

Monday Afternoon, October 31, 2011

Surface Science Division
Room: 110 - Session SS2-MoA

Molecular Ordering and Electrochemical Interfaces

Moderator: S.L. Tait, Indiana University

2:00pm **SS2-MoA1 Self-assembled Chains of 4,4'-azopyridine on Cu(100) Stabilized by Metal-Organic Coordination Interactions.** *H. Lim, S.L. Tait*, Indiana University

Understanding self-assembled molecular architectures at surfaces is essential to control and tune low-dimensional nanometer-scale organic structures. 4,4'-azopyridine (APY) has been vapor deposited on the clean Cu(100) surface in ultra-high vacuum and investigated using scanning tunneling microscopy and X-ray photoelectron spectroscopy. APY is chosen as a model building block for metal-organic frameworks, and for its conformational switching by the photoactive azo bridge. At low coverage, APY self-assembles into highly-ordered one-dimensional chains oriented along the low symmetry directions of the surface, many of which grow from the Cu step edges and some of which form tee junctions with other chains. Careful analysis of high resolution STM images points to pyridyl-Cu interactions being responsible for the high chain stability at room temperature. The related molecule, azobenzene, forms 1D chains on Au(111), but these grow side-to-side by hydrogen bonding at the azo bridge nitrogens and are only observed at cryogenic temperatures [1]. At higher coverages, APY chains align in a parallel fashion to form 2D islands, which increase in size with annealing.

[1] A. Kirakosian, M. J. Comstock, J. Cho, M. F. Crommie, *Phys. Rev. B* **71**, 113409 (2005).

2:20pm **SS2-MoA2 Molecular Self-assembly of Terephthalic Acid and Sodium Chloride on the Cu(100) Surface.** *D. Skomski, S. Abb, S.L. Tait*, Indiana University

To expand the catalogue of available interactions for the efficient self-assembly of highly-ordered nanoscale structures, we have investigated the formation of new supramolecular networks of terephthalic acid (TPA) and sodium chloride (NaCl) on the copper (100) surface. The mixture of this organic species with salt is prepared by vapor deposition in an ultra-high vacuum system and represents a model system for ionic self-assembly in two-dimensions. Several structures have been observed by means of scanning tunneling microscopy molecular resolution imaging. Chemical shifts in the sodium 1s photoelectron peak have been observed by X-ray photoelectron spectroscopy upon addition of TPA to the surface, confirming a direct interaction. Our research indicates that TPA and sodium produce new structures due to favorable ionic interactions between sodium cations and the negatively charged carboxylate groups in TPA's deprotonated form. Interactions with the metal surface and organic molecules appear to be sufficient to break the ionic bonds of the NaCl lattice. The formation of new TPA-Na structures illustrates the interplay between adsorbate-substrate and ionic interactions and opens new possibilities for ionic self-assemblies at surfaces with highly ordered structure and specific chemical function.

2:40pm **SS2-MoA3 Characterization of Azulene-Based Self-Assembled Monolayer Films.** *C.L. Berrie, M. Barybin, B. Neal, A. Dela Rosa*, University of Kansas

Azulene has been predicted to have attractive electronic properties for potential use in molecular electronics applications. However, examples of self-assembled monolayers (SAM) of azulene-based molecules are rare. Characterization of a variety of azulene based SAM films has been carried out using ellipsometry, contact angle, FTIR, and AFM. The role of the functional linker group on the structural properties of the film as well as the electronic properties has been investigated. In addition, the interactions with gold surfaces of azulene-based molecules with different functional groups has been studied. Specifically, the competition between isocyanozulenes and mercaptoazulenes for binding at the Au(111) surface has been examined.

3:00pm **SS2-MoA4 Formation of Closed Shell Quantum Dots as a Driving Force for Molecular Ordering.** *L. Bartels, J. Wyrick, Z. Cheng, D. Sun, D. Kim*, University of California, Riverside, *T.L. Einstein*, University of Maryland

Anthraquinone self-assembles on Cu(111) into a giant honeycomb network with exactly three molecules on each side. Here we propose that the exceptional degree of order achieved in this system can be explained as a consequence of the confinement of substrate electrons in the pores, with the

pore size tailored so that the confined electrons can adopt a noble-gas-like two-dimensional quasi-atom configuration with two filled shells. Formation of identical pores in a related adsorption system (at different overall periodicity due to the different molecule size) corroborates this concept. A combination of photoemission spectroscopy with density functional theory computations (including van der Waals interactions) of adsorbate-substrate interactions allows quantum mechanical modeling of the spectra of the resultant quasi atoms and their energetics.

The resultant pores have about 4 nm in diameter. In this study we explore how the behavior of adsorbates inside them differs from that on extended terraces. CO molecules and adlayers exhibit properties under such nanoscale confinement that markedly depart from those of extended adlayers: a) the confinement stabilizes dislocation lines (anti-phase domain boundaries) in the adlayer that affect roughly 1/4 of the adsorbed molecules; b) confinement prevents the formation of dense islands of adsorbed molecules, depending on coverage either causing dispersion of vacancies in the adlayer or preventing the growth of molecular islands; c) at a coverage of just a few molecules on the facet, we observe that a molecular shell structure is formed, resembling in its underlying mathematics the atomic model. Confined structures are an ideal test bed for measurement of the coverage dependence of molecular diffusion and in this study we find a reduction of the diffusion barrier at a slope of 57%/ML.

3:40pm **SS2-MoA6 Redox Activity and Structural Transitions at Electrochemical Interfaces.** *K.R. Wandelt*, University of Bonn, Germany
INVITED

Ordered layers of organic molecules play an increasing role in modern material science. Their electrochemical deposition from solution has several important advantages: i) Thermally unstable organic molecules which are not intact volatile may be deposited under mild conditions, ii) unlike vacuum deposition electrochemical adsorption may be performed near equilibrium, and iii) the electrochemical potential is an extra parameter which enables a controlled switching of the redox-state of the adsorbed molecules and, thereby, structural transitions of the layers. This lecture concentrates on the correlation between redox-activity and structural properties of viologen and porphyrin layers at metal – electrolyte interfaces. The selfassembly of the molecules is studied as a function of i) the nature and symmetry of the substrate (Cu(111), Cu(100), Au(111) and Cu/Au(111)), ii) the nature of the accompanying counter ions (Cl, Br, I, SO₄), iii) the concentration of the solution, and, most importantly, iv) the potential dependent redox state of the adsorbed molecules, by using in-situ ElectroChemical Scanning Tunneling Microscopy (EC-STM), in-situ Infrared Reflection Absorption Spectroscopy (IRRAS) as well as ex-situ Synchrotron X-ray Photoelectron Spectroscopy (SXPS) after air- and contamination-free transfer from the solution into the UHV analysis chamber. The lecture not only provides a deep insight into the properties of the investigated model systems but also demonstrates the status of modern electrochemical surface science.

4:20pm **SS2-MoA8 Influence of Solvent on the Chiral Resolution of Organic Molecules on Au(111): EC-STM Study of Biphenyl Dicarboxylic Acid on Au (111) in an Aqueous Environment.** *B.I. Kim, J.A. Hanson, M.W. Turner, L.J. Reeder*, Boise State University

Adsorption induced chiral resolution of organic molecules is important due to its potential applications in stereo-selective catalysis. We studied the adsorption induced chiral resolution using a model achiral molecule of 4,4'-biphenyl dicarboxylic acid (BPDA) on Au (111) in 0.1 M perchloric acid (HClO₄) by scanning tunneling microscopy (STM). The BPDA molecules are known to have chiral resolution on Au(111) in an ultrahigh vacuum (UHV). However, our experimental data show that the molecules form island structures with distinctive preferred orientations at the length scale of the molecular size, whereas they have no orientation order at the length scale bigger than the molecular size. We calculated angle dependent binding energy between the substrate and a BPDA molecule, the intermolecular interactions between the BPDA molecules and their interactions with water molecules. The calculation suggests that the absence of chiral resolution in the aqueous environment may originate from the increase of effective rotation energy barrier of the BPDA molecules due to its hydrogen bonding with the surrounding water molecules. The strength hydrogen binding between BPDA molecules is sufficient to overcome the energy barrier for chiral resolution through rotational motion in UHV, but not in an aqueous environment.

4:40pm **SS2-MoA9 Surface and Interface Forces between Dissimilar Surfaces in Aqueous Solution: The Effect of Electrochemical Surface Potentials, Surface Roughness and Hydration Layers**, *M. Valtiner, K. Kristiansen, G.W. Greene, J.N. Israelachvili*, University of California, Santa Barbara

With the rapid progress in the design and fabrication of micro- and nanometer-scaled devices at smaller and smaller length scales, a fundamental understanding of, and the ability to control the interfacial interactions between materials across ultra small distances plays a critical role in advancing these technologies. The ability to 'tune' the forces in various device components remains a critical hurdle to optimizing device performance and reliability of, for example nanofluidic and lab-on-a-chip systems, aqueous-based MEMS, sensor devices; as well as devices where adhesion and adsorption can be controlled, surface contacts and wetting properties tuned, and single molecules and bi-layer interactions manipulated. Surface morphology (including roughness) and electrostatic potential-dependent interaction forces significantly affect the physical and mechanical properties of surfaces and play a critical role in all of these systems.

We present novel setups for both an improved electrochemical AFM [1] and a newly developed electrochemical surface force apparatus [2], and compare the two techniques. We describe the results of the first surface force measurements under electrochemical potential control between a metal and a ceramic surface across a liquid medium (water). Our experiments also reveal how increasing levels of surface roughness and dissimilarity in the surface potentials of the interacting surfaces influence the strength and range of electric double layer, van der Waals, hydration, and steric forces, and how these contribute to deviations from DLVO theory, particularly at distances less than two Debye lengths, or 2-3 times the rms roughness, whichever is greater.

[1] Markus Valtiner, G. Anka, A. Bashir and F. Renner, *Rev. Sci. Instrum.* **82**, 023703 (2011)

[2] Markus Valtiner, Kai Kristiansen, George W. Greene, Jacob N. Israelachvili, *Advanced Materials*, DOI: 10.1002/adma.201003709 (2011)

5:00pm **SS2-MoA10 Diffusion of Single Water and Hydrogen Sulfide Molecules on Ag(111): A DFT Study**, *D.-J. Liu*, Ames Laboratory - US DOE

Diffusion of water (H₂O) and hydrogen sulfide (H₂S) on metal surfaces can be more complicated than single atom diffusion, even for simple hopping mechanism. Additional degree of freedom, such as rotation and tilting of the molecule, must be considered. Due to the asymmetry of the molecule, and therefore the potential energy surface, the saddle points generally deviate from any high symmetry adsorption site. We carry out a systematic study based on the density-functional theory for diffusion of H₂O and H₂S on Ag(111). For both molecules, the most stable configuration for adsorption is nearly flat and on top of a Ag atom. As it approaches the bridge site, the molecule can tilt, and in the case of H₂S, also rotate, to lower its energy. We also find that in this case, zero point vibrations contribute significantly to diffusion of the molecule.

5:20pm **SS2-MoA11 The Structure of Methylthiolate and Ethylthiolate Monolayers on Au(111): Absence of the ($\sqrt{3}\times\sqrt{3}$)R30° Phase**, *L. Tang*, University of Birmingham, UK, *F. Li*, University of Birmingham, UK & Northwestern Polytechnical Univ., P.R. China, *W. Zhou*, Northwestern Polytechnical Univ., P.R. China, *Q. Guo*, University of Birmingham, UK

Surface structures of self-assembled methylthiolate and ethylthiolate monolayers on Au(111) have been imaged with STM. For saturation coverage at room temperature, the well-known ($\sqrt{3}\times\sqrt{3}$)R30° phase routinely observed for longer chain alkanethiolates does not appear under any conditions for adsorbed methylthiolate and ethylthiolate. Instead, both thiolate species organize themselves into a well-ordered 3×4 structure with a coverage equal to 0.33 ML. We thus conclude that the stable structure for saturation coverage of methylthiolate/ethylthiolate on Au(111) at RT is 3×4, not ($\sqrt{3}\times\sqrt{3}$)R30° as generally believed.

We performed experiments by imaging methylthiolate and ethylthiolate monolayers in ultra-high-vacuum (UHV) using high-resolution STM. The methylthiolate monolayer was prepared by exposing a gold single crystal in vacuum to 10⁻⁸ mbar of dimethyl disulfide (DMDS) vapour at RT for 15 minutes. It is known that DMDS adsorb dissociatively on Au(111) at RT by forming methylthiolate. Ethylthiolate monolayer was prepared by exposing a (111) oriented gold film to 5×10⁻⁵ mbar of ethanethiol vapor at room RT for 2 hours. The much higher exposure required for ethanethiol is due to the very low dissociation probability of this molecule.

When the 3×4 phase is subjected to a gentle thermal annealing to 320 K, partial desorption takes place and a striped phase with coverage equal to 0.27 ML appears. The striped phase for ethylthiolate resembles that observed for propylthiolate and other long chain thiolates, but the striped

phase for the methylthiolate takes a unique structure of its own. Our findings suggest that the general belief that all alkanethiols form at least one common structural phase is not true and new theoretical modeling is urgently required to address the chain-length dependent property of alkanethiol monolayers.

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