Nanomaterials
Room Naupaka Salon 5 - Session NM-MoM

Nanocharacterization

Moderator: Roya Maboudian, University of California at Berkeley

8:00am **NM-MoM1 Identification of Point Defects in Transition Metal Dichalcogenides by Combining Atomic Resolution Force Microscopy, STM/STS and Density Functional Theory: Missing Vacancies in $MoSe_2$ and WS_2**, ***Frank Ogletree***, Lawrence Berkeley National Laboratory; *S. Barja,* UPV/EHU-CISC Ikerbasque, Spain; *S. Refaely-Abramson,* University of California Berkeley; *B. Schuler,* Lawrence Berkeley National Laboratory; *D. Qiu,* University of California Berkeley; *S. Wickenberg,* Lawrence Berkeley Laboratory; *J. Neaton, A. Weber-Bargioni,* Lawrence Berkeley National Laboratory

Point defects can strongly influence material properties of 2D materials including Transition Metal Dichalcogenides (TMDs), where they can modify optical and transport properties, catalytic activity, and act as single photon emitters. It has been difficult to directly correlate specific defects with macroscopic measurements of TMD optical and transport properties. Scanning transmission electron microscopy (STEM) investigations have provided significant structural information, but STEM cannot directly probe electronic structure . In addition radiation damage is a significant problem for TMDs, making it difficult to determine intrinsic defect concentrations [1].

Here we report on the first applications of atomic resolution AFM to TMD point defects [2,3]. Cryogenic AFM/STM/STS studies using a CO molecule tip, when combined with advanced density functional excited-state theory, provide sufficient information for detailed point defect characterization. The experimental methods can resolve:

1. defect location through AFM, including local strain with ~ 30 pm lateral and 3 pm vertical resolution. This is difficult to do with STM alone due to the strong convolution of geometric and electronic structure [4]
2. electronic structure, through scanning tunneling spectroscopy (STS), which identifies localized resonances and in-gap states, and STM spatial maps of localized states and orbitals
3. charge state, through Kelvin-probe AFM and STS charging peaks
4. radial and reflection symmetry breaking, for example defects in the chalcogen plane appear very different in AFM if located on the upper or lower TMD surface, while the STS maps and spectra are similar. Defects localized in the metal plane have one AFM signature for a given STS structure.

The detailed information from scanning probe studies strongly constrains geometric structural models for theoretical simulations, and the results of these simulations can be directly compared to STS maps and local spectra, allowing detailed understanding of defects.

We will report on studies on MBE-grown $MoSe_2$ and CVD-grown WS_2. Based on STEM studies, chalcogen vacancies have been identified as the most common point defects, and have been predicted to have in-gap states. While our AFM/STM studies show chalcogen site defects whose AFM contrast is consistent with Se or S vacancies, they do not show any electronic in-gap states. In combination with theory, we identify these sites as substituted oxygen, which has very low STEM contrast.

[1] Wang, Robertson, Warner, *Chem Soc Rev* 2018.

[2] Barja, Refaely-Abramson, Schuler, Qiu et al, submitted.

[3] Schuler, Kastl, Chen et al, submitted.

[4] Barja et al, *Nature Physics* 2015.

8:20am **NM-MoM2 CO-tip AFM Identification and STM-induced Luminescence of Point Defects in Monolayer WS_2**, ***Bruno Schuler,*** Lawrence Berkeley National Laboratory; *D. Qiu,* University of California Berkeley; *S. Rafaely-Abramson, C. Kastl, K. Cochrane,* Lawrence Berkeley National Laboratory; *S. Barja,* Lawrence Berkeley Lab, USA; *C.T. Chen, N. Borys, R. Koch, F. Ogletree, S. Aloni, A.M. Schwartzberg,* Lawrence Berkeley National Laboratory; *S. Louie,* University of California Berkeley; *J. Neaton, A. Weber-Bargioni,* Lawrence Berkeley National Laboratory

The advent of transition metal dichalcogenides (TMDs) and other two-dimensional (2D) materials has attracted considerable attention due to unique material properties emerging from their reduced dimensionality. Because of this strong confinement, structural defects greatly modify such properties and have therefore become of increasing interest to the 2D materials community. Particularly the creation of in-gap defect states is decisive for their optoelectronic properties and catalytic activity.

Using low-temperature scanning probe microscopy with CO functionalized tips we identified and characterized common point defects in monolayer WS_2 (see Fig. 1).

Contrary to previous reports, we suggest that the most abundant defect is an O substitution at a S site, not a S vacancy, with a distinctively different electronic structure.

In contrast to O decorated S vacancies, a W substitutional defect and pristine S vacancies create distinct defect states within the band gap of WS_2. Interestingly, both types of point defects exhibit spin-orbit split defect states with a large splitting of 80 meV and 280 meV, respectively. Moreover, these defects exhibit electron-induced luminescence with a characteristic bias dependence. Spectrally integrated luminescence maps resemble the defect orbitals.

The same sample was also characterized with nano-ARPES and photoluminescence spectroscopy, which shows that thermally grown graphene on SiC constitutes a suitable platform for cross-correlation microscopy of TMD materials (and potentially other van der Waals materials) in both, UHV and ambient conditions.

The atomic-scale characterization allows an unprecedentedly detailed picture on the structure and functionality of point defects in 2D-TMDs.

8:40am **NM-MoM3 Intermolecular and Molecule-Substrate Interactions in Surface-Supported Nanostructures Characterized by Ultrahigh Vacuum Tip-Enhanced Raman Spectroscopy**, *J. Schultz, P. Whiteman, S. Mahapatra,* ***Nan Jiang,*** University of Illinois at Chicago

In order to fully characterize molecular assemblies at the single molecular scale, advanced analytical surface techniques have to be employed. We carried out scanning tunneling microscopy (STM) experiments on two molecules (N-N'-bis(2,6-diisopropylphenyl)-perylene-3,4:9,10-bis(dicarboximide) (PDI) and subphthalocyanine (SubPc)), which are both self-assembled on noble metal substrates. The STM experiments were complemented by tip-enhanced Raman spectroscopy (TERS), surface-enhanced Raman spectroscopy (SERS) and density functional theory (DFT) calculations. In particular, we have interrogated the lifting of an accidental vibrational degeneracy of a mode of PDI on Ag(111) and Ag(100) surfaces, with the most strongly perturbed mode being that associated with the largest vibrational amplitude on the periphery of the molecule. In the other hand, the alignment between expeimental TERS of SubPc on surface and DFT calculated Raman spectrum of gas phase SubPc was quite good, which indicates that the interaction between SubPc molecules in the monlolayer is very weak. New two-dimensional molecular superstructures were discovered to consist of several distinct molecular binding configurations. Both TERS and SERS experiments of SubPc yielded nearly identical vibrational spectra for both binding configurations, consistent with their small adsorption energies (<0.2 eV) as calculated by DFT. Our results demonstrate the necessity of advanced Raman techniques such as TERS when precisely probing molecule-molecule and molecule-substrate interactions.

9:00am **NM-MoM4 Quantifying the Thermodynamics of Ligand Binding to $CsPbBr_3$ Quantum Dots via Solution ^{1}H NMR Characterization**, ***Sara Smock,*** *R.L. Brutchey,* University of Southern California

The characterization of surface ligand binding to quantum dots is important to fully understand their behavior, such as photoluminescence quantum yield. One of the most promising recent classes of quantum dot materials is the $CsPbX_3$ halide perovskites (where X = Cl^-, Br^-, I^-) because of their growing applications in LEDs, X-ray detectors, and lasers. These $CsPbX_3$ quantum dots possess bright photoluminescence and narrow emission line widths over a wide color gamut. Using the hot-injection synthesis first reported by Protesescu et al. (*Nano Lett.***2015**, *15*, 3692), the ligand shell supporting the resulting $CsPbBr_3$ quantum dots has been reported to be highly dynamic and primarily comprised of oleylammonium bromide binding to the surface in an $NC(X)_2$ fashion without accompanying oleate X-type coordination. To date, however, the characterization of ligand binding has been qualitative in nature. Herein, we will report on quantifying the thermodynamics of *n*-alkyl carboxylic acid and amine ligand binding to $CsPbBr_3$ quantum dots via ^{1}H NMR spectroscopy. ^{1}H NMR is a powerful characterization tool for organic ligands on the surfaces of nanocrystals to observe ligand binding and gain insight into the thermodynamics of ligand exchange processes. In agreement with previous studies, we find the supporting ligands to be fluxional in nature; however, both ammonium and carboxylate binding to the purified nanocrystal surface is unequivocally observed. *n*-Alkyl carboxylic acids undergo an exergonic exchange equilibrium with bound oleate (K_{eq} = 1.97) at 25 ˚C, while *n*-alkyl phosphonic acids undergo an irreversible ligand exchange. *n*-Alkyl amines exergonically exchange with oleylamine (K_{eq} = 2.52) at 25 ˚C. Exchange occurs with carboxylic acids, phosphonic acids, and amines on $CsPbBr_3$ quantum dots without etching the nanocrystal surface; increases in steady-state PL intensities are correlated with more strongly bound conjugate base ligands.

9:20am **NM-MoM5 Nanomaterials for Creating Sensitive and Selective Biosensing Interfaces***, **Leyla Soleymani**,* McMaster University, Canada **INVITED**

Biosensors bring together biorecognition and signal transduction to analyze biologically relevant targets. The performance metrics of biosensors, such as limit-of-detection and speed, are strongly influenced by their structure. Designing material architectures that increase the sensor sensitivity, decrease background signals, and reduce analysis time is critical for entering biosensors into clinical decision making and health monitoring. Through this work, we have developed strategies for creating three-dimensional electrodes, combining them with biorecognition and self-cleaning interfaces, and translating biorecognition into electrochemical signals.

Porous and wrinkled hierarchical electrodes are created through self-assembly, electroless deposition, and bulking enabled by shape memory polymer substrates. Biorecognition is achieved by combining functionalized electrodes with molecular machines created using DNA nanotechnology. Self-cleaning is achieved using strategies that transform electrodes to omniphobic surface. Signal transduction is performed by electrochemical and photoelectrochemical readout using photo-active electrodes.

Three-dimensional electrodes, biorecognition elements, and signal transduction components are integrated into microfluidic networks for sensing small molecules, nucleic acids, and proteins. This integrated biosensing platform is used for analyzing clinical samples, and a test with a clinically-relevant limit-of-detection is achieved for diagnosing endometriosis.

10:20am **NM-MoM8 Effects of Defects on Band Structure and Excitons in WS2 Revealed by Nanoscale Photoemission Spectroscopy***, **Adam Schwartzberg**, C. Kastl, S. Aloni, A. Weber-Bargioni, C.T. Chen,* Lawrence Berkeley National Laboratory

Two-dimensional materials with engineered composition and structure will provide designer materials beyond conventional semiconductors. However, the potentials of defect engineering remain largely untapped, because it hinges on a precise understanding of electronic structure and excitonic properties, which are yet not predictable by theory alone. Here, we introduce correlative, nanoscale photoemission spectroscopy to visualize how the local introduction of defects modifies electronic and excitonic properties of two-dimensional materials at the nanoscale. As a model system, we study chemical vapor deposition grown monolayer WS2, a prototypical, direct gap, two-dimensional semiconductor. By cross-correlating nanoscale angle resolved photoemission spectroscopy, core level spectroscopy and photoluminescence, we unravel how local variations in defect density influence electronic structure, lateral band alignment and excitonic phenomena in synthetic WS2 monolayers. Our results not only provide a unified picture of nanoscale heterogeneity, but they also open up the possibility to precisely understand and tailor lateral heterointerfaces in such two-dimensional materials.

10:40am **NM-MoM9 4D Nanocharacterization by Spectro-ptychography Tomography of Alumina Aerogels Coated with Zinc Oxide by Atomic Layer Deposition***, **Adam Hitchcock**, J. Wu, X. Zhu,* McMaster University, Canada*; D.A. Shapiro,* Lawrence Berkeley National Laboratory*; J.R.I. Lee, MM. Biener, S.A. Gammon, T.T. Li, TF. Baumann,* Lawrence Livermore National Laboratory

Highly porous materials with nanoscale functional coatings are of increasing technological interest in the areas of energy conversion and storage, catalysis, and sensing [1,2]. 3D nanocharacterization with explicit chemical speciation capability is important for their optimization. Here the new method of soft X-ray spectro-ptycho-tomography [3] is used to characterize Al_2O_3 aerogel samples coated with ZnO by atomic layer deposition (ALD). 4D imaging (chemical mapping in 3D by spectro-tomography) of an Al_2O_3 aerogel coated with ZnO by atomic layer deposition (ALD) was performed using both scanning transmission X-ray microscopy (STXM) and ptychography [4]. 2D and 3D spatial resolution was significantly increased by ptychography, relative to STXM. A 2D spatial resolution of 14 nm was achieved with ptychography while the spatial resolution of the 2D STXM maps was only 24 nm. The degree of ZnO coverage of the surface of the Al_2O_3 aerogel framework in 3 different samples was estimated and compared to the ALD targets. Quantitative analysis showed that the ZnO ALD coatings are non uniform. Comparisons are made to Electron microscopy imaging and X-ray fluorescence analysis results were performed, confirming the results. Other analyses of the 4D results, including 3D thickness distributions of each species and measurements of the degree of contact between Al_2O_3 and ZnO, were extracted from the reconstructed 3D data. Together the results provide useful feedback for optimization of the nanostructure of ALD coated alumina aerogels.

STXM performed using BL10ID1 at CLS and BL 5.3.2.2 at ALS . Ptychography performed using BL 11.0.2 and 5.3.2.1 at the ALS . Research supported by NSERC and the Department of Energy, Basic Energy Sciences under contracts DE-AC02-05CH11231 and DE-AC52-07NA27344. CLS is supported by the Canada Foundation for Innovation.

References

[1] J. Biener *et al.*, *Energy Environ. Sci.***4** (2011) 656.

[2] M.M Biener *et al.*, *ACS Appl. Mater. Interfaces* **5** (2013) 13129.

[3] Y. Yu *et al.*, *Nature Communications***9** (2018) 921.

[4] A.P. Hitchcock, *J. Electron Spectrosc. Rel. Phenom.* **200** (2015) 49.

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