In Situ Spectroscopy and Microscopy Focus Topic
Room: 106 - Session IS+AS+SS-TuM

In Situ Studies of Organic and Soft Materials and Liquid-Solid Interfaces
Moderator: A.I. Frenkel, Yeshiva University

8:00am **IS+AS+SS-TuM1 Solid-Vacuum, Solid-Gas, and Solid-Liquid Interfaces: Structure and Dynamics under Environmentally Relevant Conditions**, *M. Salmeron*, ***C. Escudero***, Lawrence Berkeley National Laboratory **INVITED**

Surfaces play a fundamental role in many of today's frontier topics, such as clean and renewable energies, efficient and highly selective chemical processes (green catalysis), high capacity rechargeable batteries and fuel cells, and also environmental problems. To advance our For this it is imperative to develop new fundamental approaches to the study of the interface of solid materials with gases, liquids and solids, because it is in these environments that crucial processes occur that need to be understood to enable game-changing discoveries.

One way to control the structure of interfaces and their properties is through the design of materials of nanoscale dimensions, with specific shape, size and composition. It is equally imperative to develop and use techniques for in situ atomic level structural and spectroscopic characterization of the interfaces. New advances in instrumentation are fulfilling this need. I will illustrate this with examples from research carried out in my laboratory, which include scanning tunneling microscopy (STM), photoelectron and x-ray absorption spectroscopies (PES) under ambient conditions, for studies of catalyst models, thin films, single crystals and nanoparticles, for applications in catalysis and electrochemistry. The results obtained so far demonstrate that the information obtained with these new techniques is unique and could not have been obtained or extrapolated from other more traditional surface sensitive techniques.

8:40am **IS+AS+SS-TuM3 Imaging Tagged Proteins in Whole Eukaryotic Cells in Liquid with Scanning Transmission Electron Microscopy**, ***N. De Jonge***, *D.B. Peckys*, Vanderbilt University School of Medicine **INVITED**

We have recently introduced a novel electron microscopy technique for the imaging of whole cells in aqueous media using scanning transmission electron microscopy (STEM) [1, 2]. Eukaryotic cells in liquid were placed in a microfluidic chamber with a thickness of 5 - 10 µm contained between two ultra-thin electron-transparent windows. On account of the atomic number (Z) contrast of the STEM, nanoparticles of a high-Z material (e.g., gold) were detected within the background signal produced by a micrometers-thick layer of a low-Z liquid (e.g. water, or cellular material). Nanoparticles specifically attached to proteins can be used to study protein distributions in whole cells in liquid, similar as proteins tagged with fluorescent labels can be used to study protein distributions in cells with fluorescence microscopy.

COS7 fibroblast cells were labeled with gold nanoparticles conjugated with epidermal growth factor (EGF). Intact fixed cells in liquid were imaged with STEM with a spatial resolution of 4 nm and a pixel dwell time of 20 microseconds [1]. In test experiments we demonstrated a maximal spatial resolution of 1.5 nm on gold nanoparticles placed above a water layer of a thickness of 3 micrometer, consistent with theoretical predictions, and with Monte Carlo simulations of the STEM imaging [3]. The use of quantum dots (QDs), which are fluorescent nanoparticles, allowed STEM images to be correlated with fluorescence images [4]. Eukaryotic cells were grown directly on microchips for the microfluidic chamber, fixed, and imaged with fluorescence microscopy. The intact cells were then imaged in liquid with STEM. The STEM images showed individual QDs, and their locations were correlated with the cellular regions, as imaged with fluorescence microscopy. We have also demonstrated the imaging of nanoparticle uptake in live cells [5], and the ultrastructure of pristine yeast cells was studied [6]. Liquid STEM presents an innovative approach for the imaging of whole cells, with significantly improved spatial resolution and imaging speed over existing methods.

URL: http://www.mc.vanderbilt.edu/labs/dejongelab/

References

[1] de Jonge, N., Peckys, D.B., Kremers, G.J. & Piston, D.W., Proc. Natl. Acad. Sci. 106, 2159-2164, 2009.

[2] Peckys, D.B., Veith, G.M., Joy, D.C. & de Jonge, N., PLoS One 4, e8214-1-7, 2009.

[3] Dukes, M.J., Peckys, D.B. & de Jonge, N., ACS Nano 4, 4110-4116, 2010.

[4] de Jonge, N., Poirier-Demers, N., Demers, H., Peckys, D.B. & Drouin, D., Ultramicroscopy 110, 1114-1119, 2010.

[5] Peckys, D.B. & N. de Jonge, Nano Lett. 11, 1733-1738, 2011.

[6] Peckys, D.B., Mazur, P., Gould, K.L. & de Jonge, N., Biophys. J., in press, 2011.

9:20am **IS+AS+SS-TuM5 Imaging Live Cells in Liquid with Scanning Transmission Electron Microscopy**, ***D.B. Peckys***, *N. De Jonge*, Vanderbilt University School of Medicine

We have applied a novel electron microscopy technique, referred to as liquid scanning transmission electron microscopy (liquid STEM) [1, 2] for the imaging of live eukaryotic cells. In two separate experiments, we studied a) nano particle (NP) uptake in COS-7 cells [3], a green monkey kidney fibroblast cell line, and, b) the ultrastructure of *Schizosaccharomyces pombe* cells [4], also known as fission yeast. The cells were confirmed to be alive at the onset of the liquid STEM imaging using specific fluorescent, live indicating dyes and correlative fluorescence microscopy. For the STEM imaging in liquid the cells were placed (in liquid) in a microfluidic chamber. The chamber had two ultra-thin electron-transparent windows allowing the passage of electrons and photons. The dimensions of the COS-7 cells required a thicker liquid filled space in the microfluidic chamber compared to the experiments with the fission yeast cells, and contrast was mainly obtained on the gold NP's. However, the thinner *S. pombe* cells allowed a thinner liquid layer, and images were recorded of the cellular ultrastructure.

Despite the fact, that the cells were not anymore alive after the STEM imaging, we consider the first STEM images taken from a cell or a specific cellular region, to represent the unperturbed and therefore physiological state. We derived this assumption after evaluation of the STEM images for signs of radiation damage at the achieved resolution. Our STEM results were found to be consistent with known data about intracellular NP trafficking and storage in mammalian cells and data about the dimensions and distribution of organelles in fission yeast.

In conclusion, we have demonstrated the feasibility of STEM imaging live eukaryotic cells. The advantages of this approach are a) a several-fold higher resolution than live cell imaging with conventional light microscopy, b) a much faster (hours versus days) sample preparation than needed for conventional transmission electron microscopy (TEM) imaging of cells, c) absence of artifact introduction associated with conventional TEM sample preparation, and d) no need for introducing any kind of labels in order to achieve a similar range of resolution as possible with the new nanoscopic imaging techniques.

References

[1] de Jonge, N., Peckys, D.B., Kremers, G.J. & Piston, D.W., Proc. Natl. Acad. Sci. 106, 2159-2164, 2009.

[2] Peckys, D.B., Veith, G.M., Joy, D.C. & de Jonge, N., PLoS One 4, e8214-1-7, 2009.

[3] Peckys, D.B. & N. de Jonge, Nano Lett. 11, 1733-1738, 2011.

[4] Peckys, D.B., Mazur, P., Gould, K.L. & de Jonge, N., Biophys. J., in press, 2011.

9:40am **IS+AS+SS-TuM6 Microscopic Imaging of Biological Samples using Coherent Soft X-rays from Free-Electron Laser and Synchrotron Sources**, ***T. Gorniak***, *T. Senkbeil*, *M. Beckers*, *C. Christophis*, University of Heidelberg, Germany, *K. Giewekemeyer*, University of Göttingen, Germany, *M. Grunze*, University of Heidelberg, Germany, *T. Salditt*, University of Göttingen, Germany, *A. Rosenhahn*, University of Heidelberg, Germany

Coherent X-ray microscopy of hydrated biological samples – especially in the so-called water window of 284-540 eV – is of tremendous interest for life sciences due to the high contrast of organic matter with respect to the aqueous background. Especially free-electron lasers can provide highly intense and coherent pulses, which allow single pulse imaging to overcome resolution limits set by radiation damage. We present the first holographic microscopy images of dehydrated biological material acquired in the water window with higher harmonic radiation provided by the free-electron laser FLASH. In order to increase the photon flux we used high efficiency zone plates instead of pinholes to create the divergent light cone for holography. The results pave the way to the vision of holographic imaging of hydrated biological samples with single FEL pulses. We supplement single pulse imaging experiments by ptychographic imaging with synchrotron radiation at BESSY II. This method uses coherent diffraction imaging at different

sample positions while maintaining a fixed spatial overlap between the fields of view. By introducing this spatial redundancy to the data an additional constraint for the iterative reconstruction algorithm is achieved. This enhances the convergence of phase retrieval drastically. The spatial resolution of below 50 nm and the imaging properties were characterized using lithographic and biological test samples. We also show results on resonant imaging with chemical contrast caused by both, absorption and phase shifts, in the vicinity of core level absorption edges.

10:40am **IS+AS+SS-TuM9 Surface Chemistry of Amino Acids at Near Ambient Pressure of Water Vapor**, ***A. Shavorskiy***, Lawrence Berkeley National Laboratory, *T. Eralp,* The University of Reading, UK, *F. Aksoy,* Nigde University, Turkey, *M.E. Grass, Z. Liu, H. Bluhm,* Lawrence Berkeley National Laboratory, *G. Held*, The University of Reading, UK

The co-adsorption of water with organic molecules under near-ambient pressure and temperature conditions opens up new reaction pathways on model catalyst surfaces that are not accessible in conventional ultra-high vacuum surface-science experiments. The surface chemistry of glycine and alanine at the water-exposed Cu{110} and Pt{111} interface was studied both in situ and in UHV using ambient-pressure photoemission and X-ray absorption spectroscopy techniques [1,2]. At water pressures above 10-5 Torr a significant pressure-dependent decrease in the temperature for dissociative desorption was observed for both amino acids on Cu{110}[3]. On Pt{111}, on the other hand, desorption temperature does not depend significantly on the presence of water vapor. The most likely reaction mechanism of decomposition involves dehydrogenation induced by O and/or OH surface species resulting from the dissociative adsorption of water on Cu{110}, but not on Pt{111}.

The linear relationship between the inverse decomposition temperature on Cu{110} and the logarithm of water pressure enables determination of the activation energy for the surface reaction, between 213 and 232 kJ/mol, and a prediction of the decomposition temperature at the solid-liquid interface by extrapolating towards the equilibrium vapour pressure. Such experiments near the equilibrium vapour pressure provide important information about elementary surface processes at the solid-liquid interface, which can neither be retrieved under ultra-high vacuum conditions nor from interfaces immersed in a solution.

[1] H. Bluhm, et al. J. El. Spec. Rel. Phenomena 150 (2006) 86.

[2] G. Jones, L. B. Jones, F. Thibault–Starzyk, E.A. Seddon, R. Raval, S. Jenkins, G. Held, Surf. Sci. 600 (2006) 1924.

[3] A. Shavorskiy, F. Aksoy, M.E. Grass, Z. Liu, H. Bluhm, G. Held, J. Am. Chem. Soc, 133 (2011) 17

11:00am **IS+AS+SS-TuM10 STM Tip Catalyzed Adsorption of Thiol Molecules and Functional Group-Selective Adsorption of Bi-Functional Molecule Using This Catalysis**, ***Y.H. Min***, *S. Kim, S.J. Jung, Y.-S. Youn,* Korea Advanced Institute of Science and Technology, Republic of Korea, *D.H. Kim,* Daegu University, Republic of Korea, *E.H. Park*, Korea Advanced Institute of Science and Technology, Republic of Korea

In this study, in contrast with cases in which Scanning Tunneling Microscopy (STM) tip-induced reactions were instigated by the tunneling electrons, the local electric field, or the mechanical force between a tip and a surface, we found that the tungsten oxide (WO_3) covered tungsten (W) tip of a STM acted as a chemical catalyst for the S-H dissociative adsorption of phenylthiol and 1-octanethiol onto a Ge(100) surface. By varying the distance between the tip and the surface, the degree of the tip-catalyzed adsorption could be controlled. We have found that the thiol head-group is the critical functional group for this catalysis and the catalytic material is the WO_3 layer of the tip. After removing the WO_3 layer by field emission treatment, the catalytic activity of the tip has been lost.

3-mercapto isobutyric acid is bi-functional molecule which has two functional groups, carboxylic acid group and thiol group, at each end. 3-Mercapto Isobutyric Acid adsorbs at Ge(100) surface only through carboxylic acid group at room temperature and this adsorption was enhanced by the tunneling electrons between a STM tip and the surface. Using this enhancement, it is possible to make thiol group-terminated surface where we desire. On the other hand, surprisingly, the WO_3 covered W tip of STM was found to act as a chemical catalyst to catalyze the adsorption of 3-mercapto isobutyric acid through thiol group at Ge(100) surface. Using this catalysis, it is possible to make carboxylic acid group-terminated surface where we want. This functional group-selective adsorption of bi-functional molecule using the catalysis may be used in positive lithographic methods to produce semiconductor substrate which is terminated by desired functional groups.

Min, Y. H.; Jung, S. J.; Youn, Y. -S.; Kim, D. H.; Kim, S. *J. Am. Chem. Soc.* **2010**, *132*, 9014.

11:20am **IS+AS+SS-TuM11 CO_2 Capture in Aqueous Monoethanolamine Solutions: Role of the Solution Interface Investigated with X-ray Photoelectron Spectroscopy**, ***T. Lewis***, University of California, Irvine, *B. Winter,* Helmholtz-Zentrum Berlin für Materialien und Energie, Germany, *M. Faubel,* Max-Planck-Institut für Dynamik und Selbstorganisation, Germany, *J.C. Hemminger*, University of California, Irvine

Aqueous monoethanolamine (MEA) solutions are commonly used to capture CO_2 emitted into the atmosphere from industrial processes. It is likely that interactions between MEA and CO_2 at the aqueous solution surface are important to this process, yet surprisingly very few studies have explicitly addressed the role of the solution-gas interface. In the present study, interfacial chemistry of CO_2 capture is studied by surface sensitive photoelectron spectroscopy measurements from a liquid microjet of CO_2-reacted MEA solutions with carbon loadings of 0.1 to 0.9 mol/mol. These experiments determine the spatial distribution of MEA and reaction products into the solution as a function of CO_2 loading. Results show that neutral MEA exhibits a propensity for the solution surface, whereas protonated MEA and reaction products prefer bulk solvation, suggesting enhanced reactivity at the solution interface, especially at high CO_2 loading. These observations indicate that a detailed understanding of the chemistry of CO_2 at the liquid/vapor interface and interface to bulk transport of the products will be important in understanding CO_2 capture.

11:40am **IS+AS+SS-TuM12 Fundamental Aspects of Organic Heterostructure Formation Examined using Supersonic Molecular Techniques and *In Situ* Real Time X-ray Synchrotron Radiation**, ***E.R. Kish***, *T.V. Desai, A.R. Woll, J.R. Engstrom*, Cornell University

Over the past several years significant advances have been made concerning our understanding of the growth of crystalline small molecule organic thin films consisting of a single component. An important challenge in organic electronics, photonics and photovoltaics is to develop and improve methods to integrate both *p*-type and *n*-type small molecule organic semiconductors into the same device microstructure. Thus, developing an understanding of the molecular scale events that lead to heterojunction formation is essential in these systems consisting of multiple components. Here we report on our examinations of the nucleation, growth, and dynamics of adsorption of a *n*-type organic semiconductor, *N*,*N*′-ditridecylperlyene-3,4,9,10-tetracarboxylic diimide (PTCDI-C_{13}), on SiO_2 surfaces modified by self-assembled monolayers (SAMs) and on a pre-deposited monolayer of pentacene (a *p*-type semiconductor) using supersonic molecular beam techniques, *in situ* synchrotron x-ray scattering and *ex situ* atomic force microscopy. From real-time x-ray scattering we find that PTCDI-C_{13} exhibits prolonged layer-by-layer growth for approximately the first 10 monolayers (MLs) of deposition on all three SAMs examined. Concerning the kinetics of growth we find that the adsorption probability of PTCDI-C_{13} on itself is similar to that observed on two SAMs that possess aromatic endgroups, but it differs significantly to that observed on a relatively short, methyl-terminated SAM. These differences could reflect mechanisms such as direct molecular insertion of PTCDI-C_{13} into either the existing PTCDI-C_{13} film, or the longer chain SAMs with aromatic endgroups. Concerning growth in the submonolayer regime, we find that nucleation is homogeneous, and that the absolute density of islands depends on the nature of the surface, while the relative change of the island density with increasing growth rate is essentially independent of the underlying SAM. From the latter we find that a critical island size of a single molecule of PTCDI-C_{13} can describe all the data. Finally, we will discuss our most recent results concerning the growth of heterostructures composed of a few to several monolayer stacks of PTCDI-C_{13} and pentacene. In this work we find that PTCDI-C_{13} grows in a smooth layer-by-layer fashion on pentacene, but the opposite is not true—pentacene grows in a purely 3D mode when deposited on PTCDI-C_{13}. We will discuss the implications of this observation concerning the growth of organic heterostructures for applications in electronics, photonics and photovoltaics.

Authors Index

Bold page numbers indicate the presenter