

Monday Morning, October 22, 2018

Tribology Focus Topic

Room 201A - Session TR+AS+NS+SS-MoM

Tribology Focus Session

Moderators: Mehmet Z. Baykara, University of California, Merced, Prathima Nalam, University at Buffalo - SUNY

8:20am **TR+AS+NS+SS-MoM1 Structural Superlubricity: History, Breakthroughs, and Challenges, Mehmet Z. Baykara, University of California, Merced** **INVITED**

The idea of *structural superlubricity* holds immense potential for the realization of nearly frictionless sliding in mechanical systems, with implications for fields as diverse as environmental conservation and space travel. The basic principle of structural superlubricity involves the proposition that friction should diminish at an interface formed by atomically-flat and molecularly-clean crystalline surfaces with different lattice parameters and/or incommensurate orientation. Despite the rather straightforward character of its basic principle, the realization of structural superlubricity under ambient conditions has been challenging due to the requirement of molecular cleanliness at the interface.

In this talk, we will first briefly review three decades of structural superlubricity research by emphasizing important milestones and breakthroughs. Subsequently, we will present results of nano-manipulation experiments from our lab, which demonstrate the remarkable occurrence of structural superlubricity for gold and platinum nano-islands sliding on graphite under ambient conditions. Complementary to the experiments, results of *ab initio* calculations will be discussed, which (i) reveal that the noble metal-graphite interface is expected to remain largely free from contaminant molecules, leading to structurally superlubric sliding under ambient conditions, and (ii) confirm the experimental observation of larger friction forces for platinum, attributable to higher energy barriers encountered during sliding. The experiments additionally demonstrate that the scaling power between friction force and contact size is independent of the chemical identity of the sliding atoms, but is determined by the geometric qualities of the interface. The talk will conclude with a review of remaining challenges for structural superlubricity, in particular those involving size- and deformation-related limits.

9:00am **TR+AS+NS+SS-MoM3 An Examination of the Nature of Bonding during Indentation and Sliding using MD and in-situ Nanoindentation, Judith Harrison, United States Naval Academy** **INVITED**

Adhesion between DLC tips and diamond counterfaces was examined using a nanoindenter coupled to TEM and molecular dynamics (MD). Additional MD simulations of sliding contact between the same tip-substrate materials were also carried out. Strong interactions between the surfaces in vacuum led to gradual nanoscale wear of the DLC. Force-separation curves show an approximate correlation between pull-off force and applied load for various contact points, while pull-in force was fairly constant for all contact points and independent of applied load. MD simulations were designed to replicate experiment as closely as possible and used the AIREBO and the REBO+S potentials. DLC tips with the same general shape (which often deviated from the assumed paraboloidal tip geometry due to wear) were brought into contact with diamond surfaces. MD results demonstrate that pull-off force is correlated with bonds formed during contact, providing an explanation of the trends observed in the TEM data. The effects of contact point and hydrogen-termination on pull-off forces and the nature of bond formation during sliding as a function of speed and hydrogen termination will be presented. The results of similar experiments and MD simulations using Si tips in contact with diamond counterfaces of adhesion and sliding using the ReaxFF potential will also be discussed.

9:40am **TR+AS+NS+SS-MoM5 The Chemistry of Friction, Wear, and Tribofilm Growth on 2D Materials, Jonathan Felts, Texas A&M University** **INVITED**

The evolution of a sliding interface between two objects is difficult to theorize, predict, and measure due to the complexity of the interface, which is often described phenomenologically. Here we utilized a nanometer sized single asperity of an atomic force microscope tip sliding against atomically flat graphene and graphene oxide to study the origins of friction, wear, and tribofilm growth phenomena at the atomic scale. We hypothesize that all of the observed contact phenomena at the macroscale can be described using fundamental thermochemistry. At low applied tip loads, the friction of graphene oxide is non-monotonic with tip velocity, initially increasing for speeds from 100 – 10,000 nm/s, followed by a

decrease and a subsequent increase above 50,000 nm/s. At sufficiently high applied loads, we observe wear of oxygen groups from graphene oxide at temperatures between 50-400 °C and loads between 10-700 nN, and find an exponential increase in wear rate with applied load. For the case of an electrically biased tip oxidizing pristine graphene, the oxidation rate somewhat paradoxically increases with applied load, despite previously observed enhancement in wear rate with load. All of the above observations can be understood in the context of mechanically driven thermochemical reactions. The friction behavior depends on two competing factors—aging of the sliding contact due to chemical bonding between tip and substrate, and hopping of unbonded tip atoms between graphene lattice sites. Atomic wear of graphene oxide is well described by the tilted potential energy surface theory of mechanically driven chemistry, which predicts a non-linear reduction in the energy barrier with applied load. We further show that the tilted potential energy surface model also well describes the enhancement of oxidation rate. The work presented here creates a foundation for describing the mechanics of sliding contacts as chemical processes, and further paves the way towards quantitatively understanding how mechanical force drives chemical reactions in general.

10:40am **TR+AS+NS+SS-MoM8 Nanomechanics of Soft, Hierarchical Polymer- and Biological-Networks, Prathima Nalam, University at Buffalo - SUNY** **INVITED**

Soft networks based on synthetic polymer chains or biological filaments, with architecture that are anisotropic or hierarchical in nature, offer a path towards the development of tough and reliable flexible structures. These structures find applications in numerous areas including healthcare delivery, environmental purification systems, energy storage systems, flexible electronics, and tribology. Further, the ability of these networks to present a wide range of tunable functional properties, through alterations in the chemical structure of the monomers, synthesis or operational conditions, etc., which otherwise is rarely possible with other hard materials, promise the development of smart materials. In this study, we present the nanomechanical and nanotribological behavior of two stimuli-responsive networks consisting of (a) polyelectrolyte films with a thin layer of chitosan (CH) grafted on top of poly (acrylic acid) (PAA) brushes (CH/PAA) and (b) naturally grown mycelium-based networks. The CH/PAA network is a synthetic hierarchical structure, in which each layer exhibits a strong structural change with variation in solution pH. On the other hand, Mycelium is a soft biological network (derived from mushrooms) composed of multicellular or unicellular filaments, known as hyphae, with anisotropic micro-architecture.

A detailed investigation of the depth-dependent elastic moduli on these networks is conducted using atomic force microscope (AFM, Oxford Instruments) to study the impact of local structural heterogeneity of the network on its mechanical properties. A colloid-attached AFM cantilever was employed to study the surface interactions and to indent the material in the linear elastic deformation regime. The study of the impact of the network structure on the material rigidity, measured at both nano- and macro- scales, has enabled to probe the validity of affine network deformation theories for hierarchical networks. With this understanding, the design and development of antibacterial platforms (with CH/PAA platforms) and water-filtration membranes (with mycelium networks) using hierarchical soft structures is discussed.

11:20am **TR+AS+NS+SS-MoM10 Mechanisms for Controlling Friction and New Approaches for Achieving Superlubricity Regime in 2D Materials, Diana Berman, University of North Texas; A. Erdemir, A.V. Sumant, Argonne National Laboratory** **INVITED**

Friction is an important aspect of many areas of everyday life. Varieties in mechanical systems from nano to macroscale and efforts to minimize energy losses intersect with challenges of controlling the friction. The popularity of recently discovered 2D materials and their usefulness for multiple applications enabled understanding the friction at a more fundamental level and opened new routes for manipulating friction to superlubricity or near zero friction values.

Here, we review the basic mechanisms that complies the frictional energy dissipation, such as wear, molecular deformation, thermal effect, electronic effect, bonding, environment and chemistry, phonons, and structural effect. We present the case studies highlighting how these mechanisms are controlled in 2D materials. Finally, we highlight recent advances in implementing 2D materials for friction reduction to superlubricity across scales from nano- up to macroscale contacts. We show that nanoscale superlubricity mechanisms originating from the formation of frictionless nanoscale systems, as in case of graphene-nanodiamond scrolls and carbon

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nanoscale structures, can be successfully transferred to macroscale effects. Development of 2D materials opened a new pathway for manipulating friction, which makes superlubric friction today's reality.

References:

- [1] D. Berman, et al., Approaches for Achieving Superlubricity in Two-Dimensional Materials, ACS Nano (2018)
- [2] D. Berman, et al., special issue in Diamond and Related Materials, 54, 91 (2015).
- [3] D. Berman, et al., Materials Today 17 (2014) 31-42.
- [4] D. Berman, et al., Science, 348 (2015) 1118-1122

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. Puzosky, 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.

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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*¹, *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

¹ NSTD Student Award Finalist

Tuesday Evening Poster Sessions, October 23, 2018

Tribology Focus Topic

Room Hall B - Session TR-TuP

Tribology Focus Topic Poster Session

TR-TuP1 Measurements of Microscale Friction on Molybdenum Disulfide using an Integrated Quartz Crystal Microbalance and Nanoindentation System, *Brian Borovsky, G.R. McAndrews, R.J. Wieser, St. Olaf College*

We report on experiments investigating the microtribological properties of molybdenum disulfide (MoS₂) crystals in the high-speed regime. The sliding speeds obtained are over 1 m/s, corresponding to a practical range for mechanical devices. The contacts formed are approximately 1 μm across or smaller. Measurements are performed with a shear-mode quartz crystal microbalance (QCM) integrated into a nanoindentation system. For each test, a thin MoS₂ crystal is adhered to the surface of a gold-coated QCM sensor and mechanically exfoliated. The resonant frequency and quality factor of the modified QCM undergo shifts when a spherical sapphire probe is loaded onto the top surface, allowing the detection of lateral contact forces. The shearing amplitude of the QCM is swept over its available range, with the load held fixed, to observe the transition from partial slip to full slip conditions. The contact area is inferred from the lateral stiffness at low amplitudes. We discuss the observed trends in the friction vs. load and area vs. load curves, as well as the degree to which the frictional shear strength depends on mean applied pressure. These results are compared to existing work on MoS₂ for contacts ranging from nanometers to millimeters in size, with the aim of contributing to an improved multiscale understanding of tribological phenomena.

TR-TuP2 Sliding Wear Behavior of Tool Steel Functionalized with Organic Monolayers Against Aluminum, *Stephan Prünte, D. Music, RWTH Aachen University, Germany; V.L. Terziyska, C. Mitterer, Montanuniversität Leoben, Austria; J.M. Schneider, RWTH Aachen University, Germany*

Tool steel surfaces were functionalized with methyl-terminated monolayers of phosphonic acids firmly attached by an intermediate metal-oxide adhesion layer. Their sliding behavior against aluminum was investigated with a ball-on-disc tribometer. Our results show a 3-fold reduction of friction and wear for a densely functionalized tool steel with an intermediate Cu–O adhesion layer compared to a non-functionalized sample due to small interactions between Al and the distal methyl moieties of the monolayer. However, functionalized Fe–O adhesion layers on tool steel failed to improve the sliding behavior against Al. This distinct difference may be rationalized by density functional theory calculations. The molecular monolayer attachment to the Cu–O adhesion layer yields 30% higher bond strength compared to one containing Fe–O. Hence it may be speculated that macroscopic sliding wear behavior is determined by the bond strength between the molecular monolayer attachment and the intermediate metal-oxide adhesion layer (on tool steel).

Nanometer-scale Science and Technology Division Room 102B - Session NS+AM+AS+MN+PC+PS+SS+TR-FrM

SPM – Probing Chemical Reactions at the Nanoscale

Moderators: Phillip First, Georgia Institute of Technology, An-Ping Li, Oak Ridge National Laboratory

8:20am **NS+AM+AS+MN+PC+PS+SS+TR-FrM1 Using Self-Assembly to Engineer Electronic Properties in 1D and 2D Molecular Nanostructures, Michael F. Crommie**, University of California at Berkeley Physics Dept.

INVITED

Control of chemical reactions at surfaces has created new opportunities for on-surface synthesis of low-dimensional molecular nanostructures. By designing precursor molecules it is possible to engineer new bottom-up structures with atomic precision and predetermined electronic properties. We have used this technique to confirm recent predictions that quasi-1D graphene nanoribbons (GNRs) have well-defined electronic topology. This means that when “topologically non-trivial” GNRs are fused to “topologically trivial” GNRs then a singly-occupied, topologically-protected interface state occurs at the boundary between them. This has allowed us to engineer new GNRs with unique electronic structure. We have also engineered molecular precursors to control the behavior of 2D polymers. By tuning the coupling reaction between monomers it is possible to create 2D covalent organic frameworks (COFs) that exhibit novel electronic superlattice behavior.

9:00am **NS+AM+AS+MN+PC+PS+SS+TR-FrM3 Chemical and Electronic Structure of Aniline Films on Silica Surfaces, Christopher Goodwin**, University of Delaware; *A.J. Maynes*, Virginia Polytechnic Institute and State University; *Z.E. Voras*, University of Delaware; *S.A. Tenney*, Center for Functional Nanomaterials Brookhaven National Laboratory; *T.P. Beebe*, University of Delaware

The use of silica as a substrate for polyaniline is highly appealing since silica is a common component in photovoltaics. To this end we have developed a vacuum technique for the deposition and functionalization of silica with aniline, without the need for wet chemistry. To study the chemistry of the reaction, X-ray Photoelectron Spectroscopy (XPS), Time-of-Flight Secondary Ion Mass Spectroscopy (TOF-SIMS), and Atomic Force Microscopy (AFM), among other techniques, have been used. To determine the electronic structure of the resulting films, scanning tunneling microscopy and evaluation of valence band data collected by XPS was performed. By controlling the temperature of the gas-phase reaction, two states of aniline were found to exist on the silica surface. Our interest is in determining how the two states affect the electronic band structure of the surface.

9:20am **NS+AM+AS+MN+PC+PS+SS+TR-FrM4 Electric Field Driven Chemical Reaction of Individual Molecular Subunits by Scanning Tunneling Microscopy, Tomasz Michnowicz**, Max Planck Institute for Solid State Research, Germany, Deutschland; *B. Borca*, Max Planck Institute for Solid State Research, Germany; *R. Pétuya*, Donostia International Physics Centre, Spain; *M. Prisl*, *R. Gutzler*, *V. Schendel*, *I. Pentegov*, *U. Kraft*, *H. Klauk*, Max Planck Institute for Solid State Research, Germany; *P. Wahl*, University of St Andrews, UK; *A. Arnau*, Donostia International Physics Centre, Spain; *U. Schlickum*, *K. Kern*, Max Planck Institute for Solid State Research, Germany

Understanding of elementary steps and control in chemical reactions on the atomic scale might improve significantly their efficiency and applicability. Scanning tunneling microscopy (STM) allows both investigating and stimulating chemical reactions of individual organic subunits, for example via the tunneling current, electric field or a mechanical interaction. Here we present a study of an STM stimulated desulfurization process of the thiophene functional group embedded in a tetraceno thiophene (TCT) molecule on a Cu(111) surface. Precise positioning and applying stimuli with the STM tip apex allows determination of a two-step process responsible for this chemical reaction. High resolution STM images, supported by the DFT calculations, help us to correlate the first reaction step to the breaking of one the carbon-sulfur bonds and the second to the breaking of the second carbon-sulfur bond. The latter reaction also results in a significant increase of the bond strength of the broken thiophene part to Cu surface atoms. The chemical reaction is triggered by positioning the tip apex above the thiophene part and applying a threshold voltage that depends linearly on the tip-molecule distance. This linear dependence is a hallmark of an electric field driven process. In addition, conduction measurements through single TCT

molecules before and after the reaction have been performed. Compared to the intact molecule we observed a 50% increase of conductance after the chemical reaction, which is in agreement with the finding of a much stronger bond formation between the molecule and Cu surface atoms.

9:40am **NS+AM+AS+MN+PC+PS+SS+TR-FrM5 Characterising Conjugated Polymers for Organic Electronics by High-resolution Scanning Probe Microscopy, Giovanni Costantini**, University of Warwick, UK

The structure of a conjugated polymer and its solid-state assembly are without a doubt the most important parameters determining its properties and performance in (opto)-electronic devices. A huge amount of research has been dedicated to tuning and understanding these parameters and their implications in the basic photophysics and charge transporting behaviour. The lack of reliable high-resolution analytical techniques constitutes however a major limitation, as it hampers a better understanding of both the polymerisation process and the formation of the functional thin films used in devices.

Here, by combining vacuum electrospray deposition and high-resolution scanning tunnelling microscopy (STM) we demonstrate the ability of imaging conjugated polymers with unprecedented detail, thereby unravelling structural and self-assembly characteristics that have so far been impossible to determine.

Applying this novel technique to prototypical DPP- and thiophenes-containing polymers, we show that sub-molecular resolution STM images allow us to precisely identify the monomer units and the solubilising alkyl side-chains in individual polymer strands. Based on this, it becomes possible to determine the molecular number distribution of the polymer by simply counting the repeat units. More importantly, we demonstrate that we can precisely determine the nature, locate the position, and ascertain the number of defects in the polymer backbone. This unique insight into the structure of conjugated polymers is not attainable by any other existing analytical technique and represents a fundamental contribution to the long-discussed issue of defects as a possible source of trap sites. Furthermore, the analysis of our high-resolution images, also reveals that the frequently assumed all-trans-conformation of the monomers in the polymer backbone is actually not observed, while demonstrating that the main driver for backbone conformation and hence polymer microstructure is the maximization of alkyl side-chain interdigitation.

10:00am **NS+AM+AS+MN+PC+PS+SS+TR-FrM6 Probing Electrical Degradation of Lithium Ion Battery Electrodes with Nanoscale Resolution, Seong Heon Kim**, Samsung Advanced Institute of Technology, Republic of Korea; *S.Y. Park*, *H. Jung*, Samsung Advanced Institute of Technology, Republic of Korea

The high performance of lithium-ion batteries (LIBs) is in increasing demand for a variety of applications in rapidly growing energy-related fields, including electric vehicles. To develop high-performance LIBs, it is necessary to thoroughly understand the degradation mechanism of LIB electrodes. The investigation of the electrical conductivity evolution during cycling can lead to a better understanding of the degradation mechanism in cathode and anode materials for Li-ion batteries. Here, we probed the electrical degradation of LIB electrodes with nanoscale resolution via quantitative and comparative scanning spreading resistance microscopy (SSRM). First, the electrical degradation of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA) particles which are representative LIB cathode materials was studied [1]. After 300 charge/discharge cycles, stepwise-increasing resistance distributions toward the centers of the secondary particles were observed. These distributions correspond to the degenerated granular structures of the secondary particles caused by the formation of micro-cracks. Second, the electrical degradation of LIB anodes, the blended Si-C composites with graphite (Gr) particles, was investigated using SSRM [2]. From the SSRM measurements, it was obviously demonstrated that the electrical conductivity of the Si-C composite particles is considerably degraded by 300 cycles of charging and discharging, although the Gr particles maintain their conductivity. Our approach using SSRM techniques can be a good tool to study the electrical properties of various LIB electrode materials with nanoscale resolution.

[1] S.Y. Park, W.J. Baek, S.Y. Lee, J.A. Seo, Y.-S. Kang, M. Koh, S.H. Kim, Probing electrical degradation of cathode materials for lithium-ion batteries with nanoscale resolution, *Nano Energy* 49 (2018) 1–6.

[2] S.H. Kim, Y.S. Kim, W.J. Baek, S. Heo, D.-J. Yun, S. Han, H. Jung, Nanoscale electrical degradation of silicon-carbon composite anode materials for lithium-ion batteries, Submitted.

Author Index

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