

Scanning Probe Microscopy Focus Topic Room 10 - Session SP+AS+MI+NS+SS-TuM

Probing Chemical Reactions at the Nanoscale

Moderators: Tae-Hwan Kim, Pohang University of Science and Technology, Giang Nguyen, Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

8:00am **SP+AS+MI+NS+SS-TuM-1 Single Molecule Junction: Chemical Optimization of Charge Transport through Single Benzene Derivatives**, *Parisa Yasini, S Afsari, P Pikma, E Borguet*, Temple University

Single molecules are possible components of miniaturized electronic devices. Interconversion between states using external stimuli is a convenient way to generate single molecule devices such as switches and sensors. In this study, we have devised an electromechanical single molecule junction where molecular orientation is controlled by the working electrode potential in an electrochemical environment. We used the scanning tunneling microscopy (STM)-break junction method to measure the electrical properties of benzene derivatives, e.g., tetrafluoroterephthalic acid (TFTPA), terephthalic acid (TPA) and trimesic acid (TMA), bridged between two gold electrodes (the conducting substrate and STM tip). At potentials more negative than zero charge potential, direct contact between the π -system of a benzene ring and the Au (111) electrode results in the formation of a highly ordered monolayer and a high conductance of 0.24 G_0 , 0.22 G_0 and 0.15 G_0 are detected for TFTPA, TPA and TMA, respectively. Moving to potentials more positive than the potential of zero charge triggers an order-disorder transition as revealed by STM. Our results show that charge transport through the π conjugated benzene ring increases by fluorination of TPA and decreases by an addition of a carboxylic acid functional group to the TPA. Accordingly, these results suggest that using functional groups, charge transport can be modified by manipulation of the electronic structure of molecules.

8:40am **SP+AS+MI+NS+SS-TuM-3 How is Armchair Graphene Nanoribbon Oxidized?**, *Chuanxu Ma, A Puzetky, A Baddorf*, Oak Ridge National Laboratory; *Z Xiao, W Lu*, North Carolina State University; *K Hong*, Oak Ridge National Laboratory; *J Bernholc*, North Carolina State University; *A Li*, Oak Ridge National Laboratory

The stability of graphene nanoribbons (GNRs) in air is crucial for practical applications. Here we study the temperature stability of the armchair GNR with a width of seven carbon atoms (7- α GNR) after exposed to air. Combining scanning tunneling microscopy, Raman spectroscopy, x-ray photoemission spectroscopy, and first-principles theory calculations, the oxidation of the armchair GNRs is found to start from the edges at about 520 °C, while below 430 °C the edges are unchanged. Two different types of oxygen species are atomically identified, specifically hydroxyl (OH) and atomic oxygen bridging two carbons, both of which are common oxygen forms in oxidized graphitic lattices. The bandgap is significantly reduced from 2.6 eV to 2.3 eV and 1.9 eV in the vicinity of hydroxyl or bridge O, respectively. Our results suggest that the oxidation will greatly affect the transport properties of GNRs. This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

9:00am **SP+AS+MI+NS+SS-TuM-4 Molecular Chessboard Assemblies Sorted by Site-Specific Interactions of Out-of-Plane d-Orbitals with a Semi-metal Template**, *T Jung*, Paul Scherrer Institut (PSI), Switzerland; *A Wackerlin, S Fatayer, T Nijs, S Nowakowska, S Mousavi, O Popova, Aisha Ahsan*, University of Basel, Switzerland; *C Wackerlin*, Paul Scherrer Institut (PSI), Switzerland

We present a conceptually new approach for the formation of 2D chessboard patterns of molecules which is, unlike the other approaches, not dependent on the molecules being functionalized for self-assembly. The deposited Phthalocyanines (Pcs) are sorted in alternating sequence into the 2D layer by their site-specific interaction with the native reconstruction of the bismuth thin-film. The square p -(10×10) layer of bismuth on Cu(100) is characterized by the periodic arrangement of shallow pockets which are separated by rims and nodes which originate from the limited registry between Bi and Cu(100). The symmetry and the pitch of 1.8 nm of the Bi/Cu(100) substrate matches with the 4-fold symmetry of the Pc molecules and the pitch of a Pc chessboard arrangement.

We attribute the sorting mechanism to the site-specific interactions between the Bi layer and the out-of-plane 3d states of Mn- and CoPc

leading to preferred adsorption sites. The 3d states also allow for the identification of the molecular components in the STM data: Mn and CoPc exhibit a bright contrast on the central metal atom, while Cu in CuPc in absence of such a d-state close to E_f is depicted as a depression.

Due to this characteristic difference in the 3d states, MnPc + CuPc and CoPc + CuPc sort into chessboard arrays. In these arrays, the molecules with out-of-plane 3d states (CoPc and MnPc) adsorb on the Bi-nodes and the one without (CuPc) adsorbs on the Bi-pores. If both molecules have out-of-plane 3d states around the Fermi level (CoPc + MnPc mixture), the selectivity of adsorption is insufficient and no chessboard layer is formed.

References:

[1] A. Wackerlin, *et al.*, Nano Letters 17, 1956 (2017)

11:20am **SP+AS+MI+NS+SS-TuM-11 Nanoscale Chemical Analysis with Photo-induced Force Microscopy**, *Sung Park*, Molecular Vista, Inc.

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. Due to the steep dipole-dipole force dependence on the tip-sample gap distance, PiFM spectral images have spatial resolution approaching the topographic resolution of AFM, demonstrating 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 organic, inorganic, and low dimensional materials. 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.

11:40am **SP+AS+MI+NS+SS-TuM-12 STM Studies of the Molecule-2D Heterointerface**, *Andrew Wee*, National University of Singapore, Singapore; *Y Huang*, Institute of Materials Research & Engineering, Singapore; *Y Zheng, Z Song*, National University of Singapore, Singapore; *S Quek*, Department of Physics, National University of Singapore, Singapore

INVITED

We have previously shown that the electronic and chemical properties of graphene can be controllably tuned via molecular functionalization [1]. In this talk, I will focus on our recent work on semiconducting 2D transition metal dichalcogenides (TMDs) with tunable direct bandgaps dependent on the number of atomic layers. We use high resolution scanning tunneling microscopy/spectroscopy (STM/STS) to study the atomic structure, intrinsic electronic properties, and grain boundaries of MoS₂ and WSe₂ layers on HOPG substrates [2,3]. Using PTCDA as a prototype semiconductor organic molecule, we show that a monolayer TMD can effectively screen an organic-inorganic heterointerface [4]. We have also studied how a C₆₀F₄₈ molecular acceptor layer on top of a single-layer WSe₂ acts as p-type dopant, and reveal the electronic structure at a prototypical 1D interface between intrinsic and p-doped WSe₂ [5].

[1] H.Y. Mao, Y.H. Lu, J.D. Lin, S. Zhong, A.T.S. Wee, W. Chen, Progress in Surface Science 88 (2013) 132.

Y.L. Huang, Y.F. Chen, W.J. Zhang, S.Y. Quek, C.H. Chen, L.J. Li, W.T. Hsu, W.H. Chang, Y.J. Zheng, W. Chen, A.T.S. Wee, Nature Comm. 6 (2015) 6298.

[2] Y.L. Huang, Z. Ding, W. Zhang, Y.H. Chang, Y. Shi, L.J. Li, Z. Song, Y.J. Zheng, D. Chi, S.Y. Quek, A.T.S. Wee, Nano Letters 16 (2016) 3682.

[3] Y.J. Zheng, Y.L. Huang, Y.F. Chen, W.J. Zhao, G. Eda, C.D. Spataru, W.J. Zhang, Y.-H. Chang, L.J. Li, D.Z. Chi, S.Y. Quek, A.T.S. Wee, ACS Nano 10 (2016) 2476.

[4] Z.B. Song et al., submitted.

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