-ray fluorescence instrument on *Curiosity* uses a Co x-ray source and charge-coupled device detector in transmission geometry to collect 2D Debye-Scherrer ring patterns of the <150 micron size fraction of drilled rock powders or scooped sediments. With an angular range of ~2-52° 2θ and a 2θ resolution of ~0.3°, mineral abundances can be quantified with a detection limit of ~1-2 wt.%. CheMin has returned quantitative mineral

abundances from 16 mudstone, sandstone, and aeolian sand samples so far. The mineralogy of these samples is incredibly diverse, suggesting a variety of depositional and diagenetic environments and unexpected igneous processes in different sediment source regions. Results from CheMin have been essential for assessing the habitability of ancient Mars, reconstructing the geologic history of Gale crater, and estimating the ancient inventory and evolution of CO<sub>2</sub> and water in the martian atmosphere and hydrosphere.

### CNM PLENARY Physics and Chemistry of Single-molecule Circuits

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Over the past ten years, there has been tremendous progress in the measurement, modeling and understanding of structure-function relationships in single molecule circuits. Experimental techniques for reliable and reproducible single molecule junction formation and characterization have led, in part, to this progress. In particular, the scanning tunneling microscope based break-junction technique has enabled rapid, sequential measurement of large numbers of nanoscale junctions allowing a statistical analysis to readily distinguish reproducible characteristics. In this talk, I will present methods to create single-molecule devices and measured their physical properties, including electronic, electrochemical and thermoelectric. I will then show how their molecular structure as well as the environment around these nanoscale systems can control their electronic characteristics.

### CNM PLENARY A New (X-ray) Window into the Local Chemistry of the Emergent Hybrid Perovskites

David P. Fenning

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The hybrid organic-inorganic perovskite material system has attracted widespread interest for potential applications in optoelectronics including solar cells, LEDs, lasing, detectors and more. In this talk, I will discuss how we are using the resolving power of the hard x-ray nanoprobe at CNM to investigate the relationship between the local chemistry in hybrid perovskites and their optoelectronic performance. Using a series of model materials with varying halide stoichiometry on the anion site, we have studied local heterogeneity and especially when and

where chlorine remains incorporated within perovskite films. I will also share insights from our recent *in situ* nanoprobe investigations of non-stoichiometry, defect kinetics, and stability in perovskite material and devices. By identifying and manipulating the local chemistry in the bulk and at interfaces, we aim to systematically accelerate the development of these optoelectronic materials.

### CNM PLENARY Spin Seebeck Effect in the Absence of Ferromagnetism

Anand Bhattacharya

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Magnetic thermogalvanic effects such as the anomalous Nernst effect in conducting ferromagnets, and the spin Seebeck effect involving ferromagnetic insulators have been widely studied in the context of spintronics and thermoelectrics. We have developed a technique that allows us to characterize magnetic thermogalvanic effects in patterned structures on the micron scale. We have used this approach to probe magnetic interactions in a variety of materials, leading to the discovery of the spin Seebeck effect in a paramagnetic insulator [1] that is a classical spin liquid at low temperatures and in an antiferromagnetic insulator with uniaxial anisotropy [2]. Our approach also allows us to characterize more complex magnetic structures in patterned devices that may not otherwise be possible to measure using standard magnetometry and scattering techniques. In particular, I will discuss how we characterize non-collinear magnetism in patterned wires of an MBE grown superlattice of La<sub>2/3</sub>Sr<sub>1/3</sub>MnO<sub>3</sub> (LSMO) and LaNiO<sub>3</sub> (LNO) [3].

[1] S.M. Wu et al. (2016). "Antiferromagnetic spin Seebeck effect." *Phys. Rev. Lett.* **116**: 097204.

[2] S.M. Wu et al. (2015). "Paramagnetic spin Seebeck effect." *Phys. Rev. Lett.* **114**: 186602.

[3] J. Hoffman et al. (2016). "Oscillatory Non-collinear Magnetism Induced by Interfacial Charge Transfer in Metallic Oxide Superlattices." *Phys. Rev. X* **6**: 041038.

### CNM PLENARY 2D Materials Superlubricity and How to Find It

Diana Berman

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Miniaturization of devices for a broad range of applications (from medical sensors, to micro- and nano-scaled machine technologies) calls for developing new materials that are effective at the nano- and micro-scales and may allow superior performance and long-lasting operation in a range

of micromechanical systems. Controlling the friction and wear that occur in sliding contacts under high pressures and shear stresses is a ubiquitous challenge in many of these applications.

In this talk, we will demonstrate superior performance of graphene, 2D carbon material, as a solid lubricant for the wide variety of applications, ranging in sizes from nano/micro scale (NEMS/MEMS) [1], to macroscale (moving electrical contacts, sliding/rolling, rotating and bearings, etc.) [2]. In particular, we will focus on experimental observations of superlubricity regime (near-zero friction) at macroscale [3] and highlight the new fundamental mechanism that could further predict frictional behavior of 2D materials systems, as well as offer a direct pathway for designing smart frictionless tribological systems for practical applications of industrial interest.

[1] D. Berman et al. (2015). Special issue in *Diamond and Related Materials* **54**: 91.

[2] D. Berman et al. (2014). *Materials Today* **17**: 31–42.

[3] D. Berman et al. (2015). *Science* **348**: 1118–1122.

## CNM PLENARY

### STM Manipulation of Individual Molecules: From Oligomers to Molecular Machines

Yuan Zhang

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One of the goals of nanotechnology is the development of complex molecular machines that can be operated with atomic level control in a solid-state environment. This level of control requires both a fundamental understanding of molecular mechanics and knowledge of how molecular machine components operate. Scanning probe microscope manipulation of molecules offer an opportunity to investigate individual molecules and molecular machine components on materials surfaces. At the first part of the talk, operation of two artificial molecular machines in the quantum regime will be presented. A stand-alone molecular motor was switched to rotate in a clockwise or anticlockwise direction by selective inelastic electron tunneling through different subunits of the motor. The directional rotation here originates from the sawtooth-like rotational potential, which are solely determined by the internal molecular structure and are independent of the surface adsorption sites. Moreover by introducing dipole active components in the rotor arms of the molecular motors, communication among the molecules can be introduced via dipolar interaction. In addition to single molecule operations, synchronization of molecular motors can be achieved depending on the symmetry of the molecular assemblies on surfaces and the strength of applied electric field energy.

The second part of the talk will be focused on the determination of the amount of lateral force needed to move a single molecule on a Ag(111) surface. Lateral manipulation technique of Scanning Tunneling Microscope and QPlus Atomic Force Microscope are employed to measure molecule-surface friction. Despite two different instruments and their different working mechanisms, the measured results turn out to be very similar. Our finding reveals a directional preference in the molecular self-assembly process of sexiphenyl (6p) due to preferential diffusion of these molecules.

## CNM PLENARY STUDENT INVITED TALK

### Metal Oxide Protected Lithium Anode Enabled by Atomic Layer Deposition towards Practical Applications

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Lithium metal is considered to be the “holy grail” of battery anodes due to its ultrahigh theoretical capacity (3,860 mAh/g), low potential (-3.04 V versus standard hydrogen electrode), and very low density (0.534 g/cm<sup>3</sup>). However, dendrite growth during cycling and low Coulombic efficiency, resulting in safety hazards and fast battery fading, are significant technical hurdles that prevent the commercialization of lithium metal anodes. In this work, we used atomic layer deposition to grow conformal, ultrathin Al<sub>2</sub>O<sub>3</sub> films on lithium metal in an effort to mitigate these technical problems. We employed *in situ* QCM, for the first time, to study the growth mechanism of Al<sub>2</sub>O<sub>3</sub> on lithium and found larger growth than expected during the initial cycles followed by steady growth at the expected rate. We discovered that both carbonate and ester electrolytes show enhanced wettability on Li with ALD coatings, leading to more uniform and dense SEI formation as well as enabling stable battery operation with smaller electrolyte volumes compared to the uncoated Li. Moreover, XPS investigations and *in situ* TEM demonstrate excellent Li dendrite prevention with the robust ALD Al<sub>2</sub>O<sub>3</sub>

films. As a result, ALD protected Li provides several times longer cycling life with stable Coulombic efficiency and voltage profiles than bare Li at a practical current density of 1 mA/cm<sup>2</sup>.

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*Tools at CNM used for the project: JEOL field-emission SEM 7500F.*