

Surface Science

Room: 309 - Session SS+TF-ThM

Organic Layers on Surfaces

Moderator: Edmund Seebauer, University of Illinois at Urbana Champaign

8:00am **SS+TF-ThM1 Orbital Tomography: Imaging the Wavefunctions of Adsorbed Molecules with Angle Resolved Photoemission, Michael Ramsey**, University of Graz **INVITED**

Here it will be shown that the apparently complex angular distribution of valence band photoemission can be simply and quantitatively predicted from a Fourier transform of initial state wavefunctions. This will be demonstrated for a variety of orbitals of the proto-typical pi conjugated molecules pentacene, sexiphenyl and PTCDA on a number of substrate surfaces. For adsorbate monolayers it will be shown how this orbital tomography can be used to determine molecular geometries, unambiguously determine the orbital energy ordering, gain insight into the nature of the surface chemical bond and image the orbitals in real space.

8:40am **SS+TF-ThM3 Chemical Pathways for Surface Functionalization: From Surface-“Stapled” Nanostructures to Layered Materials, Andrew Teplyakov**, University of Delaware

One of the important venues in designing novel interfaces and materials is based on the complementary functionalization of surfaces, modified molecules, and nanostructures, so that combining them would lead to layers and materials with novel chemical and physical properties. This presentation will focus of the molecular-level view of surface functionalization and extending the molecular approach to nanostructures and nanostructured layers with three-dimensional control. Classical organic reactions will be used to first build a nearly perfect layer of chemically functionalized nanoparticles on a flat surface and then the approach will be extended into the third dimension. The work will combine “click chemistry” with chemical functionalization approach and utilize surface analytical techniques including XPS, infrared spectroscopy, microscopic techniques combined with focused ion beam (FIB) sample preparation and will be complemented with the DFT studies. The spectroscopic techniques combined with DFT modeling will support the chemistry of deposition, while the electron microscopy techniques will confirm the growth of layered structures.

9:00am **SS+TF-ThM4 Observation and Trapping of Organic Reaction Intermediates for the Reaction of O(³P) with Oligo(Phenylene Ethynylene) Thiolate Self Assembled Monolayers on Au(111), Wenxin Li, G. Langlois, N.A. Kautz, S.J. Sibener**, The University of Chicago

We have taken steps to develop a methodology for observing and trapping organic reaction intermediates by exposing well-ordered self assembled monolayers (SAM) to supersonic beams of atomic oxygen. The use of a SAM stabilizes highly energetic intermediates formed from bimolecular reactions at the interface due to rapid thermal equilibration with the SAM matrix. In this presentation we will discuss the elucidation of the mechanistic details for the fundamental reaction between O(³P) and alkyne bonds by monitoring chemical and structural changes in an oligo(phenylene ethynylene) SAM reacting with O(³P) under collision conditions having specified initial reaction orientation. Utilizing time-resolved reflection-absorption infrared spectroscopy (RAIRS) and scanning tunneling microscopy (STM) under ultrahigh vacuum conditions, we have directly observed electrophilic addition of O(³P) onto the alkyne moieties, resulting in formation of a ketene intermediate via phenyl migration. Under single-collision conditions in the gas phase the vibrationally-excited ketene intermediate cleaves to release CO. In contrast to this, herein we have directly observed the formation of the condensed-phase stabilized singlet ketene by RAIRS. Moreover, we have also observed that the phenyl ring at the vacuum/film interface significantly cants towards the substrate plane as a result of this reaction. STM images of the SAM taken before and after O(³P) exposure show an expansion of the ordered lattice resulting from formation of the new nonlinear molecular structures within the adsorbed film. This approach of using pre-oriented reactive molecules in ordered self assembled monolayers in combination with angle and velocity selected energetic reagents provides a general approach for probing the geometric constraints associated with the reaction dynamics for a wide range of chemical reactions.

9:40am **SS+TF-ThM6 Relative Stability of S-Au and Se-Au Bonding in Aromatic and Aliphatic Self-Assembled Monolayers – Exchange and Ion Desorption Experiments, Jakub Ossowski, A. Noworolska**, Jagiellonian University, Poland, **S. Schuster**, University of Heidelberg, Germany, **J. Rysz**, Jagiellonian University, Poland, **A. Terfort**, University of Frankfurt, Germany, **M. Zharnikov**, University of Heidelberg, Germany, **P. Cyganik**, Jagiellonian University, Poland

Self-assembled monolayers (SAMs) are considered a model system in many areas on nanotechnology.¹ However, potential use of SAMs strongly depends on stability of their chemical bonding to the substrate. Most of the studies of SAMs have been performed using S-Au bonding.¹ More recently the Se-Au bonding is considered as an interesting alternative. However, as documented by the recent review,² there is still missing information which of these head group provides higher stability binding to the Au(111) substrate and whether or not this relative stability depends on the type of molecular backbone i.e. aliphatic or aromatic. A meaningful comparison of S-Au and Se-Au stability requires that respective molecules not only have the same carbon backbones, but also should form ordered structures with very similar molecular packing. Only under such conditions, not fulfilled by the most of previous studies, the contribution of the molecule-substrate bonding on the film stability can be elucidated. Following this idea, we will present a new data obtained for naphthalene based SAMs bound to the Au(111) substrate via S or Se atoms.³ After presenting detailed microscopic (STM) and spectroscopic (XPS, NEXAFS) characterization of these SAMs, which exhibit very similar well-ordered structure, we will show results of two independent experiments probing the stability of their bond to the Au(111) substrate using an exchange method as well as ion-induced desorption (SIMS). We will compare these results with our previous exchange⁴ and recent ion-desorption experiments⁵ of aliphatic based systems. Irrespective of the type of molecular backbone our results clearly demonstrate much higher stability of the Se-Au bond as compared to the S-Au bond.

References

- [1] C. Love, G. et al. **2005**, *Chem. Rev.*, **105**, 1103.
- [2] L. V. Romashov and V. P. Ananikov, **2013**, *Chem. Eur. J.*, **19**, 17640.
- [3] J. Ossowski, A. Noworolska, S. Schuster, J. Rysz, A. Terfort, M. Zharnikov, P. Cyganik, **2014**, *in preparation*.
- [4] K. Szelagowska-Kunstman, P. Cyganik, B. Schüpbach, A. Terfort, **2010**, *Chem. Phys. Phys. Chem.*, **12**, 4400.
- [5] J. Ossowski, J. Rysz, M. Krawiec, D. Maciazek, Z. Postawa, A. Terfort, P. Cyganik **2014**, *submitted*.

11:00am **SS+TF-ThM10 CuPc:C₆₀ Composite Films: From Sub-Monolayer to Multi-Layer Growth, Taylor Stock, J. Nogami**, University of Toronto, Canada

CuPc:C₆₀ composite films of various compositions and thicknesses grown on the Cu(111) surface have been studied using room temperature scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS). At coverages below two monolayers (ML), phase segregated, ordered films, or well mixed, disordered films can be produced depending on the particular deposition sequence. This compositional variability is achieved by exploiting the differences in the relative strengths of the various molecule-substrate and molecule-molecule interaction forces. In thicker films, the CuPc-C₆₀ intermolecular interaction dominates the growth, and for a range of concentrations these films are found to be well mixed, amorphous and thermally stable. These results provide a rationale for improvements that have been seen for organic light emitting diode (OLED) performance associated with C₆₀ doping of CuPc molecular layers. [1]

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- [1] Y. Y. Yuan, S. Han, D. Grozea, and Z. H. Lu, *Appl. Phys. Lett.* **88**, 093503 (2006).

11:20am **SS+TF-ThM11 2D Co-Crystallization of Organic Ferroelectrics, Axel Enders, D.A. Kunkel, A. Sinitskii**, University of Nebraska-Lincoln, **S. Simpson**, University at Buffalo-SUNY, **J. Hooper**, Jagiellonian University, Poland, **E. Zurek**, University at Buffalo-SUNY

We will present an experimental study on the self-assembly and electronic properties of the organic ferroelectrics, croconic acid (CA), 3-hydroxyphenalenone (3-HPLN), and the related compound rhodizonic acid (RA) on crystalline metal surfaces. Importantly, the bond polarization of the selected organics is highly planar. This provides the foundation for the development of 2D polarization patterns by design, including rather complex ones like the honeycomb pattern recently discovered by our group [1]. What is remarkable about those honeycomb networks of CA, is that the

interaction with the substrate is key to ferroelectric switching barriers. Also the structurally related 3-HPLN forms linear chains on surfaces that are expected to exhibit 2D polarization ordering within the plane of the 2D organic layer. The molecular arrangement can be manipulated through the use of the substrate and growth conditions, and we have also identified a new, chiral phase of hydrogen-bonded trimers of 3-HPLN. This surface-science approach was key to the first reported synthesis of RA crystalline structures [2]. Here we present an overview over the structural phases of select organic ferroelectrics on surfaces and how ordered 2D polarization states can emerge. Importantly, we discovered by co-deposition of CA and 3-HPLN that they form ordered 2D co-crystalline phases. The structure of the resulting networks can be tuned by varying the relative concentration of the organics. Namely, for equal ratios of CA and 3-HPLN two polymorphs are observed, while for 2/1 CA/3-HPLN ratio, only a single structure is found. Transitions from CA rich structures to CA poor structures can be induced through weak annealing, in which the smaller CA desorbs before 3-HPLN. We expect that important ferroelectric properties of organic ferroelectrics, such as their ordering temperature and switching fields, can be manipulated through co-crystallization. We will highlight how surface science studies, specifically STM, can help accelerate co-crystal discovery.

References:

- [1] D. A. Kunkel, et al. Phys. Rev. B **87**, 041402 (2012).
- [2] D. A. Kunkel, et al. J. Phys. Chem. Lett. **4**, 3413 (2013).

11:40am **SS+TF-ThM12 Phenol Adsorption on TiO₂(110): Evidence for Temperature Dependent Radical Formation**, *Matthew Patterson, M.F. DiTusa, C.A. Thibodeaux*, Louisiana State University, *R.W. Hall*, Dominican University of California, *O. Kizilkaya, R.L. Kurtz, E.D. Poliakoff, P.T. Sprunger*, Louisiana State University

We have examined the electronic structure of phenol on rutile TiO₂(110) using angle resolved photoelectron spectroscopy (ARPES), electron energy loss spectroscopy (EELS), and density functional calculations on model phenoxy/TiO₂ clusters. Previous electron paramagnetic resonance studies have shown that exposure of titania powder to phenol at 250°C results in the formation of environmentally persistent free radicals (EPFRs), which have lifetimes on the order of dozens of hours and have been shown to exacerbate negative health effects caused by particulate matter. The proposed chemisorption model of radical formation from aromatic species on metal oxides involves electron transfer from the adsorbed organic to the metal oxide, locally reducing the oxide. Resonant ARPES shows direct evidence of charge transfer from high-temperature adsorbed phenol to electronic states of TiO₂ (110) usually associated with the accumulation of charge at surface oxygen vacancies, providing direct evidence of the hypothesized reduction mechanism. Electronic EELS reveals there is an associated decrease of phenol HOMO-LUMO gap. Electronic structure calculations using model phenoxy-TiO₂ clusters give insight into the changes induced in the occupied molecular orbitals of the chemisorbed phenoxyl radical. Results will be discussed in light of other metal oxide systems

12:00pm **SS+TF-ThM13 Adsorption behavior of Zinc Tetrphenylporphyrin Molecules on a Au(111) Surface**, *Charles Ruggieri, S. Rangan, R.A. Bartynski, E. Galoppini*, Rutgers, the State University of New Jersey

The interaction between Zinc Tetrphenylporphyrin (ZnTPP) molecules and the Au(111) surface is investigated using scanning tunnel microscopy (STM), from initial adsorption sites to monolayer organization, with a particular emphasis on its relation to the surface atomic structure and reorganization. When adsorbed at room temperature, ZnTPP molecules initially decorate step edges at low coverage. As the coverage approaches 0.5 monolayer (ML), ZnTPP molecules self-organize into islands of molecules in a rectangular array that is in registry with the underlying Au(111) lattice. The molecules are oriented with their macrocycles parallel to the surface, and form islands in areas delimited by herringbone reconstruction domain walls. As the coverage approaches one ML, the adsorption geometry of the self-organized molecular layer can be fully characterized with respect to the atomic structure of Au(111) surface atoms. Moreover, ZnTPP adsorption alters the Au(111) herringbone reconstruction domain size, most likely caused by anisotropic adsorbate-induced surface stress. However, when a monolayer is prepared from desorption of a ZnTPP multilayer, a different molecular organization is observed at the surface. It is proposed that this reconstruction is enabled by the particular reconstruction of the Au(111) surface. In this configuration, the domain size of the Au reconstruction is closer to that of clean Au, due to smaller adsorbate-induced surface stress.

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