

# Thursday Evening Poster Sessions, October 24, 2019

## Nanometer-scale Science and Technology Division Room Union Station B - Session NS-ThP

### Nanometer-scale Science and Technology Poster Session

#### NS-ThP1 Probing Intermolecular and Molecule-Substrate Interactions at Angstrom Scale by Ultrahigh Vacuum Tip-Enhanced Raman Spectroscopy, *Sayantana Mahapatra, J. Schultz, N. Jiang*, University of Illinois at Chicago

Conventional spectroscopic techniques are limited by the optical diffraction limit to about half wavelength and therefore offers about 200 nm x 200 nm microscopic zone for working in the visible light range. Tip-enhanced Raman spectroscopy (TERS) emerges as an advanced analytical technique, where the plasmonically active probe is not only used to detect the tunneling current but also to interrogate the local chemical environment of surface adsorbed molecules with angstrom scale precision. In this work, we studied two regioisomers (positional isomers), *trans*- and *cis*-tetrakis(pentafluorophenyl)porphodilactone (*trans*- and *cis*-H<sub>2</sub>F<sub>20</sub>TPPDL) using scanning tunneling microscopy (STM), ultrahigh vacuum (UHV) TERS on Ag(100) with the spatial resolution down to 8 Å, which has wide range of applications in various field of surface science & nanotechnology such as regioselective catalysis reaction, chemical reactions, molecular electronics etc. We have shown, it is possible to distinguish these two structurally very similar forms with high accuracy & precision. The two-component molecular junction has been identified using high resolution two-dimensional (2D) Raman mapping. Furthermore, these new class of porphyrinoids i.e. porphodilactones (PDL) have been studied on different single crystals [Ag(100), Cu(100) and Au(100)] to probe the intermolecular and molecule-substrate interactions. This work demonstrates, STM combined with TERS is a complementary technique to characterize a system completely at angstrom scale.

#### NS-ThP4 A Nanoscopic View of Photo-induced Charge Transfer in Organic Nano-crystalline Heterojunctions, *Qian Zhang, S.R. Cohen, B. Rybtchinski*, Weizmann Institute of Science, Israel

Organic photovoltaics are promising as cost-efficient, tunable, and flexible platforms for solar energy conversion, yet their performance and stability are still far from optimal. Here we present a study of photo-induced charge transfer processes between electron donor and acceptor organic nanocrystals, as part of our path-finding effort to develop robust and efficient organic nanocrystalline materials for photovoltaic applications. We produced sub-micron to microns-long nanocrystals of perylene-diimides (PDIs) as electron acceptors, and with Copper Phthalocyanine (CuPc) as the electron donor. Three different configurations of donor-acceptor heterojunctions were prepared. Charge transfer in the heterojunctions was studied with Kelvin-probe force microscopy (KPFM) under laser or white light excitation. We also conducted theoretical calculations and time-resolved photo-luminescence measurements to understand the differences in the photovoltaic processes of these organic nanocrystals. Our work demonstrates that excitonic properties can be tuned by controlling the crystal and interface structures in the nanocrystalline heterojunctions, in order to minimize photo-voltaic losses.

#### NS-ThP5 Ferroic-ionic Interaction in Hybrid Organic Inorganic Perovskites, *Yongtao Liu<sup>1,2</sup>, L. Collins, A.V. Ievlev, A. Belianinov*, Oak Ridge National Laboratory; *M. Ahmadi*, University of Tennessee Knoxville; *S. Jesse, S.V. Kalinin*, Oak Ridge National Laboratory; *B. Hu*, University of Tennessee Knoxville; *O.S. Ovchinnikova*, Oak Ridge National Laboratory

Hybrid organic-inorganic perovskites (HOIPs) such as methylammonium lead iodide (CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>) have attracted broad research interest due to their outstanding photovoltaic performance. However, fundamental understandings of the origin of the high performance and the anomalous current-voltage (I-V) hysteresis of HOIPs solar cells still lag. Although ferroelectricity is proposed to be a reason of the related behavior, the convincing evidence supporting ferroelectricity in HOIPs is missing because the strong ion motion in HOIPs complicates the ferroic characterization. A clear understanding of the interplay between ferroic behavior and ion motion in HOIPs will be helpful for clarifying this question.

In this work, using multi-modal functional and chemical imaging methods, we unveil a ferroic-ionic interaction in CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>. In piezoresponse force microscopy (PFM) experiments, we observed ferroelastic twin domain structures in CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>. Although PFM shows 'piezoelectric-like' contrast

of the twin domains, our studies—including band excitation (BE) PFM, laser Doppler vibrometer (LDV) PFM, and BE contact resonance atomic force microscopy (BE-AFM)—unambiguously reveal the mechanical origin rather than the electromechanical origin of the 'piezoelectric-like' contrast. This ferroelastic domain was accompanied by ion segregation due to the strain-driven ion redistribution, which was observed using helium ion microscopy secondary ion mass spectrometry (HIM-SIMS) and atomic force microscopy infrared spectroscopy (AFM-IR). To further address how ion distribution affects the ferroic behavior of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>, we studied the interaction of the ion distribution and the fields (elastic field and electric field) distribution in CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>. It is shown that the ion redistribution is accompanied by a reversible change in lattice strain, suggesting the dependence of the elastic field on ion distribution. Furthermore, we found that the local ion distribution could manipulate the formation of ferroelastic twin domain. The electric field was studied by Kelvin probe force microscopy (KPFM), which indicates that the ion distribution affects local electric field intensity and the electric field distribution. By combining KPFM and time-of-flight secondary ion mass spectrometry (ToF-SIMS), we observed a screen effect of ion migration on the electric field in CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>. The remainder of the field is very small due to the compensation of ion migration. These results suggest that the ion motion can alter local field and hence local ferroic behavior of HOIPs. Overall, this work offers an understanding of ferroic-ionic interplay in HOIPs, providing a pathway to develop novel devices.

#### NS-ThP6 Processing of Nanoscale Lamellae in Bulk Al-Cu Eutectic Samples Through Selective Laser Melting, *Jonathan Skelton, J.A. Floro, J.M. Fitzgerald*, University of Virginia

Eutectic alloys with nanoscale lamellar spacing may have a wide range of applications in functional materials such as thermoelectrics and photovoltaics, as well as in enhanced mechanical properties. This is due to an intimate interleaving of two or more phases where the length scales are controlled in part by the solidification rate. Utilization of nanoscale eutectics remains limited as a result of the lack of methods available to readily produce them in bulk materials. Rapid solidification through laser irradiation has been shown to create these structures on the surface of model eutectic materials, such as Al-Cu, with an interphase spacing dependent on the scanning velocity of the laser, but the limited absorption depth of the laser frustrates formation of bulk nanostructured samples. Selective laser melting (SLM) presents an innovative solution to this problem by building 3D samples via a layer-by-layer method, where each pass is rapidly cooled by the bulk material. In this research, the relationship between the SLM processing parameters and the resulting microstructure of bulk Al-Cu eutectic samples is investigated, with a focus on controlling the interphase spacing and directionality of the lamellar microstructure. An SLM Solutions GmbH 125 system was used to process the samples in this study, operating at scan velocities ranging from 50 to 150 mm/s at a CW laser power of 100 W. Cross-sections of samples exhibited lamellar spacing of 40 to 100 nm within narrow eutectic colonies of approximately 3 μm width that extended the height of the individual scan layers (50 μm). The solidification mechanism that produced these colonies is investigated, and the fine lamellar spacing is analyzed in accordance to the Jackson-Hunt theory. Samples in this study were characterized by scanning electron microscopy (SEM), focused ion beam (FIB), and energy dispersive X-ray spectroscopy (EDS). Support for this research from the National Science Foundation grant #CMMI-1663085 is gratefully acknowledged.

#### NS-ThP8 Understanding Tip-induced Nanoscale Wear for Tomographic Atomic Force Microscopy, *Umberto Celano*, IMEC, Belgium; *X. Hu*, University of California-Merced; *L. Wouters, K. Paredis, T. Hatschel, P.A.W. van der Heide*, IMEC, Belgium; *A. Martini*, University of California-Merced

The ability of contact-mode atomic force microscopy (AFM) to remove material while scanning has repeatedly been used for surface modification and small-scale tip-induced nanofabrication.[1] In the simplest form, the physical removal of material can be achieved by scanning the nanosized probe against the surface at high enough pressure.[2] More recently, tomographic capability has been explored for various electrical AFM modes by leveraging the same concept and alternating tip-induced removal and probing, in what is often referred to as Scalpel AFM.[3] Here, high-pressure AFM scans (i.e., high load force) are used for a controlled material removal and alternated with conventional contact-mode scans (i.e., standard load force). The alternation of scanning conditions delivers a slice-and-view methodology that generates three-dimensional (3D) datasets, with nm-precision in depth. This method has found wide application in the analysis of ultra-scaled nanoelectronics, where 3D architectures are currently dominating and the probing of confined volumes is mandatory.[4]

<sup>1</sup> National Student Award Finalist

<sup>2</sup> NSTD Graduate Student Award Finalist

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However, for complex nanostructures such as integrated electronic devices, a detailed comprehension of the tip-sample interaction it's required for the precise control of the removal process in heterogenous materials. In this work, we combine experimental AFM data with molecular dynamics (MD) simulations that study the fundamentals of high-pressure tip-induced material removal for heterogenous nanostructures. Metal-oxide nanopillars (80 -120 nm diameter) embedded in SiO<sub>2</sub> are experimentally probed using high pressure sliding contacts (i.e., diamond probes). We select a regime whereby tens of nm<sup>3</sup> are removed targeting a controllable removal rate below 3 nm/scan. The impact of the tip-sample interaction inside the worn regions is investigated in order to generate understanding on the physical wear mechanisms. The experimental results are compared with MD simulations that allow us to study the removal processes as a function of different parameters of the AFM scan, including removal rate and the quality of the machined area. As such, this work paves the way for the development of accurate models to improve the quality of tip-induced material removal in complex nanostructures, with great scientific and technological interest for tomographic probing using AFM.

## References

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