

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-FrM-1 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-FrM-3 Chemical and Electronic Structure of Aniline Films on Silica Surfaces**, *Christopher Goodwin*, University of Delaware; *A Maynes*, Virginia Polytechnic Institute and State University; *Z Voras*, University of Delaware; *S Tenney*, Center for Functional Nanomaterials Brookhaven National Laboratory; *T 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-FrM-4 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 Pristl*, *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-FrM-5 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-FrM-6 Probing Electrical Degradation of Lithium Ion Battery Electrodes with Nanoscale Resolution**, *Seong Heon Kim*, Samsung Advanced Institute of Technology, Republic of Korea; *S 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 LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ (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

Bold page numbers indicate presenter

— A —

Arnau, A: NS+AM+AS+MN+PC+PS+SS+TR-FrM-4, **1**

— B —

Beebe, T: NS+AM+AS+MN+PC+PS+SS+TR-FrM-3, **1**

Borca, B: NS+AM+AS+MN+PC+PS+SS+TR-FrM-4, **1**

— C —

Costantini, G:

NS+AM+AS+MN+PC+PS+SS+TR-FrM-5, **1**

Crommie, M:

NS+AM+AS+MN+PC+PS+SS+TR-FrM-1, **1**

— G —

Goodwin, C: NS+AM+AS+MN+PC+PS+SS+TR-FrM-3, **1**

Gutzler, R: NS+AM+AS+MN+PC+PS+SS+TR-FrM-4, **1**

— J —

Jung, H: NS+AM+AS+MN+PC+PS+SS+TR-FrM-6, **1**

— K —

Kern, K: NS+AM+AS+MN+PC+PS+SS+TR-FrM-4, **1**

Kim, S: NS+AM+AS+MN+PC+PS+SS+TR-FrM-6, **1**

Klauk, H: NS+AM+AS+MN+PC+PS+SS+TR-FrM-4, **1**

Kraft, U: NS+AM+AS+MN+PC+PS+SS+TR-FrM-4, **1**

— M —

Maynes, A: NS+AM+AS+MN+PC+PS+SS+TR-FrM-3, **1**

Michnowicz, T:

NS+AM+AS+MN+PC+PS+SS+TR-FrM-4, **1**

— P —

Park, S: NS+AM+AS+MN+PC+PS+SS+TR-FrM-6, **1**

Pentegov, I: NS+AM+AS+MN+PC+PS+SS+TR-FrM-4, **1**

Pétuya, R: NS+AM+AS+MN+PC+PS+SS+TR-FrM-4, **1**

Pristl, M: NS+AM+AS+MN+PC+PS+SS+TR-FrM-4, **1**

— S —

Schendel, V: NS+AM+AS+MN+PC+PS+SS+TR-FrM-4, **1**

Schlickum, U:

NS+AM+AS+MN+PC+PS+SS+TR-FrM-4, **1**

— T —

Tenney, S: NS+AM+AS+MN+PC+PS+SS+TR-FrM-3, **1**

— V —

Voras, Z: NS+AM+AS+MN+PC+PS+SS+TR-FrM-3, **1**

— W —

Wahl, P: NS+AM+AS+MN+PC+PS+SS+TR-FrM-4, **1**