Nanometer-scale Science and Technology Division
Room A222 - Session NS+2D+AS-WeA

Probing and Modifying Surface and Interfacial Chemistry at the Nanoscale

Moderators: Phillip First, Georgia Institute of Technology, Adina Lucian-Mayer, University of Ottawa, Canada

2:20pm **NS+2D+AS-WeA-1 Bitumen's Microstructures are Correlated with its Bulk Thermal and Rheological Properties***, X Yu,* Worcester Polytechnic Institute*; S Granados-Focil,* Clark University*; M Tao,* ***Nancy Burnham,*** Worcester Polytechnic Institute

Understanding of how the chemistry of asphalt binders (i.e., bitumens) affects their bulk properties is critical for development of structure-related mechanical models and performance-based specifications for asphalt binders, including mitigation of potholes and improved recycling of this non-renewable material. However, establishing the chemical-mechanical relationships that govern asphalt binders' properties remains a challenge due to binders' complex chemical makeup [1] and the intriguing dynamic molecular interactions among binders' various chemical constituents. [2] Here, we investigate the effect of chemical composition on binders' microstructure and thermal and rheological behavior. Two virgin binders from different crude oil origins were chosen and a series of derivative binders was made by remixing different weight ratios of the asphaltenes and the maltenes obtained from the two source binders. Thermal and rheological properties of all binders were measured using modulated differential scanning calorimetry and dynamic shear rheometry, respectively. Binders' microscopic characteristics (e.g., nano- and micro-structures and their contrast in phase images) were evaluated using atomic force microscopy. In bitumens with more miscibility between the asphaltenes and maltenes, the samples appear to undergo a sol-gel transition as the asphaltene concentration increases above 25%. In less miscible bitumens, micro-scale phase segregation is readily apparent at the surface. Our results show that bitumens' characteristic microstructures, as a result of the complex molecular interactions among their various chemical components, are correlated with their bulk thermal and mechanical properties. Notably, the asphaltene/maltene ratio alone cannot predict a bitumen's bulk properties. Instead, a bitumen's distinctive microstructures and its colloidal miscibility index provide meaningful insights into the effect of chemical composition on glass transition, phase stability, and rheological properties of the bitumen, which may in turn help improve the sustainability and design of roads. [3]

1. X. Yu et al., Adv. Colloid Interface Sci. 218, 17-33 (2015).

2. X. Yu et al., Energy & Fuels 32, 67-80 (2018).

3. X. Yu et al., submitted

2:40pm **NS+2D+AS-WeA-2 Energetics and Statistical Mechanical Analysis of Complexation on Metal Surfaces***, J Lee, J Evans, T Windus, P Thiel,* ***Da-Jiang Liu,*** Ames Laboratory and Iowa State University

Stabilities of metal-ligand complexes on surfaces are crucial for the process of self assembly of 2D structures. We provide a comprehensive theoretical assessment at the level of Density Functional Theory (DFT) of the stability of various coinage metal-sulfur complexes, M_mS_n, with M=Cu, Ag, and Au, both in the gas-phase and also for these complexes adsorbed on the (111) and (100) surfaces of the same coinage metal. An early influential theoretical study on S/Cu(111) proposed that the Cu-$_3$S$_3$ complex being the most stable copper containing species. Later combined low temperature STM and DFT studies suggest that a heart-shaped Cu_2S_3 and its concatenations being more stable. Larger and even more complex Ag-S complexes have being observed for S/Ag(111). No complexation have been observed for S/Cu(100) and S/Ag(100). On the other hand, a Au_4S_5 complex and its fragmentations have being observed for S/Au(100), but no complexation is observed for S/Au(111) at low S coverage. We select a set of nine types of complexes, chosen for their proposed existences, intrinsic stabilities, and affinities for adsorption on metal surfaces. For the adsorbed species, we calculate various aspects of their energetics including their formation energy from sulfur adsorbed on terraces and from metal atoms that are in thermal equilibrium with the substrate. From this perspective, our DFT analysis shows that Ag_2S_3, Ag_3S_3 and many larger complexes on Ag(111) are strongly stable, Cu-$_2$S$_3$ is stable and some larger complexes are marginally stable on Cu(111), but only Au-$_4$S$_4$ on Au(111) is stable. In contrast, no complex is stable on Cu(100) and Ag(100), but a group of complex is stable on Au(100), with Au_4S_5. DFT results are consistent with experiments with the apparent exception of Au(111). This comprehensive assessment of energetics provides key input for statistical mechanical analysis of S adlayer ordering in the absence of complexation, and of the kinetics of complex formation and associated enhanced mass transport and surface dynamics.

3:00pm **NS+2D+AS-WeA-3 Adding the Chemical Dimension to Lithography at All Scales: Enabling Cellular Therapies & Other Adventures in Biology and Medicine***,* ***Paul S. Weiss***[1]*,* University of California, Los Angeles **INVITED**

By controlling the exposed chemical functionality of materials from the submolecular through the centimeter scales, we have enabled new capabilities in biology, medicine, and other areas. I will discuss current and upcoming advances and will pose the challenges that lie ahead in creating, developing, and applying new tools using these capabilities. These advances include using biomolecular recognition in sensor arrays to probe dynamic chemistry in the brain and microbiome systems. In other areas, we introduce biomolecular payloads into cells for gene editing at high throughput for off-the-shelf solutions targeting hemoglobinopathies, immune diseases, and cancers. These methods use specific chemical functionalization and control of surface contact and adhesion in microfluidic channels.

4:20pm **NS+2D+AS-WeA-7 STM Directed Synthesis of Armchair Graphene Nanoribbons and Their Oxidation***, C Ma,* Oak Ridge National Laboratory*; Z Xiao,* North Carolina State University*; A Puretzky,* ***Arthur Baddorf,*** Oak Ridge National Laboratory*; W Lu,* North Carolina State University*; K Hong,* Oak Ridge National Laboratory*; J Bernholc,* North Carolina State University*; A Li,* Oak Ridge National Laboratory

Highly controlled synthesis of graphene nanoribbons (GNRs) can be performed on a surface by polymerization of a selected precursor. Typically, this polymerization involves surface-assisted cyclodehydrogenations during thermal activation on catalytic metal surfaces. We have shown that armchair edge GNRs can be synthesized with 7, 14, and 21 carbon atom widths by absorbing 10,10'-dibromo-9,9'-bianthryl (DBBA) precursor molecules on Au(111).[1] Synthesis follows a two-step process of which the first step is polymerization at 470 K. The second step, cyclodehydrogenation, can be promoted globally by annealing to 670 K, or locally following hole injection using a scanning tunneling microscope (STM) tip.[2] Wider 14 or 21-aGNRs were formed when two or three 7-wide GNRs were conjugated side-by-side via inter-ribbon cyclodehydrogenation at the edge sites. Scanning Tunneling Spectroscopy (STS) reveals an electronic band gap dependent on the ribbon width. Bandgaps of ~2.6, ~0.3, and ~0.7 eV are measured for 7, 14, and 21 GNRs respectively, consistent with expectations of simple models.

For practical applications, understanding the stability of GNRs to oxidation is important. We have examined the thermal stability of 7-aGNRs after exposure to air.[2] Combining STM, Raman spectroscopy, x-ray photoemission spectroscopy, and first-principles theory calculations, the armchair GNRs are found to oxidize first at the zigzag ends while the edges remain stable. Oxygen attaches to the zigzag ends at temperatures as low as 180°C. Armchair edges are stable up to 430°C and become oxidized only above 520°C. Two oxygen species are identified, one a hydroxyl (OH) and the second atomic oxygen bridging two carbons, both of which are common in oxidized graphitic lattices. The bandgap is significantly reduced from 2.6 eV to 2.3 eV in the vicinity of the hydroxyl and to 1.9 eV near bridging O. These results suggest that the oxidization will significantly affect the transport properties of GNRs and provide parameters useful for maintaining integrity of GNRs during processing for devices.

This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

1. C. Ma, et al., *Nano Letters* 17, 6241 (2017).

2. C. Ma, et al., *Nature Communications* 8, 14815 (2017).

3. C. Ma, et al., *Physical Review Materials* 2, 014006 (2018).

4:40pm **NS+2D+AS-WeA-8 Carbon-based Two-dimensional Materials from Surface-catalyzed Reactions of Small Molecules***, M Wolf, C Gerber,* ***Rebecca Quardokus,*** University of Connecticut

Aryl halides undergo an Ullmann-like coupling reaction on surfaces to yield a carbon-based two-dimensional material. 1,2-dibromobenzene couples to Au(111) lifting the gold herringbone reconstruction. The reaction intermediates and coupled gold atoms are mobile on the surface at 4 K. The FCC and HCP sections of the underlying gold substrate shift to new positions. Annealing the dibromobenzene on Au(111) decouples the

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[1] **NSTD Recognition Award**

intermediates from the gold. The gold herringbone reconstruction returns and a covalently-bonded carbon-based network forms on the Au(111) surface.

5:00pm **NS+2D+AS-WeA-9 Bottom-up Fabrication of 2D Molecular Networks via On-surface Reactions***, **Sabine Maier,*** University of Erlangen-Nürnberg, Germany **INVITED**

On-surface synthesis has attracted significant attention in recent years due to its potential to fabricate novel low-dimensional nanomaterials with atomic precision. In order to understand and control the synthesis of high-quality low-dimensional nanostructures, many efforts have been made to steer the reaction pathway by the design of smart precursors and by applying templating effects from the substrate. One of the challenges is the fabrication of long-range ordered two-dimensional covalently-linked networks via on-surface reactions. In contrast to molecular self-assemblies that are constructed by non-covalent bonds, the irreversible nature of the covalent bonds limits the structural control, which results in small domains and defects.

In my presentation, I will focus on recent high-resolution scanning probe microscopy experiments in combination with density-functional theory about the bottom-up fabrication and electronic properties of atomically precise one- and two-dimensional molecular nanostructures on metals.[1-4] Thereby, the effect of the flexibility, the symmetry, and chirality of the precursor molecules on the structure formation of covalently-linked molecular structures will be discussed. In particular, I will outline how well-ordered nanoporous 1D and 2D covalent molecular structures can be fabricated by use of debromination coupling reactions. We demonstrate the narrowing of the electronic band gap by increasing the π-system in covalently-linked structures and also show delocalized electronic states in surface-supported organometallic networks. Finally, I will conclude with a comparison of the structure formation of molecular nanostructures on bulk insulators and metal surfaces.

[1] C. Steiner et al. *Nature Communications***, 2017**, 8, 14765.

[2] M. Ammon, T. Sander, S. Maier, *J. Am. Chem. Soc.*, **2017** 139 (37), 12976–12984.

[3] Z. Yang et al. *Nanoscale*, **2018**, 10, 3769-3776.

[4] X. Zhang et al., ACS Nano, **2019**, 13 (2), 1385–1393.

5:40pm **NS+2D+AS-WeA-11 Determining the Jahn-Teller Stabilization Energy of Surface Vacancies on Si(111)-√3 x √3:B***, **Daejin Eom,*** Korea Research Institute of Standards and Science, Republic of Korea*; C Moon,* Korea Research Institute of Standards and Science*; J Koo,* Korea Research Institute of Standards and Science, Republic of Korea

The vacancy defect on the Si surface becomes increasingly important with the device scaling because it works as the charge trapping and scattering center with varying ionization states. Yet its characteristics have not been addressed as comprehensively as the bulk vacancy in Si. In fact, its behavior would be affected by the gap state evolution and the Fermi level pinning on the Si surface. On the other hand, the (111)-surfaces of Si come to have the √3 x √3 reconstruction instead of the 7 x 7 one when they are heavily B-doped [1,2]. This √3 x √3 surface does not evolve any energy state within the band gap, being contrary to the 7 x 7 one [2]. Also, the Fermi level is shifted to the valence band maximum on the √3 x √3 surface whereas it is pinned in the middle of the gap on the 7 x 7 surface [2]. Hence the vacancy defects on the two surfaces may have dissimilar characteristics from each other. Here, we generate the vacancy defects on the √3 x √3 surface via the atom manipulation technique and measure their structural and electronic properties by using the scanning tunneling microscopy and spectroscopy. We find that, unlike the 7 x 7 surface, the vacancy defects on the √3 x √3 surface are Jahn-Teller distorted in the ground state, but undergo the symmetry-restoring transition when gated by the external bias. We also determine the energy gain or stabilization energy of the Jahn-Teller transition quantitatively. These findings would extend our knowledge on the surface vacancies on Si and eventually contribute to the fabrication of better-performing nanometer-scale devices.

[1] I.-W. Lyo, E. Kaxiras, and Ph. Avouris, Phys. Rev. Lett. **63**, 1261 (1989).

[2] D. Eom, C.-Y. Moon, and J.-Y. Koo, Nano Lett. **15**, 398 (2015).

6:00pm **NS+2D+AS-WeA-12 Influence of the Substrate on Self-Assembly: Terphenyl Monolayers investigated by NC-AFM and FM-KPFM***, **Niklas Biere**[1]**,*** Experimental Biophysics & Applied Nanoscience, University of Bielefeld, Germany*; S Koch, P Stohmann, Y Yang, A Gölzhäuser,* Physics of Supramolecular Systems and Surfaces, University of Bielefeld, Germany*; D Anselmetti,* Experimental Biophysics & Applied Nanoscience, University of Bielefeld, Germany

Carbon Nano Membranes (CNM) are mechanical stable and homogeneous quasi-2D systems, which are formed by electron radiation induced, cross-linked self-assembled monolayers (SAM). Contrary to graphene, the CNM structural and functional properties can be tailored by the selection of precursors for the SAM formation [1]. CNMs show the capability to act as a molecular sieve to filter e.g. water molecules from impurities with extraordinary efficiency [2]. While this result promises remarkable applications, the actual process of CNM formation as well as their structure and the mechanism for water permeation is still in the focus of our investigations. Furthermore, the choice of substrate influences the self-assembly of our precursor molecules more than previously expected, even with isoelectronic surfaces like gold and silver. In this work, we will present data acquired by noncontact-AFM combined with FM-KPFM under ultra-high vacuum conditions to investigate and compare the morphology of in-situ prepared SAMs and CNMs of terphenylthiols on Au(111) and Ag(111).

[1] A. Turchanin, A. Gölzhäuser, Adv. Mater. 28 (2016) 6075-6103.

[2] Y. Yang et al., ACS Nano 12 (2018) 4695-4701.

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[1] **NSTD Graduate Student Award Finalist**

Author Index

Bold page numbers indicate presenter