

## In-situ Microscopy, Spectroscopy, and Microfluidics Focus Topic

Room 202B - Session MM+AS+NS+PC-MoM

### Mechanical, Electrical, Thermal and Optical Systems for In situ TEM (9:00-10:100 am)/Beam Induced Effects and Processing in Liquid/Gas Cells for TEM/SEM (10:40-11:40 am)

**Moderators:** Suneel Kodambaka, University of California, Los Angeles, Olga Ovchinnikova, Oak Ridge National Laboratory

9:00am **MM+AS+NS+PC-MoM3 Cantilever Substrates for Quantitative Growth Experiments in the Environmental Transmission Electron Microscope, Frances Ross**, IBM T. J. Watson Research Center, MIT **INVITED** Environmental TEM is an excellent tool for obtaining quantitative information on growth processes and materials transformations. However, it is essential to measure the local temperature, pressure, and other key conditions at the sample location. Well controlled and accurately calibrated *in situ* experiments often make use of specially designed samples and involve various methods for direct measurement of the reaction parameters. Here we describe some of these strategies, but focus on one particular sample design which we suggest is well suited for experiments addressing chemical vapor deposition. In this sample design, growth takes place at the tip of a hairpin cantilever microfabricated from single crystal silicon and heated by direct current. Epitaxial growth is possible on the cantilever surfaces, and deposition on materials such as amorphous silicon nitride is achieved by first coating the cantilever. We discuss how the local temperature and pressure can be measured by monitoring a calibrated growth process. We also discuss how growth can be examined under more complex environments, such as electric fields, using designs involving multiple cantilevers and actuators. We finally discuss approaches to higher pressure than is possible in conventional ETEM by integrating cantilevers in a closed gas cell. Custom substrates based on microfabricated designs appear poised to expand the possibilities of quantitative *in situ* growth experiments to exciting new regimes and materials systems.

9:40am **MM+AS+NS+PC-MoM5 In Situ Laser Heating and Excitation in the Transmission Electron Microscope: Recrystallization, Grain Growth, Phase Separation and Dewetting in  $Ag_{0.5}Ni_{0.5}$  Thin Films, Philip D. Rack**, University of Tennessee Knoxville; *Y. Wu*, University of Notre Dame; *C. Liu*, University of Tennessee Knoxville; *T.M. Moore*, *G.A. Magel*, Waviks Inc.; *D. Garfinkel*, University of Tennessee Knoxville; *J.P. Camden*, University of Notre Dame; *M.G. Stanford*, *G. Duscher*, University of Tennessee Knoxville Motivated by the desire to image excited state and high temperature materials phenomena at the nano and atomic scale, Waviks Inc. has recently developed an *in situ* optical delivery tool for the (scanning) transmission electron microscope (S)TEM. The tool used in these experiments contains two optical delivery channels and is mounted on a Zeiss Libra 200 (S)TEM system. A 785 nm wavelength laser diode system coupled through a 5  $\mu$ m mode field diameter single-mode fiber is used to deliver >200 mW to the sample surface. The laser can be gated from a few ns to continuous wave (cw) at repetition rates up to 16 MHz. A second optical channel with a 100  $\mu$ m core diameter broad spectrum multimode fiber is also available for coupling to any excitation source in the wavelength range from 200 to 2100 nm using a standard SMA fiber connector. The system is mounted to a 3 axis (+/- x,y,z) nanomanipulator for focusing to the electron/sample coincident point (with sample tilted at ~45 degrees). The system contains a lens system to re-image the fiber optics (1x) at a working distance of ~10 mm, which is long enough eliminate charging and minimizes re-deposition of material. To demonstrate the functionality of the tool, we will show photothermal annealing results of a supersaturated  $Ag_{0.5}Ni_{0.5}$  film. We will demonstrate recrystallization, grain growth, phase separation and solid state dewetting of the films via various laser powers, pulse widths, pulse numbers, laser radius. Finally, we will demonstrate interesting *in situ* excited state phenomena via electron energy gain spectroscopy of plasmonic silver nanoparticles.

10:00am **MM+AS+NS+PC-MoM6 In situ Transmission Electron Microscopy Study of the Mechanical and Electrical Properties of Single III-V Semiconductor Nanowires, Lunjie Zeng**, Chalmers University of Technology, Gothenburg, Sweden; *C. Gammer*, Austrian Academy of Sciences, Austria; *B. Ozdol*, Lawrence Berkeley National Laboratory; *T. Nordqvist*, *P. Krogstrup*, University of Copenhagen, Denmark; *A.M. Minor*, Lawrence Berkeley National Laboratory; *W. Jäger*, *E. Olsson*, Chalmers University of Technology, Gothenburg, Sweden

III-V semiconductor nanowires possess outstanding electronic and mechanical properties that can be utilized in future high-speed electronic devices, solar cells and sensors. To better understand these properties and their relations to the microscopic structure of the nanowires, it is critical to directly correlate the structure and properties of single nanowires. However, the direct characterization of the mechanical and electrical properties of single nanowires, in particular, the correlation between them is still a challenge. In this study, we directly investigate the intrinsic mechanical and electromechanical properties of individual InAs nanowires using *in situ* transmission electron microscopy (TEM).

Quantitative stress, strain and electrical transport measurements were carried out on single InAs nanowires simultaneously. A Hysitron P195 nanoindentation TEM holder was used for the *in situ* TEM study. By using an electrical push-to-pull (EPTP) device in the *in situ* TEM holder, tensile stress was applied via the nanoindenter in the holder while the force applied on the nanowire was measured by a transducer in the holder. The EPTP device also enables current-voltage (I-V) measurements on single nanowires. Nanoscale lattice strain mapping within the nanowire was performed using scanning transmission electron microscopy (STEM) combined with nanobeam electron diffraction (NBED). NBED diffraction patterns were acquired using a Gatan K2 direct detection camera. Based on the detailed strain and stress measurements, Young's modulus and Poisson's ratio of single InAs nanowires were directly determined. The Young's modulus of single InAs nanowire is smaller than that of the bulk, while the Poisson's ratio of the InAs nanowire is similar as the bulk InAs. The electrical measurements showed that the resistivity of the InAs nanowires decreased continuously with increasing tensile stress. The piezoresistance coefficient of the nanowire was found to be significantly larger than that of bulk InAs. Moreover, significant inhomogeneous strain distribution within the nanowire under stress was unveiled by STEM-NBED strain mapping. The inhomogeneous strain distribution at nanometer scale can increase the resistivity of the nanowire by enhancing electron scattering. The findings demonstrate unique mechanical and electromechanical properties of the nanoscale InAs wires and provide new insights of the correlation between mechanical strain and electrical transport properties in free-standing nanostructures.

Financial support from Swedish Research Council and Nanoscience and Nanotechnology Area of Advance at Chalmers University of Technology are acknowledged.

10:40am **MM+AS+NS+PC-MoM8 Radiolytic Synthesis of Nanostructured Materials using In situ Liquid Cell Microscopy, Raymond Unocic**, *X. Sang*, *A. Belianinov*, *O.S. Ovchinnikova*, *K. More*, *S. Jesse*, Oak Ridge National Laboratory **INVITED**

There are a wide range of solution-based strategies available for the size- and shape-controlled synthesis of functional nanomaterials for applications in catalysis, energy storage, biomedical, optical, and electronics. To elucidate growth mechanisms, *in situ* liquid scanning transmission electron microscopy (STEM) plays a role for directly imaging and quantifying growth dynamics of nanoparticles from liquid-phase precursors. In this work, we report several strategies for the *active* controlled synthesis of metallic and bimetallic nanoscale architectures using the concept of radiolytic synthesis. In one approach, we developed a direct-write, template-free method to fabricate self-supporting, hollow, metallic nanostructures, and we interpret the formation mechanisms based on direct observations of nucleation and growth. The electron beam used for imaging stimulates radiolysis, promoting the dissociation of water ( $H_2O$ ) molecules and the formation of complex radical species such as aqueous electrons ( $e_{aq}^-$ ) and other reducing and oxidizing species. The highly reducing radiolytic species assist in the chemical reduction of metal ions from the precursor solution, resulting in the formation of a metallic nanocrystal seed, which then acts as a catalyst for  $H_2$  gas generation forming a metal encapsulated hollow nanobubble. In another approach, a custom-built electron beam nanopositioning and scan-generator system is used to precisely control the position and electron dose of the focused electron or ion beam to fabricate metallic and bimetallic nanostructured materials. These strategies enable fundamental

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electron beam interaction studies and open a new pathway for direct-write nanolithography from liquid-phase solutions.

This research was supported by the Center for Nanophase Materials Sciences, which is a United States Department of Energy Office of Science User Facility.

11:20am **MM+AS+NS+PC-MoM10 Electron Beam Induced Cross-Linking in Liquid Hydrogels**, *Tanya Gupta*, *A. Kolmakov*, National Institute of Standards and Technology (NIST)

Advances in additive manufacturing of bio-friendly polymeric materials over the last decade has revolutionized the diverse fields like rapid prototyping, tissue engineering, drug delivery etc. The technology currently relies on laser, thermal or UV induced 3D printing. Other triggers with similar effects can in principle be used as ionizing radiation to carry out the crosslinking. In this work we explore the use of electron beam to perform 3-D patterning at mesoscale and explore its potential towards rapid prototyping. In particular, knowledge of electron interaction with the printing ink allows us to predict effect of various control parameters like beam energy, current and dwell time on the topology of the features formed. A Monte-Carlo simulation coupled with a rigorous kinetic model is built to study the interplay of dose distribution, total interaction volume and diffusional effects of the active radiolytic species.

11:40am **MM+AS+NS+PC-MoM11 Nanoscale Chemical Reactor Based on Localized Surface Plasmon Energy in Environmental Transmission Electron Microscope**, *Canhui Wang*<sup>1</sup>, *W.-C. Yang*, UMD/NIST; *R. Sharma*, National Institute of Standards and Technology

Miniaturizing chemical processes in a research context has many advantages, including the ability to examine the reaction at atomic resolution, the reduced usage of costly and/or hazardous chemical reagents, and the ability to be integrated into analytical devices. [1-2] However, the current efforts of miniaturizing chemical processes have been limited by achievable minimum reaction volume and the lack of precision control over the reaction locations. Herein, we demonstrate a nanoscale chemical reactor utilizing localized surface plasmon (LSP) resonance as the energy source in an environmental transmission electron microscope (ETEM). This approach allows us to confine the reaction within proximity of the nanoparticle while taking advantage of the high spatial resolution capability of the electron microscope to monitor the reaction.

Plasmonic nanoparticles, such as Au or Ag, are placed in a reactive environment inside the ETEM. The composition and partial pressure of the gases are controlled by a gas handling system. Electron energy-loss spectra (EELS) imaging is used to acquire both elemental and LSP maps from the same nanoparticle. This allows the mapping and quantification of different gas adsorption on the nanoparticle surface. The energy required for the reaction of interest is provided by the LSP resonance excited by the high energy electron beam. The reaction location is confined within proximity of the nanoparticle due to the local field enhancement of the LSP resonance. Using a non-negative matrix factorization machine learning algorithm [3], we map the energy transfer pathways from the electron beam to the nanoparticle at nanometer spatial resolution and 0.08 eV energy resolution. The temperature distribution of the nanoparticle is monitored with few-nanometer spatial resolution using time-resolved EELS. Reaction processes, including morphological changes and transition of crystalline phases, are monitored using aberration-corrected atomic-resolution movies. By utilizing LSP resonance to initiate the reaction, we show that chemical processes can be confined in a nanometer scale volume, and modulated by electron flux. Important factors of the reaction, including composition of the reactants, adsorption of gases, transfer of energy, change of temperature, as well as reaction dynamics, can be monitored with nanometer or atomic resolution. Our approach paves the way to understanding a wide range of chemical reactions at the atomic scale.

References:

- [1] Abdelgawad, Mohamed, et al. Lab on a Chip 9.8 (2009): 1046-1051.
- [2] Williamson, M. J., et al. Nature materials 2.8 (2003): 532.
- [3] O. Nicoletti, et al. Nature 502.7469 (2013): 80.

**Nanometer-scale Science and Technology Division**

**Room 102B - Session NS+2D+AN+EM+MN+MP+PC+RM-MoM**

**IoT Session: Nanostructured Devices and Sensors**

**Moderators:** David Czaplewski, Argonne National Laboratory, Liya Yu, NIST Center for Nanoscale Science and Technology

8:20am **NS+2D+AN+EM+MN+MP+PC+RM-MoM1 Integrating Nanodiamonds with Augmented Artificial Intelligence and Digital Health to Optimize Combination Therapy**, *Dean Ho*, UCLA **INVITED**  
Dean Ho, Ph.D.

Nanodiamonds have emerged as promising candidates for clinical drug delivery due to their ability to carry a wide range of candidate therapies, unique surface properties, and biological tolerability. This lecture will highlight our recent clinical trial to validate a nanodiamond-embedded biomaterial for root canal therapy indications [1]. We will discuss the broad spectrum of efficacy, safety, characterization, and other studies that bridged in vitro with preclinical and downstream in-human studies. This lecture will also discuss upcoming clinical nanodiamond-based drug carrier studies, as well as our work in augmented artificial intelligence (AI) to develop globally optimized nanodiamond-modified therapy. Pairing nanodiamond platforms with augmented AI will lead to major advances in drug development and markedly improve response rates and treatment outcomes for a broad spectrum of disorders. Our recent clinical trials using these powerful combination therapy optimization technologies and digital health platforms to scale their implementation to usher in a new era of nanomedicine-based treatment will also be discussed [2].

1. Lee et al., Proceedings of the National Academy of Sciences, 2017
2. Zarrinpar et al., Science Translational Medicine, 2016

9:00am **NS+2D+AN+EM+MN+MP+PC+RM-MoM3 Morphology-Controlled Large-Scale Tin Oxide Nanostructures for Highly Sensitive Room Temperature Gas Sensor**, *Amrit Sharma*, Norfolk State University

Highly sensitive large-scale tin oxide (SnO<sub>2</sub>) nanostructures were grown on a glass substrate by vapor-liquid-solid (VLS) process using a mixture of anhydrous tin (II) chloride (SnCl<sub>2</sub>) and zinc chloride (ZnCl<sub>2</sub>) powders. We demonstrate a new kind of single cell vapor deposition system to precisely control nanostructural morphology by changing the weight ratio of SnCl<sub>2</sub> and ZnCl<sub>2</sub> and growth temperature. The morphology and structural property of as-grown nanostructures were characterized using scanning electron microscopy (SEM) and X-ray diffraction (XRD). The SEM images revealed that the SnO<sub>2</sub> nanostructures with different densities, sizes, and shapes can be achieved by adjusting the weight ratio of SnCl<sub>2</sub> and ZnCl<sub>2</sub>. SnO<sub>2</sub> nanostructures with diameter ~20 nm and length ~100 nm showed ~85% sensitivity and 53 seconds of response time, whereas the nanorods with diameter ~100 nm and length ~1mm showed ~50% sensitivity with 198 seconds response time. The nanostructured material with small size and shape showed better sensitivity on sensing at room temperature compared to previously reported SnO<sub>2</sub> based sensors.

9:20am **NS+2D+AN+EM+MN+MP+PC+RM-MoM4 Improving the Localized Surface Plasmonic Resonance Sensing Properties by Composite Metal/Dielectric Mixtures**, *Steven Larson*<sup>2</sup>, *Y. Zhao*, University of Georgia

Localized surface plasmon resonance (LSPR)-based sensors, whose resonance absorbance wavelength responds to the change in the local dielectric environment have attracted great attention and have been widely studied over the past decade. These sensors are traditionally improved by modifying the shape, size, and gap in the plasmonic nanostructure of the sensor. The sensitivity can also be tuned by the dielectric constant of the plasmonic material, such as noble metal alloys, but the improvements are not significant. Here we show that using a metal-dielectric composite, one can significantly improve the sensitivity of a LSPR sensor. Regular nanotriangle pattern samples composed of a mixture of Ag and MgF<sub>2</sub> with different composition ratios are prepared by combining nanosphere lithography and electron beam co-deposition. The plasmon resonance of these composite nanostructures at high Ag composition (C<sub>Ag</sub>) are shown to redshift with C<sub>Ag</sub> until a composition threshold (C<sub>Ag</sub> ≤ 90%) is met, where the resonance wavelength is nearly constant, slightly blue shifting. Multiple morphological and compositional characterization techniques are used to confirm that the shifts in the plasmonic properties are due to the change in composition and not a change in the morphology. The resulting LSPR sensor at C<sub>Ag</sub> = 90 at.% can

<sup>1</sup> NSTD Postdoc Finalist

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<sup>2</sup> NSTD Student Award Finalist

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achieve a sensitivity of 696 RIU/nm, as compared to 312 RIU/nm for the same nanotriangle with pure Ag. This significantly improved sensitivity is due to the modified dispersion relationship of the dielectric constant by the composite and will play an important role in future plasmonic material design and applications.

9:40am **NS+2D+AN+EM+MN+MP+PC+RM-MoM5 Improving the Selectivity of Tin (IV) Oxide Paper Based Gas Sensors with Plasma Surface Modification, Kimberly Hyoto, E.R. Fisher, Colorado State University**

Metal oxide nanomaterials are desirable for solid-state gas sensors because of their ability to detect a wide variety of gases through changes in resistance resulting from gas-surface interactions. When optimizing these sensors, the supporting substrate is rarely considered, resulting in devices that are often brittle and have a fixed amount of nanomaterial that can be exposed to target analytes. Recent work using paper as the supporting substrate yields more affordable sensors that are flexible, allowing for a more robust device. Furthermore, the porous morphology of the paper also provides a larger surface area to attach metal oxides when compared to a traditional flat substrate of the same dimensions. Another limitation of these metal oxide sensors is inherent in the detection method. The lack of selectivity and required operating temperature of  $\geq 300$  °C limits the widespread use of metal oxide sensors. Dopants or the addition of a filter in the device design are typical approaches to address these problems; however, this increases fabrication complexity and cost. Plasma processing is a promising strategy to address these issues because it maintains desirable bulk properties but modifies the surface of the material to enhance gas sensor performance.

Here, we describe the Ar/O<sub>2</sub> plasma modification of paper based, tin (IV) oxide (SnO<sub>2</sub>) nanoparticle devices as a function of applied rf power and precursor pressure. After plasma modification, the paper-based sensors exhibited improved response to carbon dioxide, ethanol, and benzene when compared to the untreated material on a more traditional substrate, zirconium dioxide. Additionally, sensor response to a target gas changed depending on the plasma modification parameters used, indicating the selectivity of these SnO<sub>2</sub> sensors can be easily tailored via plasma processing. Response and recovery studies of both the treated and untreated sensors will be discussed to demonstrate the dynamic behavior of these devices to the target gases as another measure of gas sensor performance and durability. Along with sensing behavior, optical emission spectroscopy and X-ray photoelectron spectroscopy provide insight into how the plasma modified the material, ultimately elucidating the relationship between material surface chemistry and sensor selectivity. Finally, preliminary work using this same fabrication process with another type of metal oxide gas sensor will be discussed to demonstrate the applicability of this method for other types of materials. Ultimately, these data work toward improved understanding of the gas sensing mechanism to design better performing gas sensors.

10:00am **NS+2D+AN+EM+MN+MP+PC+RM-MoM6 TiN@Si<sub>3</sub>N<sub>4</sub> Core-shell Heterostructures as Nanoantennas for Photocatalytic Reforming of Methanol, Alejandro Alvarez Barragan, L. Mangolini, University of California, Riverside**

The light-harvesting capacity of plasmonic nanoparticles has recently garnered attention in the synthesis of nanoantennas for photocatalysis. Aluminum, gold, and silver have been used to successfully drive hydrogen dissociation and CO oxidation reactions by injecting hot electrons into chemically active catalysts—such as platinum and palladium—adsorbed to their surface. However, the low response of aluminum at visible-near infrared (vis-NIR) wavelengths, the high cost of silver and gold, and the low thermal stability of these three metals, inspire the quest for alternative plasmonic materials that could potentially expand the field towards more ambitious and cost-effective applications. Titanium nitride (TiN) is a conductive ceramic with high hardness and bulk melting point (2930 °C). Its plasmon resonance located in the vis-NIR region, low cost relative to gold and silver, and well-understood properties as a thin film in the semiconductor industry, make it a strong alternative to mainstream plasmonic metals. The present work encompasses a comprehensive study of the oxidation kinetics of TiN particles at the nanoscale and an exploration of its role as nanoantennas for light-induced methanol reformation. TiN particles are synthesized via a scalable, modular, non-thermal plasma method. Titanium and nitrogen precursors are transported into a RF frequency plasma where TiN particles nucleate and grow. The high surface area and nitrogen deficiency of the particles facilitate the oxidation of the material and weaken its plasmonic response. The introduction of a secondary reactor with an input of SiH<sub>4</sub> as precursor gas

leads to the formation of a Si<sub>3</sub>N<sub>4</sub> coating. STEM and XPS analyses show that Si<sub>3</sub>N<sub>4</sub> acts as a diffusion barrier, dramatically reducing the oxidation of the ~8 nm TiN particles. UV-vis-NIR spectrophotometry data show that the core-shell heterostructures experience a substantial blue-shift of the plasmon peak and an increase in intensity compared to the bare TiN. Platinum nanoparticles were subsequently deposited on the TiN@Si<sub>3</sub>N<sub>4</sub> by photo-induced reduction of an aqueous solution of chloroplatinic acid. After rinsing and centrifuging, the Pt/TiN@Si<sub>3</sub>N<sub>4</sub> heterostructures were diluted in a 50:50 water/methanol solution. Upon photoexcitation via white light illumination, hydrogen generation was readily detected by gas chromatography. This work also highlights the wide range of applications available for light-induced processes, ranging from materials processing (deposition of Pt particles) to photocatalysis (methanol reforming). It also strengthens the case for alternative plasmonic materials in a field dominated by precious metals.

10:40am **NS+2D+AN+EM+MN+MP+PC+RM-MoM8 Nanostructured Sensor and Device Applications of Infiltrated Zinc Oxide, Leonidas Ocola, Argonne National Laboratory; Y. Wang, J. Chen, University of Wisconsin-Milwaukee; P. Blaisdell-Pijuan, California State University-Fullerton; R. Divan, Argonne National Laboratory**

**INVITED**

With the increased portfolio of materials deposited using atomic layer deposition (ALD) there has been an increased interest in infiltrated metal oxides such as zinc oxide for novel applications. We find that ZnO metal oxide ALD infiltration can be useful for nanoscale resolution imaging of biological samples and to fabricate novel UV and gas nanosensors with high sensitivity. The ALD infiltration utilizes similar concepts of the ALD coating process with the significant difference in process exposure times, pressure, and purpose. The purpose is to allow the precursor gases infiltrate a porous media (such as a dry biological sample or a photoresist polymer) and allow the reaction to occur inside the material matrix.

In terms of device fabrication we use SU8 as a negative resist that allows for localization of the infiltration process. We have used this property to make a device that is UV sensitive, and that is sensitive to ppm concentrations of gases by using infiltrated zinc oxide. The large bandgap and semiconductor properties of ZnO allow for a visible-blind ultra violet light sensor. We used a standard UV flashlight that emits at 408 nm as the UV source. We also tested the same device for sensing gases like nitrous oxide and formaldehyde. We show that the device can detect these gases with concentrations of 5 ppm. The change in current for such low concentrations was measured to be between 25% and 35 %.

With the purpose of investigating quantum applications of infiltrated ZnO, we also have characterized the growth of ZnO in PS-b-PMMA block copolymers (BCP) of spherical and cylindrical sub-20 nm morphologies and studied how the photoluminescence of these nanostructures varies per its seed layer. We report blue-shifted photoemission at 335nm (3.70eV), suggesting quantum confinement effects. Samples of ZnO prepared with an alumina seed layer showed additional defect state photoemission at 470nm and 520nm for spherical and cylindrical BCP morphologies, respectively. Defect photoemission was not observed in samples prepared without a seed layer. No Raman peaks were observed for any samples with less than four cycles of ZnO, implying the absence of phonons and the functionality of these ZnO nanostructures as isolated emitters. To that effect we have demonstrated a fabrication path to isolate single infiltrated cylinders, paving the way for further studies of optical properties of individual 20 nm ZnO nanostructures.

- Use of the Center for Nanoscale Materials an Office of Science user facility, was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

11:20am **NS+2D+AN+EM+MN+MP+PC+RM-MoM10 Templates for the Investigation of Size-Selected Nanocluster Networks, Patrick Edwards, V.V. Kresin, University of Southern California**

The study of metal nanoclusters has revealed quantum nanoscale effects unique to the fully size-resolved regime. A highly notable example is electronic shell structure, akin to that in atoms and nuclei, which arises when confined conduction electrons organize into discrete energy levels. One consequence is the possibility of dramatic enhancement in electron Cooper pairing. Recent research from our group has provided evidence of this enhancement in certain free Al nanoclusters, with the electronic transition taking place at a temperature two orders of magnitude above that of bulk aluminum. We now aim to take advantage of this phenomenon by exploring the pairing transition in size-selected nanoclusters soft-landed on an appropriate substrate. Of particular interest are graphene and nanotube device architectures which provide unique templates for

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organizing nanocluster arrays. For example, a network of such superconducting nanoislands may induce superconductivity in graphene even at low coverages. Theory also predicts that an array of nanoclusters will not only support, but even enhance the Josephson current by 2-3 orders of magnitude. Carbon allotropes offer two distinct advantages for our system. First, the weak out-of-plane bonding provides a surface with less potential to disturb the structure of the soft-landed nanoclusters. Second, the tunability of graphene and carbon nanotube-based field effect transistors offers a versatile probe of nanocluster properties. We are also investigating the use of biological nanowires (bacterial flagella) as potential scaffolds upon which to deposit such nanocluster networks. These abundant and naturally occurring nanowires could serve as low cost and highly reproducible alternatives to the more common metallic or semiconductor templates.

Research supported by the Army Research Office (W911NF-17-1-0154).

11:40am **NS+2D+AN+EM+MN+MP+PC+RM-MoM11 High Performance Detection for X-ray and  $\gamma$ -ray with MAPbX<sub>3</sub> Perovskite Single Crystals**, X. Wang, Z. Zhu, Q. Li, J. Wu, X. Zhang, B. Wang, **Wei Lei**, Southeast University  
Recently, organometallic lead trihalide perovskites have emerged as a new generation of opto-electronic materials. However, the high performance detection for x-ray and gamma-ray with MAPbX<sub>3</sub> is still a big challenge. For x-ray and gamma-ray detections, the detectors should have high sensitivity. If the photon counting method is adopted, the high energy resolution and high time resolution are also required. In this work, the large area MAPbBr<sub>3</sub> single crystal has been fabricated with a facile methodology. Due to the quite thick active material and large carrier mobility, the x-ray photons and gamma-ray photons can be absorbed with high efficiency. The photo generated electrons and holes can also be collected effectively with the large electric field. To decrease the dark current in the detection, a novel photo-diode structure is proposed here. In crystallization process of MAPbI<sub>3</sub> single crystal, the p-n junction can be formed with doping of selenium atoms into MAPbI<sub>3</sub> single crystal.

With various temperature method, the 30mm×30mm×7mm MAPbBr<sub>3</sub> single perovskite crystal is fabricated. As the experimental results shown, almost all of the 100 keV x-ray photons are absorbed when the MAPbBr<sub>3</sub> SPC is 7mm thick. The detection sensitivity is as high as 305  $\mu\text{C Gy}_{\text{air}}^{-1}\text{cm}^{-2}$  when the anode voltage of x-ray tube is 30 kV.

To reduce the dark current in the detection, two type of photo diode structures have been proposed here. Firstly, a photo diode with structure of Au/TPD/MAPbBr<sub>3</sub> PSC/C<sub>60</sub>/PCBM/Ag has been fabricated with spin coating and sputtering methods. Although the dark current density can be reduced to 20 nA/cm<sup>2</sup> with -30V bias voltage, the temporal response time is nearly 50  $\mu\text{s}$  due to the defects on the interfaces between PSC and carriers transport layers. Then, by doping selenium (Se) in MAPbI<sub>3</sub> perovskite single crystals (DPC) crystallization process, low dark current p-n junctions were fabricated without any organic layers. This photodiodes gives the high detection sensitivity as 21000  $\text{mC Gy}_{\text{air}}^{-1}\text{cm}^{-2}$  and 41  $\text{mC Gy}_{\text{air}}^{-1}\text{cm}^{-2}$  for 60 keV x-ray and 1.33 MeV gamma-ray respectively. In this photodiode, the transition time becomes shorter under higher electric field, and the carrier lifetime also becomes shorter due to the dopant of Se atoms. Finally, the temporal response time is measured as 3  $\mu\text{s}$  by experiments. The FWHM width of energy spectrum is decreased to 3.2%@1330 keV.

## In-situ Microscopy, Spectroscopy, and Microfluidics Focus Topic

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### X-ray and Electron Spectromicroscopy in Liquids and Gases & Flash Networking Session

Moderator: Piran Kidambi, Vanderbilt University

1:20pm **MM+AS+NS+PC+SS-MoA1 Bridging the Material and Pressure Gap in Synchrotron based Photoelectron in Situ/Operando Studies**, **Luca Gregoratti**, **M. Amati**, **P. Zeller**, Elettra-Sincrotrone Trieste, Italy **INVITED**  
Modelling the real behavior of technologically relevant materials at typical laboratory environmental conditions is a longstanding challenge. Not only classical pressure conditions are generally far from usual industrial environments (pressure gap) but also heterogeneous materials are very different from those often used to simplify the modelling strategies (material gap). For instance to monitor in-situ/operando the lateral distribution of the chemical state of surfaces and interfaces during a catalytic or electrochemical reaction at sub-micron level at environmental conditions as close as possible to the operational ones is of crucial importance to shed light on the running processes. But the possibility to investigate chemical reactions with X-ray photoelectron spectroscopies by overcoming material and pressure gaps is still a challenge also for modern experimental setups.

The Escamicroscopy team of Elettra which operates a Scanning Photoemission Microscope (SPEM) has recently developed novel concepts for a new generation of SPEM working under more realistic pressure conditions. The graphene sealed cells, combined for the first time with XPS by A. Kolmakov [1], allow the possibility to investigate systems which require an ambient pressure regime (e.g. liquid/solid interfaces). Despite the huge ongoing progress in the development and performance of these cells several crucial issues are unsolved and will be addressed by this presentation.

Another recent development is an effusive cell for near-ambient pressure SPEM setups where the highest static pressure achievable is around 1 mbar. Samples are encapsulated in a vacuum sealed cell and located behind a 200  $\mu\text{m}$  diameter size pinhole through which the focused X-ray beam illuminates surfaces and photoelectrons reach the high vacuum path towards the electron analyzer [1].

2:00pm **MM+AS+NS+PC+SS-MoA3 Transition Metal Complexes in Aqueous Solutions Characterized by Liquid Jet Ambient Pressure X – ray Photoelectron Spectroscopy**, **Jared Bruce**, **J.C. Hemminger**, University of California, Irvine

Transition metals in aqueous solution have been investigated by a multitude of techniques and are a cornerstone of many aspects of chemistry. Recently, the atmospheric chemistry community has begun to shift their attention to iron, manganese and copper containing aqueous solutions due to their propensity to generate hydroxyl radicals at the air/water interface through a Fenton mechanism. Understanding the chemical state of the transition metal present at the air/water interface, in addition to the distribution as a function of depth, would provide critical insight to the active species of hydroxyl generation. Solvation effects have been shown to significantly affect the distribution of small ions as a function of depth from the vacuum/water interface; first through molecular dynamics (MD) simulations then corroborated by liquid – jet X – ray photoelectron spectroscopy (LJ-XPS). Solvation of transition metals in aqueous solution have added complexity compared to small ions because of complexation of ligands and equilibria with the surrounding solvent.

In our work, using both a lab – based LJ - XPS and synchrotron measurements at the Advanced Light Source, we have shown the distribution of chemical states on a model Fenton reagent,  $\text{Fe}^{2+}_{(\text{aq})}$ , change with depth relative to the air/liquid interface. The chemical state is also sensitive to “spectator” ions in the solution. The presence of  $\text{Cl}^-$  leads to a binding energy shift in the Fe 2p spectra and a change in the distribution as a function of depth. This is also observed in the Cl 2p spectrum where a binding energy shift of 0.3 eV indicates the presence of an inner sphere Cl that follows the distribution change in the Fe 2p spectrum

2:20pm **MM+AS+NS+PC+SS-MoA4 Interfacial Electrochemistry in Liquids Probed with Photoemission Electron Microscopy**, **S. Nemsak**, Forschungszentrum Juelich GmbH, Germany; **E. Strelcov**, NIST Center for Nanoscale Science and Technology; **Tomas Duchon**, Forschungszentrum Juelich GmbH, Germany; **H.X. Guo**, National Institute of Standards and Technology; **J. Hackl**, Forschungszentrum Juelich GmbH, Germany; **A. Yualev**, NIST Center for Nanoscale Science and Technology; **I. Vlasiouk**, Oak Ridge National Laboratory; **D.N. Mueller**, **C.M. Schneider**, Forschungszentrum Juelich GmbH, Germany; **A. Kolmakov**, NIST Center for Nanoscale Science and Technology

The use of photoemission spectromicroscopy as a probe of liquid electrolytes has been an elusive goal, motivated by the breadth of information the technique can provide, but hindered by many technical difficulties. Here, we present a universal multichannel array platform employing graphene capping that allows for investigation of interfacial liquid electrochemistry via soft x-ray absorption and photoemission spectromicroscopy. The methodology is demonstrated in the case of copper electroplating from a sulphuric acid solution, that, along with cycles of copper deposition on gold electrodes, reveals hindered nucleation at the electrified graphene membrane evidenced by the presence of stable  $\text{Cu}^+$  ions.

3:40pm **MM+AS+NS+PC+SS-MoA8 Practical Liquid Cell Microscopy - Opportunities and Challenges**, **Daan Hein Alsem**, **K. Karki**, Hummingbird Scientific; **J.T. Mefford**, **W.C. Chueh**, Stanford University; **N.J. Salmon**, Hummingbird Scientific **INVITED**

Transmission electron microscopy (TEM), scanning electron microscopy (SEM) and synchrotron X-ray microscopy (XRM) are powerful characterization tools and are routinely used to study a wide range of material-systems at the nanoscale. This has generated strong interests in acquiring more reliable quantitative *in-situ* and *operando* measurements in realistic reaction environments, as is possible with liquid environmental cells. This approach has already started to produce new insights on the dynamics and structural changes during electrochemical processes as lithium ion insertion/extraction, dendrite formation, metal nucleation and corrosion. However, practical aspects of replicating representative electrochemical data reminiscent of bulk behavior are still a challenge in these systems.

Here, we will discuss practical aspects of conducting *operando* liquid cell microscopy experiments relating to the typical geometry of these liquid-cell microscopy systems as well as artifacts coming from the microscope during *operando* experiments. We will also present a TEM/SEM/XRM microscopy platform that enables true electroanalytical measurements mimicking bulk behavior of the material system.

The example study shown here is performed using electrochemical cells, which consist of two microfabricated chips sandwiched with transparent  $\text{SiN}_x$  membranes for encapsulating liquid and viewing in the microscope. A newly developed hardware system and specially optimized electrochemistry chips with a custom configuration for working electrode (WE), counter electrode (CE) and reference electrode (RE) allows quantitative measurements of electrochemical processes with details resembling the complete cycle of the bulk. As illustrations, we present cyclic voltammetry (CV) studies of some model compounds such as 0.1M  $\text{CuSO}_4$  and 20 mM  $\text{K}_3\text{Fe}(\text{CN})_6$ /20 mM  $\text{K}_4\text{Fe}(\text{CN})_6$  in 0.1M KCl solutions. In the former case, the copper deposition and stripping occurs at the working electrode at distinct redox peaks in liquid cell and the result mimics the bulk electrochemical cells with large electrode areas and larger volume of electrolyte solution. This work highlights the fact that with suitable hardware systems and with knowledge and correction of microscope-induced artifacts, bulk behavior of the electrochemical processes can be both observed and measured quantitatively.

4:20pm **MM+AS+NS+PC+SS-MoA10 Observation of Electric Double Layer under Graphene by Scanning Electron Microscopy**, **Hongxuan Guo**, **A. Yulaev**, **E. Strelcov**, National Institute of Standards and Technology (NIST)/University of Maryland, College Park; **A. Tsellev**, CICECO and Department of Physics, University of Aveiro, Portugal; **A. Kolmakov**, National Institute of Standards and Technology

The formation of the electric double layer is a fundamental phenomenon occurring at electrified solid-liquid electrolyte interfaces and which has a key importance for energy devices, chemical engineering and biomedical applications. The structure and composition of electric double layer can be accessed using optical methods<sup>1</sup>, and more recently with X-ray spectroscopy<sup>2,3</sup>, as well as scanning probe microscopy<sup>4</sup>.

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In this presentation, we demonstrate the feasibility of *in-situ* scanning electron microscopy to observe the changes in electric double layer in different electrolytes upon polarization. We designed an electrochemical liquid cell with electron transparent electrode made of bilayer graphene.<sup>5,6</sup> We monitored the changes in secondary electron yield from the graphene-liquid interface upon electrolyte polarization. We found that the normalized SEM image contrast is linear with the applied bias voltage and is related to the concentration and distribution of the ions at the interface. The analysis of SEM videos provide insight on long term kinetics of ionic moieties in electrolyte during polarization. This experimental methodology will be helpful for understanding the structure, property, and dynamics of the electric double layer at solid -electrolyte interfaces.

## Reference

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- [4]. J. M. Black, M. Zhu, P. Zhang, R. R. Unocic, D. Guo, M. B. Okatan, S. Dai, P. T. Cummings, S. V. Kalinin, G. Feng, and N. Balke, Scientific Reports 6 (2016), 32389
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## Nanometer-scale Science and Technology Division Room 102B - Session NS+2D+AS+PC-MoA

### SPM - New Imaging and Spectroscopy Methodologies

**Moderators:** Aubrey Hanbicki, Naval Research Laboratory, Sidney Cohen, Weizmann Institute of Science, Israel

#### 1:20pm **NS+2D+AS+PC-MoA1 A Connection Between Stability of STM Control System and Local Barrier Height: Implications on Imaging and Lithography**, *S.O. Reza Moheimani*, University of Texas at Dallas **INVITED**

Poor performance of the Scanning Tunneling Microscope (STM) control system may result in tip-sample crash, a prevalent failure in STMs. Since its invention, about thirty-five years ago, few attempts have been made to improve the STM control system. Consequently, nearly all STMs are today operated with experimentally selected fixed-gain PI controllers. Selection of controller gains is often done without much attention to the electromechanical dynamics of the scanning tunneling microscope. Performance of such poorly-tuned controllers is limited and a key contributor to the tip-sample crash.

We perform closed loop system identification on a scanning tunneling microscope and show that the system DC gain is proportional to the square root of Local Barrier Height (LBH), a quantum mechanical property of the sample and/or tip that affects the tunneling current. We demonstrate that during a scan the LBH may undergo significant variations and thus it may adversely affect the closed-loop stability if the controller parameters are fixed. Feedback instabilities increase the risk of tip-sample crash in STMs.

In order to improve the closed loop performance, we estimate the LBH, on the fly, and use this information to adaptively tune the PI controller parameters. Experimental results obtained with the self-tuning PI controller confirm the improved STM performance compared to the conventional fixed gain PI controller. Further experiments confirm effectiveness of the proposed method in extending the tip lifetime by lowering the chance of the tip/sample crash.

#### 2:00pm **NS+2D+AS+PC-MoA3 Distinctive Microstructures in a Complex Polymer Evolve with Time and Composition**, *x. Yu*, Worcester Polytechnic Institute; *S. Granados-Focil*, Clark University; *M. Tao*, *Nancy Burnham*, Worcester Polytechnic Institute

The diverse microstructures observed by atomic force microscopy (AFM) in asphalt binder – a complex polymer – suggest complicated intermolecular associations. These microstructures contribute to binders' bulk mechanical properties; therefore, it is essential to understand chemical-microstructural-mechanical relationships for optimal design of binder-related applications, which range from roads to roofs. The US market for asphalt binders in 2019 is predicted to reach 148 million barrels. [1]

Binders annealed at room temperature for over two months showed time-dependent microstructures, which correlate well with room-temperature steric hardening behavior as verified by other researchers using modulated differential scanning calorimetry. Microstructures of the binder films stabilized after different annealing durations, depending on the dimensions of the molecular structures and the complexity of the molecular interactions among the multiple phases in each bitumen. Distinctive microstructures were observed for remixed binders with increasing asphaltene concentrations. Consistency between our observations [2] and other literature suggests that microstructures observed by AFM are probably not just a surface phenomenon.

Furthermore, the complex nature of binder and the various influencing factors often lead to practical challenges in investigation of its microstructures and their chemical origins. Some of the main concerns related to AFM characterization of binders' microstructures, namely the dependence of the microstructures on such factors as sample preparation methods, annealing conditions and durations, and chemical composition, were also addressed in this study.

The above findings provide practical knowledge and deeper insights into the establishment of the complicated chemical-mechanical relationships for asphalt binders that pave the way toward tuned binder performance.

[1] <https://www.reportlinker.com/p0158665/US-Asphalt-Industry.html>

[2] "Time- and composition-dependent evolution of distinctive microstructures in bitumen." X. Yu, S. Granados-Focil, M. Tao, and N.A. Burnham, Energy Fuels 32, 67-80 (2018).

#### 2:20pm **NS+2D+AS+PC-MoA4 Offering new Characterization Capabilities at the XTIP beamline by Combining Scanning Tunneling Microscopy with Synchrotron Radiation**, *Volker Rose*, *H. Chang*, *M. Fisher*, *S.W. Hla*, *N. Shirato*, Argonne National Laboratory

The race is on for chemical x-ray imaging with nanoscale resolution. Specifically, there are currently substantial efforts underway at synchrotron facilities worldwide that aim to combine x-rays with scanning probe microscopy. Recently, substantial progress was made on Argonne's Synchrotron X-ray Scanning Tunneling Microscopy (SX-STM) project. SX-STM enables an entirely new view into the nanoworld by combining the best of two worlds: the exceptional chemical, magnetic, and structural sensitivity of synchrotron x-rays combined with the high spatial resolution of scanning probe microscopy accompanied by its ability to engineer and manipulate surfaces down to the level of single atoms.

To fully exploit the special capabilities of a unique new cryogenic x-ray microscope, XTIP, a dedicated beamline for SX-STM will become available at the Advanced Photon Source in early 2019. To meet the scientific objective of the nanoscience and nanomagnetism communities most effectively, we are going to build a soft x-ray beamline with full polarization control operating over the 500-1600 eV energy range. The dedicated XTIP beamline will provide researchers access to a one-of-a-kind instrument. Among the potential breakthroughs are "designer" materials created from controlled assembly of atoms and molecules, and the emergence of entirely new phenomena in chemistry and physics.

#### 2:40pm **NS+2D+AS+PC-MoA5 Scanning Probe Microscopy Based Spectroscopy Measurement for Nanoscale Chemical Identification**, *Chanmin Su*, Bruker-Nano, Inc. **INVITED**

Scanning probe microscopy has been instrumental for physical property characterizations at the nanometer scale, primarily for mechanical, electromagnetic and thermal properties. Recent progresses were focused on chemical identification based on mid-IR spectroscopy, pushing FTIR mapping to a resolution at or beyond 10 nm. This presentation will review technology advances in both scanning near field optical microscopy and photothermal based IR spectroscopy. Each of the techniques is discussed and benchmarked by detection limit, spatial resolution and signal to noise ratio, which ultimately determines the chemical mapping efficiencies. We will highlight techniques that address correlative imaging where physical and chemical properties at the same nanoscale location being acquired either concurrently or sequentially. As an example, PeakForce tapping based chemical and physical measurements will be explained in detail with the applications ranging from 2D materials to polymer complexes. The presentation will also highlight major challenges for scanning probe based measurements to be broadly adopted as the premier tool for nanoscale chemical fingerprint mapping.

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3:40pm **NS+2D+AS+PC-MoA8 Quantifying Tip-Sample Interactions in Vacuum Using Cantilever-based Sensors: An Analysis**, *O.E. Dagdeviren, C. Zhou, E.I. Altman, Udo D. Schwarz*, Yale University

To achieve as much quantitative information on a surface as possible, the local measurement of tip-sample interaction potentials has recently gained much popularity in particular under well-defined ultrahigh vacuum conditions, where such measurements can be carried out with great accuracy both in terms of spatial as well as force resolution. To this end, either the oscillation frequency or the oscillation amplitude and phase of the vibrating force-sensing cantilever are recorded as a function of tip-sample distance and subsequently converted into quantitative values for the force or interaction potential. Here, we theoretically and experimentally show that the force law obtained from such data acquired under vacuum conditions using the most commonly applied methods may deviate more than previously assumed from the actual interaction when the oscillation amplitude of the probe is of the order of the decay length of the force near the surface, which may result in a non-negligible error if correct absolute values are of importance [1]. Caused by approximations made in the development of the mathematical reconstruction procedures, the related inaccuracies can be effectively suppressed by using oscillation amplitudes sufficiently larger than the decay length. To facilitate efficient data acquisition, we propose a novel technique that includes modulating the drive amplitude at a constant height from the surface while monitoring the oscillation amplitude and phase. Ultimately, such amplitude sweep-based force spectroscopy enables shorter data acquisition times and increased accuracy for quantitative chemical characterization compared to standard approaches that vary the tip-sample distance. An additional advantage is that since no feedback loop is active while executing the amplitude sweep, the force can be consistently recovered deep into the repulsive regime.

[1] O. E. Dagdeviren et al., *Physical Review Applied* **9**, 044040 (2018).

4:00pm **NS+2D+AS+PC-MoA9 AFM + Nanoscale Vis-IR Spectroscopy via Photo-induced Force Microscopy**, *Derek Nowak, T. Albrecht, S. Park*, Molecular Vista

Photo-induced Force Microscopy (PiFM) [1] combines optical spectroscopy and atomic force microscopy (AFM) via illumination of the tip-sample junction with tunable laser light and mechanical detection of forces acting on the tip in response to interaction of light with the sample. With infrared (IR) source, PiFM can map the IR absorption of the sample as a function of IR wavelength and position and achieve nm-scale resolution in displaying the locations of heterogeneous materials on the surface of a sample. Even for samples without active IR absorption band, PiFM can be used to acquire nanoscale mapping based on the dielectric constant of the sample surface; dielectric constant mapping also allows high resolution sub-surface mapping. With tunable visible and near infrared (VisNIR) laser source, PiFM can map exciton resonances with similar spatial resolution even on monolayer samples. Examples from various classes of samples including organic, inorganic, and 2D materials will be presented. We will also present PiFM spectroscopy data that show excellent correlation with bulk FTIR spectra despite the fact that PiFM acquires local chemical information from regions in the range of 10 nm in extent.

[1] D. Nowak et al., *Sci. Adv.* **2**, e150157 (2016).

## Processing and Characterization of Air-Liquid, Solid-Liquid and Air-Solid Interfaces Focus Topic

Room 202A - Session PC+AS+BI+NS+PB+SS-TuM

### Solid-Liquid and Gas-Liquid Interfacial Processes and Characterization

**Moderators:** Stephen Nonnenmann, University of Massachusetts - Amherst, Juan Yao, Pacific Northwest National Laboratory

8:00am **PC+AS+BI+NS+PB+SS-TuM1 Liquefied Gas Electrolytes for Electrochemical Energy Storage Devices**, *Y.S. Meng*, University of California San Diego; *Yangyuchen Yang*, University of California at San Diego **INVITED** Electrochemical energy storage devices, such as Li-ion batteries and electrochemical capacitors, have seen little change in their electrolyte chemistry since their commercialization. These liquid electrolytes often limit the energy density and low-temperature operation of these devices, which hinder many potential applications. Our work uses electrolytes based on solvent systems which are typically gaseous under standard conditions and show excellent performance in electrochemical energy storage devices. It has demonstrated that these novel solvents have superior physical and chemical properties which are attributed to excellent performance over an extended temperature range and a wide potential window of stability with unique safety features. The use of fluoromethane as solvent for lithium batteries shows excellent low-temperature operation down to -60 °C with high capacity retention. The liquefied gas electrolytes also show a high coulombic efficiency for cycling dendrite-free lithium metal anodes.

8:40am **PC+AS+BI+NS+PB+SS-TuM3 An In situ Molecular-scale View of Nucleation and Self-assembly at Solid-liquid Interfaces**, *James De Yoreo*, Pacific Northwest National Laboratory **INVITED**

Nucleation and self-assembly from solutions are seminal processes in the formation of ordered structures ranging from simple inorganic crystals to macromolecular matrices. Observations over the past fifteen years have revealed a rich set of hierarchical nucleation pathways involving higher-order species ranging from multi-ion clusters to dense liquid droplets, as well as transient crystalline or amorphous phases. Despite their complexity, a holistic framework for understanding particle-based pathways to crystallization that extends classical concepts emerges when the coupled effects of complexity of free energy landscapes and the impact of dynamical factors that govern particle formation and interaction are considered. Here I use a series of in situ TEM and AFM studies on inorganic, organic, and macromolecular systems to illustrate that framework via the evolution in nucleation and growth processes as these complexities and dynamical factors come into play. The results show that the introduction of either size-dependent phase stability associated with the high surface-to-volume ratios of nanoparticles, or high driving force coupled with the existence of metastable polymorphs leads to two-step pathways characterized by the initial appearance of a bulk precursor phase. The creation of micro-states, which represent local minima in free energy stabilized by configurational factors associated with structural elements of molecules, can also lead to hierarchical pathways, but the intermediates are microscopic transient states that do not appear on a bulk phase diagram. However, small changes in molecular structure can eliminate these transient states, leading to a direct pathway of nucleation. Limitations on molecular mobility, either through large barriers to changes in coordination or conformation, reduced temperature, or introduction of ion-binding polymers, can freeze non-equilibrium states into place for dynamical reasons. Analysis of sub-critical cluster evolution and subsequent nucleation shows that these dynamical constraints can lead to density fluctuations in accordance with classical descriptions even when non-classical pathways dominate. The findings from these in situ studies provide a common basis for understanding the development of order in systems as diverse as simple salt crystals, branched semiconductor nanowires, and microbial membranes.

9:20am **PC+AS+BI+NS+PB+SS-TuM5 Non-linear Surface Spectroscopy at the Aerosol Particle/Gas Interface**, *Geiger, Ariana Gray Be*, Northwestern University **INVITED**

While the interface of the aerosol gas and particle phase is the first entity encountered by incoming gas phase species, accessing it with bond-specific methods has been hindered due to a lack of tools that can operate under ambient pressure and temperature conditions. Here, we overcome this

hurdle by using nonlinear optics and demonstrate the utility of vibrational sum frequency and second harmonic generation for probing the surfaces of sea spray aerosol, secondary organic aerosol, and anthropogenic influence on them. By following the heterogeneous physical and chemical processes that drive gas-to-particle conversion, aerosol formation, their transformations and phase transitions, and reactivity, we provide the molecular origin for cloud activation.

11:00am **PC+AS+BI+NS+PB+SS-TuM10 The Influence of Electrochemical Potential and Water Vapor on Ionic Liquid Binding Energy Shifts Examined by AP-XPS**, *Meng Jia*, University of Delaware; *A. Broderick, J.T. Newberg*, University of Delaware

Ionic liquids (ILs) have relatively high electrochemical and thermal stability, good conductivity and low volatility, making them inherently “greener and safer” compared to the conventional electrolytes. The application of ILs in the field of electrochemistry has identified many opportunities for their use as electrolytes in electrochemical devices. Due to the ubiquity of water and the hydrophilic nature of ILs, water can either be unintentionally present or often intentionally added to alter IL properties including density, viscosity, friction, and electrochemical window. Ambient pressure X-ray photoelectron spectroscopy (AP-XPS) is sensitive to both the chemical and electrical states of materials, which makes it an ideal method for studying surface potentials in electrochemical devices. In this work we examine the IL-gas interface of 1-butyl-3-methylimidazolium acetate, [BMIM][OAc], deposited on an Au foil via AP-XPS as function of electrochemical potential and surrounding water vapor pressure. The electrochemically induced binding energy shifts ( $\Delta BE/\Delta E$ ) of carbon, nitrogen, and oxygen species of the IL were analyzed. Results reveal that in the absence of water vapor there is an ohmic drop between the electrode-IL interface and the IL-vacuum interface, giving rise to a  $\Delta BE/\Delta E$  value of less than one. Upon introducing water vapor, forming an IL/water mixture, the  $\Delta BE/\Delta E$  approaches a value of one as a function of increasing pressure. We attribute this behavior to a decrease in the ohmic drop as the IL/water mixture becomes more conductive. These results suggest that the electrochemical potential of the IL-gas interface is influenced by both an external bias and by varying the surrounding relative humidity. The same is likely true for the IL-electrode interface where water is known to be present.

11:20am **PC+AS+BI+NS+PB+SS-TuM11 Role of Air Gas at the Interface between Water and Graphite Surfaces**, *Ing-Shouh Hwang*, Institute of Physics, Academia Sinica, Taiwan, Republic of China; *C.W. Yang, C.K. Fang*, Institute of Physics, Academia Sinica, Taiwan, Republic of China; *Y.H. Lu*, Institute of Physics, Academia Sinica, Taiwan, Republic of China; *H.C. Ko*, Institute of Physics, Academia Sinica, Taiwan, Republic of China

The saturation concentrations of nitrogen and oxygen in water under ambient conditions are very small (~10 ppm), thus their roles have been largely ignored. Using advanced atomic force microscopy, we study the evolution of gas-containing structures at graphite/water interfaces at room temperature. Our study indicates that gas (mainly nitrogen and oxygen) molecules dissolved in water tend to adsorb onto hydrophobic/water interfaces [1]. In gas-undersaturated water, we observe gradual nucleation and growth of small two-dimensional (2D) ordered domains over time on graphite surfaces [2]. The ordered structures may eventually cover the entire interface. When water is gas-supersaturated or when fresh DI water is briefly heated, we observe cap-shaped fluid nanostructures in addition to the ordered domains [3]. The cap-shaped nanostructures are the so-called interfacial nanobubbles (INBs) or surface nanobubbles, whose nature, stability, and formation remain controversial. When water is slightly gas-supersaturated, we see evolution of the fluid-like structures. The fluid phase first appears as a circular wetting layer ~0.3 nm in thickness and is later transformed into a cap-shaped INB [4]. 2D ordered domains are nucleated and grow over time outside or at the perimeter of the fluid regions, eventually confining growth of the fluid regions to the vertical direction. We determined that INBs and the fluid layers have very similar mechanical properties, suggesting low interfacial tension with water and a liquid-like nature.

Our study suggests that, in gas-undersaturated water, dissolved gas molecules may mainly be in the dispersed monomer form. Their rearrangement with water molecules at hydrophobic/water interface may lead to gradual nucleation and growth of the ordered domains. In gas-supersaturated water, some dissolved gas molecules are well dispersed in water, but others may aggregate into clusters. Adsorption of gas clusters leads to the formation of circular fluid layers at the graphite/water interface. The work clearly shows the crucial role of gas molecules at



# Tuesday Morning, October 23, 2018

hydrophobic/water interfaces and has broad implications in diverse research fields.

[1] H.-C. Ko, W.-H. Hsu, C.-W. Yang, C.-K. Fang, Y.-H. Lu, I.-S. Hwang, *Langmuir***32**, 11164 (2016)

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[4] C.-K. Fang, H.-C. Ko, C.-W. Yang, Y.-H. Lu, I.-S. Hwang, *Sci. Rep.* **6**, 24651 (2016).

11:40am **PC+AS+BI+NS+PB+SS-TuM12 Probing Cluster and Nanoparticle Growth Processes with X-Ray Spectroscopy and Mass Spectrometry**, **Musahid Ahmed**, **O. Kostko**, Lawrence Berkeley National Laboratory

## INVITED

Tunable synchrotron radiation (VUV and X-rays) provides a universal, yet selective scalpel to decipher molecular information in complex chemical systems when coupled to mass spectrometry and X-Ray spectroscopy. This provides profound insight into molecular growth mechanisms, solvation and electronic structure in clusters, complexes and nanoparticles. In the first part, I will describe how single photon ionization mass spectrometry may be applied to molecular beams to probe molecular growth that is mediated either by ion or neutral pathways. The association and dissociation pathways in acetylene clusters where bonding can change from van der Waals to covalent upon ionization leading to the formation of benzene will be described.<sup>1</sup> I will follow up with very recent results on association of water with “hydrophobic” naphthalene & “hydrophilic” glycerol where subtle non covalent interactions can lead to surprising results in electronic structure and its effect on the hydrogen bonding network of water.

X-ray spectroscopy provides a local probe of a sample’s electronic structure with elemental and site-specificity and is thus ideally suited for probing solvation. Since X-rays can probe surfaces, interfaces and bulk, and more important penetrate matter, it provides for interrogation of buried and confined spaces. Here I will describe a new approach, Velocity Map Imaging X-Ray Photoelectron Spectroscopy coupled to nanoparticle beams<sup>2</sup> that allows for the visualization of dynamic processes in solvation and molecular growth processes. I will describe its’ implementation on aqueous arginine aerosols, where by varying the pH of the constituent solution, evidence is provided that the guanidinium groups are protonated even in a very basic solution (pH 13).<sup>3</sup> A molecular level picture of how charge and proton transport in aqueous solutions of arginine occur emerges by analyzing the energy shifts on the C and N X-ray photoelectron spectra. I will conclude by suggesting new approaches to probe gas liquid interactions and chemistry with X-Ray spectroscopy and microfluidic devices allowing access to liquids in vacuum.<sup>4</sup>

[1] T. Stein, B. Bandyopadhyay, T.P. Troy, Y. Fang, O. Kostko, M. Ahmed, M. Head-Gordon, PNAS (2017), DOI 10.1073/pnas.1616464114

[2] O. Kostko, B. Xu, M.I. Jacobs, M. Ahmed, J. Chem. Phys. DOI: 10.1063/1.4982822

[3] B. Xu, M.I. Jacobs, O. Kostko, M. Ahmed, Chem. Phys. Chem. DOI 10.1002/cphc.201700197

[4] J. Yao, D. Lao, X. Sui, Y. Zhou, S. K. Nune, X. Ma, T. P. Troy, M. Ahmed, Z. Zhu, D. J. Heldebrant, X-Y. Yu, Phys. Chem. Chem. Phys. DOI: 10.1039/C7CP03754F

## Processing and Characterization of Air-Liquid, Solid-Liquid and Air-Solid Interfaces Focus Topic

Room 202A - Session PC+AS+BI+EM+NS+PB+SS-TuA

### Progress in Industrial Processes and Characterization of Interfaces and Gas-Solid Interfacial Processes and Characterization

**Moderators:** Jeffrey Fenton, Medtronic, Xiao-Ying Yu, Pacific Northwest National Laboratory

2:20pm **PC+AS+BI+EM+NS+PB+SS-TuA1 Near Ambient Pressure XPS as a Standard Tool for True Non-destructive High-throughput Surface Chemical Analysis in Industrial Applications, Andreas Thissen, P. Dietrich, SPECS Surface Nano Analysis GmbH, Germany; M. Kjaervik, W.E.S. Unger, Bundesanstalt für Materialforschung und -prüfung (BAM), Germany**

**INVITED**

Since many decades X-ray excited Photoelectron Spectroscopy (XPS) or Electron Spectroscopy for Chemical Analysis (ESCA) is a well-accepted standard method for non-destructive chemical analysis of solid surfaces. Over the last years it has been possible to develop XPS instrumentation, that can work far beyond the standard conditions of high or ultrahigh vacuum: Near Ambient Pressure (NAP)-XPS, or ESCA under environmental conditions has become a method, that enters the field of standard surface chemical analysis and thus also the industrial sector. The main reason for this is the extremely fast solid surface analysis of any (degassing or non-degassing) material. Furthermore the environmental conditions around the sample avoid strong surface degradation due to vacuum or photon stimulated desorption. Even during the analysis the sample stays under its equilibrium conditions. Last, but not least the surrounding gas pressures of a couple of mbar acts as built-in charge neutralization on any type of material. This Environmental Charge Compensation (ECC) also decreases the negative influences of the characterization on the sample constitution. All this considered, NAP-XPS is capable of true non-destructive high throughput analysis of sample surfaces. The influence of the ambient conditions on quantification in XPS will be demonstrated and discussed.

After a short summary of the relevant development steps in NAP-XPS instrumentation over the last forty years, this presentation summarizes results of surface chemical analysis on insulating polymer samples, showing the spectroscopic resolution for C1s, F1s and O1s emission lines as a comparison for PET and PTFE. Using this, the application of ECC to bulk insulators (polymeric materials, ceramics), food samples, pharmaceuticals, and different biological materials is demonstrated. The unique ability to measure liquids, like water or aqueous solutions allow for studies of drying processes of liquid containing materials, like paper or absorber materials and finally also opens the field to medical applications, especially to studies of drug uptake into gram-negative bacteria embedded in biofilms.

The last part summarizes methods to analyze materials and device under working conditions. As examples reduction and reoxidation of catalytically active compounds and operando electrochemistry will be presented. An outlook to future industrial applications will be given.

**ACKNOWLEDGEMENTS:** This project has received funding from the EMPIR programme co-financed by the Participating States and from the European Union's Horizon 2020 research and innovation programme.

3:00pm **PC+AS+BI+EM+NS+PB+SS-TuA3 Surface Modifications in the Medical Device Field – Understanding of Methods to Control Adhesion and Reactions That Materials Undergo, Jeffrey Fenton, B. Theilacker, A. Belu, B. Tischendorf, Medtronic**

**INVITED**

Advances in materials chemistry have increased the need for deep understanding of process-material interactions and their role in device or component longevity. In the medical device industry advances are due in part to operating in a federally regulated environment where it may be necessary to understand not only what is the surface chemistry, but how various chemistries interact with the body, what is clean, or where does a foreign material originate. This presentation will highlight case studies where microscopy and surface characterization techniques were successfully applied to help further understand materials performance and interactions with the body.

Polymers used in the medical industry often undergo numerous clinical trials, laboratory testing, and development to understand the body and polymer interactions. The interactions these materials often undergo may potentially be at odds with the bulk material properties. For example, it

may be desirable to modify surface properties of PTFE for polymer adhesion or modify a surface chemistry to improve bio compatibility. Methods of polymer surface modification will be presented that either enable or hinder the adhesion of a material to the surface.

Lithium ions generated during battery discharge may undergo interactions with components in or near the battery forming chemistries that may degrade battery performance or material stability. For example, lithium ions are known to interact with silica containing glass to form lithium silicide. The formation of these silicides can degrade the hermetic seal of feedthroughs. One method of studying these interactions is in-situ interfacial reactions characterization. This facile method of generating ions in-situ can be leveraged to understand what reactions may occur at a substrate surface.

The application of surface characterization techniques such as X-ray photoelectron spectroscopy (XPS), Time of Flight-Secondary Ion Mass Spectrometry (TOF-SIMS), and Scanning Electron Microscopy (SEM) provide unique insights into surface modifications and can help ensure the reliability of medical devices. These techniques support the development and manufacturing of Medtronic products such as packing and perfusion devices to improve processing conditions, understand failure modes, and surface-tissue interactions.

4:20pm **PC+AS+BI+EM+NS+PB+SS-TuA7 Ambient Pressure X-Ray Photoelectron Spectroscopy Studies of Catalytically Active Interfaces using Electron Transparent Graphene Membranes, R. Mom, L. Frevel, Fritz-Haber Institute of the Max Planck Society, Germany; J.J. Velasco-Velez, MPI CEC Mülheim, Germany; T.E. Jones, M. Plodinec, Fritz-Haber Institute of the Max Planck Society, Germany; R. Schlögl, MPI CEC Mülheim, Germany; Axel Knop-Gericke, Fritz Haber Institute of the Max Planck Society, Germany**

**INVITED**

Green production of hydrogen will be an important building block in the transition to a carbon-balanced economy and could be realized by electrolytic water splitting powered by cheap renewable energy sources. Water electrolysis is currently limited by the oxygen evolution reaction (OER) and development of the associated catalysts is proceeding slowly, mainly due to missing descriptors for activity and stability of working OER catalysts. Herein, we contribute to that emerging field with in situ XPS and NEXAFS on iridium anodes. In our in situ cell the catalyst is probed through a graphene layer, which traps an electrolyte layer around the catalyst and provides electrical contact for separated iridium nanoparticles. In this way we enhance spectroscopic signal from the active surface relative to the bulk of the catalyst and reduce mass transport problems. In taking advantage of these benefits, we found that the two well-known oxidation waves occurring before the OER onset are connected to the development of two different types of electron deficient oxygen species, which are bound to one ( $\mu_1$ ) or two ( $\mu_2$ ) iridium atoms. It appears that oxygen is not only a “non-innocent ligand”, but rather a protagonist in the catalysis of the OER.

During the electrochemical reduction of oxygen, platinum catalysts are often (partially) oxidized. While these platinum oxides are thought to play a crucial role in fuel cell degradation, their nature remains unclear. We studied the electrochemical oxidation of Pt nanoparticles using in situ XPS. By sandwiching the particles between a graphene sheet and a proton exchange membrane that is wetted from the rear, a confined electrolyte layer was formed, allowing us to probe the catalyst under wet electrochemical conditions. We show that the behavior at the onset of Pt oxidation is influenced by the choice of proton exchange membrane, yet universally involves PtO<sub>2</sub> formation. The oxidation process is fast: even bulk oxide growth occurs on the sub-minute timescale. Thus, our observations indicate that PtO<sub>2</sub> may take part in the transient processes that dominate Pt electrode degradation.

5:00pm **PC+AS+BI+EM+NS+PB+SS-TuA9 The Influence of Density and Chemical Bonding on Atomic and Molecular Structures of Alcohols, Water and Oxides, Gabor A. Somorjai, University of California at Berkeley** **INVITED** Alcohol oxidation reaction over platinum nanoparticles with size ranging from 2 to 8 nm deposited on mesoporous silica MCF-17 was studied in the gas and liquid phases. Among methanol, ethanol, 2-propanol, and 2-butanol oxidations, the turnover frequency increased as the nanoparticle size became large in both reaction phases. The activation energy in the gas phase was higher than that in the liquid phase. Water co-adsorption decreased the turnover rate of all the gas and liquid phase oxidations except for the gas-phase 2-butanol case, while certain amount of water promoted 2-propanol oxidation in the liquid phase. Sum frequency generation vibrational spectroscopy (SFG) study and DFT calculation

# Tuesday Afternoon, October 23, 2018

revealed that the alcohol molecules pack horizontally on the metal surface in low concentration and stand up in high concentration, which affects the dissociation of  $\beta$ -hydrogen of the alcohol as the critical step in alcohol oxidation.

Ice surfaces have water layers with thickness ranging from one monolayer at 100K to 30 layers of 273K. At the interfaces of two ice cubes, ice layers grow at the disappearing water interfaces (regelation). SFG studies of water surfaces show three peaks in the vibrational spectrum; "free OH", liquid like hydrogen bonded water, with half bilayer termination, and ice-like water, with bilayer termination, with more hydrogen bonds.

Most nanocatalysts are composed of highly dispersed transition metal nanoparticles on oxides. The interface between the metal nanoparticles and the oxides plays a crucial role in determining the catalytic performance of nanocatalysts. Due to non-adiabatic electronic excitation, energetic electrons in metals can be generated during exothermic chemical processes. The energy barrier formed at the metal-oxide interfaces leads to the irreversible transport of energetic, or hot, electrons. The dopants and impurities present on the oxides can generate additional charge carriers or oxygen vacancies that affect the catalytic activity. The accumulations or depletion of hot electrons on the metal nanoparticles, in turn, can also influence the catalytic reactions. In this talk, we outline recent studies of the role of metal oxide interfaces and characteristics of fast charge transfer between metals and oxides that lead to ionization of molecules at the interface. The molecular ions produce so-called acid-base reactions. The electronic configuration of metal-oxide nanocatalysts during catalytic reactions will be introduced and its influence on heterogeneous catalysis will be outlined.

5:40pm **PC+AS+BI+EM+NS+PB+SS-TuA11 Atomic Scale Observation of Oxidation and Reduction of Palladium Surface**, *Takehiro Tamaoka, H. Yoshida, S. Takeda*, Osaka University, Japan

Reaction processes on metal surfaces under gas environment have been investigated in various research fields such as catalysis, gas sensing, and many more. Palladium is a well-known material which is used for hydrogen storage, hydrogen sensing, and exhaust catalysis. Therefore, the phase transition of palladium in hydrogen or oxygen has been extensively investigated by means of environmental transmission electron microscopy (ETEM). However, the oxidation and reduction process of palladium surface at the atomic scale remain poorly understood.

Here, we investigated the surface structure of a wedge-shaped palladium specimen in both hydrogen and oxygen by means of in-situ atomic resolution ETEM. Under ambient condition the surface of palladium is oxidized by several nanometers. After introducing hydrogen (100 Pa) in ETEM, the native oxide layer (PdO) was reduced to metallic fcc palladium even at room temperature. After exposure and exhaustion of hydrogen, we introduced oxygen (100 Pa) in ETEM. The palladium oxide was reproduced and the ETEM results show that the oxidation started from step edges and terraces and proceeded until the palladium surface was completely covered by the palladium oxide.

We also show that oxidation of palladium is dependent on the history of hydrogen exposure. When the duration of hydrogen exposure was over 90 min., we found that the surface was not oxidized. This was not due to bulk hydrogenation as demonstrated by our electron energy loss spectroscopy (EELS) results. We performed similar studies for the surface of platinum in oxygen after prolonged hydrogen exposure. However in platinum, the oxidation of the surface was not suppressed. This suggests that the process for suppression of oxidation, after prolonged hydrogen exposure, exists for palladium and not for platinum.

From these results, we hypothesize possible processes that explain how the prolonged hydrogen exposure suppresses the oxidation of palladium surface. We will also present atomic-scale in-situ movies on the surface dynamics in palladium and platinum in various processing.

6:00pm **PC+AS+BI+EM+NS+PB+SS-TuA12 Polymorphism of Hydrogen-Bonded Clusters at the Vacuum-Solid Interface**, *Angela Silski, J. Petersen*, University of Notre Dame; *R.D. Brown*, Clarkson University; *S. Corcelli, S.A. Kandel*, University of Notre Dame

Molecular self-assembly is an attractive bottom-up approach to nanostructure fabrication. Using molecules as building blocks and carefully tuning the non-covalent intermolecular interactions, unique nanostructured architectures can be designed. Given the structure/function relationship on the nano- and meso-scale, this bottom-up approach to designing new architectures is critical in the careful design of novel materials with desired chemical properties. In this study, the role

of hydrogen bond donor/acceptor position in metastable cluster formation is explored using scanning tunneling microscopy (STM) with complementary density functional theory (DFT) calculations. We observe a metastable cyclic pentamer for isatin (1H-indole-2,3-dione) with DFT providing support for a cyclic structure stabilized by both NH...O and CH...O hydrogen bonds between neighboring molecules. The CH...O hydrogen bond is made between the 7-position proton acting as the hydrogen bond donor and the 3-position carbonyl as the hydrogen bond acceptor, and calculations indicate that the isatin pentamer structure is 12 kJ/mol more stable than the dimer on the per molecule basis. To probe the importance of the CH...O hydrogen bond in stabilizing the isatin pentamer, we compare to isatin derivatives: we replace the 3-position carbonyl with a methyl group (3-methyl 2-oxindole), the 7-position proton with a fluorine (7-fluoroisatin), systematically move the location of the hydrogen bond donor/acceptor by one position, (phthalimide), and remove of the primary hydrogen bond donor (1,2-indandione and 1,3-indandione). We show that cyclic pentamer formation is either altered or precluded as a result of these substitutions. Additionally, the importance of CH...O bonding in forming isatin pentamers is supported by electrospray ionization mass spectrometry (ESI-MS) measurements, which include a magic-number isatin pentamer peak, whereas the derivative molecules show little clustering under the same conditions. This work is significant in understanding the role that the position of the hydrogen bond donor/acceptor groups has on the resulting 2D supramolecular assemblies.

## Processing and Characterization of Air-Liquid, Solid-Liquid and Air-Solid Interfaces Focus Topic

Room Hall B - Session PC+AS+BI+EM+NS+PB+SS-TuP

## Processing and Characterization of Gas-Liquid, Solid-Liquid, and Gas-Solid Interfaces

**PC+AS+BI+EM+NS+PB+SS-TuP1 Operando Photoelectron Spectroscopic Study of Copper-based Oxide Semiconductor Interface with Water,** *Pitambar Sapkota, S. Ptasinska*, University of Notre Dame; *A. Cabrera*, Instituto de Física, Pontificia Universidad Católica de Chile

The quest for suitable semiconductor photoelectrodes to build efficient and stable photoelectrochemical (PEC) cells for solar water splitting is continually growing in the material sciences and solar energy community. Along with good stability in aqueous media, such photoelectrodes should have suitable band-edges and band-gap energies properly matching both the water oxidation-reduction potential and the solar spectrum, respectively. Copper-based oxide semiconductors are promising candidates fulfilling these criteria, but little is known about the interfacial properties of these compounds with H<sub>2</sub>O under operational conditions. Therefore, knowledge of their surface dynamics and interfacial reactions under realistic conditions is essential to improve our understanding of water-splitting mechanism, as well as to increase the stability and efficacy of PEC devices. Ambient pressure X-ray photoelectron spectroscopy was used to characterize the semiconductor surface and study the chemical reactions occurring at the interface under the reaction conditions. In this study, thin films of CuFeO<sub>2</sub> and CuFe<sub>1-x</sub>Ga<sub>x</sub>O<sub>2</sub> composites were exposed to various H<sub>2</sub>O pressures and temperatures. Water interactions with the Cu-based oxide surface and the electronic structures of the surface atoms were evaluated from the Cu 2p, Fe 2p, C 1s and O 1s photoemission spectra to identify surface species newly formed.

**PC+AS+BI+EM+NS+PB+SS-TuP2 Interfacial Water in Silicon-based Catalytic Motors,** *Jordi Fraxedas, K. Zhang, B. Sepulveda, M.J. Esplandiu*, Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and BIST, Spain; *X. Garcia, J. Llorca*, Institute of Energy Technologies, Department of Chemical Engineering and Barcelona Research Center in Multiscale Science and Engineering. Universitat Politècnica de Catalunya, Spain; *V. Perez-Dieste, C. Escudero*, Alba Synchrotron Light Source, Spain

Self-propelled motors that can harvest chemical energy from their surroundings to convert it in mechanical energy are at the cutting edge of nanotechnology for their appealing applications in e.g., environmental remediation and nanobiomedicine. A full understanding of the propulsion mechanism is crucial to improve their performance and controllability. Recently, a simple motor made of silicon and a noble metal that can operate with visible light has been developed [1]. The photoactivation mechanism and consequent motion is essentially based on the formation of electron/hole pairs. The holes are strong oxidizing agents for the species in the fluid producing protons and the electrons can diffuse towards the metal surface and participate in the counterpart reduction reaction. As a result, a gradient of proton concentration is formed in the fluid which builds-up an electric field driving the motion of the fluid through electro-osmosis. A mechanism that competes with the electro-osmotic process is based on diffusion-osmosis and is triggered by the redox decomposition exclusively at the metal surface and is not light responsive. We have recently shown that it is possible to enhance/suppress one mechanism over the other by tuning the surface roughness of the micromotor metal. Thus, the actuation mechanism can be switched from light-controlled electrokinetics to light-insensitive diffusio-osmosis by only increasing the metal surface roughness [2].

We have recently performed near ambient pressure photoemission studies of Pt/Si micromotor surfaces activated by oxygen plasma in water atmosphere at the NAPP endstation of the CIRCE beamline at the ALBA synchrotron near Barcelona. We have used p-type silicon substrates with one half covered with a Pt film with a thickness of about 50 nm grown by both e-beam and sputtering deposition. The results reveal a chemical gradient at the Si/Pt edge with a reduction of the Pt species. The analysis has to carefully consider the photochemical reactions induced by the combined action of the impinging beam and the water condensed at the surfaces. The beam induced damage evolves in two regimes: an initial preferential reduction of Pt<sup>4+</sup> species and then the reduction of Pt<sup>2+</sup> species, which increases the metallic character of the surface.

[1] M.J. Esplandiu, A. Afshar Farniya, A. Bachtold, ACS Nano, 9, 11234 (2015).

[2] K. Zhang, J. Fraxedas, B. Sepulveda, M. J. Esplandiu, ACS Appl. Mater. Interfaces 9, 44948 (2017).

**PC+AS+BI+EM+NS+PB+SS-TuP3 Chiral Modification of Oxide-Supported Pt Surfaces: An in-situ ATR-IR Study,** *Yufei Ni*, University of California, Riverside; *F. Zaera*, University of California, Riverside

The synthesis of enantiopure compounds is of great significance to the designing of pharmaceuticals and agro products. Possible methods for the manufacture of enantiopure chemicals include the separation of racemic product mixtures and reactions with other chiral chemicals, but perhaps the most promising procedure is the use of enantioselective heterogeneous catalysis. Chiral modification of catalytically active metals such as Pt and Ni is believed to be the most feasible approach to produce chiral heterogeneous catalysts. In this context, the use of cinchona alkaloids-modified Pt for the hydrogenation of activated ketones has drawn particular attention in the past few decades. A better understanding of how these chiral modifiers work to bestow enantioselectivity is still a prerequisite for the design of such catalysts.

In this project, we have used attenuated total reflection infrared absorption spectroscopy (ATR-IR) to investigate the details of the adsorption of such cinchona-alkaloid chiral modifiers on the Pt surfaces of supported catalysts in situ at the liquid-solid interface. It was determined that adsorption can be only observed after H<sub>2</sub> pretreatment of the catalyst. A comparison study in terms of adsorption strength was carried out using not only cinchona alkaloids such as cinchonidine and cinchonine but also simpler alternatives such as (R)- or (S)-(-)-1-(1-naphthyl) ethylamine (NEA), naphthylmethyl amine, and dimethyl naphthyl ethylamine. The adsorption strength of the different modifier molecules was found to be quite different among those compounds. This is illustrated by the fact that quinoline can displace s-NEA from Pt but not vice versa, for instance, and by the observation that when Pt is exposed to a solution containing both quinoline and s-NEA only the quinoline's signature peaks can be detected by ATR-IR spectroscopy. The ordering of the modifiers studied in terms of adsorption strength was found to correlate with their ability to chirally modify the Pt catalyst during the hydrogenation of unsaturated aldehydes.

Finally, it was found that NEA bonds to the metal through the nitrogen atom of its amine moiety, and not through the aromatic ring as commonly believed.

**PC+AS+BI+EM+NS+PB+SS-TuP4 Wettability Behaviour of Synthesized Carbon Nanospheres and its Application as a Photocatalyst,** *Sonal Singhal, A.K. Shukla*, IIT Delhi, India

Superhydrophobic and superhydrophilic surfaces have been widely investigated due to their diverse range of applications such as self-cleaning, microfluidic application in biotechnology, corrosion, Anti-reflecting coatings and microelectronic mechanical system etc. Here, a facile chemical vapour deposition method is reported for the synthesis of carbon nanospheres (CNSs). Henceforth, the morphology of as-synthesized sample is characterized using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). X-ray diffraction (XRD), Raman spectroscopy and FTIR spectroscopy are used to determine the phase purity, chemical composition and presence of chemical bonds on the surface of synthesized CNSs. TEM and SEM results reveal the presence of CNSs with a diameter ranging from 50 nm to 400 nm. Raman spectroscopy confirms the presence of disordered carbon and low graphitization, which are also confirmed by TEM and XRD results. Optical properties of as-synthesized CNSs is investigated by UV-Vis spectroscopy and photoluminescence. Wettability behaviour of as-synthesized carbon nanospheres is investigated by contact angle measurements. CNSs shows a water contact angle of 152°, which confirms the fabrication of superhydrophobic carbon nanosphere surface. After the proper explanation of wettability behaviour, it also discusses the application of as-synthesized CNSs as a photocatalyst. As it is well known, catalyst enhances the chemical reaction rate without changing its properties. Therefore, various kind of catalysts has been developed for the purpose to enhance the catalysis for environmental applications. Among different materials, carbon-based materials are widely used as a catalyst support due to their excellent properties. Considering these facts, the degradation of an organic pollutant under UV light is discussed here using CNSs.

# Tuesday Evening Poster Sessions, October 23, 2018

**PC+AS+BI+EM+NS+PB+SS-TuP5 Thermally Driven Solid-solid Li<sup>+</sup> Transfer into Nanostructured TiO<sub>2</sub>**, *Tiffany Kaspar, T. Varga*, Pacific Northwest National Laboratory; *D.A. Shapira*, Advanced Light Source, Lawrence Berkeley National Laboratory; *A. Martinez, Y. Shin, K.S. Han, M.-S. Lee, S. Thevuthasan, V. Murugesan*, Pacific Northwest National Laboratory

Due to their good chemical stability, strong oxidation capability, and desirable lithium electrochemical activity, nanostructured titanium dioxide (TiO<sub>2</sub>) anode materials have received considerable attention recently. Decreasing the particle size to 10-20 nm can increase the electrochemical capacity to 200-300 mAhg<sup>-1</sup>. Furthermore, nanostructured TiO<sub>2</sub> anodes are non-toxic and would be suitable for cost effective mass production. Among the rutile, anatase, and brookite polymorphs of TiO<sub>2</sub>, anatase nanoparticles have shown the best Li ion insertion properties and maximum reduction, indicating increased Li ion intercalation into the material. Here, we have synthesized 10-20 nm anatase TiO<sub>2</sub> nanoparticles and contacted them with solid Li- bis(trifluoromethanesulfonyl)imide (LiTFSI) as a function of temperature to understand the chemical and structural effects associated with thermally driven solid-solid Li<sup>+</sup> transfer to, and intercalation in, TiO<sub>2</sub> nanoparticles. We have used a combination of x-ray photoelectron spectroscopy (XPS), Ti L-edge scanning transmission x-ray microscopy (STXM), Raman spectroscopy, and nuclear magnetic resonance (NMR) spectroscopy to gain a fundamental understanding of the structural evolution of TiO<sub>2</sub> nanoparticles during Li<sup>+</sup> intercalation. Our results indicate that thermally driven solid-solid Li<sup>+</sup> transfer to TiO<sub>2</sub> has occurred, and altered the TiO<sub>2</sub> structure at the edges of the agglomerated nanoparticles.

## Processing and Characterization of Air-Liquid, Solid-Liquid and Air-Solid Interfaces Focus Topic

Room 202A - Session PC+AS+BI+EM+PB+SS-WeM

### Novel Approaches and Challenges of Interfaces

**Moderators:** Andrei Kolmakov, National Institute of Standards and Technology (NIST), Xiao-Ying Yu, Pacific Northwest National Laboratory

8:00am **PC+AS+BI+EM+PB+SS-WeM1 Probing Chemical Species and Potential Profiles of Electrified Interfaces, Ethan J. Crumlin**, Advanced Light Source, Lawrence Berkeley National Laboratory **INVITED**  
Interfaces play an important role in nearly all aspects of life, and are essential for electrochemistry. Electrochemical systems ranging from high temperature solid oxide fuel cells (SOFC) to batteries to capacitors have a wide range of important interfaces between solids, liquids, and gases which play a pivotal role in how energy is stored, transferred, and/or converted. This talk will focus on our use of ambient pressure XPS (APXPS) to directly probe the solid/liquid electrochemical interface. In particular, I will discuss how we were able to probe the potential drop within the electrochemical double layer (EDL) as well as the potential of zero charge under polarization conditions. This unique approach was accomplished by measuring spectral changes observed in both the electrolyte (water) and a neutral spectator probing molecule (pyrazine). By combining these experiments with numerical simulations provided the ability to discern the shape of the electrochemical double layer profile as a function of both electrolyte concentration and applied potentials. Extending beyond the EDL, I will highlight some of our recent investigations into both the oxygen evolution reaction on a platinum electrode as well as a magnesium electrode in a non-aqueous electrolyte. Information gained from these studies will aid in the guided design and control of future electrochemical interfaces.

8:40am **PC+AS+BI+EM+PB+SS-WeM3 Observation of Electron Transfer in Riboflavin Reduction by In Situ Liquid SIMS, Rachel Komorek, X.F. Yu, Z.H. Zhu, X-Y. Yu**, Pacific Northwest National Laboratory

Riboflavin is of vital significance in living processes as a precursor of the two important coenzymes flavin mononucleotide (FMN) and flavin adenine dinucleotide (FAD).[1] The isoalloxazine ring in riboflavin plays an important role in energy supplementation and cellular respiration, since it has the capability to accept electrons in some redox reactions.[2] Understanding riboflavin reduction could potentially bring insight into the electron transfer process between cell surfaces and conductive materials.

Thus, the electrochemical reduction process of riboflavin has drawn increasing attention. In this study, the riboflavin reduction mechanism in an aqueous solution has been investigated using time-of-flight secondary ion mass spectrometry (ToF-SIMS) with the electrochemical cell.[3, 4] Positive and negative ion mode mass spectra were used to depict the molecular information of species dissolved in the electrolyte. The distribution of key reduction intermediates were mapped at the electrode-electrolyte interface using dynamic depth profiling. To examine product formation as a function of applied potentials, measurements were made by holding the potential at 0, -0.3, 0.3, and 0.6 V respectively, once interesting electrochemistry was determined using the cyclic voltammogram. Furthermore, gold and graphite electrodes were both used in our experiment to investigate if the electrode surface plays a role in the electrochemical reaction mechanism. Preliminary spectral principal component analysis (PCA) results have shown key chemical distinctions in the electrolyte at 0, -0.3, 0.3, and 0.6 V. Selected peak spectral PCA is required to gain a better understanding of this observation, which will allow for a more comprehensive chemical profile of the electron transfer process in riboflavin redox reactions.

**Key words:** in situ liquid SIMS, SALVI, riboflavin reduction, electrochemistry, electron transfer

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3. B Liu, et al., In situ chemical probing of the electrode-electrolyte interface by ToF-SIMS. *Lab Chip* (2014), **14**, 855-9.

4. J Yu et al., Capturing the transient species at the electrode-electrolyte interface by *in situ* dynamic molecular imaging. *Chem. Comm.* (2016), **73**, 10929-11206.

9:00am **PC+AS+BI+EM+PB+SS-WeM4 Electrowetting of Liquid Drops Revisited by XPS, Sefik Suzer, P. Gokturk, B. Ulgut**, Bilkent University, Turkey

Electrowetting behavior of liquid drops has been followed in-situ and in-vacuum using XPS in a chemically resolved fashion, under both dc and ac excitations. Various Liquid drops, compatible with the UHV conditions, consisted of an Ionic Liquid (DEME-TFSI), Poly-ethylene-glycol (M.W. ~600 amu) and their mixtures. For the dielectric substrate, a ~300 nm thick silicon oxide (SiO<sub>2</sub>/Si) without and with a thin hydrophobic coating (CYTOP) has been employed. XPS data have been recorded both in the conventional scan- and also in the fast (<1s) snap-shot modes. Intensity and position of the peaks, representing the liquid drops (F1s in the case of the IL, or C1s/O1s of the PEG) as well as those of the substrates (Si2p for the oxide only and F1s for the hydrophobic coated one) have been recorded under various electrical excitations. Under ac excitation at a fixed frequency, intensity modulations in the XPS peaks reveal geometrical changes of the drops, while the peak position modulations reveal electrical potentials developed. Monitoring position modulations as a function of the changes in the ac frequency (10<sup>-2</sup> – 10<sup>5</sup> Hz) allows us to tap into ionic, dipolar and electrical contributions of the dielectric susceptibility of both the liquid drops and the substrates. Experimental details and various application will be presented and discussed.

\*This work is partially supported by TUBITAK through Grant No. 215Z534

9:20am **PC+AS+BI+EM+PB+SS-WeM5 Probing Interfaces in Heterogeneous Catalysts at Atomic Scale: Current and Emerging STEM Techniques, M. Chi, Wenpei Gao**, Oak Ridge National Laboratory **INVITED**

Chemical reactions take place on the surfaces and interfaces of heterogeneous catalyst systems. Depending on the phase of the reactant, the reactive interfaces include those between solid-gas, solid-liquid, and triple-phase interfaces of solid-gas-liquid. At these interfaces, the catalyst provides active sites where the reactants are adsorbed, activated, and converted to new chemical species that are eventually released from the catalyst surface. The ability of catalysts in promoting these reactions is determined by the surface binding energy, which can be modified by tuning the interfacial atomic arrangements or by forming new interfaces, e.g., forming core-shell structures. Understanding the formation of these interfaces during synthesis and their structural and chemical evolution during operation are important to the rational design of future high-performance catalysts. Probing these dynamically evolving interfaces at a sufficient spatial resolution, however, presents many challenging. Recent work on elucidating the formation and the operation mechanisms of interfaces in precious metal-based heterogeneous catalysts using *in situ* atomic-scale scanning transmission electron microscopy (STEM) techniques will be discussed. Several emerging STEM-based methods, such as vibration spectroscopy and atomic-scale differential phase contrast imaging that are currently under development within the microscopy community will be introduced, and their prospective influence on future studies to design functional interfaces in heterogeneous catalysts will be discussed.

**Acknowledgements:** Research supported by the Center for Nanophase Materials Sciences, which is a U.S. Department of Energy (DOE) Office of Science User Facility.

11:00am **PC+AS+BI+EM+PB+SS-WeM10 From 2D to Advanced 3D Surface Functionalization using Self-limiting Reactions in the Fluidized Bed Reactor Technology, Didier Arl, T. Da Cunha, N. Adjeroud, K. Menguelti, M. Gerard, D. Lenoble**, Luxembourg Institute of Science and Technology (LIST), Luxembourg

The integration of novel functional nanomaterials like high specific surface powders in polymeric or inorganic matrices requires a fine control of their properties. The design of these nanoscopic agents is linked to the development of nanotechnology processes which can be transferred from planar substrates to complex 3D surfaces. In this framework we showed how self-limiting reactions inspired by Atomic Layer Deposition can be applied to functionalize powder by using a specifically designed Fluidized Bed Reactor. A specific interest has been given to work in non-saturated regime with nickel or Cobalt acetylacetonate to obtain well controlled metal nanocatalysts of 5-10nm diameter. Depending on the process window, some interesting properties have been demonstrated such as ferromagnetic behavior or the systematic recover of the Metal-Carbide phase that increase the throughput of Carbon Nanotubes growth. These

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activated nanostructures can expressly improve the electrical, the thermal or the mechanical properties of some related composites depending on how some processing parameters such as exposure time, pressure or local temperature can be tailored.

## Nanometer-scale Science and Technology Division Room 203A - Session NS+MN+PC+SS-WeA

### IoT Session: Bio at the Nanoscale

**Moderators:** Juraj Topolancik, Roche Sequencing Solutions, Liya Yu, NIST Center for Nanoscale Science and Technology

#### 3:00pm NS+MN+PC+SS-WeA3 Nanoscale Label-free Imaging of Protein Molecules via Photo-induced Force Microscopy, D. Nowak, Sung Park, Molecular Vista

Nanoscale real space imaging of biological and biomaterial surface is not straightforward even with advances in microscopy techniques. Photo-induced Force Microscopy (PiFM) [1] combines infrared (IR) absorption spectroscopy and atomic force microscopy (AFM) via illumination of the tip-sample junction with tunable IR laser light and mechanical detection of forces acting on the tip in response to absorption of light by the sample. By mapping the IR absorption of the sample as a function of IR wavelength and position, nm-scale resolution is achieved in displaying the locations of heterogeneous materials on the surface of a sample. For protein molecules, amide I and II bands are readily accessible via tunable quantum cascade laser and provide ways to interrogate the molecule's local chemical environment. PiFM can provide both high resolution spectral imaging at a fixed wavenumber and full PiFM spectrum (analogue to FTIR spectrum) with a spectral resolution of  $1\text{ cm}^{-1}$  and spatial resolution of sub-10 nm. Results on collagen molecules, individual icosahedral protein cages, and nanoparticle/protein systems will be presented.

[1] D. Nowak et al., *Sci. Adv.* **2**, e150157 (2016).

#### 3:20pm NS+MN+PC+SS-WeA4 Evaluating Reaction-diffusion Immunoassays via High-resolution Imaging Techniques, Imanda Jayawardena, University of Queensland, Australia; S. Corrie, Monash University, Australia; L. Grøndahl, University of Queensland, Australia

Immunodiffusion is a simple assay used for the determination of a target protein concentration in a biological sample using a distance-based measurement. The assay allows the sample containing the antigen of interest to combine with an antiserum in a gel-based substrate leading to the formation of a ring-shaped precipitate ('precipitin ring'), the size of which is proportional to target protein concentration.<sup>1</sup> Using the malarial antigen HRP2 and antisera from immunized rabbits as the model system, for the first time, we are investigating transforming the current immunodiffusion assays into a more rapid and sensitive format.

The traditional assay substrate, agarose, is a severely diffusion limited system. The porosity of the gel is a key determinant of diffusion properties and is an essential parameter required for the study and modification of the assay. However, the scientific data on agarose pore size determination is based on artefact laden microscopy images of agarose hydrogels. Thus, we have performed an in-depth investigation on best imaging techniques for accurate pore size determination. The precipitin ring structure is a band of antigen-antibody precipitate, in significant contrast with the surrounding gel substrate. A brief preliminary investigation has been reported by Fedorov et al. on precipitin ring structure<sup>2</sup>, and we have extended this work by applying microscopic imaging techniques.

For imaging hydrogels, high pressure frozen gels were subjected to cryo-SEM<sup>3</sup>, and was established as the most accurate technique to study the native structure of the gel. Atomic force microscopy was found to complement cryo-SEM data while CLSM due to its limited resolution was found to be inadequate for the imaging of hydrogels. For imaging the protein-rich precipitin ring structure, high pressure frozen ring sections were subjected to cryo-SEM, however, more meaningful insight on the ring structure was obtained in this instance through CLSM studies.

Herein, we aim to present our work described above on imaging agarose hydrogels for accurate pore size determination and imaging precipitin ring structures associated with immunodiffusion assays.

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#### 4:20pm NS+MN+PC+SS-WeA7 The Last Nanometer – Hydration Structure of DNA and Solid Surfaces Probed by Ultra-High Resolution AFM, Uri Sivan, K. Kuchuk, I. Schlesinger, Technion - Israel Institute of Technology, Israel INVITED

Recent advancements in atomic force microscopy facilitate atomic-resolution three-dimensional mapping of hydration layers next to macromolecules and solid surfaces. These maps provide unprecedented information on the way water molecules organize and bind these objects. Since the hydration structure governs the energetics of solvation and interactions between objects immersed in solution, the new data are invaluable when trying to resolve fundamental questions such as identification of molecular binding sites and interaction mechanisms.

After a short presentation of our home-built microscope, characterized by sub 0.1 Å noise level, the talk will focus on two representative studies. The first one will disclose our recent finding that in solutions in contact with atmosphere, hydrophobic surfaces are generically coated with a dense layer of adsorbed gas molecules. This layer renders the hydrophobic interaction a certain universality, regardless of the underlying surface. The second study will present our recent success in obtaining ultra-high resolution images of DNA and 3d maps of its hydration structure. This study shows that labile water molecules concentrate along the DNA grooves, in agreement with known position of DNA binding sites.

#### 5:00pm NS+MN+PC+SS-WeA9 Open-hardware, High-speed Atomic Force Microscopy using Photothermal Off-resonance Tapping, Georg Fantner, École Polytechnique Fédérale de Lausanne, Switzerland INVITED

Self-assembly of protein complexes is at the core of many fundamental biological processes. To reach a comprehensive understanding of the underlying protein self-assembly reactions, high spatial and temporal resolution must be attained. This is complicated by the need to not interfere with the reaction during the measurement. Since self-assemblies are often governed by weak interactions, they are especially difficult to monitor with high-speed atomic force microscopy due to the non-negligible tip-sample interaction forces involved in current methods. Here we develop a high-speed atomic force microscopy technique, photothermal off-resonance tapping (PORT), which is gentle enough to monitor self-assembly reactions driven by weak interactions. Using photothermal actuation on ultra-small HS-AFM cantilevers we perform force-distance curves at two orders of magnitude higher rates than in conventional off-resonance methods. From the time-domain tip sample interaction we extract tip-sample force curves to quantify the "static" forces due to the cantilever deflection, and the "impact" forces due to the rapid deceleration of the cantilever tip upon impact. Experimental characterization of the tip-sample forces in HS-tapping mode-AFM and PORT revealed that imaging forces in PORT are less than  $1/5^{\text{th}}$  of those exerted in conventional HS-AFM.

One of the key enabling factors for PORT is the real time control of the cantilever position using photothermal excitation. This requires low level, control of the feedback architecture and optimized AFM instrumentation. I will discuss the relevant components developed in my laboratory and explain how we share them with the broader scientific community using an open-hardware scheme.

We apply PORT to dissect the self-assembly reaction of SAS-6 proteins, which form a nine-fold radially symmetric ring-containing structure that seeds formation of the centriole organelle present in all eukaryotic cells. Using machine learning algorithms we traced hundreds of molecules over time to extract reaction kinetics from single molecule interactions. These measurements show that 9-fold closed SAS-6 rings are under pre-tension in their natural state. Due to the high temporal and force resolution provided by PORT, we found that, contrary to the current belief, more than one assembly route exists to reach the nine fold symmetry. These observation resets our current thinking about the assembly kinetics of this crucial step in cell replication.

#### 5:40pm NS+MN+PC+SS-WeA11 Development of Multimodal Chemical Nano-Imaging for in situ Investigations of Microbial Systems, A. Bhattarai, B.T. O'Callahan, P.Z. El Khoury, Scott Lea, Pacific Northwest National Laboratory; K.-D. Park, E.A. Muller, M.B. Raschke, University of Colorado Boulder

Existing genomic and biochemical methods cannot directly probe the physical connections involved in microbial metabolic processes over relevant length scales, spanning the nano-meso-micrometer spatial regimes. Determining the location and function of such biomolecules would aid in identifying the mechanisms governing microbial interactions. We are addressing these technical and conceptual gaps by developing a



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single multimodal chemical imaging platform that can interrogate biomolecules in living systems using three complementary label-free, nanoscale, ultrasensitive chemical imaging techniques:

Infrared scattering scanning near-field optical microscopy (IR s-SNOM)

Tip-enhanced Raman nano-spectroscopy (TERS)

Multimodal hyperspectral optical nano-spectroscopy.

We have built and developed these imaging modalities independently prior to integration into a single, multimodal chemical nanoscope. As part of our benchmarking experiments, we performed TERS measurements targeting prototypical systems and constructs and demonstrated <1 nanometer precision in ambient TERS chemical imaging measurements.<sup>[1]</sup> We also established an overall broader scope of TERS<sup>[2]</sup> and illustrated that TERS is not restricted to nanoscale chemical imaging, but can also be used to probe different aspects of local fields confined to a few nanometers. Our new setup, equipped with a hyperspectral imager, enables hyperspectral fluorescence, optical absorption, dark-field scattering, Raman scattering, and topographic imaging. Recently, we used this capability to visualize pigments in lipid monolayers and within a single live *T. lutea* cell in solution.<sup>[3]</sup> For IR s-SNOM, we are working on developing an AFM capable of bottom illumination and collection of IR light to support measurements in aqueous environments. The approach would use a piezoelectric scanner mounted ZnSe prism to enable evanescent wave illumination and collection of scattered IR light. We are also benchmarking the IR s-SNOM with the TERS and hyperspectral imaging modalities on a number of model biological systems including bacteria, collagen, and cytochromes.

This unique AFM-based instrument could be used to investigate a wide range of biomolecules through their characteristic electronic and vibrational signatures, over the nano-meso-micrometer scales. This platform will not only enable recording chemical images of single microbial cells at the subcellular level, but it will also enable mapping entire microbial communities with chemical selectivity.

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## Plasma Biology, Agriculture, and Environment Focus Topic Room 104A - Session PB+BI+PC+PS-WeA

### Plasma Agriculture & Environmental Applications

Moderator: Deborah O'Connell, University of York, UK

#### 2:20pm PB+BI+PC+PS-WeA1 Pulsed Power Applications for Farming and Food Processing, Koichi Takaki, Iwate University, Japan INVITED

High-voltage and plasma are useful in several stages in agriculture, fishery and food processing including contribution to the food safety. Pulsed high-voltage produces intense high-electric field which can cause some biological effects such as stress response (stimulation) and electroporation. Types of pulsed power that also have biological effects are caused with gas discharges and water discharges which include reactive species such as ROS and RNS. We developed repetitively operated compact pulsed power generators with a moderate peak power for the agricultural applications.

The pulsed repetitive discharge were used for promoting growth of the vegetables and fruits. The growth rate of the vegetables and sugar content in the strawberry harvested after the cultivation increased by the plasma irradiation to the hydroponic solution [1]. The plasma was irradiated in the drainage water for 10 and 20 minutes each day. The leaf size of the plants increased with plasma treatment time. Number of colony forming units (CFU) of *R. solanacearum* in the liquid fertilizer decreased from  $10^7$  to  $10^2$  CFU/mL using the discharge plasma treatment [2]. Seedlings with discharge plasma treatment were relatively healthy; in contrast, all seedlings in the positive control wilted and died from infection of *R. solanacearum* after 12 days. The yielding rate of Shiitake mushroom (*L. edodes*) was also improved with the high-voltage stimulation in fruit-body formation phase [3].

Electrostatics effect were used for keeping freshness of not only agricultural products [4, 5], but also marine products [6]. In postharvest phase of agriculture, keeping freshness in storage house and in transportation container is important. The electrostatic effects can contribute to remove airborne bacteria and fungi spore from the storage house and container [4]. This removal contributes to reduce the infection risk with fungi and bacteria. Some kinds of fruit and vegetable emit the ethylene gas which accelerate a degradation of other kind fruits and

vegetables. The plasma can contribute the ethylene removal via oxidation reaction [5]. The AC electric field induces a conformational change of protein. This technologies can contribute to extend the freshness of marine products [6].

#### References:

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#### 3:00pm PB+BI+PC+PS-WeA3 Stimulus Control on Organisms Using Pulsed Power Technology, Douyan Wang, T. Namihira, Institute of Pulsed Power Science, Kumamoto University, Japan INVITED

Pulsed power is instantaneous ultra-high power with high energy density ( $10^5$ - $10^7$ J/m<sup>3</sup>). By controlling and utilizing it in a narrow space and an instantaneous time, phenomena and reactions that are not attained by conventional and ordinary methods can be achieved. For instance: electromagnetic field, discharge plasma, shockwaves, intense light emission, etc. By selecting or combining some of these physical phenomena, it is able to control the degree of output performance. Bioelectrics refers to the use of pulsed power, powerful pulsed electric or magnetic field for extremely short periods of time, non-thermal plasmas in gases or liquids and shock waves, in order to give novel physical stresses to biological cells, tissues and/or organisms as well as bacteria. Bioelectrics is an interdisciplinary academic field over physics, chemistry, biology, medical science, agriculture, environmental, mechanical and electrical engineering, and is expected to open up new science and technology.

By controlling the degree of electrical stimulations using pulsed power, it is possible to either inactivate biological targets or keep them alive and activate their functions. Examples of inactivation are given as: sterilization of liquids, treatment of algae and marine harmful organisms, growth inhibition of plants. On the other hand, more delicate stress control enables the activation of living organisms such as transcriptional activation of genes, substance transduction into cells, growth enhancement of plants. Both direct and indirect stimuli are useful. Here, aerial, liquidus and edaphic environmental control are examples of the indirect stimulus.

#### 4:20pm PB+BI+PC+PS-WeA7 Synthesis of Nitrates by Atmospheric Microplasma in Aqueous Solution, Nicolas Maira, F. Reniers, Universit e Libre de Bruxelles, Belgium

For many years, cold atmospheric plasma techniques have been used for a large variety of applications such as surface modification, film deposition, nanoparticles synthesis or pollutants degradation. One of their main advantage is the possibility to work with a gaseous, liquid or solid phase. In this study, the plasma water treatment is investigated for a potential application in agriculture. When water solutions are treated by plasma, in air environment, several reactive oxygen and nitrogen species (RONS) are generated [1,2]. The main RONS are hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), nitrites (NO<sub>2</sub><sup>-</sup>) and nitrates (NO<sub>3</sub><sup>-</sup>). Nitrates are one of the most essential molecules for plants because, together with ammonium, they represent an important source of nitrogen which is mandatory for DNA, RNA, enzymes, chlorophyll, ATP and many other molecules. For some applications such as hydroponics or urban agriculture, the local production of pure nitrates fertilizers directly available in the flowing water feeding system would be of great interest.

In this study, a DC atmospheric microplasma system is used for the investigation of the formation mechanism of NO<sub>3</sub><sup>-</sup> in water. The liquid phase is analyzed by Ionic Chromatography (IC), UV-visible spectrometry (UV-vis) and pH-metry, whereas the gas phase is probed by Optical Emission Spectroscopy (OES) and atmospheric Mass Spectrometry (MS).

Firstly, the influence of the inner diameter of the microplasma stainless steel needle is investigated (internal diameter of 0,76 mm, 0,50 mm and 0,20 mm). The amount of NO<sub>x</sub><sup>-</sup> (NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup>) synthesized varies with the diameter and the shape of the plasma is different for a larger internal diameter. Furthermore, the total amount of NO<sub>x</sub><sup>-</sup> formed in a solution shows a linear trend with the total charge injected into the plasma with, however different slopes for nitrites and nitrates.

The oxidation mechanism of NO<sub>2</sub><sup>-</sup> to NO<sub>3</sub><sup>-</sup> is then explored and the influence of other reactive species on this mechanism is then studied. Indeed, it is known from the literature that H<sub>2</sub>O<sub>2</sub> may play a role in the process for different atmospheric plasma systems [2]. The formation of oxygenated

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water and its role as an oxidant is highlighted in the microplasma system. Therefore, the amount of  $H_2O_2$  synthesized by microplasma is compared to other plasma systems. The nature of the atmosphere above the solution is modified in order to determine the species formed in the gaseous phase and their respective influence.

The authors would like to thank the financial support of NITROPLASM (EOS Project 30505023)

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5:00pm **PB+BI+PC+PS-WeA9 Design Considerations for Plasma-based Water Purification Reactor Scale-up**, John Foster, S.M. Mujovic, J.R. Groele, J.C.Y. Lai, The University of Michigan-Ann Arbor

**INVITED**

Plasma-based water purification has been proven viable in laboratory demonstration experiments, highlighting its effectiveness at the removal of contaminants of emerging concern and at disinfection. While these small scale experiments bolster the promise of plasma based advanced oxidation, translating demonstration experiments to practice has proven challenging. A chief challenge is the scale up of plasma-based methods to a viable water treatment technology that is both robust and usable at treatment flow rates of interest. Presented here is an attempt to frame the scope of the challenge, the current state of the art in plasma water purification, and scale up design considerations both from plasma science and engineering standpoints. The objective here is to summarize key challenges to scale-up and implementation as well as elaborate on approaches to achieving a high throughput plasma-based water treatment system. Two illustrative reactor examples amenable to scale up are highlighted along with associated performance data. The pathway from bench-top demonstration of plasma-based systems to piloting and ultimately to the reduction of the technology to practice is also elaborated upon.

5:40pm **PB+BI+PC+PS-WeA11 Radicals and Ozone Generated in Ar/He and Ar/He/H<sub>2</sub>O Plasma by using Atmospheric Pressure Plasma Jet Systems and their use in Methylene Blue Degradation**, J.H. Hsieh, YijinWei Wei, Ming Chi University of Technology, Taiwan, Republic of China; C. Li, National Yang Ming University, Taiwan, Republic of China

Optical emission spectroscopy (OES) and UV absorption spectrometry were first used to gather information about the excited species present near/in the plasma plume generated using Ar/He and Ar/He/H<sub>2</sub>O gases with an atmospheric pressure plasma jet (APPJ). Afterward, the APPJ system was used to study its efficiency in degrading methylene blue as a function of radical and ozone density. According to the results, it was found that the degradation of methylene blue was directly related to the ozone concentration and, perhaps, OH radical density. Additional moisture may be used to control the ratio of ozone and OH radical density, resulting in the variation of degradation rate. Complete degradation of MB can be achieved in 80 seconds.

## Nanometer-scale Science and Technology Division Room 102B - Session NS+2D+AS+MN+PC-ThA

### SPM – Probing Electronic and Transport Properties

**Moderators:** Ondrej Dyckoe, Oak Ridge National Laboratory, Sergei Kalinin, Oak Ridge National Laboratory, Indira Seshadri, IBM Research Division, Albany, NY

#### 2:20pm NS+2D+AS+MN+PC-ThA1 Imaging Currents in Two-dimensional Quantum Materials, *Katja Nowack*, Cornell University **INVITED**

Magnetic imaging is uniquely suited to the non-invasive imaging of current densities, particularly in two-dimensional devices. In this talk, I will showcase this approach by discussing measurements on HgTe quantum well devices in the quantum spin Hall (QSH) regime. In a nutshell, we scan a superconducting quantum interference device (SQUID) to obtain maps of the magnetic field produced by the current flowing in a device. From the magnetic image we reconstruct a two-dimensional current distribution with a spatial resolution on the micron scale. This allows us to directly visualize that most of the current is carried by the edges of the quantum well devices when tuned into their insulating gaps - a key feature of the QSH state. I will both discuss routes towards improving the spatial resolution of our measurements to sub-micron length scales through a combination of improved image reconstruction and smaller sensor sizes.

#### 3:00pm NS+2D+AS+MN+PC-ThA3 Side-gate Construct for Probing Active Energy Levels in Electron Transport through a Solid-state Surface-bound Protein Monolayer, *Sidney Cohen, B. Kayser, C. Gua, M. Sheves, I. Pecht, D. Cahen*, Weizmann Institute of Science, Israel

Electron transport studies provide an excellent platform to deduce electronic structure in molecular electronics studies, enabling control and understanding of the pathways and mechanisms involved. Due to their complexity, proteins are used only infrequently in this context, despite convenient properties such as selective binding, self-assembly, light sensitivity, and the possibility to (bio) chemically tailor properties. Here, we study electron transport in monolayer films of Azurin, using a 3-electrode configuration with a novel side-gate. The source and drain are gold substrate and conductive atomic force microscope (C-AFM) probe, respectively. The measuring devices were prepared in a two-step electron beam lithography process, whereby interdigitated drain and gate electrodes with separation of 80 nanometers are patterned from macroscopic electrodes, the latter formed optically on a silicon oxide substrate. The gold electrodes are patterned with the gate elevated by 20 nm for improved coupling with the drain. After deposition of the Azurin monolayer on this structure, the carrier chip was wire-bonded for insertion into the AFM. Azurin was incorporated in the device both as copper-containing holo-Azurin, and as apo-Azurin with the Cu ion removed. Stability of source-drain vs.  $V_{\text{source-drain}}$  curves, as well as gate-drain leakage were monitored for validity.  $I_{\text{source-drain}}$  vs.  $V_{\text{source-drain}}$  curves were acquired at different gate voltages, and  $I_{\text{source-drain}}$  at  $0 V_{\text{source-drain}}$  was measured while sweeping  $V_{\text{gate}}$  in both polarities. Asymmetry of current onset for opposing gate biases points to a low-lying LUMO transport level for holo-Azurin. For apo-Azurin this level is shifted to higher values and hence inaccessible. Semi-quantitative location of the tail of this LUMO, as well as value of gate coupling were estimated by changing the work function of the drain electrode, i.e. C-AFM probe, from Pt ( $\phi = -5.3$  eV) to Au ( $\phi = -4.9$  eV). The observations can be rationalized by considering previous electrochemical and theoretical studies.

#### 3:20pm NS+2D+AS+MN+PC-ThA4 Adding Electrons One at a Time to Electrostatically Confined Graphene Quantum Dots, *Daniel Walkup, C. Gutierrez, F. Ghahari*, National Institute of Standards and Technology (NIST)/ University of Maryland, College Park; *C. Lewandowski*, MIT; *J. Rodriguez-Nieva*, Harvard University; *T. Taniguchi, K. Watanabe*, National Institute for Materials Science (NIMS), Japan; *L. Levitov*, MIT; *N.B. Zhitenev, J.A. Stroscio*, National Institute of Standards and Technology (NIST)

The Coulomb blockade of adding charges to isolated metallic systems is one of the most characteristic phenomena of quantum dots (QDs). Here, we created circular graphene QDs in a backgated graphene-hexagonal boron nitride (hBN) device by locally ionizing defects in the hBN layer, using the electric field from the tip of a scanning tunneling microscope (STM). Scanning tunneling spectroscopy (STS) enables us to image the local density of states outside and within these circular graphene resonators. At weak magnetic fields, confinement of graphene electrons is poor and Coulomb blockade is not observed. At higher fields, however, the graphene electrons

form quantized Landau levels (LLs) separated by energy gaps. In the area of the QD, the LLs are bent by the electrostatic potential creating metallic (compressible) rings where a LL crosses the Fermi energy, separated by circular insulating barriers (incompressible strips), which isolate the dot from the graphene and enable the onset of Coulomb blockade. Tunneling  $dI/dV$  spectra inside the QD reveal a series of Coulomb blockade peaks, which shift as a function of back gate voltage. In the plane defined by gate voltage and sample bias, these peaks form Coulomb lines, whose slope is governed by the relative capacitances between the dot, tip, gate, and sample bias electrodes, and whose relative offsets reveal the addition spectrum of the quantum dot. A characteristic feature of the Coulomb blockade in these systems is the presence of different families of charging lines, one for each LL, which intersect each other and experience avoided crossings. The avoidance pattern of these anticrossings is novel: at the strongest fields, it somewhat resembles the predictions of simple models of electrostatically-coupled QDs, but at weaker fields it diverges very strikingly, and new modeling is needed to reproduce it. This avoidance pattern reflects the interaction of electrons in different LLs, occupying different parts of the QD, and is tunable via the magnetic field and gate voltage. By moving the STM tip, we can tune the tip-dot capacitance, and tunnel into different parts of the dot, enabling a full characterization of the anticrossings in these novel electronic nanostructures.

#### 4:00pm NS+2D+AS+MN+PC-ThA6 Bulk and Surface Contribution to the Charge and Spin Transport in Topological Insulators Observed with a Four-Probe Scanning Tunneling Microscope, *Wonhee Ko, G.D. Nguyen*, Oak Ridge National Laboratory; *H. Kim, J.S. Kim*, Pohang University of Science and Technology, Republic of Korea; *A.-P. Li*, Oak Ridge National Laboratory

Topological insulators are fascinating materials for future electronics because of its superior charge and spin transport characteristics stemming from their topological nature. However, topological insulators realized in actual materials have both bulk and surface carriers, where the former significantly hampers the topological transport of the later. In this talk, we utilize four-probe scanning tunneling microscope to investigate bulk and surface contribution to the charge and spin transport in bulk-insulating topological insulator  $\text{Bi}_2\text{Te}_2\text{Se}$ . The relative contribution of bulk and surface was varied by changing temperature and transport area, which was measured by variable probe-spacing spectroscopy. The surface dominant regime was already reached at 82 K, where the sample exhibited superior transport properties such as a large surface mobility and high spin polarization. At this regime, the contact to external probes also transforms from Schottky to Ohmic junction. Our result indicates that controlling bulk and surface contribution to the transport is crucial for realizing topological devices.

#### 4:20pm NS+2D+AS+MN+PC-ThA7 Modulation of Single-Walled Carbon Nanotube Electronic Structure by External Electronic Perturbations: Scanning Tunneling Spectroscopy and Density Functional Theory, *Benjamin Taber<sup>1</sup>, G.V. Nazin*, University of Oregon

Understanding the local impact of environmental electronic perturbations on the local density of states (LDOS) of single-walled carbon nanotubes (CNTs) is critical for developing CNT-based devices. We present scanning tunneling microscopy and spectroscopy (STM/STS) investigations of CNTs adsorbed on both a metal, Au(111), and a dielectric, monolayer RbI on Au(111), serving as models for stronger and weaker electrostatic interactions, respectively. In both cases, STS revealed modulations in the CNT LDOS corresponding to features in the underlying material. We then corroborate our STM/STS results with density functional theory calculations of the electronic structure of semiconducting CNTs in the presence and absence of an external dipole (a pair of opposite charges). DFT-calculated CNT LDOS quantitatively matched STM/STS results, providing key insight in to the local impact external charges have on CNT electronic structure.

#### 4:40pm NS+2D+AS+MN+PC-ThA8 Single Charge and Exciton Dynamics probed on the Molecular Scale, *Anna Roslawaska, P. Merino, C. Grosse, C.C. Leon, O. Gunnarsson, M. Etzkorn, K. Kuhnke, K. Kern*, Max Planck Institute for Solid State Research, Germany

The performance of organic optoelectronic devices depends on the dynamics of charges and excitons (electron-hole pairs). The relevant processes have been mostly studied by time-resolved techniques with a spatial resolution limited by optical diffraction. In order to overcome this limit, a nanoscale scanning probe approach that enables addressing

<sup>1</sup> NSTD Postdoc Finalist

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individual light emitters is preferred. Here we introduce time-resolved scanning tunneling microscopy-induced luminescence (TR-STML) and use it to explore locally the single charge and single exciton regime. The excitonic light originates from structural defects in  $C_{60}$  thin films on Au(111) that act as charge and exciton traps. Such a defect is a single photon emitter, whose spectrum has a sharp electron-hole recombination feature [1,2]. By measuring the time-resolved electroluminescence due to individual injected charges, it is possible to analyze the formation and recombination processes of single excitons and determine their characteristic time constants[3].

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5:00pm **NS+2D+AS+MN+PC-ThA9 Microscopic Understanding of the Temperature-dependent Carrier Transport in Ge Nano - Crystals Films, Dan Shan**, Yangzhou Polytechnic Institute, China; *J. Xu*, Nanjing University, China

Silica-based semiconductor nano-crystals have attracted much interest in recent years due to their possible applications in many kinds of nano-electronic and optoelectronic devices. Compared with Si, Ge has larger electron and hole mobility. Furthermore, Ge has a narrower band-gap and high phonon responsivity in the near-infrared region, so it is suited to many near-infrared applications. In order to further improve the device performance, detailed knowledge of transport mechanisms across these nano-crystals becomes necessary and is considered indispensable.

In this work, hydrogenated amorphous germanium films were prepared by a plasma enhanced chemical vapor deposition technique. Ge nano-crystals (Ge NCs) films were obtained by thermal annealing the as-deposited samples. P-type behavior in Ge NCs films without any external doping is attributed to the holes accumulation caused by acceptor-like surface states. It can be found that the dark conductivity and Hall mobility reach to as high as 25.4 S/cm and 182  $\text{cm}^2/\text{V}\cdot\text{s}$  in the Ge NCs film, which are much higher than the previously reported data. Carrier transport mechanisms of Ge NCs films were investigated by temperature-dependent Hall measurement. Three kinds of temperature-dependent conductivity behaviors, which exhibit the linear relationships of the  $\ln \sigma$  versus  $T^{-1/4}$ ,  $T^{-1/2}$  and  $T^{-1}$ , respectively, were observed in the temperature regions of 10-500 K. It can be confirmed that the thermal activation conduction in the extended states dominated the carrier transport process above 300 K (300-500 K). Below room temperature, the carrier transport process was dominated by the percolation-hopping conduction at 90-230 K and turned to Mott-VRH conduction when the temperature falling below 50 K (10-50 K).

Furthermore, the different scattering mechanisms in carrier transport process were found in different temperature regions, which were evaluated via temperature-dependent Hall mobilities. In the low temperature region (10-50 K), the carrier Hall mobility is almost temperature independence ( $\mu \sim T^0$ ), revealing the neutral impurities' scattering mechanism dominated the carrier transport process. When increasing the temperature (50-190 K), the carrier transport properties were controlled by the grain boundary scattering mechanism, where the carrier Hall mobility was increased with temperature and exhibited the thermally activated behavior. However, the relationship of  $\mu \sim T^{-0.9}$  was observed above room temperature (300-500 K). It is suggested that the carrier transport is dominated by a superposition of grain boundary scattering and acoustic phonon scattering within the high temperature region.

## 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.

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Thevuthasan, S.: PC+AS+BI+EM+NS+PB+SS-  
TuP5, **13**  
Thissen, A.: PC+AS+BI+EM+NS+PB+SS-TuA1,  
**10**  
Tischendorf, B.: PC+AS+BI+EM+NS+PB+SS-  
TuA3, **10**  
Tselev, A.: MM+AS+NS+PC+SS-MoA10, **5**  
— U —  
Ulgut, B.: PC+AS+BI+EM+PB+SS-WeM4, **14**  
Unger, W.E.S.: PC+AS+BI+EM+NS+PB+SS-  
TuA1, **10**  
Unocic, R.R.: MM+AS+NS+PC-MoM8, **1**  
— V —  
Varga, T.: PC+AS+BI+EM+NS+PB+SS-TuP5, **13**  
Velasco-Velez, J.J.: PC+AS+BI+EM+NS+PB+SS-  
TuA7, **10**  
Vlassioug, I.: MM+AS+NS+PC+SS-MoA4, **5**  
Voras, Z.E.: NS+AM+AS+MN+PC+PS+SS+TR-  
FrM3, **21**  
— W —  
Wahl, P.: NS+AM+AS+MN+PC+PS+SS+TR-  
FrM4, **21**  
Walkup, D.: NS+2D+AS+MN+PC-ThA4, **19**  
Wang, B.: NS+2D+AN+EM+MN+MP+PC+RM-  
MoM11, **4**  
Wang, C.: MM+AS+NS+PC-MoM11, **2**  
Wang, D.: PB+BI+PC+PS-WeA3, **17**  
Wang, X.: NS+2D+AN+EM+MN+MP+PC+RM-  
MoM11, **4**  
Wang, Y.: NS+2D+AN+EM+MN+MP+PC+RM-  
MoM8, **3**  
Watanabe, K.: NS+2D+AS+MN+PC-ThA4, **19**  
Wei, Y.J.: PB+BI+PC+PS-WeA11, **18**  
Wu, J.: NS+2D+AN+EM+MN+MP+PC+RM-  
MoM11, **4**  
Wu, Y.: MM+AS+NS+PC-MoM5, **1**  
— X —  
Xu, J.: NS+2D+AS+MN+PC-ThA9, **20**  
— Y —  
Yang, C.W.: PC+AS+BI+NS+PB+SS-TuM11, **8**  
Yang, W.-C.: MM+AS+NS+PC-MoM11, **2**  
Yang, Y.: PC+AS+BI+NS+PB+SS-TuM1, **8**  
Yoshida, H.: PC+AS+BI+EM+NS+PB+SS-  
TuA11, **11**  
Yu, x.: NS+2D+AS+PC-MoA3, **6**  
Yu, X.F.: PC+AS+BI+EM+PB+SS-WeM3, **14**  
Yu, X.-Y.: PC+AS+BI+EM+PB+SS-WeM3, **14**  
Yualev, A.: MM+AS+NS+PC+SS-MoA4, **5**  
Yulaev, A.: MM+AS+NS+PC+SS-MoA10, **5**  
— Z —  
Zaera, F.: PC+AS+BI+EM+NS+PB+SS-TuP3, **12**  
Zeller, P.: MM+AS+NS+PC+SS-MoA1, **5**  
Zeng, L.J.: MM+AS+NS+PC-MoM6, **1**  
Zhang, K.: PC+AS+BI+EM+NS+PB+SS-TuP2,  
**12**  
Zhang, X.: NS+2D+AN+EM+MN+MP+PC+RM-  
MoM11, **4**  
Zhao, Y.: NS+2D+AN+EM+MN+MP+PC+RM-  
MoM4, **2**  
Zhitenev, N.B.: NS+2D+AS+MN+PC-ThA4, **19**  
Zhou, C.: NS+2D+AS+PC-MoA8, **7**  
Zhu, Z.: NS+2D+AN+EM+MN+MP+PC+RM-  
MoM11, **4**  
Zhu, Z.H.: PC+AS+BI+EM+PB+SS-WeM3, **14**