



MOLECULAR FOUNDRY USER MEETING

AUGUST 11–12, 2016



Abstract Booklet

Poster Session

August 11, 2016 | 4:00 pm to 6:30 pm

Posters are organized by the facility of the Molecular Foundry with which the work is most closely associated.

Biological Nanostructures

BI.01

Generation of inorganic-organic hybrid nanomaterials using bacterial S-layer protein arrays

Francesca Manea, LBNL

Advancements within nanotechnology are driven by the ability to fabricate tailored functional architectures with nanoscale precision. We aim to exploit the intricate self-assembly pathway of S-layer proteins to construct molecular-diverse, highly-ordered nanostructures. These proteins, localised on the outer cell wall of bacteria and archaea, organize into two-dimensional crystalline arrays and serve as exceptional organic nanoscaffolds.

We employ several protein engineering approaches, including modification of unstructured C-terminal sequences, peptide chemistry and thiol chemistry to develop protein-based surfaces for the controlled deposition of metal nanoparticles and oxides. In particular, the generation of highly-coordinated bimetallic surfaces will allow the generation of nanoscale alloys with enhanced catalytic properties. Rational embellishment of S-layer arrays with magnetite, a magnetic iron oxide, will produce artificial biocomposites with potential applications in optical and magnetic sensing and as adsorbents in the bioremediation of heavy metals.

Our developed nanomaterials will be investigated via a range of electron microscopy techniques, including matched illumination and detector interferometry (MIDI)-STEM, which has the ability to image soft heterogeneous structures at atomic resolution. Ultimately, we hope to incorporate our engineered S-layer arrays onto the surface of bacteria to produce custom-made, economical microorganisms.

BI.02

Biohybrid Structures Electron Conduits for Improved Microbial Electrochemical Systems

Jose Comejo, LBNL

Co-authors: *Heinz Frei, Caroline Ajo-Franklin*

Extracellular electron transfer (EET) between microorganisms and solid substrates has been the main focus in the process of improvement and better understanding of microbial electrochemical technologies. Despite recent developments, further efforts are needed to make this technology economically viable. A major constraint is the high internal resistance in electrochemical cells used for evaluation and development. Here we present nanopatterned biohybrid structures that act as well defined electron conduits. As a result, this approach is capable of alleviating power losses due to high internal resistance by reducing larger, constraining features in electrochemical cells. These biohybrid structures consist of silica membranes with embedded molecular wires of p-oligo(phenylenevinylene). This platform is used to redirect electrons that are harvested by microorganisms to inorganic catalysts. We utilized microbial cultures of *Shewanella oneidensis* to evaluate electrochemical performance and biofilm surface coverage. We find that the LUMO energy can be tuned by assembly of layers that can conduct electrons from bacteria to inorganic catalysts. Here we will present electrochemical studies describing EET through the incorporated materials used for membrane support. Chronoamperometry and cyclic voltammetry will be discussed as tools for characterization of EET between microbes and solid substrates acting as terminal electron acceptors. In addition, we employed biofilm imaging and HPLC techniques to support evidence of adequate microbial metabolism and EET. This novel biohybrid interface will provide

controlling EET through well-ordered, high surface area molecular structures in the nanoscale.

BI.03

pH-mediated Hybridization of Complementary Dynamic Covalent Oligomers

Megan Dunn, University of Michigan

Co-authors: *Tao Wei, Timothy F. Scott*

Dynamic covalent chemistry has been introduced as a method of assembling molecular architectures that are both durable and precise when compared to classic molecular self-assembly mechanisms. We incorporate boronic acid and catechol moieties into peptoid-based oligomers that were designed to undergo a dynamic covalent reaction and assemble into molecular ladders. Here we describe the synthesis of the precursor oligomers and the resulting assembled structures from reactions between homopolymers of boronic acids and catechols as well as the hybridization of single complementary oligomer chains that were comprised of both dynamic covalent functional groups. The generated structures were characterized using matrix-assisted laser desorption/ionization mass spectrometry confirming successful molecular ladder fabrication. The described work is helping to lay the foundation for a method that will enable a route to the facile fabrication of complex and robust proteomimetic nanostructures.

BI.04

Glycosylated peptoid nanosheets as a multivalent scaffold for protein recognition

Alessia Battigelli, Molecular Foundry

Peptoids, or N-substituted glycines, are peptidomimetic polymers, which differ from peptides as the side chains are appended to the nitrogen rather than the α -carbon. The sequence of the peptoid can be opportunely designed to self-assemble into highly stable two-dimensional materials, able to free-float in water. These peptoid nanosheets are highly stable in aqueous solution and they are hundreds of micrometers in length and width, and only two molecules thick (3nm), as revealed by atomic force microscopy (AFM) and X-ray diffraction (XRD) measurements.

The highly ordered bidimensional structure and the large surface area make this new material a perfect scaffold for the molecular recognition and the detection of threat agents, like toxins, bacteria, viruses.

In this poster, the versatility of the material to recognize different multivalent proteins will be described. One important advantage of using peptoids is their synthesis, which allows the complete control of the polymer length and the side-chain chemistry. In this study we incorporate a hydrophilic loop in the middle of the nanosheets-forming polymer strand. Exploiting click chemistry, peptoids are then functionalized with different carbohydrates on the loop insert. This design allows the formation of nanosheets characterized by sugars displayed on their surface. The binding between the resulted materials and specific multivalent proteins is then studied, revealing the selectivity and the specificity of the interaction.

BI.05

Engineering core/shell structured NaErF₄:Yb upconversion nanocrystals for brighter single-imaging probes

Bining Tian, Molecular Foundry

Co-authors: *Angel F. Bravo, Cheryl Tajon, Emory M. Chan, P. James Shuck, Bruce E. Cohen*

Upconversion nanoparticles (UCNPs), which convert near infrared

have taken UCNP studies down to single-particle level but opened the door for better understanding upconversion properties. The biggest challenge for the development of upconverters is the limited upconverted luminescent (UCL) intensity, especially for sub-10nm sized particles because of enlarged surface quenching and reduced crystal sites for hosting upconverting centers and sensitizers. Against conventional knowledge of concentration quenching, we designed core/shell structured NaErF₄:Yb UCNPs enhancing activator from ~20 to 100%. At single imaging level, these UCNPs exhibit 1 order magnitude lower luminescent threshold and 1 order magnitude higher UCL intensity at high excitation density.

BI.06

Nondestructive Surface Modification of CdSe/CdS Quantum Dots by Copper(I)-Catalyzed Azide-Alkyne Cycloaddition

Victor Mann, Molecular Foundry

Co-authors: Alexander Powers, Bruce Cohen

One of the main weaknesses of quantum dot-based fluorescent labels are the methods of introducing functionality to the surface. They are too large, nonspecific or damaging to the optical properties of the nanocrystal. The copper-catalyzed azide-alkyne cycloaddition (CuAAC) reaction is among the most prolific bioconjugation and synthetic chemistry reactions, and could function as a small and highly specific labeling system. However, copper ions are potent quenchers of quantum dot luminescence, at concentrations as low as nanomolar range. A combinatorial, high-throughput screening method was designed to sample large areas of the parameter space of this reaction, including copper(I)-coordinating ligands, reaction pH, buffering conditions, and reducing agent concentration in order to optimize the CuAAC reaction under conditions that yield low fluorescence quenching and high reaction yield. This screen was based on Forster resonance energy transfer (FRET) between azide-functionalized CdSe/CdS core-shell quantum dots and an alkyne-functionalized organic dye, Cy5. An examination of the data points to a strong pH and coordinating ligand dependence, affecting the initiation and cyclization stages of the catalytic cycle. Using conditions optimized in this screen, a QDot-biomolecule construct was synthesized and successfully used in targeted cell imaging experiments.

BI.07

Nanodiscs Stabilize Anabaena Sensory Rhodopsin for Transcriptional Regulation Studies

Jenny Cappuccio, Humboldt State University

Co-authors: Joshua M. Massey, Alexis D. Aguiar, Edward I. Sandoval

Anabaena Sensory Rhodopsin (ASR) is a retinal containing photoactive membrane protein, from the cyanobacterium *Anabaena* sp. PCC 7120. ASR undergoes an orange light-induced conformational change associated with release of a bound transducer protein ASRT. This protein complex has been proposed to directly control the transcription of the *cpc*-genes involved in chromatic adaptation. However, direct binding of DNA with ASR has not been demonstrated. Hindering such binding studies is the lack of a system to stabilize ASR in an accessible native-like phospholipid bilayer. To overcome this barrier we isolated and characterized ASR from engineered *E. coli* for construction of self-assembled protein lipid nanodiscs. Our ASR nanodiscs are soluble and allow for protein access from the top and bottom of the bilayer. Our UV-visible spectrophotometric spectra show that isolated ASR nanodiscs possess a retinal absorbance shift in response to light exposure (~548-537nm). Dynamic light scattering of ASR nanodisc fractions, separated by size exclusion chromatography, displayed two populations of distinct diameters (21.9 +/- 6.3 and 31.1 +/- 12.5 nm). The two populations may represent different oligomeric states of ASR in nanodiscs. We conclude that ASR is stabilized in the soluble lipid bilayer of the nanodiscs and represents a practical platform to enable further investigation of ASR's unique role in the transcriptional control of chromatic adaptation. Our next steps will involve examination of the lipid environment and to investigate DNA binding. Results of these studies may allow for future use of these proteins as photo-active transcriptional regulators.

BI.08

Probing ion channel activation with tarantula toxins conjugated to environment-sensitive fluorophores

Sebastian Fletcher-Taylor, University of California, Davis

Co-authors: Mark Lillya, Parashar Thapa, Joyce Huang, Rayan Kaakati, Michael Kirmiz, Kenneth S. Eum, Bruce E. Cohen, Jon T. Sack

The extent of voltage-gated ion channel activation is a functional readout of electrical signaling in excitable cells. Voltage activation of ion channels can be monitored by tracking "channel activity probes" that selectively bind to different voltage sensor conformations (PNAS 2014, 111:E4789). Here we

show that channel activity probes can be fluorescently labeled such that their fluorescence emissions shift in wavelength upon binding to voltage-gated ion channels in live cells. We synthesized azide-functionalized derivatives of the red fluorescent dye aminophenoxazone, which responds to the polarity of its chemical environment with large shifts in its excitation and emission maxima. To produce a channel activity probe we synthesized variants of the guangxitoxin-1E tarantula venom peptide, which binds Kv2 voltage-gated potassium channels with an affinity that varies with membrane voltage. For conjugation to azide groups, alkyne groups were inserted at locations on the peptide predicted to interact with the outer leaflet of the membrane when the peptide binds channels. Electrophysiology indicates that the fluorescent channel activity probes selectively bind Kv2.1 channels. The fluorescence emission spectrum of probes bound to Kv2.1 was blue-shifted compared to an aqueous environment, suggesting that when bound to channels, the probe is oriented to position the fluorophore in a less polar chemical environment, consistent with membrane embedding. The emission spectrum was more blue-shifted in cells with more negative membrane potential, consistent with the toxin's specificity for resting-conformation voltage sensors. Deconvolution of the spectra shows that the emission spectra at different voltages can be characterized by sums of different ratios of intensities of a blue-shifted spectrum and a red-shifted spectrum, consistent with different ratios of Kv2.1-bound probe and aqueous probe.

BI.09

Fabricating Novel Optical Sensors by Embedding Gold Nanoparticles Inside Peptoid Nanosheets

Kathleen Chen, Wellesley College

In the venture to improve chemical sensing techniques, biomimetic materials research has received a considerable amount of interest because the biological selectivity of natural materials like proteins is still currently unsurpassed. Peptoids, or N-substituted glycines, are enormously promising because they are biomimetic, sequence-defined polymers that can be designed to fold into bilayer nanosheets that are structurally similar to proteins, yet they offer some advantages over proteins such as chemical diversity and environmental stability. Previous work on peptoids has focused on displaying functional sites on the nanosheet surface for binding chemical and biological species. Here, we present our work on improving upon the functional nanosheet scaffold by creating an "all in one" sensor. By taking advantage of the nanosheet assembly mechanism via monolayer collapse at the oil-water interface, plasmonic nanoparticles can be embedded inside the sheets to provide a feedback system for analyte binding. We have successfully fabricated temporally stable nanosheet/AuNP composites using (Nae-N3mpe)₄-(Nce-N3mpe)₄ peptoids and dodecanethiol functionalized AuNPs. Preliminary findings from calcium ion binding studies indicate that the composites are efficacious in producing a response upon analyte binding.

BI.10

Investigating peptoid nanosheet porosity using droplet interface bilayers

David Hastman, Department of Homeland Security / LBNL

Peptoids are a class of bioinspired polymers composed of repeating N-substituted glycine monomer units. Through precise control of chain length and sequence design, peptoids can be engineered to assemble into higher order structures, such as 2D peptoid nanosheets. Recently, molecular simulations have shown that small pores can exist in peptoid nanosheets, yet no experimental data has confirmed these predictions. Here we form droplets of aqueous nanosheet-forming peptoid solution, and suspend the droplets in mineral oil. After a peptoid monolayer is formed at the droplet/oil interface, two drops are brought into contact with one another, creating a bilayer at the interface between the two droplets. To confirm bilayer formation and investigate the bilayer porosity, one of the aqueous peptoid droplets was loaded with fluorescently labeled dextran. Two different molecular weight (MW) dextrans were used, 70,000 and 3,000. The 70,000 MW dextran was unable to diffuse through the interface between the droplets, thus confirming bilayer formation. The 3,000 MW dextran was able to diffuse through the bilayer at a rate < 10% of the diffusion rate without bilayer formation and < 1% of the diffusion rate without peptoid present in the droplets. From this diffusion data we conclude that the bilayer structure contains pores on the scale of ~ 1-1.5nm, which agrees with molecular simulations. The presence of pores within peptoid nanosheets indicates their potential as size exclusion membranes capable of nanofiltration.

BI.11**Peptoid nanosheet adhesion to intact Escherichia coli cells**

Lisa Yun, Lawrence Berkeley National Laboratories

Co-authors: Ronald N. Zuckermann

Peptoid nanosheets are two-dimensional protein-mimetic nanostructures that can be synthesized to exhibit a variety of surface functionality. Their lateral dimensions are in the 10s of microns, making it possible to explore the selective adhesion to micron-scale objects. Here, we incorporated mannose into the peptoid sequence in order to bind whole bacterial cells. To image the interactions, we moved from the traditional method of imaging nanosheets immobilized on flat agarose slabs, to 3D imaging of the sheets in free suspension. Using confocal microscopy and fluorescently labeled samples, we can directly observe the interaction of nanosheets with cells. We compare the interaction of the mannose-nanosheets to Escherichia coli cells that do and do not express mannose receptors. Preliminary results indicate that the nanosheets are stable to the cell-binding interaction. If successful, this strategy could be used to selectively remove or neutralize harmful bacteria from a variety of samples.

Imaging and Manipulation of Nanostructures**IM.01****Room temperature skyrmion ground state stabilized through interlayer exchange coupling**

Arantzazu Mascaraque, Universidad Complutense de Madrid

Co-authors: Gong Chen, Alpha T. N'Diaye, Andreas K. Schmid

New fast, ultra-high density and low power consumption devices are desirable to face the new demands for today's IT technology. In view of the severe limitations that semiconductors are facing for their performance in the future, scientists are looking for a new and radically different paradigm that has to be a breakthrough in the actual archetype of magnetic storage. In this sense, spintronic technologies have been recently identified as the most likely technology for the next generation of magnetic memory.

Skyrmions may be described as an exotic cylindrical magnetic domain with a chiral spin texture. They can be created, erased and manipulated using and electric or spin current. Recently, we have demonstrated an experimental approach to stabilize a room temperature skyrmion ground state in chiral magnetic films via exchange coupling across non-magnetic spacer layers. Using spin polarized low-energy electron microscopy to measure all three Cartesian components of the magnetization vector, we image the spin textures in Fe/Ni films. The stabilization of a chiral stripe phase, a skyrmion phase, and a single domain phase can be selected by tuning the thickness of a copper spacer layer between chiral Fe/Ni films and perpendicularly magnetized Ni layers. This strategy to stabilize skyrmion ground states can be extended to other magnetic thin film systems and may be useful for designing skyrmion based spintronics devices.

IM.02**Nanoscale Chemical Imaging with Photo-induced Force Microscopy**

Robert Kertayasa, Molecular Vista

Co-authors: Sung Park, Tom Albrecht

Infrared Photo-induced Force Microscopy (IR PiFM) is based on an atomic force microscopy (AFM) platform that is coupled to a widely tunable mid-IR laser. PiFM measures the dipole induced at or near the surface of a sample by an excitation light source by detecting the dipole-dipole force that exists between the induced dipole in the sample and the mirror image dipole in the metallic AFM tip. This interaction is strongly affected by the optical absorption spectrum of the sample, thereby providing a significant spectral contrast mechanism which can be used to differentiate between chemical species. Due to its AFM heritage, PiFM acquires both the topography and spectral images concurrently and naturally provides information on the relationship between local chemistry and topology with sub 10 nm spatial resolution on a variety of samples. PiFM spectral images surpass spectral images that are generated via other techniques such as scanning transmission X-ray microscopy (based on synchrotron source), micro confocal Raman microscopy, and electron microscopes, both in spatial resolution and chemical specificity. The breadth of the capabilities of PiFM will be highlighted by presenting data on various polymer systems. By enabling imaging at the nm-scale with chemical specificity, PiFM provides a powerful new analytical method for deepening our understanding of nanomaterials and facilitating technological applications of such materials.

IM.03**Electron Diffractometry of Superstructures in Low-Dimensional Materials**

Brian Shevitski, Molecular Foundry

Electron microscopy and diffractometry are powerful techniques for probing the fundamental properties of 2D materials. Electron diffraction patterns provide a snapshot of a crystal's reciprocal lattice and are routinely used to deduce the atomic structure of 2D materials. However, these diffraction patterns can contain Bragg peaks not attributable simply to the reciprocal lattice of the material under study. These additional diffraction peaks can be attributed to crystalline domains, phase segregation, dynamical diffraction effects, rotational faults, and charge-density-wave induced Peierls distortion of the crystal lattice. We present a powerful methodology for classifying these anomalous peaks and show how they can be used to determine the nature of the fundamental underlying phenomena that produce them.

IM.04**Remodeling of RecG Helicase by SSB Protein: Direct Observation of Sliding after Remodeling**

Mohtadin Hashemi, University of Nebraska Medical Center

Co-authors: Zhiqiang Sun, Hui Yin Tan, Piero Bianco, Yuri L. Lyubchenko

The orderly progression of genomic replication is challenged by encounters with template damage, slow moving and arrested polymerases, and other DNA-protein complexes that stall the replication fork. Stalled forks must be repaired and replication continued in order to maintain genomic stability. RecG is a key protein in the replication fork stall and regression process that contributes to maintaining high fidelity. Although crystallographic data provide a model for RecG interaction with the replication fork, a number of questions remain unclear. Our recent AFM studies of RecG bound to the replication fork provided further insight into RecG behavior and led to a novel model according to which interaction of SSB with RecG induces remodeling of RecG, enabling the protein to translocate along the DNA duplex. Here we tested the model, specifically the prediction that remodeling changes RecG interaction with DNA allowing the protein to slide along the DNA. Time lapse HS-AFM visualization confirmed the model and showed that RecG is only capable of translocation along the DNA in the presence of SSB. A single base pair mismatch drastically decreased then translocation distance, supporting the translocation model. Additional factors were also identified; the fork polarity contributes to the RecG loading in such a way that the complex is formed with the yield ratio 1.8:1 for the fork with 3' end compared to the reverse polarity. Overall the results obtained reveal novel properties of RecG and highlight a new chaperone-type role of SSB in the DNA repair process.

IM.05**Intercalation-Induced Modulation of Electronic Structure in Layered Vanadium Oxide Bronzes**

Luis De Jesus, Texas A&M University

Co-authors: Gregory A. Horrocks, Abhishek Parija, Justin L. Andrews, Yufeng Liang, David Prendergast, and Sarbajit Banerjee

Layered materials have been extensively studied due to their facile ability to reversibly incorporate cations and molecular species in interlayer sites and the pronounced modifications to electronic structure that can be achieved upon dimensional reduction to a two-dimensional (2D) structure. As a case in point, the discovery of graphene and its thickness-dependent electronic structure that diverges sharply from its 3D counterpart graphite, has inspired the search for single- and few-layered materials that manifest new physical phenomena. Comprehensive nanoscale characterization is essential to understand how the loss of 3D structural coherence, induced either as a result of ion intercalation or exfoliation to 2D sheets, alters the electronic structure of these materials. Novel physical phenomena derived from dimensional reduction and the electronic structure peculiarities of 2D materials hold promise for applications in areas such as catalysis, energy conversion, and electronics. My research focuses on spatially mapping heterogeneities in the electronic structure of layered nanomaterials and interfaces using X-ray microscopy in tandem with first principles density functional theory calculations with a focus on various $\text{Li}_x\text{V}_2\text{O}_5$ phases, MoS_2 polytypes, and exfoliated $\delta\text{-Sr}_x\text{V}_2\text{O}_5$.

IM.06**Investigating dynamical nanoscale processes using cathodoluminescence microscopy**

Rebecca Wai, UC Berkeley

Co-authors: Connor Bischak, Clarice Aiello, Craig Hetherington, Zhe Wang, Shaul Aloni, Frank Ogletree, Naomi Ginsberg

Imaging nanoscale dynamics using established microscopy techniques is inherently difficult due to the short time and length scales over which these processes occur. Traditional optical microscopy is diffraction limited, far-field super-resolution optical microscopies are limited to specific fluorophores, and electron microscopy can damage soft samples. Alternatively, cathodoluminescence (CL) microscopy is a method of interrogating the nanoscale optical properties of a sample with high image acquisition rates, which can be implemented in addition to electron microscopy. With home-built CL detection, developed in collaboration with Foundry staff, we perform CL microscopy at low electron beam exposure to study dynamic processes in hybrid materials, such as light-induced phase separation in organic-inorganic perovskites. We have also been able to infer lifetime characteristics of upconverting nanoparticle aggregates by time-resolved CL microscopy, enabled by repurposing the beam blaster and developing time-resolved photon counting capabilities.

Soft materials, however, including biological samples, will inevitably be damaged by exposure to the electron beam. To image these samples with high spatial and temporal resolution, we have developed a super-resolution optical imaging method called cathodoluminescence-activated imaging through near-field resonance energy transfer (CLAIRE). CLAIRE uses nanoscale optical excitation in an ultrathin scintillator film, generated by a low-energy electron beam, to interrogate an adjacent sample by taking advantage of near-field interactions, such as Forster Resonance Energy Transfer. Using CLAIRE, we imaged plasmonic metal nanostructures with 46 nm-resolution and obtained sub-diffraction resolution images of organic light-emitting polymers that would otherwise be damaged by direct electron excitation. We have begun imaging photosynthetic membranes and the motions of metal nanoparticles moving in low vapor pressure liquids.

IM.07

Resonant Soft X-Ray Scattering: A Versatile Technique for Spatio-Chemical Characterization of Electrochemical Materials

Isvar Cordova, LBNL - Advanced Light Source

Co-authors: Gregory Su, Michael Brady, Cheng Wang, David Kilcoyne

Conventional "hard" X-ray scattering is a high-resolution nondestructive structural probe that can interrogate a statistically significant 3-dimensional sample area. However, the physical nature of the scattering process at these energies limits its applicability to materials that possess significantly different electron densities. Unfortunately, the performance of many electrochemical materials often hinges on subtle heterogeneities that do not possess sufficiently distinct electron densities to provide significant contrast. To help address this challenge, resonant soft X-ray scattering (RSoXS) uses tunable "soft" X-rays to dramatically enhance the scattering cross sections from heterogeneous regions when the X-ray photon energy is judiciously chosen to coincide with favored transitions near their absorption edges. In recent years, RSoXS performed near the C K-edge has proven to be very useful for soft matter researchers interested in defining chemical structure and molecular orientation of complex materials with nm-scale spatial sensitivity. Still, the full potential of RSoXS to study these processes is far from being fully explored by inorganic material scientists and electrochemists.

In this presentation, we will show some of the first experimental results demonstrating how RSoXS can be a powerful tool for the electrochemistry community. Specifically, we will expound on its ability to simultaneously interrogate the bulk, surfaces, and buried interfaces of low-Z element materials (including many transition metals), such as those used as nanostructured electrodes, catalysts, and ion exchange membranes. In addition, we will present recent developments made working with the Molecular Foundry to enable in-situ and operando RSoXS characterization of electrochemical materials in liquid and gaseous environments.

IM.08

Nanoscale photocurrent imaging of monoclinic BiVO₄ films via atomic force microscopy

Johanna Eichhorn, Lawrence Berkeley National Laboratory

Co-authors: Jason K. Cooper, Lucas H. Hess, Dominik Ziegler, David M. Larson, Mary K. Gilles, Ian D. Sharp, Francesca M. Toma

Bismuth vanadate (BiVO₄) is a promising photoanode material for artificial photosynthesis. However, under relevant operating conditions, pristine BiVO₄ thin films are subjected to degradation at the exposed surface facets. The degradation is accelerated by trapping of photogenerated charge at localized surface sites. Therefore, developing approaches to stabilize these efficient semiconductor nanostructures requires a detailed understanding of the interplay between the morphological and electronic structure at the nanoscale. Here, we use photoconductive atomic force microscopy to correlate local surface morphology with generated photocurrent at individual grain facets in polycrystalline thin films. In this

context, we discuss the impact of surface structure and different working conditions on the photocurrent generation.

IM.09

AFM-based infrared spectroscopy - nanoscale chemical analysis with monolayer sensitivity

Eoghan Dillon, Anasys Instruments

This talk will focus on techniques and instrumentation for measuring chemical and optical properties of materials with nanometer scale spatial resolution. Conventional infrared spectroscopy is one of the most widely used tools for chemical analysis, but optical diffraction limits its spatial resolution to the scale of many microns. Atomic force microscopy (AFM) enjoys excellent spatial resolution, but has historically lacked the ability to perform robust chemical analysis. This presentation will discuss two techniques (1) AFM-based infrared spectroscopy and (2) scattering scanning near field optical microscopy (s-SNOM). Both of these techniques overcome the diffraction limit, providing the ability to measure and map chemical and optical properties with nanometer scale spatial resolution. As complementary techniques, AFM-IR and s-SNOM together provide an unrivaled capability to perform nanoscale chemical analysis on a diverse range of organic, inorganic, photonic and electronic materials. This talk will show AFM and s-SNOM applications on samples from fields including polymers, life sciences, semiconductors, graphene and nanoantennas.

IM.10

Blue, green, red and near-infrared lasing action from lanthanide doped upconversion nanocrystals in microcavities

Angel F. Bravo, Molecular Foundry

Co-authors: Emory M. Chan, Cheryl Tajon, Bining Tian, Bruce E. Cohen and P. James Schuck

Light amplification has been pursued in photonics, energy and sensing among the most relevant areas. Furthermore, achieving efficient light amplification into cavities can lead to miniaturization, cost effective and highly sensitive devices, highlighting a variety of important features to be applied in very diverse scientific scenarios. Rare earth upconversion nanocrystals enable large anti-Stokes shifts with relatively sharp emission and long excited-state lifetimes, useful in a variety of fields. Fundamental aspects however had hindered a more general applicability where the requirement of lower irradiances has precluded this materials from being practical. Nevertheless, this problematic can be addressed from different angles; in this work unique core-shell nanocrystals where the active upconverting material is encapsulated by a protective shell are systematically investigated as optical gain and lasing media as a function of dopant type and concentration. Polystyrene microbeads of an average size of 5 μm are coated with nanocrystals and used as resonators to achieve upconversion lasing by excitation of whispering gallery modes (WGM). These may greatly extend the broad functionality of UCNPs for background free imaging, theranostics, volumetric displays, active waveguiding and photonics structure assembly. We observe that the concentration of lanthanides in the crystal lattice reveal a correlation with lasing thresholds and optical gain, and measure lasing thresholds as low as 1 $\mu\text{W cm}^{-2}$ in pulsed excitation.

IM.11

Energy transfer from quantum dots to 2D materials

Archana Raja, Stanford University and Columbia University

Co-authors: Andrés Montoya-Castillo, Johanna Zultak, Xiao-Xiao Zhang, Ziliang Ye, Cyrielle Roquelet, Daniel A. Chenet, Arend M. van der Zande, Pinshane Huang, Steffen Jockusch, James Hone, David R. Reichman, Louis E. Brus, Tony F. Heinz

Electronic processes at the interfaces of nanoscale heterostructures are an important area of research, both from the fundamental and application points of view. 0D semiconductor quantum dots and 2D van der Waals material heterostructures have been recently explored for energy and charge transfer, with potential photovoltaic and optoelectronic applications. In this work, we experimentally demonstrate highly efficient non-radiative energy transfer (NRET) from core-shell quantum dots to monolayer and few layer graphene, a semi-metal and MoS₂, a semiconductor. The NRET rates were experimentally obtained via time resolved photoluminescence and theoretically studied using a classical electromagnetic theory. Increasing the number of layers in the acceptor van der Waals material results in surprisingly contrasting trends in the rate of NRET. The rate increases significantly with increasing layer thickness for graphene, but decreases with increasing thickness for MoS₂ layers. We interpret the contrasting behavior in terms of the interplay between dielectric screening and absorption of the 2D material. We also extend our treatment to predict

the type of NRET behavior for the near-field coupling of a chromophore to a wide range of semiconducting and metallic thin film materials.

IM.12
Crystalline Dielectric Materials for High Energy Density Capacitors

Shilpa Worlikar, Capacitor Sciences, Inc.
Co-authors: Paul Furuta, Pavel Lazarev, Yan Li, Hoang Ly, Ian Kelly-Morgan, Daniel Membreno, Matthew Robinson, Barry Sharp

Meta-dielectric materials will enable energy storage devices with both high energy density and high power density. Meta-dielectrics are crystalline thin films comprising densely arranged polarizable units electrically isolated by insulating envelopes. Insulating alkyl or fluoro-alkyl substituents covalently bonded to the polarizable unit provide the resistive envelopes and influence the degree of order and orientation in the films. We study the supramolecular structural order in coated films of densely packed, highly polarizable molecules of two types: 1) perylene and perylene diimide "cores, and 2) co-polymers with ionic side-chains and enveloping alkyl chains. We will employ advanced AFM and optical microscopy at MF and SAXS/WAXS at ALS. We look forward to working with Molecular Foundry staff and other MF users to evolve our understanding of the structure-function properties of meta-dielectrics.

IM.13
Nanoscale Optical, Thermal and Elemental Analysis at the Foundry

Frank Ogletree, Molecular Foundry
Co-authors: Shaul Aloni, Ed Barnard

This poster briefly outlines resources in the Imaging Facility for Cathodoluminescence, a tool for nanoscale imaging of optical properties; Nano Auger for surface analysis of materials; TDTR for Nanoscale Thermal Characterization; and the ScopeFoundry software framework for smart microscopy.

IM.14
Orientation manipulator for Projective image via Dynamic DNA Origami Structure

Chao-Min Huang, The Ohio State University
Co-authors: Hai-Jun Su, Carlos E. Castro

Transmission electron microscopy (TEM) has been widely used to obtain projective images of nanostructures in many applications. Instead of tilting the whole specimen to reconstruct in 3D, we attempt to use DNA origami technique to locally orient the nanostructure of interest into three orthogonal views. Scaffold DNA origami is a recently developed nanotechnology that provides a bottom-up methodology to fabricate nanostructures by programming the folding of a long single-stranded DNA strand (called the scaffold) into 3D nanostructures using many short single-stranded DNA strands (called staples) based on DNA base pairing. Recently, we have demonstrated this technology can be used to design and fabricate dynamic nanomechanisms with multiple degrees of freedom that we refer to as DNA origami mechanisms (DOM). We have also shown these DOM can be actuated using the DNA staple displacement method for precise motion control.

IM.15
Design of Metal Oxide Photonic Crystals and Plasmonic Nanoparticles for CO₂ Reduction

Laura Loebbert, JCAP
Co-authors: E. Ashley Gauldin, Austin G. Li, Erin Creel, Ian D. Sharp, Francesca M. Toma

Existing systems for CO₂ reduction share common limitations related to high energy requirements for CO₂ conversion and product selectivity. Photoelectrocatalytic reduction of CO₂ is an attractive opportunity to study the effect of light on product distribution. Specifically, photonic crystals have attracted growing interest due to their potential to manipulate light with their photonic band structure. In addition, nanoparticles that are used as catalysts for CO₂ reduction can bear interesting plasmonic properties under illumination. A significant increase of adsorption in the visible spectrum and generation of hot carriers may lower the energy barriers requirement to produce certain CO₂ reduction reaction products.

In this work, we design photonic crystals of semiconductor materials where the photonic bandgap is tuned by varying the polystyrene sphere sizes (50 nm - 1000 nm) of the opal template used for the semiconductor material growth. We report here the optimization of the opal structures to produce highly periodic films on the order of nano- and millimeter scale by tuning different parameters (e.g. deposition method, solvent, surfactant, evaporation rate/ temperature, substrate tilt angle) during deposition. In addition, we attempted electrodeposition of copper(I) oxide as

photocathode material for CO₂ reduction to yield the inverse opal crystal structure upon removal of the polystyrene opal template.

IM.16
A Nanodiamond is Forever: Redefining the Boundaries of Optical Imaging and Diagnostics

Roger York, Bikanta
Co-authors: Ambika Bumb

The sensitivity and resolution of fluorescence-based imaging in-vivo is often limited by autofluorescence and other background noise. To overcome these limitations, we have developed a wide-field background-free imaging technique based on magnetic modulation of fluorescent nanodiamond (FND) emission. FNDs are bright, photo-stable, biocompatible nanoparticles that are promising probes for a wide range of in-vitro and in-vivo imaging applications. Due to the fact that the intensity of the fluorescent emission of FNDs can be a function of magnetic field, unlike other fluorescent compounds, difference imaging (with and without a magnetic field in the range of 300-2000T) allows us to select the FNDs in a strongly autofluorescent background, such as biological tissue. This technique has the potential to significantly improve and extend fluorescent nanodiamond imaging capabilities on diverse fluorescence imaging platforms, ranging from gel imagers to whole animal scanners to clinical instruments. We discuss light source properties, such as wavelength and intensity, nanodiamond concentration, nanodiamond size, imaging depth and other experimental parameters in the context of signal to noise ratio and compare this difference imaging to existing methods—such as spectral unmixing—that are designed to select a given molecule in a strong background signal.

1) Sarkar, S.K. et al. Biomedical Optics Express Vol. 5, Issue 4, pp. 1190-1202 (2014)

Inorganic Nanostructures

IN.01
HERMAN: High-throughput Experimentation Robot for Multiplexed Automation of Nanosynthesis

Thomas Bischof, LBNL
Co-authors: Emory Chan

The development of a new nanocrystalline material requires the optimization of a variety of parameters, such as size, shape, composition, and surface functionalization. Exploring this parameter space at the benchtop scale can be time-consuming, wasteful of material, and prone to variability. By adopting high-throughput methods for automated synthesis and characterization, we can rapidly screen materials for particular applications with high fidelity. We use these high-throughput methods to explore the optical performance of core/shell nanoplatelets produced by repeated colloidal atomic layer deposition (c-ALD).

IN.02
Far-field optical nanothermometry using individual sub-50 nm upconverting nanoparticles

Andrea Pickel, UC Berkeley
Co-authors: Jacob D. Kilbane, Emory M. Chan, Christian Monachon, Nicholas J. Borys, Elizabeth S. Levy, Jeffrey J. Urban, P. James Schuck, and Chris Dames

As device length scales continue to decrease, nanothermometry – the measurement of temperature at the nanoscale – becomes increasingly important. In addition to characterizing device hotspots, the ability to probe thermal transport at nanometer length scales is needed to study the fundamentals of nanoscale thermal transport. While some near-field or contact techniques can achieve spatial resolution on the order of 10 nm, these methods are afflicted by unknown contact resistances and parasitic heat sinking. Meanwhile, the spatial resolution of far-field optical techniques is typically diffraction limited. Nanoparticle luminescence thermometry, in which temperature is obtained using the ratio of luminescence from two thermally-coupled energy levels, is an established technique with well-understood temperature dependent physics. However, previous single particle temperature measurements have used particles on the order of hundreds of nanometers. Here, we demonstrate far-field optical thermometry using individual sub-50 nm upconverting NaYF₄ nanoparticles doped with 2% Er³⁺ and 20% Yb³⁺. The luminescence thermometry response is characterized between 300 K and 400 K and a standard Arrhenius model used for larger particles can still be accurately applied to these sub-50 nm particles. With spatial resolution well below the diffraction limit, this technique has the potential to be applied to both fundamental studies and industrial applications.

IN.03**Li₂S Nano Spheres Anchored to Single-layered Graphene as a High-performance Cathode Material for Lithium/sulfur Cells**

Dan Sun, LBNL

Fully lithiated lithium sulfide (Li₂S) has become a promising cathode material for Li/S cells due to its high theoretic capacity (1166 mA·h g⁻¹) and specific energy (2600 W·h Kg⁻¹). However, low utilization of sulfur and poor rate capability still hinder the practical application of the Li/S cells. In this paper, a carbon coated Li₂S/graphene composite (Li₂S/G@C) was developed by incorporating Li₂S nano spheres with single-layered graphene and further forming a durable protective carbon layer on the surface of the Li₂S particles using a facile CVD method. The high rate capability and remarkable cycle life of the Li₂S/G@C cathode were demonstrated, which was mainly attributed to the unique structure of the Li₂S/G@C that can significantly improve not only the electrical conductivity, but also the mechanical stability of the sulfur cathode.

IN.04**High-Throughput Synthesis of Lanthanide-Doped NaYF₄ Upconverting Nanoparticles**Deepak Subramanian, The University of Texas at Austin
Co-authors: Thomas Bischof, Emory Chan

Upconverting nanoparticles have potential uses in biological imaging and single-nanoparticle temperature sensing. Lanthanide-doped NaYF₄ upconverting nanoparticles were synthesized using both conventional thermolytic synthesis procedures and high-throughput automated synthesis procedures. In order to determine the optimal reaction conditions to produce monodisperse nanoparticles with uniform shape and phase, parameters such as surfactant concentration, reaction temperature, temperature ramp rate, solvent concentration, and sodium to rare earth ratio were modified to elucidate their effects on the physical and optical properties of the synthesized nanoparticles. We were able to determine a robust set of conditions that allow for synthesis of β-phase NaYF₄ nanoparticles with sizes ranging from 100 nm to 350 nm, and can produce both nanorods and hexagonal prisms.

IN.05**A Nano-flake Model for Medium-range Structure in Vitreous Silica**

Shangcong Cheng, Corning retiree

Vitreous silica is the simplest silicate glass. Understanding its structure is fundamental to deciphering the structure of all other silicate glasses. The most common model for vitreous silica is the continuous random network theory (CRN) It is based on the original idea of Zachariasen and X-ray diffraction studies by Warren. According to the original CRN theory, Si and O atoms form a nearly perfect SiO₄ tetrahedron that serves as the basic building block for the silica network. These tetrahedra are randomly linked at all four corners to form a continuous 3-dimensional network. Although the original CRN model is presented in many textbooks, it has to be regarded as a first-order approximation of the glass structure. Many experimental data show that in the medium range (about 0.5 nm to 2 nm), the SiO₄ tetrahedra are not randomly connected, but has some unidentified ordering.

In order to describe the medium-range ordering (MRO) in vitreous silica, various models have been proposed and explain some of the contradicting data, but not all of them. This talk will present a new nano-flake model from well-known X-ray diffraction data and from the differences of vitreous silica and β-cristobalite crystal in their early formation processes. The newly proposed model is found to be consistent with various analytical data.

IN.06**The Indentation Cracking Behaviors and Nano-phase Structures of Glasses**

Shangcong Cheng, Corning retiree

Co-authors: C. Song, P. Ercius, C. Cionea and P. Hosemann

Glasses as the classical brittle materials do not show delayed failure like ductile metals; and their catastrophic mechanical failures are predominant. The contact damage resistance properties of glasses are of fundamental importance for their applications in architectural, automobile, display devices and many others. One technique to evaluate the mechanical properties of glasses is the micro/nano-indentation method.

Vickers indentation was employed to study the cracking behaviors of soda-lime-silica glass, sodium borosilicate glass and fused silica glass. Fresnel contrast technique of transmission electron microscopy (TEM) was used to reveal the nano-phase separation structures of the glass specimens. It is found that the indentation cracking behavior of glasses is related to the

types of the phase separation structures in glasses. The normal cracking behavior of soda-lime-silica glass is caused by its spinodal nano-phase structure, in contrast to that the anomalous cracking behavior of fused silica is due to the uniform single phase structure. The commercial borosilicate glass has the droplet nano-phase structure and shows intermediate cracking behavior.

IN.07**Carrier Scattering at Alloy Nanointerfaces Enhances Power Factors in PEDOT:PSS Hybrid Thermoelectrics**Edmond Zaia, LBNL (Molecular Foundry)/ UC Berkeley
Co-authors: Ayaskanta Sahu, Preston Zhou, Madeleine P Gordon, Jason Forster, Shaul Aloni, Yi-Sheng Liu, Jinghua Guo, Jeffrey Urban

This work demonstrates the first method for controlled growth of heterostructures within hybrid organic/inorganic nanocomposite thermoelectrics. Using a facile, aqueous technique, semimetal-alloy nanointerfaces are patterned within a hybrid thermoelectric system consisting of tellurium (Te) nanowires and the conducting polymer poly(3,4-ethylenedioxythiophene): poly(styrene-sulfonate) (PEDOT:PSS). Specifically, this method is used to grow nanoscale islands of Cu_{1.75}Te alloy subphases within hybrid PEDOT:PSS-Te nanowires. This technique is shown to provide tunability of thermoelectric and electronic properties, providing up to 22% enhancement of the system's power factor in the low-doping regime, consistent with preferential scattering of low energy carriers. This work provides an exciting platform for rational design of multiphase nanocomposites and highlights the potential for engineering of carrier filtering within hybrid thermoelectrics via introduction of interfaces with controlled structural and energetic properties.

IN.08**Magnetic NanoBeads: a versatile platform for cell sorting, controlled drug delivery, imaging and magnetic hyperthermia**Maria Elena Matera, Istituto Italiano di Tecnologia/Molecular Foundry
Co-authors: Teresa Pellegrino

Magnetic NanoBeads (MNBs) represent a multifunctional water soluble platform suitable for multiple purposes including cell sorting and targeting, magnetic resonance and fluorescent imaging, controlled drug delivery and magnetic hyperthermia. MNBs consist of magnetic nanoparticle clusters enwrapped in a polymer shell. By varying different reaction parameters (the number of polymer molecules, the combination of solvents, the addition rate of the solvent, the shaking speed, etc.), it is possible to tune the size of the beads within 50 to 400 nm and also, to some extent, the shape of the beads. Furthermore, when using the amphiphilic poly(maleic anhydride-alt-1-octadecene) as polymeric shell many types of surface functionalization with charged and bioactive molecules or pH-/T-responsive polymers have been proven and some of those materials have shown that can be used as drug, nanoparticles or gene carriers. Instead, fluorescence signal is introduced into the beads by simultaneous encapsulation of magnetic and fluorescent nanoparticles (QDs or Upconverting NPs) into the same nanobead. It is also possible to further improve the magnetic response of the MNBs using highly magnetic iron oxide nanoparticles with cubic shape which ensure a fast collection to an external magnet and at the same time, the ability to heat up the beads under the application of an alternating magnetic field. Here, we provide an overview of such nanobead platform.

IN.09**High throughput synthesis and characterization of Prussian Blue analogues**

Kevin Hurlbutt, Cuberg, Inc.

Co-authors: Richard Wang, Mauro Pasta, Emory Chan

At the Molecular Foundry, Cuberg is using high throughput robotic synthesis and characterization to study combinatorially the effect of transition metal ion composition on the physical and chemical properties of Prussian Blue analogues (PBAs) for applications as battery materials. PBAs are a family of materials that have an open framework, face-centered cubic structure of ferrocyanide complexes connected by transition metal ions. The crystals' interstices can accommodate and conduct alkali metal ions, and this property has been exploited to make PBA cathodes. PBAs also have several properties that are highly tunable based on the transition metal ions that bridge the ferrocyanide complexes. These properties include electronic conductivity, ionic conductivity, ferrocyanide vacancy number, zeolitic water content, particle size, thermal stability, and even electrochemical stability against negative electrode materials of interest. PBAs are easily made in a rapid co-precipitation reaction to which robotic synthesis techniques are well suited. We will characterize the PBAs using high throughput X-ray diffraction (XRD), inductively coupled plasma – optical emission spectrum (ICP-OES), dynamic light scattering (DLS),

Raman spectroscopy, and UV-vis spectroscopy. The most promising or interesting reaction conditions from each synthesis will guide subsequent iterations that narrow the search space for the PBA candidate with ideal properties for battery applications.

IN.10

Toward picosecond time-resolved X-ray absorption studies of interfacial photochemistry

Das Pemmaraju, LBNL

Co-authors: Stefan Nepl, Johannes Mahl, David Prendergast, Oliver Gessner

We report on the progress toward developing a novel picosecond time-resolved transient X-ray absorption spectroscopy (TRXAS) capability for time-domain studies of interfacial photochemistry. The technique is based on the combination of a high repetition rate picosecond laser system with a time-resolved X-ray fluorescent yield setup that may be used for the study of radiation sensitive materials and X-ray spectroscopy compatible photoelectrochemical (PEC) cells. The mobile system is currently deployed at the Advanced Light Source (ALS) and may be used in all operating modes (two-bunch and multi-bunch) of the synchrotron. The use of a time-stamping technique enables the simultaneous recording of TRXAS spectra with delays between the exciting laser pulses and the probing X-ray pulses spanning picosecond to nanosecond temporal scales.

First results are discussed that demonstrate the viability of the method to study photoinduced dynamics in transition metal-oxide semiconductor (SC) samples under high vacuum conditions and at SC-liquid electrolyte interfaces during photoelectrochemical water splitting. Opportunities and challenges are outlined to capture crucial short-lived intermediates of photochemical processes with the technique.

IN.11

A Self-Assembled Bulk Hybrid 2D Semiconductor

Tess Smidt, Molecular Foundry

Co-authors: Mary S. Collins, Behzad Rad, Paul D. Ashby, Jeffrey B. Neaton, J. Nathan Hohman

A recurring theme in nanoscience is that new properties emerge in materials with reduced dimensionality. Although layered transition metal dichalcogenides (TMDs) are typically indirect band gap semiconductors in their bulk crystalline form, TMD monolayers possess direct band gaps and high charge carrier mobilities, a consequence of isolating their constituent two-dimensional (2D) semiconductor layers. These new properties have attracted interest for a variety of device applications, but exploiting monolayers technologically is complicated by the strict requirement for physical isolation. For example, the unique properties of 2D monolayers are lost rapidly with increasing layer number because of strong interlayer coupling. Here, we report the synthesis, characterization, and theoretical density functional model of 'mithrene,' or silver benzeneselenolate, $[\text{AgSePh}]_{\infty}$. This compound is a semiconducting material that retains 2D electronic properties in bulk multilayers. It is an air-stable metal-organic crystal comprised of ultrathin silver selenide layers, decoupled by covalently linked organic spacers. It self-assembles in one step from small-molecule building blocks at ambient temperature and pressure, is a direct band gap semiconductor that exhibits intense blue fluorescence at 467 nm, and requires no physical exfoliation to exhibit its 2D properties. Ab initio calculations confirm that the layers in the bulk crystal are direct band gap semiconductors and electrically isolated. Van der Waals (vdW) interactions between the arene rings hold the layers together in 3D. Furthermore, our ab initio calculations show that ligand design may present opportunities for manipulating the optoelectronic properties of a new class of hybrid vdW solids, the metal-organic chalcogenide assemblies.

IN.12

Soft PEDOT:PSS Aerogel Architectures for Thermoelectric Applications

Madeline Gordon, Molecular Foundry

Co-authors: Edmond W. Zaia, Preston Zhou, Boris Russ, Nelson E. Coates, Ayaskanta Sahu, Jeffrey J. Urban"

In this study, we present the first characterization of pure PEDOT:PSS aerogels fabricated via a facile and reproducible freeze-drying technique using no additional crosslinking agents, and demonstrate that these materials provide a promising path to new classes of polymeric thermoelectric materials. The morphology, chemical composition, and thermoelectric properties of these robust and mechanically stable aerogels are investigated upon treatment with ethylene glycol. By direct comparison to fully dense PEDOT:PSS thick films, we show that the electronic portion of thermoelectric transport in PEDOT:PSS is remarkably unaffected by morphological porosity.

Nanofabrication

NF.01

Imaging and Characterization of Chemically and Electrochemically Etched Porous Si and Si Nanowires for Thermoelectric Energy Conversion

Yong Gan, Cal Poly Pomona

In this work, vertically aligned porous Si nanowire (SiNW) arrays were successfully fabricated on two sides of an n-type Si wafer substrate. Ag nanoparticles (NPs) were first deposited onto the Si substrate via two different deposition methods, chemically and electrically (cyclic voltammetry), afterwards the metal assisted chemical etching (MaCE) technique was implemented to fabricate the SiNWs. The thermoelectric property of the SiNWs/Si/SiNWs structure was characterized by the Seebeck coefficient (S) which was measured at room temperature. Our results show a higher S when Ag NPs were electrodeposited onto the Si wafer piece compared to chemical deposition. The S enhancement is ~3 times and ~2 times in comparison to that of bulk Si and Ag chemical deposition samples, respectively. The electrodeposition created a strong adhesion between the Ag NPs and Si substrate which ensured a more uniform dispersed SiNWs producing a higher S. The improved thermoelectric performance coupled with electrodeposition of Ag indicates that the SiNWs/Si/SiNWs structure is an excellent candidate for the application in high-performance thermoelectric devices.

NF.02

The Application of Black Silicon for Nanostructure-Initiator Mass Spectrometry

Jian Gao, Lawrence Berkeley National Laboratory

Co-authors: Markus de Raad, Benjamin P. Bowen, Ronald N. Zuckermann, Trent R. Northen

Nanostructure-Initiator Mass Spectrometry (NIMS) is a matrix-free desorption/ionization technique with high sensitivity for small molecules. Surface preparation has relied on hydrofluoric acid (HF) electrochemical etching which is undesirable given the significant safety controls required in this specialized process. In this study, we examine a conventional and widely-used process for producing black silicon based on sulfur hexafluoride/oxygen (SF_6/O_2) inductively coupled plasma (ICP) etching at cryogenic temperatures and we find it to be suitable for NIMS. A systematic study varying parameters in the plasma etching process was performed to understand the relationship of black silicon morphology and its sensitivity as a NIMS substrate. The results suggest that a combination of higher silicon temperature and oxygen flow rate gives rise to the formation of black silicon with fine pillar structures, whose aspect ratio are ~8.7 and depth are < 1 μm resulting in higher NIMS sensitivity which is attributed to surface restructuring caused by their low melting point upon laser irradiation.

NF.03

Electronic Transport Through Amorphous ALD TiO₂

Paul Nunez, California Institute of Technology

Co-authors: Shu Hu, Christopher Roske, Matthias Richter, Nathan Lewis

Amorphous TiO₂ deposited by atomic layer deposition (ALD) has been recently used as a means to protect photoanodes from harsh operating conditions. The use of this protection layer has enabled the use of semiconductors (e.g. GaAs, GaP, CdTe) that were previously not feasible due to their stability. The TiO₂'s intrinsic stability makes it an ideal candidate for as a protecting layer. The band alignment of TiO₂ should make it such that photogenerated holes are not able to pass through the TiO₂; however, photogenerated holes are able to. It has been suggested that mid-gap states are the source of the TiO₂'s ability to allow photogenerated holes to traverse the dielectric; however, these mid-gap states and their relation to the electrical transport of this amorphous film have not been fully investigated. Thus, in this work we grow the amorphous TiO₂ film on p+Si, demonstrate the role of the mid-gap states towards conduction and conduction mechanism, the relation of these mid-gap states to the top contact as well as adventitious integration methods to enable the TiO₂ for water oxidation in acidic environments.

NF.04

Optoelectronic properties of cesium lead halide perovskite nanocrystals organized in ordered nanoscale assemblies

Erika Penzo, Molecular Foundry

The outstanding optoelectronic properties of metal halide semiconductors with perovskite crystal structure have recently drawn considerable attention. In particular, hybrid organic-inorganic lead halide perovskites

have shown great potential as both light-absorbing and light-emitting direct-bandgap solution-deposited semiconductors. Similarly high optoelectronic quality have been demonstrated by fully inorganic cesium lead halide perovskite nanocrystals (NCs) (CsPbX_3 , $X = \text{Cl, Br, I}$, and mixed Cl/Br and Br/I systems) which display remarkably bright photoluminescence (PL) characterized by high quantum yield (QY) of 50-90% and narrow emission line widths of 12-42 nm.

In this work we engineer the spatial organization of green emitting CsPbBr_3 NCs with nanoscale precision, which allows for the study of the exciton transport mechanism. CsPbBr_3 NCs are synthesized with ~ 10 -15 nm side length and are soluble in apolar solvents (hexane, octane, and toluene). They show affinity to hydrophobic surfaces and they assemble into a monolayer when spin-coated onto a surface pre-covered with a hydrocarbon polymer. These monolayers are made of ordered sub-domains, about 100 nm in size, inside which the nanocubes are aligned to each other and their edges are parallel. Combining lithographic patterning and self-assembly, the CsPbBr_3 NCs can be confined not only in the z direction, but also in x and y. Trenches 60 nm deep and 250 nm, 100 nm and 50 nm wide are patterned with electron beam lithography and inductively coupled plasma (ICP) etching. A 60 nm thick layer of amorphous Si is deposited by plasma-enhanced chemical vapor deposition (PECVD) on a 20 nm thick alumina layer deposited by atomic layer deposition (ALD). The alumina works as an etch-stopping layer producing etched features with sharp corners and a flat bottom. Due to capillary forces the NCs preferentially deposit inside the trenches, where the reduced available space improves the alignment of the nanocubes into orthogonal arrays, extending the scale of the organized monolayer domains and guiding the exciton diffusion along preferred directions.

NF.05 Characterization of Imaging Systems at Nanoscale using Modulation Transfer Function

Keiko Munechika, aBeam Technologies

Any metrology system is as good as it is characterized, where the characterization requires well known test samples. Such samples exist at a 2-Angstrom scale for TEM and at a micron scale and larger for optics, but scales between an angstrom and a micron are not readily available. Results of this work have enabled nanoscale characterization of imaging systems.

The modulation transfer function (MTF), or contrast transfer function, is the most comprehensive characteristic of any tool. It describes loss of contrast while reducing feature sizes and characterizes the system over its entire dynamic range. The MTF is widely used to characterize optical systems, and has allowed optical systems to be perfected down to their diffraction limit. There were attempts to use the MTF to characterize nanometrology systems such as SEMs, but the absence of samples with known spatial frequencies in the required dimensional range was a common problem. We developed a solution to measure MTF at the nanoscale involving the use of a test sample and analysis software. An image is taken by the system to be characterized (SEM, AFM, optical or other system) and the software automatically extracts the MTF.

In order to enable characterization at ultimately small dimensions, the minimum feature sizes of a test sample should be comparable to the tool resolution. In this work, a variety of test samples were fabricated for tools of various resolutions; the minimum feature size on a test sample was 1.5 nm. Optical and interferometric microscopes require larger samples; test samples with minimum feature sizes from 300 nm to 2.4 mm were also fabricated.

NF.06 Simple Fabrication and Optical Characterization of a WS₂ Based Photonic Crystal

Jacopo Pedrini, Università degli Studi di Milano-Bicocca
Co-authors: Christopher Chen, Giuseppe Calafiore, Christoph Kastl, Shaul Aloni, Stefano Cabrini, Adam M. Schwartzberg

Photonic crystals (PCs) control light propagation via a photonic band gap, originated when a periodic lattice of alternating refractive index (n) is present. A higher n contrast between the periodic nodes and imbedding medium produces better photonic properties, but the fabrication of large area, homogeneous and high quality PCs is complex due to the poor processability of high-n materials. Transition metal dichalcogenides (TMDs) have a high n ($n > 3$) through the visible and near-infrared spectrum, making them promising for visible light PCs. However, the production of TMD-based PCs is limited by complex chemical interactions in high-resolution etching which reduce the resolution or completely destroy the material. We have developed a new method that does not require the direct etching or

processing of TMD to produce TMD-based PCs. The PC structure is etched into quartz ($n \sim 1.5$), then the TMD is conformally deposited using atomic layer deposition (ALD) to produce a high efficiency PC. The fabricated PC shows intense resonances due to the high n-contrast between the TMD film and the quartz substrate. Moreover, we show that changing the feature size and the thickness of the PC layer can modulate these resonances significantly. This is a new class of 3-D photonic crystal which is simple to fabricate, but produces large optical modulations.

NF.07 Nanoimprinted photonics on a fiber

Alexander Koshelev, aBeam Technologies

Integration of complex photonic structures onto optical fiber facets represent a powerful platform which can provide both optical functionalities and the ease of use at the same time. Conventional nanofabrication technologies, however, do not permit viable integration of complex photonic devices onto optical fibers owing to their low throughput and high cost associated with fabrication. Here, we report on novel fabrication of 3d free-form structures on the edge of a fiber by nanoimprint lithography (NIL). NIL was chosen as it offers the capability to pattern nano/micro structures into high refractive index material, which is a key feature that enable the use of the imprinted fibers for immersion applications. Also, NIL is a low-cost technology suitable for manufacturing disposable fiber probes. We present fabrication and optical measurements for high refractive index Fresnel lens, vortex phase plate and diffractive beam splitter on a fiber done by NIL. Such photonic structures on a fiber have applications in integrated optics, optical trapping, and sensing.

NF.08 THz-Field Enhancement on Nano-Slit Arrays for Nonlinear Studies of Dynamics in Complex Materials

Zhiren Zheng, Lawrence Berkeley National Laboratory
Co-authors: T. Rittmann, S. Dhuey, A. Liehl, J.H. Buss, M. Amani, S. Cabrini, R. A. Kaindl

Extraordinary optical transmission in sub-wavelength metal structures has unleashed great opportunities for strong field nonlinear studies in complex materials. Narrow slits in thin metal films behave like capacitors charged by field-induced surface charges and thus provide local field enhancement near the gap. Since the charge concentration increases with decreasing frequency and gap width, nano-scaled slits are ideally suited for applications at low terahertz (THz) frequencies. Reported local field enhancements by two orders of magnitude combined with high intensity THz setups open possibilities for nonlinear THz experiments on 2D materials like graphene, quantum wells or dichalcogenide monolayers.

Here, we both experimentally and numerically investigate the field enhancement spectra in gold nano-slit arrays for varying slit widths and periodicities within a broad range of 70 - 300 nm and 2 - 50 nm, respectively. These structures are fabricated on single crystal quartz substrates using e-beam lithography and evaporation of a 60 nm gold layer. After microscopic characterization, the resulting enhancement spectra are determined by transmission measurements with THz time-domain spectroscopy.

Besides demonstrating the general $1/w$ - and $1/f$ -dependency, we observe a stagnating enhancement below a certain saturation frequency, which increases for decreasing periodicities due to the spatial limitation of contributing carriers. These results are accurately consistent with our model simulation using frequency domain finite element methods and provide essential figures of merit for optimization of possible nonlinear experiments. With high-repetition rate systems, such sensitive studies will allow to explore the limits of quasiparticle transport or to modify the electronic structure in light-induced phases.

NF.09 Design of Photonic and Plasmonic Materials for Photocatalytic CO₂ Reduction

E. Ashley Gaulding, Lawrence Berkeley National Lab (JCAP)
Co-authors: Laura Lobbert, Austin Li, Christopher Chen, Jacopo Pedrini, Adam Schwartzberg, Ian Sharp, Francesca Toma

The objective of our work is to explore the independent and coupling effects of photonic structures and the localized surface plasmon resonance (LSPR) of plasmonic particles on CO₂ reduction reactions (CO₂RR) under illumination. The photonic bandgap of an inverse opal structure can be tuned by the material and pore size/periodicity. These photonic properties control how the incoming light is reflected and refracted within the material. We investigate a variety of photonic crystal materials, such as metal oxides, by infilling the voids of an opal template of polystyrene (PS)

spheres via electrodeposition and sol-gel methods to obtain an inverse opal photonic crystal by subsequently removing the PS spheres. Similarly, the LSPR can be tuned in metal or degeneratively doped semiconductor nanoparticles by tuning the size, shape, and material composition to enhance absorption near the resonance peak. Additionally, hot carriers can be generated as the LSPR decays, providing potential access to kinetic pathways for desired products that are otherwise energetically prohibitive. Since we can tune the photonic bandgap simply by changing the size of the PS spheres in the template, we can investigate how matching the photonic bandgap with the plasmonic resonance of a metal/catalyst particle affects product selectivity of CO₂ reduction as the photonic bandgap and LSPR are brought in and out of resonance. We use UV-Vis/NIR transmission and reflectance spectroscopy to characterize the optical properties of Cu₂O and TiO₂ inverse opals with different inverse opal periodicities. We will then pair the experimental data with simulations to help us understand the optical features. A combination of SEM, TEM, and XRD are used to analyze the morphological structure and crystallinity of our materials as well as material composition via EDX. Initial photocurrent measurements show that Cu₂O maintains its photoactivity under CO₂ reduction conditions when patterned in an inverse opal structure.

NF.10

Accessing control of crystal growth and morphology of halide perovskite materials

Nicola Cefarin JCAP

Co-authors: Alessandro Cian, Agnese Sonato, Alessandro Pozzato, Zekarias Teklu, Ian D. Sharp, Francesca M. Toma, Massimo Tormen

Organolead halide perovskites have been studied in recent years for a variety of optoelectronic applications, including as photovoltaic (PV) devices, light emitting diodes (LEDs), lasers, and photodetectors. To achieve better performance and tunable optoelectronic properties, control of crystal growth is essential. For instance, single crystal domains are desirable for PV devices since they can be characterized by low trap densities and long carrier diffusion lengths.

Herein, we explore three different synthetic strategies, namely i) three-step deposition, ii) hydrophobic/hydrophilic patterning, and iii) thermal nanoimprint lithography to control the crystal growth of the methylammonium lead halide perovskite. Each of these approaches allows access to different morphologies, such as well-faceted crystals, micron-sized crystals, and V-groove shapes, respectively. These synthetic methodologies provide a path to improved tuning of optoelectronic properties in advanced hybrid halide perovskite-based materials and devices.

NF.11

High density, multifunctional neural probes for massively parallel read-out and control

Melanie West, Molecular Foundry

To advance the understanding of brain function and behavior at the synaptic, circuit and systems level, it is necessary to record and directly manipulate neural activity with high resolution. By implementing electrophysiological recordings and optogenetic intervention in tandem, this provides a major advantage for most physiological experiments aimed at addressing the neural basis of sensation and behavior.

In this work, we propose to fabricate multifunctional silicon probes for the polymodal recording and manipulation of neural activity. The probes will have two basic elements: recording electrodes and optical waveguides. The recording electrodes sample action potentials and the waveguides provide excitation light for optogenetic actuators or sensors. The probes are fabricated using a wafer-scale process where electrodes are fabricated by electron beam lithography for high density integration, the critical dimensions of the insertion shank are smaller than the current state of the art to minimize tissue damage, and single mode waveguides are designed with diffractive gratings and ring resonators for localized light extraction and enhanced spatial resolution.

National Center for Electron Microscopy

EM.01

Capturing the Genuine Structure of Materials and Their Time Evolution by Low Dose-Rate In-Line Holography

Christian Kisielowski, Molecular Foundry

In the wake of DOE's TEAM project, it became obvious that any further development of atomic resolution electron microscopy is primarily limited by electron beam-sample interactions because the probing radiation

actively alters the genuine structure of any material on the nanoscale. In fact, this aspect is not intrinsic to the use of electron beams but applies generally to any radiation of great intensity that is needed to deliver atomic resolution. Consequently, solutions are urgently sought to overcome this bottleneck. In this context, low dose / low voltage electron microscopy is developed, which effectively exploits reversible object excitations to minimize radiation-induced object alterations to an unexplored end. The holographic method exploits the extraordinary resolution and stability of the TEAM 0.5 microscope to recover quantitatively the electron exit wave function at atomic resolution with single atom sensitivity. It provides the complete information about the elastic electron scattering process while using the fewest amount of electrons possible. This poster highlights emerging capabilities that are of significant interest to users of the Molecular Foundry in particular in the context heterogeneous systems made from single-digit nanoparticles, two-dimensional materials and the emerging field of electron microscopy for sustainable energy research. In addition, time-resolved investigations of functionality on a single atom level are enabled even in environmental meaningful conditions (elevated T, p).

EM.02

Special TEM specimen preparation and application to lithium rechargeable battery

Xiangyun Song, ESDR Energy Storage & Distributed R Lawrence Berkeley National Laboratory

Co-authors: Changan Yang, Huali Wang, Yanbao Fu, Chengyu Song, Xiaobo Chen, Gao Liu, Vince Battaglia*

Due to complex component and sensitive to the air and water of the lithium rechargeable battery, how to prepare a practical useful TEM specimen from Li-ion cell has been critical to the TEM application in new generation batteries. We have developed an efficient way to prepare a TEM specimen from Lithium ion cells that prevents electrode materials contamination and chemical reaction from water or air and damage from mechanical stress. By using our special technique for TEM specimen preparation, two Li/SnO₂ cells with different electrochemical performance were investigated. Furthermore, their failure mechanism was revealed by TEM investigation.

EM.03

TEM and EELS investigation of the nanostructure and composition in SEI layer

Xiangyun Song, ESDR Energy Storage & Distributed R Lawrence Berkeley National Laboratory

Co-authors: Weifeng Mao, Yanbao Fu, Chengyu Song, Philip Ross, Vince Battaglia

Solid-electrolyte-interphase (SEI) layer formation and its microstructural properties are crucial in the failure of lithium ion batteries. Many scientists have tried to know the nano structural property and composition of the SEI layer by using various advanced instruments. Some possible compounds and crystals have been suggested. However, the exact really nano-crystal related with its structure, composition and morphology in SEI layer have not been fully reported yet, because of difficult to get the SEI layer from cycled negative electrode surface.

By using our special technique of the TEM specimen preparation SEI layer in Li(NiMnCo)O₂/graphite cell has been investigated. The MnF₂ nano-crystal with tetragonal structure in SEI layer was found and identified by HRTEM and EELS. Furthermore, the morphology of MnF₂ nano-grains, its nucleation, its distribution and SEI layer thickness were studied.

EM.04

Measuring temperature using the thermal diffuse scattering in transmission electron microscope diffraction patterns

Geoff Wehmeyer, UC Berkeley

Co-authors: Karen Bustillo, Andrew M. Minor, Christopher Dames

In-situ temperature measurements in an electron microscope could be used to map temperature with single-nanometer spatial resolution, to detect hotspots in operating microelectronic devices, or to quantifying electron beam heating. Several recent exciting demonstrations of temperature measurements using scanning transmission electron microscopy (STEM) have been based on thermal expansion: these signals have a thermal coefficient on the order of 30 ppm/K. Thermometries which are based on temperature dependent electron-phonon scattering (such as resistance thermometry) regularly show much larger coefficients (>1000 ppm/K), but have not been implemented in TEM to date.

Here, we measure the temperature dependent thermal diffuse scattering in electron diffraction patterns. Using 4D-STEM and a temperature-controlled sample holder, we obtain diffraction patterns over many locations of an isothermal gold film and compare the average diffuse scattering fraction at

room temperature and liquid nitrogen temperature. We measure spatially averaged thermal coefficients of 1500 ± 500 ppm/K, demonstrating the potential for diffuse scattering measurements in electron microscopes. However, by mapping the diffuse scattering fraction we also show that variations in the sample microstructure and local imaging conditions have a strong influence on the local diffuse scattering fraction. Future work will reduce the temperature measurement uncertainty by implementing localized Joule heating for fast thermal cycling and a lock-in technique to obtain the thermal coefficient of the Annular Dark Field (ADF) signal.

EM.05
Probing the Surface Structures of Polyol-synthesized High-voltage Cathode Materials

Hyeseung Chung, University of California, San Diego

Using a novel polyol synthesis method, our group has successfully synthesized two types of high-voltage cathode materials – spinel-structured $\text{LiNi}_0.5\text{Mn}_1.5\text{O}_4$ and olivine-structured LiCoPO_4 . Polyol process is a synthesis method that utilizes high-boiling, multivalent alcohol as a reaction medium. This medium acts as both solvent and chelating agent, allowing more delicate control in the product particles' size and morphology.

After successfully synthesizing pure spinel and olivine phase of $\text{LiNi}_0.5\text{Mn}_1.5\text{O}_4$ and LiCoPO_4 , we have observed the materials' atomic structures in pristine and cycled state using the double aberration-corrected scanning TEM (TEAM 0.5 at NCEM). While both $\text{LiNi}_0.5\text{Mn}_1.5\text{O}_4$ and LiCoPO_4 material synthesized via polyol maintained their original structure after cycling, $\text{LiNi}_0.5\text{Mn}_1.5\text{O}_4$ synthesized via conventional sol-gel method went through structural transformation at the surface. As the surface structure changed from Fd-3m spinel to Fm-3m rocksalt, sol-gel $\text{LiNi}_0.5\text{Mn}_1.5\text{O}_4$ experienced more significant capacity decay.

For this project, we gratefully acknowledge funding from U.S. Department of Energy, the Advanced Research Projects Agency-Energy (ARPA-E) under Grant No. DE-AR0000396.

EM.06
Speciation of Air Particulate Matter for Improved Health Outcomes

Valerie Leppert, UC Merced
Co-authors: Kennedy Nguyen

Five of the ten worst polluted cities in the United States are in California's Central Valley. Improvements in air quality in the region have historically been obtained through measures that aim to reduce the total mass of particulate matter emitted into the atmosphere. However, progress in improving air quality and human health outcomes have recently stalled due to the difficulty and expense of reducing particulates below historic background levels for the Valley. New measures adopted in 2013 by the San Joaquin Valley Air Pollution Control District aim to target particulate sources for mitigation that present the highest health risk to area residents. The success of this "Health-Risk Reduction Strategy" requires a better understanding of the details of the chemistry of particulate matter from various sources and resulting mechanisms of respiratory injury in order to prioritize specific sources for mitigation, since the characterization of particulate matter to date has focused mainly on elemental analysis and quantification of the total mass of material emitted. Here, we describe the use of advanced characterization using transmission electron microscopy and microanalysis to understand the details of the chemistry of air particulate matter collected from various Central Valley locations. Also described is the use of this information to create well-controlled synthetic particulate matter systems for cell culture studies in order to elucidate source dependent mechanisms of lung inflammation and injury.

EM.07
Electron-beam-assisted variation of deformation behavior in small-sized metallic glass particles

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Co-authors: Jinwoo Kim, Koji Nakayama, Andrew M. Minor, Eun Soo Park

Mechanical responses of small-sized metallic glasses (MGs) have been investigated in a bid to understand the fundamentals of MG deformation, thereby to overcome brittleness that limits their structural application despite the outstanding strength and resilience. In regard to deformation mode transition and increase in strength upon size reduction, discussions based on Griffith criterion and defect density have been provided, but there is still a lack of understanding from the perspective of deformation unit.

To elucidate the structural origin of size effect, we fabricated small-sized MG particles in a spherical shape thereby enabling intermittent flows even for relatively large samples that fracture in a brittle manner, and compared the size scaling behavior of intermittent flows in particles of different sizes.

Moreover, we introduced a competing condition between relaxation and rejuvenation for particles by illuminating electron beam through in-situ experiment inside electron microscope and investigated variations in the deformation behavior. These results could provide effective guidelines for evaluating nanomechanical properties and understanding the fundamentals of MG deformation.

Organic and Macromolecular Synthesis

OR.01
Femto Satellite Propulsion by nano printed gold four leaf bowties and directed electron discharge

Peter Ateshian and Andy Filo, Naval Postgraduate School

Femto satellites weighing a few grams and 3 mm x 3 mm size are best candidates for initial deep space voyages to Alpha Centauri about 4.4 LY away. Proposals for sub-light speed propulsion with laser photons seems still too distant with 20+ year travel times. The Molecular Foundry studies of nano physics reveals alternative means of propulsion. Directed Kelvin temperature electron discharge may be one of two such alternatives and Xray and photon emissions by laser illuminated four leaf gold bow-ties may be another means. Combining the two may provide a booster and sustainer propulsion system. Mars in a few days?

OR.02
Tetraoxydiboron Reagents Mediate Catalytic H Atom Transfer From Water in Alkene and Alkyne Hydrogenation Reactions

Steven Cummings, University of California, Merced
Co-authors: Thanh-Ngoc Le, Lorenzo G. Quiambao, Benjamin J. Stokes

We recently described a new method for the hydrogenation of alkenes and alkynes at ambient temperature using water as the H atom donor in the presence of tetraoxydiboron reagents and catalytic Pd/C. The reaction proceeds at ambient temperature in organic solvents or water, and boric acid is the only byproduct. Herein, we present the results of our latest efforts to extend this method to include alkyne semi-hydrogenation and semi-deuteriation reactions. We also discuss our latest mechanistic insights including our efforts towards a well-defined catalyst.

OR.03
Ligand-Mediated Synthesis of Colloidal Cesium Lead Bromide Perovskite Nanocrystals

Aizhao Pan and Yi Liu, Molecular Foundry, Organic Facility
Co-authors: Bo He, Xiaoyun Fan, Zeke Liu, Jeff Urban, Paul A. Alivisatos, Ling He, Yi Liu

While convenient solution-based procedures have been realized for the synthesis of colloidal perovskite nanocrystals, the impact of surfactant ligands on the shape, size and surface properties still remains poorly understood, which calls for a more detailed structure-morphology study. Herein we have systematically varied the hydrocarbon chain composition of carboxylic acids and amines to investigate the surface chemistry and the independent impact of acid and amine on the size and shape of perovskite nanocrystals. Solution phase studies on purified nanocrystal samples by ^1H NMR and IR spectroscopies have confirmed the presence of both carboxylate and alkylammonium ligands on surfaces, with the alkylammonium ligand being much more mobile and susceptible to detachment from the nanocrystal surfaces during polar solvent washes. Moreover, the chain length variation of carboxylic acids and amines, ranging from 18 carbons down to two carbons, has shown independent correlation to the size and shape of nanocrystals in addition to the temperature effect. We have additionally demonstrated that employing a more soluble CsOAc precursor in place of the universally used Cs_2CO_3 results in enhanced processibility without sacrificing optical properties, thus offers a more versatile recipe for perovskite nanocrystal synthesis which allows the use of organic acids and amines bearing chains shorter than eight carbon atoms. Overall our studies have shed light on the influence of ligand chemistry on crystal growth and stabilization of the nanocrystals, which opens the door to functionalizable perovskite nanocrystals through surface ligands manipulation.

OR.04
Mesoporous PbI_2 Scaffold for High-Performance Planar Heterojunction Perovskite Solar Cells

Qin Hu, Peking University and Lawrence Berkeley National Laboratory
Co-authors: Tanghao Liu, Qin Hu, Ke Chen, Feng Liu, Jiang Wu, Cheng Wang, Hong Lu, Shuang Jia, Thomas Russell, Rui Zhu, Qihuang Gong

Thin film solar cells based on organo-lead iodide perovskite, $\text{CH}_3\text{NH}_3\text{PbI}_3$, have attracted much attention during the past few years. In the traditional

sequential deposition process of CH₃NH₃PbI₃, PbI₂ was first coated onto mesoporous TiO₂ scaffolds and subsequently converted into CH₃NH₃PbI₃. The conversion of PbI₂ to CH₃NH₃PbI₃ can be incomplete if the PbI₂ layer forms a dense, pinhole free film. To address this issue, mesoporous PbI₂ thin film deposition is developed, providing channels for molecular diffusion and thus enhancing the perovskites conversion efficiency. The morphologies of the PbI₂ scaffolds, can be programmed by a controlled nucleation and growth mechanism, providing a new handle on perovskite morphology control. Using this strategy, perovskite solar cells with planar heterojunction structures delivered a power conversion efficiency (PCE) of 17.6%, and the inverted devices achieved a PCE of 15.7% with virtually no hysteresis. Correlations between the PbI₂ film morphology and device performance have been established.

OR.05

Deep absorbing porphyrin molecules and their applications in organic solar cells

Ke Gao, South China University of Technology

A new category of conjugated small molecules (DPPEZnP-TRs) using porphyrin rings as the donor and diketopyrrolopyrrole as the acceptor. The resultant material showed a broad light absorption covering the UV-vis-NIR region while maintaining a deep HOMO energy level. Thus, a cohesive enhancement in both short circuit current and open circuit voltage is seen in solar cell devices. A remarkable current density of ~20 mA/cm² is generated, which is the highest in small molecule-based organic photovoltaics and the overall efficiency reached 9.06%, making these materials among the best deep absorbing light-harvesting materials. Also, we extended the application of the material into ternary solar cells and tandem solar cells. A PCE of above 11% was achieved for the ternary solar cells and the PCE was improved with a large range of the second donor ratio from 10% to 70%, making it the best ternary solar cells. When applied to the tandem solar cells, a PCE of 12% was achieved, which is the highest reported solution-processed organic solar cells. When applied them into flexible tandem solar cells, a PCE of over 10% make it the best flexible organic solar cells reported.

Theory of Nanostructured Materials

TH.01

High throughput search of field-induced topological ferroelectrics in ABX₃ (X=Cl,Br,I)

Sebastian Reyes-Lillo, Molecular Foundry, LBNL
Co-authors: Aris Ioannou, Jeffrey B. Neaton

Using first principles density functional theory calculations, we perform a high throughput search of topological phases in a newly-identified class of ferroelectric and antiferroelectric materials in the Inorganic Crystal Structure Database (ICSD) within the halide ABX₃ (X=Cl,Br,I) family of compounds. Accurate band gaps of selected compounds are obtained with hybrid functionals, including spin-orbit interactions. We find several ABX₃ (X=Cl,Br,I) materials that, upon stabilization in the perovskite structure, display a small energy difference (~10meV) between the polar ferroic R3c (a-a-a- in Glazer notation) and the nonpolar antiferrodistortive Pnma (a-a-b+ in Glazer notation) distortions, characteristic of antiferroelectricity. We predict trivial ferroelectrics and antiferroelectrics, whose competing R3c polar phase display promising semiconducting properties for photovoltaic applications such as small band gaps of ~1eV and macroscopic polarization of ~10uC/cm². In addition, we predict that the hypothetical perovskites RbSnI₃ and RbSnBr₃ are bulk topological insulators in the reference cubic Pm-3m phase and the metastable polar R3c distortion, but correspond to trivial insulators in the nonpolar Pnma structure. These compounds, are therefore antiferroelectrics that display an induced topological ferroelectric phase, even in the presence of oxygen octahedral rotations, through the application of an external electric field. We explore the structural and electronic properties that lead to such behavior by computing surface states and topological invariants, and suggest possible technological applications, such as switchable photovoltaic devices with combined structural, electronic and optical functionalities.

TH.02

Accurate Level Alignment in Molecule-Metal Interfaces with Optimally-Tuned Range-Separated Hybrid Functionals

Zhenfei Liu, LBNL
Co-authors: David A. Egger, Sivan Refaely-Abramson, Leeor Kronik, Jeffrey B. Neaton

Molecule-metal interfaces are ubiquitous in nanoscale functional materials and energy related applications. Characterizing the electronic structure at

molecule-metal interfaces, especially the level alignment between molecular frontier orbitals and the Fermi level of the combined system, is crucial for understanding charge dynamics. Density functional theory (DFT) has been successful in computing binding geometries and adsorption energies, but much less successful in predicting level alignment. This is because the latter depends on quasiparticle excitation energies, typically believed to be outside the reach of DFT. In this work, we generalize the recently developed optimally-tuned range-separated hybrid functional to the electronic structure of several molecule-metal interfaces, and elucidate parameters leading to agreement with experiment and with many-body perturbation theory.

TH.03

First-principles study on the role of N,N'-dimethylethylenediamine (mmen) molecule in mmen-M2(dobpdc) metal organic frameworks

Jung-Hoon Lee, UC Berkeley
Co-authors: Jeffrey B. Neaton

mmen-M2(dobpdc) metal organic frameworks (MOFs) are currently being investigated since mmen-M2(dobpdc) MOFs recently showed a good CO₂ adsorption performance¹. Here we have investigated the role of N,N'-dimethylethylenediamine (mmen) molecule in mmen-M2(dobpdc) MOFs by exploiting vdW-corrected first-principles calculations density functional theory (DFT). Our DFT calculations demonstrate that mmen molecule enhances the CO₂ binding energy as well as the CO₂ adsorption selectivity. More importantly, the present calculations reveal that it is able to maintain the CO₂ adsorption process under humid condition without degradation. Interestingly, water molecules increase the CO₂ binding energy via hydrogen bonding by 33 kJ/mol. This is due to its unique CO₂ capture process. We have also shown that mmen significantly enhances the mechanical property of M2(dobpdc) MOFs. These results suggest that functionalized molecule such as mmen can be used as a control parameter to optimize the gas adsorption properties of MOFs.

1. McDonald, T. M. et al. Cooperative insertion of CO₂ in diamine-appended metal-organic frameworks. *Nature* 519, 303-308 (2015).

TH.04

Modeling the interaction of EUV radiation with photoresist materials from first principles

Kristina Closser, Lawrence Berkeley National Laboratory
Co-authors: David Prendergast, Musa Ahmed, Paul D. Ashby, Suchit Bhattarai, Oleg Kostko, Yi Liu, D. Frank Ogletree, Deirdre L. Olynick, Daniel Slaughter, Bo Xu, Patrick Naulleau

Thoroughly understanding the initial absorption of extreme ultraviolet radiation (EUV) and subsequent relaxation of both electrons and nuclei is critical for effectively designing improved resist materials. Using a first principles based approach, this work focuses on computing critical properties of the system, such as the initial optical absorption, the energy of primary and secondary electrons, and the potential photo-products, and correlating these to desired resist properties, such as high resolution, low line width roughness, and high sensitivity.

Throughout this work, various flavors of density functional theory (DFT) are used. The methodology is general and its utility is demonstrated by application to a series of halogenated model materials. The computed optical cross-sections which describe the initial absorption, electron loss functions which give information about the interaction of emitted electrons with surrounding material, and ab initio molecular dynamics which can determine possible photo-products, are discussed. The electronic structure of the system yields important information on the nature of the absorption, and it is seen that more tightly bound states are preferentially ionized by EUV photons. These states are highly localized and may ultimately lead to selective photo-fragmentation and increased resolution.

TH.05

Phonon dispersion of solid naphthalene using van der Waals-corrected density functional theory

Florian Brown-Altwater, UC Berkeley/Molecular Foundry
Co-authors: Tonatiuh Rangel, Jeffrey B. Neaton

Acene molecular crystals are interesting testbeds for study of phenomena relevant to organic optoelectronics, including charge separation and carrier transport. In such processes, scattering from lattice vibrations is an important dissipation mechanism. Despite their central role in dissipation processes, there are few calculations of phonon spectra in acene crystals. Here, we show that van der Waals-correction is essential to accurately and predictively calculate the ground-state structure and phonon band structure of acene molecular crystals. We use a finite-differences method, and compare the performance of several density functional theory approaches - including standard local density approximations (LDA), generalized

gradient approximations (GGA), such as PBE, and vdW density functionals -- to neutron scattering, IR, and Raman experiments of solid naphthalene. This work was supported by the DOE; computational resources provided by NERSC.

TH.06
Exploring the Electronic Structure of Aluminum: X-Ray Absorption Spectroscopic Investigations of Aluminum Coordination Complexes and Materials

Alison Altman, UC Berkeley
Co-authors: John Arnold, Alexandra Brown, Stefan G. Minasian, C. Das Pemmaraju, David Prendergast, David K. Shuh, Tolek Tyliczszak

Aluminum is an essential part of numerous important scientific and industrial technologies. For many of these applications, aluminum can be described as an electropositive, Lewis acidic metal, although it is known that low-valent aluminum behaves as an electron pair donor. Recent research has demonstrated that aluminum can be reduced under mild conditions, suggesting new characterization tools may be useful in harnessing novel chemistry with aluminum. Metal K-edge X-ray Absorption Near Edge Spectroscopy (XANES) is an established technique for evaluating electronic structure in bioinorganic and inorganic compounds. However, studies at the Al K-edge have been limited for molecules and materials.

Here, we present our efforts to explore Al K-edge XANES as a unique probe of electronic structure in aluminum molecules and materials. Measurements were conducted at Advanced Light Source Beamline 11.0.2, and spectral interpretation was informed by spectra calculated using the eXcited electron and Core Hole approach. Initial efforts focused on aluminum hydrides, Al(I) analogues and other related molecules. Spectroscopy, theory and reactivity studies suggested that some aluminum hydride bonds exhibit covalent character, and a bridging hydride Ti-Al bimetallic was synthesized to further study aluminum-hydride reactivity. Additionally, Al K-edge XANES was used to probe the electronic structure of lanthanide and actinide dialuminide alloys. Theoretical investigations of simple closed shell analogues aided in the full assignment of the XANES spectra for these complex materials. It was found that metal valence plays a significant role in determining the relative amounts of aluminum 3p and metal d character that make up the conduction band.

TH.07
Many-body perturbation theory: a predictive simulation approach for energy related applications

Tonatiuh Rangel-Gordillo, The Molecular Foundry

Many-body perturbation theory (MBPT) has proven to be a successful theory to simulate excited-state properties of materials from first principles, treating finite and periodic systems on equal footings. We present a brief overview of the theory and highlight its potential and application to a broad range energy related applications. In particular, we illustrate the predictive power of MBPT to simulate photovoltaic properties of organic molecules and semiconductors, inorganic molecules and metal-organic frameworks.

TH.08
First-principles study of charge-order-induced ferroelectricity in LaVO₃/SrVO₃ superlattices

Se Young Park, Rutgers University
Co-authors: Anil Kumar, Karin M. Rabe

The structure and properties of the 1:1 superlattice of LaVO₃ and SrVO₃ are investigated with a first-principles density-functional-theory-plus-U (DFT+U) method. The lowest energy states are antiferromagnetic charge-ordered Mott-insulating phases. In one of these insulating phases, layered charge ordering combines with the layered cation ordering to produce a polar structure with nonzero spontaneous polarization normal to the interfaces. This polarization is produced by electron transfer between the vanadium 3+ and 4+ layers, and is comparable to that of conventional ferroelectrics. The energy of this polar state relative to the nonpolar ground state is only 3 meV per vanadium. Under tensile strain, this energy difference can be further reduced, suggesting that the polar phase can be induced by applied electric field, yielding an antiferroelectric double-hysteresis loop. If the system does not switch back to the nonpolar state on removal of the field, a ferroelectric-type hysteresis loop could be observed.

TH.09
vdW-DF hybrids as an approach for accurate, general-purpose density functionals

Yang Jiao Chalmers, University of Technology
Co-authors: Kristian Berland, Tonatiuh Rangel, Elsebeth Schroder, Per Hyldgaard

The vdW-DF method, which accounts for non-local van der Waals (vdW) interactions in the framework of density functional theory (DFT), has shown success in both dispersion bound systems and also densely packed systems, and has been demonstrated being a good framework for developing successively improved functionals. It describes truly nonlocal correlations in a term derived from the adiabatic connection formula using a single-plasmon-pole approximation for the response captured by an underlying semilocal-functional starting point.

In recent efforts we have launched consistent-exchange (spin) vdW-DF formulations where the same plasmon-pole approximation is used to specify all functional components. Also, the approach lends itself naturally to define hybrids where long-range exchange interaction is taken along with the non-local correlation by hybridising with exact exchange. We have thus constructed vdW-DF-cx (where the plasmons are set as in the original vdW-DF), alternative versions, vdW-DF2-csx and vdW-DF-cpx (where other formal many-particle physics results define different but related starting points), and associated hybrids. The set of consistent-exchange vdW-DF versions and hybrids have been implemented in Quantum Espresso package.

Benchmarking has been performed on a wide range of model systems, atomisation energies for a set of small molecules in the G1 set, binding energies of small molecules with varied dominant interactions in S22 set, chemical reaction energies for molecules in extended G2 set, bulk element structures and atomisation energies, oxides and layered materials. This study covers a wide range of electronic systems and illustrates the reliability of the vdW-DF hybrids as a general purpose functional.

TH.10
Combining Theory and Experiment to Explore the Structure of Semiconducting Polymers with Soft X-rays

Gregory Su, Lawrence Berkeley National Lab

A comprehensive understanding of the connections among chemistry, structure, and dynamics of polymers is needed to improve performance and efficiency in numerous polymer-based applications. However, these relationships can be difficult to probe, especially under in situ or operando conditions, and proper simulations are needed to complement and unravel experimental results. We show an example of how first-principles calculations of X-ray absorption spectroscopy can be used to understand the fundamentals of electronic structure in conjugated polymers, and help elucidate structural parameters such as backbone tilt or polymer chain axis orientation. The important effects of various molecular parameters such as polymer chain length, side chain atoms, and backbone orientation on simulated spectra is demonstrated for model conjugated polymers. In addition to core-level spectroscopy, which is sensitive to chemical moieties and electronic structure, soft X-rays provide the ability to probe spatial information, dynamics and chemical kinetics through transmission microscopy, resonant scattering and photon correlation spectroscopy, and this suite of soft X-ray methods is naturally complementary. Advancements in X-ray methodologies and complementary theory will drive capabilities to probe chemistry and morphology of polymers and soft matter in a time-resolved manner.

TH.11
Energy level alignment of self-assembled linear chains of benzenediamine on Au(111) from first principles

Guo Li Lawrence, Berkeley National Lab
Co-authors: Tonatiuh Rangel, Zhen-Fei Liu, Valentino R. Cooper, Jeffrey B. Neaton

Using density functional theory (DFT) with a van der Waals density functional, we calculate the adsorption energetics and geometry of benzenediamine (BDA) molecules on Au(111) surfaces. Our results demonstrate that the reported self-assembled linear chain structure of BDA, stabilized via hydrogen bonds between amine groups, is energetically favored over previously studied monomeric phases. Moreover, using a model, which includes nonlocal polarization effects from the substrate and the neighboring molecules and incorporates many-body perturbation theory calculations within the GW approximation, we obtain approximate self-energy corrections to the DFT highest occupied molecular orbital (HOMO) energy associated with BDA adsorbate phases. We find that, independent of coverage, the HOMO energy of the linear chain phase is lower relative to the Fermi energy than that of the monomer phase, and in good agreement with values measured with ultraviolet photoelectron spectroscopy and x-ray photoelectron spectroscopy.

TH.12 X-ray Absorption Spectroscopy study of processing effects on Graphene: Experiment and Theory

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Co-authors: A. D. Winter, S. Kim, A. D. Williams, C. Weiland, E. Principe, D. A. Fischer, D. Prendergast, J. Grote, and E. M. Campo

Nanoelectronics applications based on graphene will owe its effectiveness to processing and large area fabrication. Current processing schemes aim at transferring methods to achieve homogeneous, defect-free, graphene layers onto flexible and non-flexible substrates with the purpose of preserving mobility. Although structural properties of as-grown graphene on Cu and SiC are well documented, further research is required to analyze the resulting lattice structure and strain dynamics (responsible for transport properties) as a consequence of transfer.

One approach to assess strain in small molecules is through Near Edge X-Ray Absorption Fine Structure (NEXAFS) spectroscopy. In the experimental realm, studies have confirmed a linear correlation between σ^* resonances and molecular bond lengths, which theoretical models had predicted earlier.

In this work, we apply similar arguments to graphene, and use a combination of X-ray spectroscopy experiments and ab-initio simulations to extend the validity of this correlation. This approach has enabled the prediction of average bond lengths and lattice parameters of single and multiple graphene-transferred layers onto a variety of substrates. The eXcited electron and Core-Hole (XCH) approach was followed to simulate NEXAFS spectra based on constrained-occupancy Density Functional Theory.

This analysis aims at establishing a correlation between growth and processing, making use of experimental and theoretical data to predict optimum graphitic quality, and ultimately, to inform fabrication routines. The proposed approach suggests NEXAFS spectroscopy, in both its experimental and theoretical modalities, is a powerful technique in the assessment and prediction of structural properties of graphene.

TH.13 Ab initio design of low work function complex oxides for thermionic energy conversion

Stephanie Mack, UC Berkeley
Co-authors: Guo Li, Jeffrey B. Neaton

Understanding and controlling work functions, or band edge energies, is of interest for a variety of applications in optoelectronics and energy conversion. In particular, while recent advances in device design have improved the feasibility of thermionic generators, new low work function materials are needed to enable their widespread use. Perovskite-based oxides (ABO₃) are a diverse class of materials that, depending on the transition metal atoms on the A and B sites, can give rise to myriad emergent and collective phenomena. Here, we use density functional theory calculations to examine how the work function of one such oxide, SrRuO₃ (SRO), can be tuned by ultrathin layers of polar or near-polar oxides. With a single monolayer the shifts in work function are on the order of tenths of an eV, although the calculated reduction in work function is still an order of magnitude less than would be expected from the bulk polarization. We also consider non-centrosymmetric bilayers on the SRO substrate. The SRO work function can be tuned by over 1 eV with bilayers. We understand the variation in work function via a detailed analysis of Born effective charges at the surface, which are as small as 10% of their bulk values, and atomic displacements at the surface.

TH.14 Engineering high-valence metal sites for water oxidation

Xueli Zheng, University of Toronto

Electrochemical reduction of carbon dioxide into value-added fuels will reduce today's dependence on conventional fossil fuels, mitigating net CO₂ emissions¹⁻⁴. Unfortunately, the electrical-to-chemical power conversion efficiency of the overall reaction is limited by the sluggish anodic oxygen evolution reaction (OER) in pH-neutral CO₂-saturated solution. In the best catalysts reported to date, the overpotential of OER in pH-neutral electrolytes exceeds 460 mV at 10 mA/cm², degrading the efficiency of renewable energy storage systems^{3, 5-7}. We took the view that generating transition metal sites with high valence at low applied bias should improve the activity of neutral OER catalysts^{5, 10-12}. Here we report a new approach, one that seeks to minimize the formation energy of high-valency active sites, and find that the new design strategy leads to dramatic reductions in neutral OER overpotential. Using density functional theory, we find that the formation energy of desired Ni⁴⁺ sites is systematically modulated using the combination of Co, Fe and non-metal

phosphorus. We synthesized NiCoFeP oxyhydroxides and probed their oxidation kinetics employing in situ soft X-ray absorption (sXAS). These first-ever in operando sXAS studies of neutral pH OER catalysts indicate ready promotion of Ni⁴⁺ under record-low overpotential conditions. The new catalyst exhibits exceptional OER performance, with a 330 mV overpotential at 10 mA/cm² in CO₂-saturated 0.5 M KHCO₃ electrolyte. The new catalyst outperforms the leading precious metal oxide IrO₂ and retains its performance following 100 hours of operation. Finally, we achieved a 1.99 V cell voltage at 10 mA/cm², reducing CO₂ into CO and oxidizing H₂O to O₂ with a new record 67% electricity-to-chemical-fuel efficiency by coupling NiCoFeP oxyhydroxides as OER catalysts and ultrasharp nanoneedles as CO₂ reduction catalysts.

TH.15 X-ray Spectroscopy of the Aqueous Carbonate System

Royce Lam, UC Berkeley / LBNL
Co-authors: Alice England, Jacob Smith, Orion Shih, Anthony Rizzuto, David Prendergast

The solvation of carbon dioxide (CO₂) in water and its subsequent hydrolysis to form carbonic acid (H₂CO₃), bicarbonate (HCO₃⁻), and carbonate (CO₃²⁻) comprise a central process in both biological buffer systems and the global carbon cycle. Despite enormous effort, there have been very few successful spectroscopic studies of dissolved CO₂ and aqueous H₂CO₃ – a result of their intrinsic instabilities in aqueous solution. We have recently characterized the electronic structure and hydration environment of the various carbonate species, including dissolved CO₂ and aqueous H₂CO₃, by X-ray absorption spectroscopy (XAS) and X-ray Photoelectron Spectroscopy (XPS) using a fast-flow liquid microjet mixing system to protonate a bicarbonate solution to generate aqueous H₂CO₃ and dissolved CO₂. Interpretation of the measured spectra via a combination of molecular dynamics simulations and first principles electronic structure calculations establish the detailed hydration properties of the aqueous carbonate system.

TH.16 Fluidic Platforms with SWNT Channels for Membrane Applications and Fundamental Studies of Ionic Transport

Steven Buchsbaum, Lawrence Livermore National Laboratory
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Carbon nanotubes (CNTs) exhibit remarkable fluidic properties which make them very attractive materials for next-generation composite membrane fabrication. Many membrane applications require CNT pores with high density, vertical alignment, and small diameters for enhanced flux and selectivity. Despite significant work to this end, fabricating membranes satisfying these conditions has proven very difficult. Here, we demonstrate square cm, free-standing, flexible SWNT based membranes with well aligned tubes at loadings 10x greater than previously reported films [1]. Membranes are manufactured using an LPCVD CNT growth process followed by polymer or SiN infiltration to fill inter-channel gaps. Fabricated membranes show remarkable ion, water and gas transport rates which are several orders of magnitude above typical continuum and Knudsen based models. Additionally, CNT pores display transport selectivity based on analyte size and charge.

Several studies have reported huge ionic transport rates in CNTs driven by an electric field. The origin of large ionic conductance, however, is poorly understood: literature reports often disagree in the magnitude of the sh different transport mode contributions to the measured ionic current and even in what ions are carrying the current; moreover, results obtained with single pore measurements differ frequently from those with membranes containing billions of open CNTs [2]. Toward shedding light on these phenomena, we have combined our CNT membrane fabrication with a focused ion beam (FIB) based platform which allows for activation of individual (or a few) tubes. By employing this platform, we observe giant ionic currents in CNT channels and a power-law increase of conductance with KCl concentration, a behavior that seems unique to CNTs. The findings and implications of this behavior are presented here.

[1] Guo, S., et al. (2015) Adv. Mater., 27: 5726

[2] Bui, N., et al. (2016) Adv. Mater., 28: 6020