



MOLECULAR FOUNDRY USER MEETING



AUGUST 11-12, 2016

Abstract Booklet

Plenary Session

August 11, 2016 | 9:00 am to 4:00 pm | Building 50 Auditorium

Organizers: User Executive Committee

9:00 am

Welcome

User Executive Committee

9:05 am

Molecular Foundry Update

Jeffrey Neaton, Director of the Molecular Foundry, Berkeley Lab; Professor of Physics UC Berkeley

9:30 am

Keynote Address: Evolving Click Chemistry → SuFEx

K. Barry Sharpless, W. M. Keck Professor of Chemistry, The Scripps Research Institute

What does it take to move fluoride and aryloxy ligands around between the coordination spheres of S(VI) and Si(IV), and very quickly, too? The answers are still up in the air, but I'll tell you what I know so far. This is another intermolecular linkage process, which like its old sibling CuAAC, provides yields above 99%, even when run in a serial fashion for 100 linear steps.

10:10 am

Nanoparticle-Polymer Conjugates for Near-Infrared Biomolecular Detection"

Markita Landry, UC Berkeley

Co-authors: Linda Chio, Travis del Bonis O'Donnell, Abraham Beyene

To visualize an important (but invisible) biomolecule inside an optically-opaque sample such as a living organism, two challenges must be overcome: (i) detecting a molecule for which there may exist no molecular recognition conjugate, and (ii) detecting a molecule deep inside a sample that is not transparent. Single-walled carbon nanotubes (SWNT) are unique near-infrared emitters, making them well-suited for use as fluorescence-based optical sensors: SWNT have essentially infinite lifetimes and emit in an optical window where tissues, cells, blood, and other biological materials are maximally transparent. We show that selective modulation of SWNT infrared fluorescence by a target biological analyte can be accomplished by adsorbing synthetic amphiphilic polymers onto SWNT surfaces [1]. The immediate utility of this platform is demonstrated in the discovery of synthetic sensors for small molecule metabolites, hormones, neurotransmitters [2, 3], proteins [4], and reactive oxygen and nitrogen species [5, 6]. We discuss several brief examples in which SWNT-based molecular sensors have been instrumental in advancing technologies at the interface of nanomaterial and molecular biosciences.

1. Zhang, J., et al., Molecular recognition using corona phase complexes made of synthetic polymers adsorbed on carbon nanotubes. *Nat Nanotechnol*, 2013. 8(12): p. 959-68.
2. Landry, M.P., et al., Experimental tools to study molecular recognition within the nanoparticle corona. *Sensors*, 2014. 14(9): p. 16196-211.
3. Landry, M.P., et al., Neurotransmitter detection using corona phase molecular recognition of fluorescent single-wall carbon nanotube sensors. *JACS*, 2014. 136(2): p. 713-724
4. Bisker, G., et al., Protein-targeted corona phase molecular recognition. *Nat Commun*, 2016. 7: p. 10241.
5. Giraldo, J.P., et al., Plant nanobionics approach to augment photosynthesis and biochemical sensing. *Nat Mater*, 2014. 13(4): p. 400-8.
6. Giraldo, J.P., et al., A Ratiometric Sensor Using Single Chirality Near-Infrared Fluorescent Carbon Nanotubes: Application to In Vivo Monitoring. *Small*, 2015. 11(32): p. 3973-84.

11:00 am

New capabilities at the Molecular Foundry

Mike Brady – SAXS-WAXS

Emory Chan – HERMAN

Shaul Aloni – 2D Materials

Frank Ogletree – Nano-Auger

Peter Ercius – Direct Electron Detection

Alex Muller – Cryo FIB stage

Frances Allen – He-ion Microscope

David Prendergast – Theory & Computation

11:40 am

Core-Shell Micro-Tube Array for Closing the Artificial Photosynthesis Cycle on a Nanometer Scale

Eran Edri, Berkeley Lab

Co-author: *Heinz Frei*

There is a growing interest for designs that can compartmentalize two reactions yet keep the two electronically and ionically connected on a nanometer scale. The separation of the reactions minimizes crossover and destructive reactions while keeping the separation to nanoscale minimizes transport losses and obviates the need for extreme ionic conditions. We demonstrate a design that closes the photosynthetic cycle on a nanometer scale with spatially and chemically separated reaction environments. The design consists of a centimeter-squared array of tubes, each of micron scale diameter and with a few nanometer thick walls. The inner layer of the tube-wall is made of an earth abundant water oxidation catalyst. The outer layer of the tube is a composite organic-inorganic membrane layer (~2 nm) decorated externally with photocatalysts for CO₂ reduction. The ultra-thin membrane is made of dense phase amorphous silica enclosing embedded conjugated molecules. Other than the conjugated molecules, which are oxidatively protected by surrounding silica, all components of this system are inorganic oxides and use earth abundant elements, properties that are essential for durability and scalability. Furthermore, nanofabrication and chemical methods used in making this design are also scalable. We confirm by photo-electrochemistry, that the conjugated molecules transport electronic charge at specific energy levels between the reduction-oxidation sites. We also find by impedance spectroscopy, that the dense phase silica is gas impermeable and can be made proton conductive by chemical doping. Using ultra fast transient spectroscopic measurements provide insight into the mechanism and kinetics of charge transport through conjugated molecules embedded in insulating inorganic layer. Lastly, using isotope labeling we confirm the photocatalytic production of CO and O₂ from H₂O vapor and CO₂ when light at 355 nm is shone on the tube array in which the outside silica surface of each tube has attached heterobinuclear ZrOCo light absorbers.

12:00 pm

Fabricating and Actuating DNA Origami Mechanisms

Alexander Marras, The Ohio State University

Co-authors: *Lifeng Zhou, Hai-Jun Su, Carlos E. Castro*

DNA origami enables the precise fabrication of nanoscale geometries. We demonstrate an approach to engineer complex and reversible motion of nanoscale DNA origami mechanisms. Following a traditional macroscopic machine design approach, we developed flexible DNA origami rotational and linear joints that integrate stiff double-stranded DNA components and flexible single-stranded DNA components to constrain motion along a single degree of freedom and demonstrate the ability to tune flexibility and range of motion. Linear motion was achieved by folding a tube concentrically around a track through a novel approach of programmed sequential folding so the track folds first, and then the tube is constrained to assemble around the track. Multiple joints were then integrated into higher order mechanisms. One mechanism is a crank–slider that couples rotational and linear motion, and the other is a Bennett linkage that moves between a compacted bundle and an expanded frame configuration with a 3D motion path. With the help of the Molecular Foundry, we are exploring ways to obtain 3D structural information about these mechanisms using transmission electron microscopy. We have also demonstrated multiple actuation methods to achieve reversible conformational changes via input strands to form new connections distributed throughout the mechanisms. We recently developed an approach for reversible actuation that relies on transient binding of many weak affinity input strands. Our results demonstrate programmable motion of 2D and 3D DNA origami mechanisms constructed following a macroscopic machine design approach with steps towards fast mechanical actuation.

2:00 pm

Keynote Address: New Insights into Oxygen Electrochemical Reactions on (La,Sr)MnO₃

Sossina M. Haile, Walter P. Murphy Professor of Materials Science and Engineering, Professor of Applied Physics, Northwestern University

Lanthanum strong manganite is the canonical cathode for solid oxide fuel cells. It offers a valuable balance between electrochemical activity, chemical stability, and thermomechanical compatibility with the widely used electrolyte, yttria stabilized zirconia (YSZ). Despite its widespread implementation, questions regarding the reaction pathway for oxygen electroreduction on this material remain open. Here, a fundamental study of the reduction mechanism is carried using thin film methods. Libraries of (La_{0.8}Sr_{0.2})_{0.95}MnO_{3+δ} (LSM) thin film microelectrodes with systematically varied thickness or growth temperature were prepared by pulsed laser deposition, and a novel robotic instrument was used to characterize these libraries in automated fashion by impedance spectroscopy. All impedance trends are consistent with a reaction pathway involving oxygen reduction over the LSM surface followed by diffusion through the film and into the electrolyte substrate. The surface activity is found to be correlated with the number of exposed grain boundary sites, which decreases with either increasing film thickness (at constant growth temperature) or increasing film growth temperature (at constant thickness). These findings suggest that exposed grain boundaries in LSM films are more active than exposed grains towards the rate-limiting surface process, and that oxygen ion diffusion through polycrystalline LSM films is faster than several prior studies have concluded.

2:40 pm

Study of Plasmonic Behavior of Nanoantennas via Transmission Electron Microscopy

Braulio Archanjo, National Institute of Metrology, Quality and Technology (Brazil)

Co-authors: *Thiago L. Vasconcelos, Frances Allen, Chengyu Song, Gustavo Cançado, Ado Jorio, Carlos A. Achete, Peter Ercius*

Localized surface plasmons are a collective oscillation of conduction electrons occurring on the surface of metal nanostructures. A remarkable characteristic of the localized surface plasmon resonance (LSPR) phenomena is that the resonance energy can be tuned by changing the size, shape and material of the host nanostructure. In this work, we use scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) to study the effect of 3D morphology on plasmonic properties of nanoscale tips or nanoantennas. The tips are created by template stripped processing and helium ion lithography and the goal of the project is to

develop new nanoscale tips for apertureless scanning near-field optical microscopy (apertureless-SNOM), which allows chemical and structural characterization at the nanoscale, with spatial resolution higher than the diffraction limit of the light. Also efforts in using the new designed tips for tip enhanced Raman spectroscopy (TERS) in a home built system will be shown.

3:00 pm

New Half-Metallic Ferromagnets Induced by a Quantum Critical Point from First Principles

Sinead Griffin, Berkeley Lab and UC Berkeley

Co-author: Jeffrey Neaton

Most theoretical and experimental efforts in the Fe-pnictide class of superconductors aim to optimize the superconducting T_c . Significant substitution with other transition-metal ions is detrimental to superconductivity, however recent experiments on doped $BaMn_2As_2$ point to its potential as a half-metallic ferromagnet. Using ab initio calculations we investigate Mn-based structures as a new family of half-metallic ferromagnets, and explain the appearance of ferromagnetism by a quantum critical point. We also discuss tuning the chemical composition and physical parameters for optimal performance.

3:20 pm

Probing Atomic and Electronic Structure Effects of Halide Composition in Perovskite Photovoltaics

Walter Drisdell, Berkeley Lab

Co-authors: Linn Leppert, Carolin Sutter-Fella, Quynh (Skye) Ngo, Yufeng Liang, David Prendergast, Francesca M. Toma, Ian D. Sharp

Since methylammonium lead halide perovskites were first demonstrated as photovoltaic materials in 2009, reported efficiencies have skyrocketed from 3.9% to more than 22%. This rapid advancement has outstripped a fundamental understanding of the atomic and electronic structure responsible for increased performance in these materials. In particular, synthesizing perovskites with mixed halides (e.g. I/Br, I/Cl) allows tuning of the bandgap and can dramatically increase carrier diffusion length, but the origin of these effects is not understood. By utilizing High Energy Resolution Fluorescence Detection (HERFD) X-ray Absorption Spectroscopy (XAS), we resolve distinct spectral changes in the Pb L₃-edge spectrum as a function of I/Br composition. By coupling with first-principles density functional theory (DFT) computations performed at the Molecular Foundry Theory of Nanostructured Materials Facility, we explain the spectral changes in terms of competing effects: different bond lengths for Pb-I versus Pb-Br, and the difference in electronegativity of I versus Br. Halide identity therefore has a strong impact on the electronic structure at the Pb octahedra in these materials. Our combined HERFD-XAS / DFT approach provides a highly local probe of electronic effects at the Pb centers, which has significant advantages over other characterization techniques; implications and further studies are discussed.

3:40 pm

The Joint Genome Institute & Emerging Single-Cell Genomic Technologies

Devin Doud, Berkeley Lab

Abstract not available.