Scanning Probe Microscopy Focus Topic
Room: 202 C - Session SP+AS+BI+MI+NS+SS-ThM

Advances in Scanning Probe Imaging

Moderator: S. Allen, The University of Nottingham, UK, A.P. Li, Oak Ridge National Laboratory

8:00am **SP+AS+BI+MI+NS+SS-ThM1 Inelastic Imaging of Single Molecule Dynamics**, ***W. Ho***, University of California, Irvine **INVITED**

A greater part of chemistry is designed to probe the encounter of reactants to form products through a sequence of reaction steps that involve reaction complexes as intermediates. The detection of these complexes is an important step to reveal the reaction mechanisms and advance our understanding and control of chemistry. While sophisticated spectroscopic techniques have been developed to provide properties of the complexes in the energetic and temporal domains, much less is known about the spatial properties. Advances made over the last 15 years in scanning tunneling microscopy (STM) have led to direct characterization and imaging of reaction complexes that are formed by controlled manipulation of the reacting molecules to separate from each other at distances from non-interaction to those approaching the transition state. Changes in their vibrational properties can be monitored as a function of the spatial separation by inelastic electron tunneling spectroscopy (IETS) with the STM. Both spectroscopic information (vibrational energies, intensities, and lineshapes) and inelastic images can be obtained by STM-IETS. These results provide sub-THz spectral characterization and spatial visualization of chemical reactions with sub-Angstrom spatial resolution.

8:40am **SP+AS+BI+MI+NS+SS-ThM3 Tunneling Resonances Into Engineered Nanoscale Cavities on a Noble Metal Surface**, ***A. DiLullo***, *D. Acharya*, Ohio University, *N. Takeuchi*, Universidad Nacional Autónoma de México, *S.-W. Hla*, Ohio University

Variations in surface topologies such as step edges and surface defects are known to alter the electrochemical properties of the surfaces. The ability to directly alter surface topologies on the nanoscale in order to achieve desired properties is useful. We report on the direct modification of local surface topologies and the resulting changes in local electronic properties. Surface vacancies on a Ag(111) surface are created by probe manipulations using a scanning tunneling microscope operated at 78 K. Tunneling resonances, found at certain probe-sample biases, are determined by analysis of spatial height-differential mapping (dz/dV). The resonances, when considered over paths crossing the induced surface vacancies, significantly shift when comparing clean terraces to vacancy positions. These resonances originate as a result of field emission where the emitted electron has greater energy than the surface potential (work function) at the probe lateral position. By fitting these resonances to the Gundlach equation describing resonant tunneling it is possible to extract the tip work function, sample work function at probe position, and absolute tip height from the sample. The shift in resonances at vacancy locations is related to the variation in the work function due to local topology. It is important to be able to tune the work function as it plays a large role in many surface processes and properties. The created surface vacancies may then be considered local wells having work functions differing from the supporting substrate, with resonances tunable by probe manipulations, and may be useful for nanotechnological applications.

9:00am **SP+AS+BI+MI+NS+SS-ThM4 Real-space Spectroscopy and Microscopy of Tunneling Electron Induced Light Emission from Single Gold Nanoclusters**, ***S.W. Li***, *A.X. Yu, G. Czap, W. Ho*, University of California, Irvine

Historically, gold has been treasured for its beauty and permanence. In the quantum regime, gold nanoclusters gain even more reputation from their unique power as photocatalysts. To better understand the optical properties of nanoclusters, we investigated Scanning Tunneling Spectroscopy and tunneling electron induced light emission of single Au nanoclusters deposited on Al_2O_3 / NiAl(110) surface. In this electron-in-light-out experiment, optical phenomena are probed with sub-Ångström spatial resolution.

9:20am **SP+AS+BI+MI+NS+SS-ThM5 Spatial Mapping of Surface Plasmons in Nanoscale Ag Islands on Graphite using Scanning Probe Energy Loss Spectroscopy**, ***K. Bauer***, *S. Murphy, L. Tang, R.E. Palmer*, University of Birmingham, UK

A scanning STM tip operated at high voltage can be used to obtain localized spectroscopic information from surfaces via energy loss measurements [1]. In this technique, known as Scanning Probe Energy Loss Spectroscopy (SPELS), the STM tip is used as a localized source of field-emitted electrons, which, upon backscattering from a surface, are analyzed by an energy-dispersive detector to obtain localized energy loss spectra. Characteristic surface excitations such as plasmons and excitons (as well as secondary electrons) can be probed with a spatial resolution below 50 nm and an energy resolution approaching 0.3 eV [2].

We report the development of a new generation SPELS instrument utilizing a 400-channel electron detector. This allows sufficiently fast sampling of the energy loss spectra to obtain 2D spatially-resolved maps of energy loss features in a reasonable timeframe. We demonstrate the new instrument by mapping plasmons in (thermally evaporated) Ag nano-islands on the surface of graphite and illustrate the various mechanisms give rise to the contrast obtained in the energy-resolved maps.

[1] A. Pulisciano, S.J. Park and R. E. Palmer, Appl. Phys. Lett. 93, 213109 (2008).

[2] F. Festy and R. E. Palmer, Appl. Phys. Lett. 85, 5034 (2004).

9:40am **SP+AS+BI+MI+NS+SS-ThM6 Development of a Synchrotron X-Ray Assisted STM**, ***H. Kersell***, *S.-W. Hla*, Ohio University, *N. Shirato, V. Rose*, Argonne National Laboratory

Scanning tunneling microscopy (STM) yields substantial information about surface properties of conductive materials by probing the electronic properties of samples under investigation. However, the nature of STM's reliance on the sample density of electronic states often limits the elemental contrast of resulting images. By targeting samples with high energy X-rays, such as those generated by a synchrotron light source, core level electrons may be excited and subsequently measured as a contribution to the tunneling current in STM. Since core level energies are chemically specific, this technique can be used to gain elemental sensitivity in STM imaging, providing enhanced understanding of molecule-substrate and intermolecular interactions. We present the development of a synchrotron-assisted STM (SXSTM), for this purpose.

10:40am **SP+AS+BI+MI+NS+SS-ThM9 High-Speed AFM Studies of Cell Membrane Dynamics**, ***A. Slade***, *S.C. Minne*, Bruker Nano Inc.

Bacterial membranes have a much more complex structure than mammalian cell membranes. As such, knowledge of bacterial membrane composition and organization, as well as characterization of the molecular-level responses to drug interactions, is critical to the development and assessment of effective antibacterial drug formulations. Cellular drug responses involve highly dynamic processes. However, the ability to image live cells with nanometer resolution on timescales relevant to dynamic cellular events has proven challenging. With traditional AFM systems, the typically longer image acquisition times required to obtain a single high-resolution image (~minutes) has limited the ability to investigate dynamic biological processes. While recent years have shown significant progress in the development of high-speed atomic force microscopy (HS-AFM), the nature of the instrumentation that has been developed has several drawbacks in specimen size, requiring small scan sizes and flat sample surfaces. As such, the majority of biologically-related HS-AFM studies have concentrated on imaging single biomolecules with little focus on using HS-AFM to examine cellular processes. With the rapidly growing antibiotics crisis, antimicrobial peptides (AmP) are increasingly being investigated as therapeutic alternatives. Key to their success is an understanding of the mechanisms by which AmPs interact with the cell membrane and facilitate cellular death. Using HS-AFM, we have obtained the first high-resolution time sequence images of the native structure of a bacterial outer membrane, obtained directly on the surface of live *Escherichia coli* cells. The increased time resolution of HS-AFM allowed us to observe dynamic changes in the nanoscale structure of the outer membrane in direct response to the AmP CM15, at timescales relevant to the mechanism of AmP-induced cell death. To understand how CM15 interacts with the bacterial inner membrane, we also conducted HS-AFM imaging on supported model membranes that mimic the composition of the inner membrane of *E. coli*. Our results revealed the formation of circular, pore-like defects within specific lipid domains upon exposure to the AmP. The results of these HS-AFM studies have provided the first opportunity to resolve the dynamics of AmP-mediated cell death in a native cell membrane environment in real-time and with nanoscale resolution.

11:00am **SP+AS+BI+MI+NS+SS-ThM10 Photothermal Excitation for Reliable and Quantitative AFM**, ***A. Labuda***, *D. Walters, D. Bocek, M. Rutgers, J. Cleveland, R. Proksch*, Asylum Research, an Oxford Instruments Company

Since the advent of atomic force microscopy, cantilevers have predominantly been driven by piezos for AC imaging and data acquisition. The ease of use of the piezo excitation method is responsible for its ubiquity. However, the well-known "forest of peaks", which is clearly observed while tuning a cantilever in liquids, renders AC imaging in liquids problematic because the peaks move around with time (see Figure). Effectively, these shifting peaks result in a setpoint that changes with time causing stability problems while AFM imaging. Furthermore, the same "forest of peaks" prevents the quantitative interpretation of forces in liquids[1], air[2], and vacuum environments[3], even if the cantilever tune looks clean. Dissipation studies in all these environments have especially suffered due to piezo excitation of the cantilever.

Photothermal excitation is an alternative method for exciting a cantilever by heating/cooling the base of the cantilever to drive the cantilever. Photothermal excitation results in a repeatable, accurate and time-stable cantilever tunes, as seen in the Figure. Therefore, the setpoint remains truly constant while imaging, preventing tip crashes, or unwanted tip retractions. A true atomic resolution image of calcite in water, shown in the inset of the Figure, were made for hours with no user intervention, testifying to the stability of photothermal excitation. Unlike other specialized drive methods, photothermal excitation is compatible with almost any cantilever and with all AFM techniques. The introduction of a blue laser into the AFM also enables several other functionalities, such as tuning the temperature of the cantilever. Furthermore, because the photothermal tune represents the true cantilever transfer function, existing AFM theories can be applied to accurately recover conservative and dissipative forces between the tip and the sample. This is especially important for force spectroscopy, dissipation studies, as well as the frequency modulation AFM techniques.

Our recent developments in perfecting photothermal excitation [4] and its benefits to the AFM community will be discussed in this talk.

[1] A. Labuda, K. Kobayashi, *et al*. AIP Advances **1**, 022136 (2011)

[2] R. Proksch and S. V Kalinin, Nanotechnology **21**, 455705 (2010)

[3] A. Labuda, Y. Miyahara, *et al*. Phys. Rev. B **84**, 125433 (2011)

11:20am **SP+AS+BI+MI+NS+SS-ThM11 Minimally Invasive AFM for Imaging Biomolecules in Liquid**, ***B.W. Hoogenboom***, University College London, UK **INVITED**

Atomic force microscopy (AFM) is a unique tool in combining nanometre spatial resolution and high temporal resolution with the ability to visualise biological molecules in their native environment, i.e., aqueous solution. Its ultimate resolution on such samples depends on the strength of the interaction between the sample and the AFM probe: Too weak an interaction means low contrast, too high an interaction usually results in molecules being distorted or dislodged. I will discuss our recent work on minimising the invasiveness of AFM in liquid, resulting among others in the first observation of the DNA double helix on a single molecule in aqueous solution [Nano Lett. 2012, 12(7), pp. 3846-3850].

Authors Index

Bold page numbers indicate the presenter