

## Nanometer-scale Science and Technology Division Room 102B - Session NS+AM+MI+MN+SS+TR-TuA

### SPM – Probing and Manipulating Nanoscale Structures

**Moderators:** Renu Sharma, NIST Center for Nanoscale Science and Technology, Carl Ventrice, Jr., SUNY Polytechnic Institute

2:20pm **NS+AM+MI+MN+SS+TR-TuA1 Building Artificial Quantum Matter with Dopant Atoms, *Sven Rogge***, University of New South Wales, Australia  
**INVITED**

Atomic-scale engineering reached the level of control where single-atom devices can be reproducibly fabricated with high yield. This talk focuses on the progress of single dopant atom placement in the context of engineered quantum matter. Silicon offers a particularly interesting platform for single dopants because when isotopically purified it acts as a “semiconductor vacuum” for spins. This leads to extraordinary coherence that is used to realise donor atom based qubits. Spatially resolved tunnelling experiments reveal the spectrum and quantum state image of single atoms and tunnel coupled arrangements of atoms. These measurements grant access to the wavefunction of donors in the silicon lattice that makes it possible to pinpoint the dopants to their exact position in the lattice that is essential in the evaluation of engineered quantum matter. A first step towards engineered Hamiltonians for Fermionic systems in the form of atomic chains was taken where interacting dopants were employed to simulate a two-site Hubbard Hamiltonian at low effective temperatures with single-site resolution. Quasi-particle tunnelling maps of spin-resolved states with atomic resolution reveal interference processes from which the entanglement entropy and Hubbard interactions are quantified. We will present dopant based multi-electrode devices fabricated by the scanning probe hydrogen depassivation and decoration technique where the quantum state of the device can be manipulated and imaged in situ. The aim of this work is to build a two dimensional array of up to 30 spins in the solid state to implement complex highly correlated systems.

3:00pm **NS+AM+MI+MN+SS+TR-TuA3 Scanning Tunneling Microscopy Study of Structure Control of a Nanocarbon Catalyst through a Surface-Activated coupling Reaction, *Jeremy Schultz, P. Whiteman, N. Jiang***, University of Illinois at Chicago

In order to optimize nanocarbon materials for metal-free catalysis, the structure must be controlled and characterized at the nanoscale. One method for the bottom-up assembly of nanocarbon catalysts is through an Ullmann-type coupling reaction induced by a metal substrate, where a halide leaving group allows covalent intermolecular coupling. Scanning tunneling microscopy has been applied to a fundamental study of 3,6-dibromo-phenanthroquinone (DBPQ), a molecule selected for its catalytically active diketonic groups. Conjugated polymers formed from DBPQ have been found to be capable of catalyzing alkane oxidative dehydrogenation (ODH) reactions as well as nitrobenzene (NB) reduction reactions.

Different surfaces were investigated for their role in the surface-activated coupling reaction. Intact monomer molecules were found to self-assemble through hydrogen and halide interactions on Ag(100), resulting in well-packed molecular islands which impacted the organometallic structure ultimately formed after reaction. On Au(100), two competing intermediate dimers were observed resulting from a chiral covalent bond between base DBPQ molecules. Cis dimers were found to result in reaction products that became stuck as tetramers without the potential for further polymerization. Utilization of increasing coverage and a new surface identity that arose from the leaving Bromide resulted in selective formation of longer conjugated polymer chains composed of trans dimers. This study characterizes the ability of initial self-assembly and leaving groups to steer reaction dynamics and control the structure of a nanocarbon catalyst.

3:20pm **NS+AM+MI+MN+SS+TR-TuA4 Detecting the Tip Shape Dependence of the Plasmonic Photon Emission under STM, *Songbin Cui***, Pohang University of Science and Technology, Republic of Korea; *U. Ham*, Institute for Basic Science (IBS), Republic of Korea; *T.-H. Kim*, Pohang University of Science and Technology, Republic of Korea

Photon signal can be enhanced significantly by modifying the plasmonic nanocavity. This enhancement becomes an important issue in super-resolution microscopy and high resolution spectroscopy, such as scanning tunneling microscopy (STM) electroluminescence [1], surface enhanced Raman spectroscopy, tip enhanced Raman spectroscopy [2], and so on. Low temperature STMs can allow us to achieve less than 1nm tip-sample

gap stably. This gap-mode plasmonic nanocavity between an STM tip and surface realizes sub-molecular photon spectroscopy [1]. A few works demonstrated that light emission signal can be effectively enhanced by certain resonant plasmonic spectral peaks, which can be modified by tip indentation [2] and showed theoretically that the larger tip aperture causes a blue shift and the sharper apex curvature results in higher intensity in a photon spectrum [3]. However, the tip shape dependence of the plasmonic nanocavity remains unclear. In this work, we experimentally present the role of tip shape in surface plasmonic light emission. We have used Ag tips and a Ag(100) substrate, and photon signals have been measured from both side of the STM tip simultaneously. We dipped STM tips into the substrate with controlling the dipping depth and the lifting speed in order to change the tip shape, and then, the tip shape subsequently was checked through STM profiles. We found that changing small parts of tip apex (<3nm tip direction) can differ the photon spectrum significantly. Furthermore, the plasmonic photon emission from different direction from a STM tip could be quite different due to tip shape asymmetry. This finding can help us to tune the plasmonic photon emission spectra more efficiently.

[1] R. Zhang et al., *Nature* 498, 82–86 (2013).

[2] Z. C. Dong et al., *Nature Photonics* 4, 50–54 (2010).

[3] J. Aizpurua et al., *Physical Review B* 62, 2065-2073 (2000).

4:20pm **NS+AM+MI+MN+SS+TR-TuA7 Advances in SPM Methods for Energy-relevant Materials, *Marina Leite***, University of Maryland College Park  
**INVITED**

The scientific understanding of nanoscale materials and devices is continuously growing ever since atomic force microscopy (AFM) has enabled us to image these systems at similar length scale. Specifically, there is a pressing need for functional imaging as energy-relevant technologies are becoming dominated by nano- and mesoscale constructs. In this presentation I will review my group’s recent research discoveries based on new AFM methods to measure and determine how the electrical, chemical, and/or optical properties influence overall photovoltaic device behavior [1,2]. We realize novel functional imaging AFM-based methods to elucidate the driving forces for the dynamic response of the perovskites upon and post-illumination [3], and polycrystalline materials for solar cells [4,5]. We map nanoscale variations in open-circuit voltage  $V_{oc} > 300$  mV under 1-sun illumination, not revealed by conventional AFM tools. Using fast-KPFM (16 seconds/scan) while maintaining high spatial sensitivity, we map, in real-time, the dynamics of the  $V_{oc}$  in perovskite solar cells with spatial resolution  $< 100$  nm. Unexpectedly, we identify a ‘residual  $V_{oc}$ ’ post-illumination, attributed here to iodine ion migration, a process that takes place in a time scale of several minutes. We foresee our functional imaging tool to be implemented in the identification of stable perovskite compounds, ranging from lead-free and non-toxic alternatives to new options for tandem designs.

[1] *ACS Energy Letters* 2, 2761 (2017). [Invited Review](#).

[2] *ACS Energy Letters* 2, 1825 (2017). [Invited Perspective](#)

[3] *Nano Letters* 17, 2554 (2017).

[4] *ACS Energy Letters* 1, 899 (2016).

[5] *Advanced Energy Materials* 5, 1501142 (2015).

5:00pm **NS+AM+MI+MN+SS+TR-TuA9 Coherent Electrical Contact to Semiconducting Graphene Nanoribbon, *Chuanxu Ma, L. Liang***, Oak Ridge National Laboratory; *Z. Xiao*, North Carolina State University; *A.A. Puzetzy, K. Hong*, Oak Ridge National Laboratory; *W. Lu, J. Bernholc*, North Carolina State University; *A.-P. Li*, Oak Ridge National Laboratory

High quality electrical contact to low-dimensional semiconductor channel materials is the key to unlocking their unique electronic and optoelectronic properties for fundamental research and device applications. Inappropriate contacts create interfacial states that can pin the Fermi level and form a large Schottky barrier. For 2D transition metal dichalcogenides (TMDs), a route to a high-performance contact has recently been proposed by using a phase transition that converts a hexagonally packed semiconductor (2H) phase into a distorted octahedrally packed metallic (1T') phase. However, a similar approach is not available for 1D materials. Conceptually, an ideal contact would be a metal-semiconductor interface formed with native covalent bonds without introduction of any structural or electronic boundaries. Realization of such a seamless contact in 1D materials such as graphene nanoribbons (GNRs) requires atomically precise development of a heterostructure from well-defined atomic or molecular precursors.

# Tuesday Afternoon, October 23, 2018

Here we report on a successful approach for making seamless contacts in 1D materials through the formation of GNR staircase heterostructure. The coherent staircase is made of GNRs with widths varying from 7, 14, 21 and up to 56 carbon atoms. The graphitic heterostructures are synthesized by a surface-assisted self-assembly process with a single molecular precursor. While the 7-atom-wide GNR is a large-gap semiconductor, the conjugated wide GNRs are either quasi-metallic or small-gap semiconductors, similarly to the 2D metals. Our study, which combines STM and Raman measurements with DFT calculations, reveals that the heterointerface consists of native  $sp^2$  carbon bonds without localized interfacial states. Such a seamless heterostructure offers an optimal electrical contact to the wide-gap 1D semiconductor.

explore dimensionality effects in biological systems, including proteins confined within membranes.

5:20pm **NS+AM+MI+MN+SS+TR-TuA10 Visualizing Coordination Structures of Small Gas Molecules to Metallo-porphyrin on Au(111) Using Scanning Tunneling Microscopy, MinHui Chang**, Korea University, Republic of Korea; *Y.H. Chang, N.Y. Kim*, Korea Advanced Institute of Science and Technology (KAIST); *U.S. Jeon, H. Kim*, Korea University, Republic of Korea; *Y.-H. Kim*, Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea; *S.-J. Kahng*, Korea University, Republic of Korea

Binding reaction between small molecules and metallo-porphyrins play crucial roles in functional processes of biological systems such as oxygen delivery, muscle contraction, and synaptic transmission. Their geometrical structures such as tilted binding of NO to metallo-porphyrin have been recently confirmed by high-resolution scanning tunneling microscopy (STM) images at the single molecule level. Here, we present STM images of further systems, di, tri, and quadra-atomic small molecules, coordinated to metallo-porphyrin on Au(111). We observed square ring, rectangular ring, and center-bright structures for three different small molecules. With the help of density functional theory (DFT) calculations, we reproduce the experimental STM images in the simulated images. Thus, our study shows that geometric structures of small molecules coordinated to metallo-porphyrins can be probed with STM combined with DFT methods.

5:40pm **NS+AM+MI+MN+SS+TR-TuA11 Effects of Dimensionality on the Reactivity of Carboxylic-Acid-Terminated Monolayers, Dominic Goronzy<sup>1</sup>**, *E. Avery, N.M. Gallup*, University of California, Los Angeles; *J. Staněk, J. Macháček, T. Baše*, Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic; *K.N. Houk*, Chemistry and Biochemistry, University of California, Los Angeles; *P.S. Weiss*, University of California at Los Angeles

Self-assembled monolayers (SAMs) are an advantageous construct to modify surfaces and thereby to tune material properties. Three major determinants affect the spontaneous assembly of monolayers: the substrate-monolayer interface, the interactions between the adsorbate molecules, and the monolayer-environment interface. By controlling the exposed functional groups in the SAM, this interface between the surface and the environment can be probed and manipulated. To examine how exposed carboxyl functional groups modulate the properties of SAMs, we have tethered thiol-functionalized carborane cage molecules with and without a carboxyl group to Au{111} surfaces. Using scanning tunneling microscopy (STM), visualization of the *para*-functionalized carboxylic acid carboranethiol was only possible in the form of a mixed monolayer of functionalized and unfunctionalized molecules. These experiments demonstrated that the functionalized molecule adopted the same nearest-neighbor spacings on the surface as the unfunctionalized *para*-carboranethiol, approximately 7.2 Å. By comparison, in our study of carboranethiols with a carboxylic acid functional group attached in the *meta* position, we have been able to image pure functionalized monolayers via STM with these molecules showing nearest-neighbor spacings of 8.4 Å, approximately 1 Å larger than the unfunctionalized carboranethiols. Studies of two different isomers of *meta*-carboranethiolate carboxylic acids yielded similar results. In order to examine the effects of changing dimensionality from a 3D solvent system to a 2D thin film, we applied contact angle titration to probe the reactivity of the carboxylic acid head group. These experiments demonstrated a substantial shift from a  $pK_a$  of 3-3.2 in solution (3D) to an apparent surface  $pK_a$  of approximately 6.5-7.5. Density functional theory calculations were performed to test the effects of desolvation by 2D confinement and showed shifts in  $pK_a$  consistent with the experimental data. Together, these results support the concept that the confinement in a 2D environment induces significant changes in reactivity in the molecules, as evidenced by the  $pK_a$  shift. Thus, precise positioning of functional groups in SAMs is an important tool to investigate the behavior of surface-confined molecules. This system may also serve as a model to

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

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