Biomolecules at Aqueous Interfaces Focus Topic
Room: 203 A - Session BA+AI+AS+BI+IS+NL-MoM

Biomolecules at Aqueous Interfaces
Moderator: P. Koelsch, University of Washington

8:20am **BA+AI+AS+BI+IS+NL-MoM1 Selected Studies of Biomolecular Interactions**, ***K.B. Eisenthal***, *B. Doughty, Y. Rao, S.M. Kazer, S.J.J. Kwok, N.T. Turro*, Columbia University **INVITED**

The work reported here utilizes a sensitive method for the investigation of biomolecular interactions that has the important characteristic of not requiring chemical labels, e.g. fluorophores, nor invasive detection methods. The surface selective second order spectroscopies, second harmonic, SHG, and sum frequency generation, SFG, allow one to probe equilibrium properties and time dependent changes in the electronic and vibrational structure of molecules located at interfaces. In addition they have the special feature of being able to monitor changes in the electrical charge of the interacting molecules. 1) A new way is presented to measure the binding constants of molecules, e.g. drugs and proteins, with DNA tethered to colloidal microparticles suspended in aqueous solution. 2) Time resolved second harmonic generation was used to observe the binding of an enzyme to its recognition site on DNA, followed by the cleaving of DNA into a small and a large fragment, and the subsequent DNA rehybridization dynamics. 3) The relative orientation of two molecules bound to DNA is manipulated by changing the number of nucleotide base pairs separating them. The interference between the SH electric fields generated by the pair of molecules is modulated because their relative orientation changes as the number of nucleotide base pairs separating them is changed. With this method we have a new way to probe structural changes in DNA due to the binding **of** biomolecules to it.

9:00am **BA+AI+AS+BI+IS+NL-MoM3 Probing Nanoparticle-lipid Bilayer Interactions with Nonlinear Optics**, ***F. Geiger***, Northwestern University **INVITED**

The interaction of engineered nanoparticles with biological membranes is an important and necessary first step for cellular uptake. Here, we probe this interaction by applying second harmonic and vibrational sum frequency generation as well as the Eisenthal chi(3) method to supported bilayer-based model systems as well as shewanella and daphnia magna, chosen as important biological endpoints, exposed to 4 nm sized noble metal nanoparticles surrounded by negatively and positively charged ligands. Our studies are complemented by a plethora of supporting experiments based on quartz crystal microbalance, zeta potential, and related experiments. We find that Coulomb's law dictates much of the interactions in the particular systems studied here.

9:40am **BA+AI+AS+BI+IS+NL-MoM5 Characterizing the Protein-Surface Interactions that Control Diatom Biomineralization**, ***J.E. Baio***, Oregon State University, *M. Bonn, T. Weidner*, Max Planck Institute for Polymer Research, Germany

The assembly of mineralized tissues can be initiated and controlled by proteins. One such system, is the formation of silica-based cell walls in marine, single celled organisms, where biomineralization is regulated by protein−mineral interactions. The diatom species *Cylindrotheca fusiformis* assembles supramolecular silica structures via proteins called sillafins. In a silicic acid solution, specific repeat units within this protein, SSKKSGSYSGSKGSKRRIL (R5), induce the formation of silica-protein composite nanoparticles. The protein−surface interaction that drives self-assembly is likely controlled by both the secondary structural motifs of the protein and specific contacts between the surface atoms and key protein side chains. In this study, we characterized the R5-SiO_2 interactions that drive this self-assembly process by both near edge x-ray absorption fine structure (NEXAFS) spectroscopy and *in situ* sum frequency generation (SFG) spectroscopy. Two peaks within the amide I vibrational band of the SFG spectra, 1640 and 1670 cm^{-1}, indicate that the R5 peptide retains a beta sheet conformation when interacting with SiO_2. Expanding upon this characterization of secondary structure, the introduction of isotopic labeled amino acids within the peptide allowed us to probe the orientations of individual side chains by SFG. This SFG characterization was complemented by the observed polarization dependence of the NEXAFS C1s to π^* transition which provided details of the binding geometry of the single tyrosine within R5.

10:00am **BA+AI+AS+BI+IS+NL-MoM6 Probing the Effects of Different Ions on the Formation of Microstructure Within Collagen Hydrogels by Second Harmonic Generation (SHG) Microscopy**, ***X. Lang***, *J.G. Lyubovitsky*, University of California, Riverside

In this study we aimed to explore the nucleation, assembly and the 3-D microstructure of collagen hydrogels *in situ* with second harmonic generation (SHG) microscopy. Transmission electron microscopy (TEM) and optical density (OD) were carried out as well in order to complement the SHG measurements. The goal was to generate the knowledge to accelerate rational design of collagen-based biomedical products. In this work, we employed 0, 150, 300, 600, 900 mM NaCl concentrations and in a separate experiment 0, 5, 10, 20, 50, 75, 100, 150, 300 mM Na_2SO_4 concentrations of salts needed for the assembly of collagen hydrogels. Specifically, we characterized collagen hydrogels prepared from 2 g/l and 4 g/l initial collagen concentrations as well as several incubation temperatures. For samples incubated with NaCl, incubation under the room temperature (RT) and 27°C gave similar OD values. These OD values were higher than the OD values for 37°C incubated samples. Delay time became shorter upon elevating the polymerization temperature. For samples incubated with Na_2SO_4, there were two regimes for collagen polymerization, Na_2SO_4 concentration 5 mM – 50 mM and 100 mM -300 mM. Fibers were longer when NaCl concentration was 150-600 mM compared to 0 and 900 mM NaCl for both collagen concentrations under RT, 27°C and 37°C. In general, fibers were small when incubated at 37°C compared to fibers formed under RT and 27°C. TEM measurement showed that there were collagen fibers with a characteristic striation structure in all collagen and NaCl concentrations. The fibrils exhibited a twisted morphology in 2 g/l collagen hydrogels.

10:40am **BA+AI+AS+BI+IS+NL-MoM8 Sum Frequency Generation (SFG) Vibrational Spectroscopy Studies of Molecules at Solid-Liquid and Solid-Gas Interfaces**, ***G.A. Somorjai***, University of California, Berkeley and Lawrence Berkeley National Laboratory, *X. Cai*, Lawrence Berkeley National Laboratory **INVITED**

Construction of a femtosecond broad-band laser enables us to simultaneously monitor the CH and CO vibrational SFG spectra, thus allowing more actual characterization of reaction intermediates at solid-liquid and solid-gas interfaces. Using a picosecond laser we compare the spectroscopy using these two different laser systems and they will be discussed in some detail. In addition, sum frequency generation vibrational spectroscopy, high-pressure scanning tunneling microscopy and ambient-pressure X-ray photoelectron spectroscopy as well as other synchrotron-based techniques (X-ray adsorption) that enable the investigation of surfaces under reaction conditions on the atomic and molecular level will be reviewed.

We investigate solid-liquid and solid-solid interfaces (buried interfaces) as they adsorb and react with diatomic and organic molecules in dynamic state at various pressures and temperatures.

11:20am **BA+AI+AS+BI+IS+NL-MoM10 A Molecular View of Water Interacting with Climate-active Ice Nucleating Proteins**, *R. Pandey*, Max Planck Institute for Polymer Research, Germany, *J. Fröhlich, U. Pöschl*, Max Planck Institute for Chemistry, Germany, *M. Bonn*, ***T. Weidner***, Max Planck Institute for Polymer Research, Germany

Specific bacteria, such as *Pseudomonas syringae*, effectively attack plants by using ice-nucleating proteins anchored to their outer cell surfaces. Ice nucleating proteins promote the local crystallization of ice at temperatures that would otherwise not allow ice formation. The frost damage caused by ice crystals then facilitates bacterial invasion of the affected plants. Ice nucleating proteins not only play an important role for agriculture, but are also very important for atmospheric processes: airborne ice-nucleating proteins have been shown to be among the most effective promoters of ice particle formation in the atmosphere. A recent survey of microorganisms in the troposphere biome by NASA has discovered massive emissions of biogenic ice nucleators from large forest areas like the amazon, which likely change precipitation patterns and may affect the global climate. To understand biogenic ice formation, a detailed molecular level picture of the mechanism by which ice-nucleating proteins interact with water molecules is important. Sum frequency generation (SFG) spectroscopy – owing to its inherent interface sensitivity – is ideally suited to determine the structure and dynamics of water molecules at interfaces. We have investigated the interaction a monolayer of the ice-nucleating protein inaZ with water using static and time-resolved SFG spectroscopy. When cooling the sample from room temperature to near-freezing temperatures (~5°C for D_2O), inaZ significantly increases the structural order of water molecules in contact with inaZ proteins. This effect was not observed for liquid water surfaces

without the protein or for protein monolayers which are not ice nucleators. SFG spectra in the CH and the amide I region also indicated a change of protein structure near the nucleation temperature. Femtosecond, time-resolved 2-dimensional SFG spectroscopy is used to quantify the heterogeneity of protein-bound water molecules and their structural dynamics.

Biomaterial Interfaces
Room: 201 B - Session BI+AS+IS+NL-MoM

Surfaces to Control Cell Response
Moderator: H.E. Canavan, University of New Mexico

8:20am **BI+AS+IS+NL-MoM1 Modulation of Cell Behaviour using Self–assembled Binary Colloidal Crystals**, ***P.Y. Wang***, *P. Kingshott*, Swinburne University of Technology, Australia

The control of cell behaviour on surfaces is the key to a broad range of biomedical applications. Biomaterial surfaces with tuneable surface topographies and chemistries can profoundly influence the development of advanced biomaterials used in applications including tissue engineering and regenerative medicine. Recently, we developed an elaborate and feasible method to display an ordered surface topography with tuneable surface chemistry using binary colloidal crystal particles. Using this binary colloidal system, various combinations of particle size and surface chemistry can be readily employed. In this study, two combinations of binary colloidal crystals, i.e. PS-COOH (2 μm)/PMMA (0.4 μm) and SiO_2 (2 μm)/PMMA (0.4 μm) were assembled on ozone-treated silicon wafers. The preliminary results of cell attachment and morphology of L929 fibroblasts and MG63 osteoblasts were studied after 24h.

In general, cells had a small projection area rather than fully spread morphology on the crystal surfaces compared with the flat control. Fibroblasts have abundance of cell protrusions called filopodia which can be observed using scanning electron microscopy (SEM), whilst osteoblasts don't have. Fibroblasts had long and thin extended filopodia on the PS/PMMA crystal surfaces, whilst they had short and thick filopodia on the SiO_2/PMMA crystal surfaces. Regarding the surface chemistry, both SiO_2 and PMMA particles were not as favourable as the PS-COOH particles for fibroblasts attachment, and resulted in the cell projection area on the PS/PMMA being larger compared to the SiO_2/PMMA crystal surfaces. On the contrary, the cell projection area of osteoblasts didn't have significant differences between these two crystal surfaces. After fibronectin coating, cell projection area of osteoblasts on SiO_2/PMMA crystal surfaces increased significantly, whilst fibroblasts didn't, suggesting that different cell types respond to surfaces differently.

These results show for the first time that cell-substrate interactions can be easily controlled by precise positioning of different particles with various sizes and chemistries. The present results will help gain a more thorough understanding of cell-material interactions benefiting the development of advanced biomaterials and materials for tissue engineering.

8:40am **BI+AS+IS+NL-MoM2 Achieving Differential Cell Adhesion with Novel Polymer Surfaces Identified using Microarrays**, ***F.A. Simoes***, *C. Alexander, G. Mantovani, L. Buttery, M.R. Alexander*, University of Nottingham, UK

Stem cells have the ability to repair, replace or regenerate tissues. As a result their potential for regenerative medicine is vast. The processing of cells for therapeutic use and clinical diagnostics will rely on cell sorting steps to ensure a homogeneous population is obtained.[1]

Several techniques exist to achieve this, which rely on the physical properties of cells but tend to provide poor specificity.[2-4] Fluorescence Activated Cell Sorting (FACS) and Magnetic-Activated Cell Sorting (MACS) rely on specific biomarkers. However cells require labelling and label removal steps, which can affect the phenotype.[5]

There is a need for a fully synthetic, inexpensive, label-free separation system, capable of sorting cells with minimum manipulation. In order to generate robust surfaces for such a system, we have developed a method to immobilize thiol-functionalised materials to a polymer substrate using thiol-ene "click" chemistry in a high throughput format. Microarrays of these functionalised polymers comprising of 6 replicates, are fabricated using pin printing to generate a combinatorial library of materials. A mixture of differentiated cells derived from mouse embryoid bodies are then seeded onto the arrays.

Immunohistochemistry techniques are employed to track the differentiation of cells into different lineages, thus enabling the visualisation of multiple cell lines. These techniques also allow for the high throughput quantification of attachment by the means of automatic fluorescence microscopy.

Surface characterisation of the "click" immobilization procedure is performed by X-Ray Photoelectron Spectroscopy. In contrast the characterisation of microarrayed materials is performed using Time of Flight - Secondary ion Mass Spectrometry, which is followed by the ranking of materials using Partial Least Square (PLS) regression analysis. This process allows for the correlation of cell attachment with key molecular ions generated from each material by mass spectrometry.

Successful materials that selectively induce cell attachment are identified and investigated further. This is the first step in the generation of new surface-based devices that have the capacity to be fully synthetic, selective, inexpensive and disposable.[6]

1. McIntyre C. *et al*., *Bioprocess International*, 2010, 44-53.

2. Chabert M. and Viovy J., *PNAS*, 2008, **105**, 3191-3196.

3. Shim S. *et al*., *Integrative Biology*, 2011, **3**, 850-862.

4. Kose A. R. *et al*., *PNAS*, 2009, **106**, 21478-21483.

5. Bulte J. W. M. *et al*., *Blood*, 2004, **104**, 3410-3413.

6. Singh A. *et al*., *Nature Methods*, 2013, **10**, 438-444

9:00am **BI+AS+IS+NL-MoM3 Interaction of Hematopoietic and Leukemic Cells with their Microenvironment**, ***A. Rosenhahn***, Ruhr-University Bochum, Germany, *M. Hanke, C. Christophis,* Karlsruhe Institute of Technology, Germany, *I. Taubert, N. Baran, P. Wuchter, A.D. Ho*, University of Heidelberg, Germany

Especially for leukemic and haematopoietic cells, the interaction with their microenvironment is of upmost importance for extravasation and homing. One key mechanism is the interaction of the CD44 receptor with extracellular hyaluronan (HA) binding motifs. To quantitatively assess the interaction, a microfluidic experiment has been developed that allows studying the interaction of cells with interfaces under well-defined flow conditions [1]. Shear flow activated catch bond interaction is well characterized for selectin mediated extravasation of leukocytes [2]. We recently found that also the CD44 interaction with HA requires a minimum shear stress to become activated and enable cells to roll on HA surfaces [3]. Similar critical shear values were found for rolling on mesenchymal stroma cells, which are present in the bone marrow niche creating the microenvironment required for haematopoietic stem cell renewal. Interestingly not only hematopoietic stem cells but also acute leukemic blasts show a shear flow induced rolling. The proportion of rolling cells will be discussed on the basis of the pathogenesis of the disease.

[1] C. Christophis, M. Grunze, A. Rosenhahn, PCCP 2010, 12, 4498.

[2] E.B. Finger, K.D. Puri, R. Alon, M.B. Lawrence, U.H. von Andrian, T.A. Springer, Nature 1996, 379, 266

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9:20am **BI+AS+IS+NL-MoM4 The Creation of Polymeric Biointerfaces using Non-Contact Dispensing Technology**, ***C. Dufresne***, Scienion

Polymeric surfaces of varied composition have been created in high density microarray formats. These patterned surfaces have been used to study a number of biointerface processes such as stem cell differentiation, and bacterial adhesion. Scienion offers non-contact picoliter dispensing technology that enables the creation of such surfaces. The inert glass capillaries allow for the use of a wide range of chemical reagents. Precision positioning enables drop-on-drop dispensing and mixing. Image analysis of the substrates in turns makes it possible to accurately dispense the materials onto almost any surface. This presentation will cover how Scienion technology is implemented for the production of polymeric surfaces.

9:40am **BI+AS+IS+NL-MoM5 The Role of Cell-Substrate Interactions on Cell Stiffness and Cell Volume**, ***D.A. Weitz***, Harvard University **INVITED**

Cell stiffness is often observed correlate with the stiffness of the substrate on which the cells are grown. This talk will present data which suggest that cell-substrate interactions are more diverse, and depend as well on the adhesion area. It will discuss the impact of the substrate on cell volume and the consequences of this on cell stiffness. The data presented will suggest that cell volume is a control for cell stiffness.

10:40am **BI+AS+IS+NL-MoM8 Quantitative, Predictive Models of Adhesion of Cells to Polymers**, ***V.C. Epa***, *D.A. Winkler*, CSIRO Materials Science & Engineering, Australia, *A.L. Hook, C. Chang, J. Yang*, University of Nottingham, UK, *R. Langer, D.G. Anderson*, MIT, *P. Williams, M.C. Davies, M.R. Alexander*, University of Nottingham, UK

Designing materials to control biology is an intense focus of biomaterials and regenerative medicine research. Discovering and designing materials with appropriate biological compatibility or active control of cells, tissues, or pathogens is being increasingly undertaken using high throughput synthesis and assessment methods.

In particular, culture of multipotent cells such as stem cells is a major research focus in regenerative medicine. Much research effort is focused on designing chemically defined, serum-free, feeder-free synthetic substrates and media to support robust self-renewal of pluripotent cells. Changes in cellular properties such as adhesion, morphology, motility, gene expression and differentiation are influenced by surface properties of the materials on which cells have been cultured. Similarly, designing new materials to control the growth of pathogens on implantable and indwelling devices such as pacemakers, and catheters, is critical given the high level of device-centred infections.

We report a relatively simple but powerful machine-learning method of generating models that link microscopic or molecular properties of polymers or other materials to their biological effects. We illustrate the potential of these platform modelling methods by developing the first robust, predictive, quantitative, and purely computational models of adhesion of human embryonic stem cell embryoid bodies, and three clinically important pathogens, *Staphylococcus aureus*, *Pseudomonas aeruginosa*, and uropathogenic *Escherichia coli*, to the surfaces of 496 polymers.

11:00am **BI+AS+IS+NL-MoM9 Smart Surfaces for Studies of Real-Time Dynamic Cell Behavior**, ***M.N. Yousaf***, York University, Canada

Active migration, local tissue invasion and seeding of distant metastases are all characteristics of malignant cells. These complex cellular events require the integration of information derived from soluble growth factors with positional information gained from interactions with the extracellular matrix and with other cells. The biochemical events of the signaling cascades occur in a spatially and temporally coordinated manner that then dynamically shape the cytoskeleton in specific sub-cellular regions. Therefore cell migration and invasion involve a precise but constantly changing subcellular nano-architecture. To fully understand the complex signaling and cytoskeletal aspects of the cellular nano-architecture during migration requires a multidisciplinary coordinated effort. The long-term goal of this research program is to develop new surface chemistry and cell biological tools to generate a class of tailored dynamic nanopatterned substrates for a variety of cell adhesion and migration experiments. The combined application of dynamic smart substrates, molecular surface gradients and in vivo biosensors will potentially allow for the analysis and quantitation of the events of cell migration at each step from initial engagement with extracellular matrix ligands, to localized activation of signaling proteins, to organization and activation of the cytoskeleton, to overall movement of the cell.

11:20am **BI+AS+IS+NL-MoM10 What Makes the Heart Grow Fonder? Chemically Diverse Polyacrylate and Polyacrylamide Surfaces for Human Cardiomyocyte Culture and Their Effect on Phenotype**, ***A.K. Patel***, University of Nottingham, UK, *D.G. Anderson, R. Langer*, Massachusetts Institute of Technology, *M.C. Davies, M.R. Alexander, C. Denning*, University of Nottingham, UK

Human pluripotent stem cell (hPSC) derived cardiomyocytes hold the potential to strengthen pharmaceutical toxicity testing and to provide disease models for development of treatment targets1. The maturation and maintenance of the cardiomyocyte phenotype may be controlled by the manipulation of the substrate supporting the cells2. However, the surfaces currently in use still fall short of producing cardiomyocytes of adult maturity. Standard culture-ware requires coating with biological substrates such as fibronectin which can be expensive and subject to poor reproducibility due to batch variation. We are exploring an alternative, combinatorial materials high throughput screening approach3 to identify novel materials that can improve cardiomyocyte culture. Polymer microarrays comprising of 6 replicates of 116 acrylates and acrylamides are fabricated using contact printing. Cardiomyocytes derived from the HUES7 human stem cell line are seeded onto the arrays. Immunostaining of nuclei (DAPI) and the cardiomyocyte specific motor protein, sarcomeric alpha actinin is performed to visually estimate cell function and maturity and enable quantification of cell attachment in a high throughput manner using automated fluorescence microscopy and image analysis software. Surface characterisation of the arrays is performed using time of flight secondary ion mass spectrometry. Partial least squares (PLS) regression analysis allows for correlation of cell attachment with key molecular ions identified from mass spectrometry4.

Successful monomers that permit cardiomyocyte attachment, spreading and contraction are identified from the first generation homopolymer microarray and are mixed pair-wise to form second generation microarrays. This diverse library of copolymers enables unique combinations of chemical moieties to be investigated. Hit monomers and combinations identified to be synergistic can be analysed for their effect on cardiomyocyte function including electrophysiology measured by patch clamping, myofibril alignment and gene expression.

The lead materials generated by this approach are the first step in a discovery process for novel synthetic biomaterials capable of enhancing the culture of cardiomyocytes to move towards more reproducible, economical and defined conditions.

References:

1. Matsa E. et al. European Heart Journal. 2011;32(8):952-62

2. Engler A. et al.The Journal of Cell Biology. 2004;166(6):877–887

3. Hook A. et al. Biomaterials. 2010;31(2):187–198

4. Yang J. et al.Biomaterials. 2010;31(34): 8827–8838

11:40am **BI+AS+IS+NL-MoM11 Selectivity in Platelet Activation by the Titania Surface: A Model System for In Vitro Modulation of Platelet Activity**, *S. Gupta*, CIC biomaGUNE, Spain, ***I. Reviakine***, Karlsruhe Institute of Technology, Germany

Platelet are anuclear cell fragments circulating in blood. Their major function is haemostasis: they catalyze the formation of the fibrin clot that stops the bleeding. Recently it was shown that they have a multitude of other functions in processes such as the immune response, inflammation, angiogenesis, implant rejection or integration.

Platelets circulate in the blood in a quiescent form. They become activated at wound sites, implant surfaces, or through the action of soluble agonists secreted by activated platelets or produced in the blood as a result of the clotting process. Activated platelets express on their surface a variety of protein and lipid receptors that catalyze the clotting process, interact with other platelets, leukocytes, and endothelial cells, and adhere to the extracellular matrix exposed at the wound sites. The also secrete a variety of active substances, including growth factors, that are stored inside special granules within the platelets.

Recently discovered diversity of platelet functions implies a tight regulation of the activation processes. Indeed, there is evidence to suggest that platelet activation is a selective process with a spectrum of activated states, rather than a two-state process involving quiescent vs. pro-coagulant platelets. In this context, we have previously shown that platelet activation profile on TiO_2 depends on the surface-bound Ca. Here, we measure intracellular calcium currents in surface-adsorbed platelets in order to understand how this manifestation of platelet activation selectivity is related to the internal signaling pathways. Such an understanding is a prerequisite for designing new, platelet-based approaches to the treatment of haemostatic and inflammation-based disorders, to enhancing implant integration and wound repair, and to tissue engineering applications.

Biomaterial Interfaces
Room: 201 B - Session BI+AI+BA+IS-MoA

Biofouling
Moderator: D.E. Barlow, Naval Research Laboratory

2:00pm **BI+AI+BA+IS-MoA1 Biofouling of Carbon Steel: Effects of Microstructure and Test Media on Initial Bacterial Attachment and Subsequent Corrosion**, *M.A. Javed, P.R. Stoddart, S.M. McArthur,* ***S.A. Wade***, Swinburne University of Technology, Australia

Biofouling of surfaces causes numerous problems in a wide range of industries such as shipping, health care, oil and gas production and food production. Of specific interest to the current work is the accelerated corrosion of metals that can arise as a consequence of bacterial biofilm formation, which is commonly known as microbiologically influenced corrosion (MIC).

The initial attachment of bacteria to a surface is one of the first steps in the process of biofouling. The attachment is dependent upon a large number of factors, which are broadly related to the properties of the bacteria, substrate/surface and environment. Changes in these properties can not only influence the initial attachment step, but also the interrelated production of extracellular polymeric substances (EPS) by the bacteria and the subsequent corrosion.

A large amount of the work performed to date on bacterial attachment in relation to MIC has focused on stainless steels, possibly due to reports of rapid failures of these materials such as through thickness pitting of piping welds. These studies have highlighted how a range of material properties (e.g. chemical composition, surface roughness, grain size and boundaries) can influence attachment and biofilm formation on steel surfaces. This range of influences means that a high level of care must be taken when designing and carrying out bacterial attachment tests in order to avoid the situation where a number of material variables affect the outcome of a single test. For example one of the criticisms of some of the previous work in this area is the lack of control of surface roughness of the substrates used in the studies.

In this work we will report results of studies of the initial attachment and EPS production of *E. coli* bacteria on highly polished carbon steel samples, with a number of different microstructures, for a number of different test media. We have found that the microstructure and test medium can have a significant effect on the rate of bacterial attachment, the distribution of attached bacteria, the onset of EPS production and the corrosion of samples immersed in *E. coli* inoculated test media.

2:20pm **BI+AI+BA+IS-MoA2 Charged SAMs as Model Surfaces to Understand Anti-fouling Properties of Zwitterionic Coatings**, ***S. Bauer***, University of Heidelberg, Germany, *J. Finlay, M.E. Callow, J.A. Callow,* University of Birmingham, UK, *A. Rosenhahn*, Ruhr-University Bochum, Germany

Zwitterionic surfaces are a class of coatings that receive increasing attention due to their good antifouling performance.[1] Since early work on protein resistance of mixed, charged self-assembled monolayers (SAMs), charge neutrality seems to be a prerequisite for their inert properties. [2,3] Similar to established non-fouling ethylene glycol chemistries, zwitterionic systems rely on a strong hydration of the coating. In this study we attempt a systematic analysis to which extend charge neutrality and the chemical nature of the charged groups affect their antifouling performance. Positively charged trimethylammonium terminated thiols were therefore mixed with sulfonate-, carboxylate- and phosphonate-terminated undecanethiols in varying ratios. Optimized preparation conditions and surface analysis will be presented that demonstrates successful assembly of the coatings and characterizes their physicochemical properties. The antifouling properties were tested against a range of laboratory organisms such as diatoms and spores of algae and compared to protein resistance. The obtained trends will be discussed and correlated with field experiments in the real marine environment.

(1) Chen, S.; Jiang, S. **2008** A new avenue to nonfouling materials. *Advanced Materials*, 20, 335-338.

(2) Holmlin, R. E.; Chen, X. X.; Chapman, R. G.; Takayama, S.; Whitesides, G. M. **2001** Zwitterionic SAMs that resist nonspecific adsorption of protein from aqueous buffer. *Langmuir*, 17, 2841-2850.

(3) Chen, S. F.; Yu, F. C.; Yu, Q. M.; He, Y.; Jiang, S. Y. **2006** Strong resistance of a thin crystalline layer of balanced charged groups to protein adsorption. *Langmuir*, 22, 8186-8191.

2:40pm **BI+AI+BA+IS-MoA3 The Role of Bacterial Physiology in Biodeterioration of Polyurethane Coatings**, *S. Zingarelli,* Air Force Research Laboratory, *D.E. Barlow, J.C. Biffinger,* Naval Research Laboratory, *L.J. Nadeau,* Air Force Research Laboratory, *D. Babson,* Naval Research Laboratory, *B.W. Stamps,* University of Oklahoma, *R.K. Pirlo,* Naval Research Laboratory, *C.N. Drake,* Air Force Research Laboratory, *B.S. Stevenson,* University of Oklahoma, *J.N. Russell, Jr.,* Naval Research Laboratory, ***W.J. Crookes-Goodson***, Air Force Research Laboratory **INVITED**

Microbial biofilms frequently contaminate surfaces and can cause degradation of polyurethane coatings that are intended to protect against environmental degradation. Historically, investigations of polyurethane biodeterioration have focused on identification and characterization of the organisms and 'polyurethanase' enzymes involved in the degradation process. However, many questions remain unanswered. For example, microbes capable of polymer degradation are ubiquitous in the environment, yet only affect polymers under some circumstances. What controls the production of polyurethanases? What is the role of planktonic vs. biofilm populations in the biodeterioration process? The goal of our research is to define the parameters and regulatory mechanisms that result in polyurethane biodeterioration by *Pseudomonas protegens Pf*-5, with a focus on environmental conditions (nutrients, pH, oxygen) and microbial 'lifestyles' (planktonic vs. biofilm populations). First, we screened a variety of carbon sources with a polyurethane agar plate-clearing assay using the polyester polyurethane Impranil DLN. Results showed that strain *Pf*-5 could grow on a variety of carbon sources but that degradation of polyurethane varied depending on the carbon source. We observed strong polyurethane degradation in the presence of M9-citrate medium but severely reduced clearing of polyurethane when glucose was provided as a carbon source. Subsequent studies with planktonic cultures of *P. protegens Pf*-5 verified the inhibitory effect of glucose on polyurethanase activity. Using proteomic tools, activity in citrate-grown planktonic culture supernatants was ascribed to two esterases, polyurethane esterases A and B. Currently the regulation of these enzymes is being investigated through a combination of genetic and transcriptomic approaches. Biofilms were grown on Impranil DLN in M9-citrate or -glucose to determine if these nutrients also regulated polyurethanase secretion in biofilms. Micro ATR-FTIR surface chemical analysis of the coatings after biofilm removal showed that degradation proceeds through preferential loss of the ester component. However, optical microscopy and profilometry clearly show that subsequent bulk coating loss can occur under certain conditions, resulting in complete loss of the original coating surface, and eventually complete loss of the coating. Transmission FTIR microscopy was also used to detect bulk coating degradation in a biofilm culture plate assay we developed to complement the Impranil clearing assay. This assay demonstrated significant Impranil coating degradation from citrate-grown biofilms versus minor degradation for glucose-grown biofilms.

3:40pm **BI+AI+BA+IS-MoA6 Multifunctional Active Nano and Microstructured Surfaces for Biofouling Management**, ***G.P. López***, Duke University **INVITED**

This talk will present (i) recent developments of stimuli responsive surfaces that exhibit dynamic structure on lateral length scales of the order of 10 microns and below, (ii) a prospectus for the formation of multifunctional bioactive surfaces based on such dynamic micro- and nanostructured materials, and (iii) results from study of bioadhesion and biorecognition on these surfaces. Stimuli responsive polymer surfaces include patterned polymer brushes and elastomers; biological systems of interest include protein solutions, adherent mammalian cell lines, as well as marine and infectious bacteria. Our previous studies have demonstrated that stimuli responsive polymers can be used to control the adhesion of such systems and, in this presentation, we will provide our latest advancements in this line of study, as regards to both molecular and cellular biointerfacial phenomena. Methods for preparing dynamic micro- and nanopatterns of stimuli responsive polymers will be presented, along with characterization of their structure, dynamic behavior and bioadhesion resistant character.

4:40pm **BI+AI+BA+IS-MoA9 Roles of Extracellular DNA in the Development and Expansion of Bacterial Biofilms**, ***C.B. Whitchurch***, University of Technology, Sydney, Australia **INVITED**

Biofilms are multicellular communities of bacteria that are often found attached to surfaces and cause significant problems in medical, industrial, and marine settings. Cells within biofilms are enmeshed in an extracellular polymeric matrix comprised of polysaccharides, proteins, lipids, and nucleic acids. Over the past decade, extracellular DNA (eDNA) has been found to be essential for biofilm formation by many species of bacteriawhere it is

thought to function as an intercellular "glue" that binds cells together. Interestingly, whilst it has been known for over a decade that eDNA is essential during the early stages of biofilm development by the opportunistic pathogen *Pseudomonas aeruginosa*, the precise roles of eDNA in this process have yet to be elucidated. We have used advanced techniques in microscopy, computer vision and image informatics to explore the roles of eDNA during early biofilm development and during active expansion of biofilms formed by *P.aeruginosa*. Many species of bacteria, including *P. aeruginosa* utilize type IV pili mediated twitching motility to actively translocate across solid and semi-solid surfaces. Twitching motility can manifest as a complex, multicellular behavior that enables the active expansion of bacterial biofilms. Under appropriate conditions, such as those encountered at the interface of a glass coverslip and semi-solid nutrient media, the expanding biofilm can develop dramatic networks of intersecting trails. Our analyses reveal that at the leading edge of the interstitial biofilm, highly coherent groups of bacteria migrate across the surface of the semi-solid media, and in doing so, create furrows along which following cells preferentially migrate. This leads to the emergence of a network of trails that guide mass transit toward the leading edges of the biofilm. We have determined that eDNA facilitates efficient traffic flow throughout the expanding biofilm by maintaining coherent cell alignments, thereby avoiding traffic jams and ensuring an efficient supply of cells to the migrating front. Our analyses reveal that eDNA also co-ordinates the movements of cells in the leading edge rafts and is required for the assembly of cells into aggregates that forge the interconnecting furrows. Our observations have revealed that large-scale self-organization of cells in actively expanding biofilms of *P. aeruginosa* occurs through construction of an intricate network of furrows that is facilitated by eDNA.

5:20pm **BI+AI+BA+IS-MoA11 Sample Preparation and Optimization for Bacterial Identification by Raman Spectroscopy**, ***M.M. Hlaing***, *M. Dunn, S.M. McArthur, P.R. Stoddart*, Swinburne University of Technology, Australia

The characterisation and identification of individual bacteria using Raman spectroscopy can aid in rapid, in situ microbiological diagnosis and hence timely, appropriate treatment and control measures [1, 2]. Appropriate sample preparation methods and experimental conditions are crucial to avoid some potential difficulties in analysing the information-rich Raman spectra from bacterial cells. In this study, the Raman spectra of fresh and stored samples of bacterial isolates (*Escherichia coli*) were analysed to determine any variations caused by sample processing. Analysis based on principal components suggests that different methods of sample preparation and storage affect the spectral components associated with different biochemical compounds in bacterial cells. The effect of long term storage in glycerol stock at freezing temperatures on the Raman spectrum of cells from the early exponential phase was observed in this study and found to modify the bacteria cells. Furthermore, the presence of extracellular polymeric substance (EPS) matrix around bacterial cells at later stages of the growth cycle provide higher resistance to environmental stress compared with other phases. Based on these results, a specific experimental protocol has been developed in order to obtain interpretable, comparable and reliable Raman data from bacterial samples.

Keywords: Raman spectroscopy; Bacterial identification; Sample preparation.

References

[1] W. E. Huang, R. I. Griffiths. Anal. Chem. 2004, **76**(15): 4452-4458.

[2] T. J. Moritz, S. T. Douglas. J. Clin. Microbiol. 2010, **48**(11): 4287-4290.

Ions at Aqueous Interfaces Focus Topic
Room: 203 A - Session IA+AI+BI+IS+NL+SS-MoA

Ions at Aqueous Interfaces
Moderator: M.H. Grunze, University of Heidelberg, Germany

2:00pm **IA+AI+BI+IS+NL+SS-MoA1 Sum-frequency Vibrational Spectroscopy for Studies of Ions Emerging at Water Interfaces**, ***Y.R. Shen***, University of California, Berkeley **INVITED**

Ions at water interfaces can significantly change the chemical and physical properties, and hence the functionality, of the interfaces. They play a key role in many important processes in many disciplines. In recent years, sum-frequency vibrational spectroscopy(SFVS) has been demonstrated to be a unique, effective tool to study such interfaces. We discuss here SFVS investigations of ions at various water interfaces: soluble ions at air/water interfaces, ions attached to Langmuir monolayers on water, and hydrophilic and hydrophobic water interfaces. Formation of an electric double charge layer by ions near an interface usually occurs. It induces significant polar reorientation of interfacial water molecules and alters their vibrational spectra that can be detected by SFVS. Useful structural information can be deduced from the results, but work is still needed for complete understanding of the results.

2:40pm **IA+AI+BI+IS+NL+SS-MoA3 Experimental Quantification of Surface Propensity of Halide Ions by Femtosecond Surface Vibrational Spectroscopy**, ***M. Bonn***, Max Planck Institute for Polymer Research, Germany, *H.J. Bakker*, FOM Institute AMOLF, Netherlands, *Z. Zhang, E.H.G. Backus*, Max Planck Institute for Polymer Research, Germany, *L. Piatkowski*, FOM Institute AMOLF, Netherlands **INVITED**

We investigate the vibrational dynamics and energy transfer between interfacial water molecules, in the presence of sodium chloride and sodium iodide salts, using 2-dimensional, femtosecond surface-specific vibrational spectroscopy. We find that both the vibrational lifetime and the intramolecular energy transfer for anion associated interfacial water molecules is slower than for non ion-bound interfacial water molecules. The analysis of the time-dependent slope of the 2-dimensional sum frequency response reveals that the intermolecular resonant energy transfer between the interfacial water molecules is significantly slowed down by the presence of ions. Accordingly, the decay of the frequency-frequency correlation function is slower for NaI than for NaCl solution. This finding provides direct evidence of the higher surface propensity for iodide than for chloride ion, and allows for the quantification of interfacial density of halide ions for both systems.

3:40pm **IA+AI+BI+IS+NL+SS-MoA6 Specific Ion Effects on Acid-Base Equilibria at the Planar Silica/Water Interface**, ***J.M. Gibbs-Davis***, University of Alberta, Canada

The interaction of ions with biological and environmental interfaces depends not only on their valency but also their identity. These specific ion interactions can influence other processes like deprotonation at mineral oxide interfaces. To monitor such interactions we utilized surface specific second harmonic generation (SHG) to report on changes in the surface charge density of silica in real time. We observe that the intrinsic equilibrium constant of the silanol groups is sensitive to the identity of the alkali ion. In contrast, varying the identity of the anion does not affect the intrinsic acidity of the sites but rather their mechanism of deprotonation. Specifically, positive cooperativity is observed in the deprotonation of silanol groups with increasing anion size and polarizability. These results and complementary measurements of the water structure using sum frequency generation spectroscopy will be discussed.

4:00pm **IA+AI+BI+IS+NL+SS-MoA7 Molecular Insight Into the Preferential Adsorption of Monovalent Ions to Selected Polar Surfaces: A Vibrational Sum Frequency Study**, ***E.C. Tyrode***, *R. Corkery*, KTH Royal Institute of Technology, Sweden

Vibrational Sum Frequency Spectroscopy (VSFS) has been used to systematically study the preferential adsorption of a series of monovalent ions to charged and uncharged fatty acid monolayers. Ion enrichment is mainly determined indirectly by targeting surface water vibrational modes. In selected cases however, the ion presence is also directly determined by targeting the fatty acid carboxylate headgroups. A major effort is made to understand the effect of co-ions in the molecular properties of these biophysically relevant interfaces.

4:20pm **IA+AI+BI+IS+NL+SS-MoA8 Dielectric Interfacial Effects**, ***R. Netz***, FU Berlin, Germany **INVITED**

The molecular layer of water molecules on surfaces, the so-called hydration layer, is important for a whole number of properties of biological as well as technological surfaces. Insight can be gained from all-atomistic simulations in conjunction with appropriate continuum modeling.

- Dielectric properties of interfacial water layers are important for the design of high-power capacitors, and can be resolved using simulations.

- At the same time, ions accumulate into a highly condensed interfacial layer, leading to the well-known saturation of the electro-osmotic mobility at large surface charge density regardless of the hydrodynamic boundary conditions. The experimentally well-established apparent excess surface conductivity follows for all hydrodynamic boundary conditions without additional assumptions.

- Hydration water at biological membranes absorbs electromagnetic radiation specifically in the 0.1-10 GHz range that is used for radio communication. Possible health issues are discussed.

5:00pm **IA+AI+BI+IS+NL+SS-MoA10 Liquid Jet –XPS Studies of Ions and Nitriles at the Aqueous Interface**, ***K.A. Perrine***, *M.H.C. Van Spyk, A.M. Margarella,* University of California, Irvine, *H. Bluhm,* Lawrence Berkeley National Laboratory, *B. Winter,* Helmholtz-Zentrum Berlin für Materialien und Energie/Elektronenspeicherring BESSY II, Germany, *M. Faubel,* Max Planck Institute for Dynamik und Selbstorganisation, Germany, *J.C. Hemminger*, University of California, Irvine

Acetonitrile in water is known to exhibit non-ideal behavior. At low concentrations, acetonitrile molecules migrate towards the solution interface leaving water mostly in the bulk. At 0.2 mole fraction, the surface saturates with a full monolayer. Above 0.2 mf, the acetonitrile signal at the surface is enhanced relative to that of the bulk with increasing solution concentration. In the bulk, acetonitrile and water form clusters between 0.2 and 0.7 mole fraction and interact with each other through dipole interactions. Propionitrile, another nitrile with a lower solubility, is also shown have a propensity for the surface of aqueous solutions.

Ions have been shown to impact the properties and solvation structure of aqueous solutions, both at the surface and in the bulk of solution. Potassium iodide (KI) was added to acetonitrile and propionitrile aqueous solutions to observe the effects of ions on nitrile distributions. Liquid jet-X-ray photoelectron spectroscopy (LJ-XPS) was used to characterize the elemental compositions of ions and nitrile species. By tuning the incident photon energy, different depths of the solutions is observed; at low kinetic energies the solution surface is probed and the high kinetic energies the bulk of solution is probed. After adding KI, the interfacial photoelectron spectroscopy signal reveals a reduction in nitrogen and carbon signals in acetonitrile, demonstrating the salting-in effect. With addition of ions to aqueous propionitrile solutions, nitrogen and carbon signals are increased, suggesting a salting-out effect. Sodium chloride ions are also added to aqueous propionitrile studies to determine differences between ions effects from the KI and NaCl salts on propionitrile solutions. These studies help elucidate the role ions play at the interface of aqueous organic solutions.

5:20pm **IA+AI+BI+IS+NL+SS-MoA11 Study of the Structural and Adhesion Forces in Highly Concentrated Electrolytes using Atomic Force Microscopy (AFM)**, ***T. Baimpos***, *M. Valtiner*, Max Planck Institut fur Eisenforschung GmbH, Germany

The understanding of the surface interaction in electrolyte solutions is of paramount importance in many fields such us biology, electrochemistry and surface chemistry. Aqueous solutions of high concentrations are mainly interesting from practical point of view (batteries). In principle, AFM through the Force versus Distance curves (F-D) can be successfully used to probe the electrolyte layering at solid-liquid interfaces and investigate the nature of hydration forces in the presence of various electrolytes of different ion valency, ion concentration or pH [1].

In the current work AFM has been used to measure hydration forces between a non-coated Silicon colloid probe and atomically smooth, flat freshly cleaved Mica surfaces, in highly concentrated monovalent electrolytes (LiCl, NaCl, CsCl). The effect of i) the cation hydration diameter (Li^+>Na^+>Cs^+) and ii) the electrolyte's concentration (0.05-3.0 M), on both the structural (F_{STR}) and adhesion (F_{ADH}) forces are studied. In all environments, F_{ADH} values pass through a minimum as a function of electrolyte's concentration, while for each salt solution, the frequency of structural events is calculated as a function of its concentration. The number of the F-D curves, were classified in appropriate tables according to the number of the structural hydration layers observed. Furthermore, depending on the concentration, 1, 2 or even up to 5 consecutive hydration layers can be clearly distinguished in the same F-D curve from which both the force and the range of each layer can be measured. These results are compared with the hydrated radii of the above ions enabling the extrusion of useful statements concerning the re-arrangement of the structured cation/water layer at the liquid/solid interface.

Applied Surface Science
Room: 204 - Session AS+BI+IS-WeM

Ambient Ionization Mass Spectrometry
Moderator: C. Szakal, National Institute of Standards and Technology, K. Artyushkova, University of New Mexico

8:20am **AS+BI+IS-WeM2 Rapid Evaporative Ionization Mass Spectrometry - Principles and Applications**, *Z. Takats,* Imperial College, London, ***J. Balog***, MediMass Ltd., Hungary **INVITED**

Development of ambient ionization methods lifted some of the constraints on the applications of mass spectrometry regarding sample pre-treatment and accessibility. However, even these techniques failed to offer a general solution for in-vivo analysis. Rapid Evaporative Ionization Mass Spectrometry (REIMS) has been developed to fill this gap and bring metabolic/lipidomic phenotyping into interventional medical environment. Origins of REIMS technique were based on the observation that thermal evaporation of tissues during surgical intervention produces gaseous ions corresponding to complex lipid species. Furthermore, these complex lipid fingerprints were found to show excellent histological specificity, similarly to those obtained by MALDI or DESI. Following the development of REIMS-based intra-surgical tissue identification technology, the mechanism of the technique was studied in details, and a wide variety of further applications were proposed. Observations strongly suggest that the REIMS technique – similarly to sonic spray ionization – transfers pre-formed ions from solution to gas phase. Electric current and power setting studies revealed minor dependence of the ionization efficiency on the AC frequency, while increasing power (and hence current) settings improved ion yield in the studied ranges. Studying the effect of atmospheric interface settings led to the conclusion that gaseous ionic species detected in the mass spectrometer are formed in the intermediate vacuum regime via cluster-surface collision phenomena. The assumption was further supported by cluster pick-up experiments where various parts of the ion optics were labelled with low volatility compounds (Rhodamine 6G, arginine) and surface re-ionization was studied during REIMS process. Based on these observations, a new type of atmospheric inlet was built, featuring a target surface for surface-induced dissociation of large molecular clusters accelerated by free jet expansion. The ions formed on collisions are collected by a ring electrode trap which is coupled to the ion optics of the mass spectrometer. Based on the results of mechanistic and earlier surgical studies, a number of new applications were developed ranging from the analysis of arbitrary liquid samples through identification of bacterial strains to imaging analysis.

9:00am **AS+BI+IS-WeM4 A Microplasma VUV Photoionization Source for Ambient Mass Spectrometry**, ***J.M. Symonds***, *R.D. Gann, F. Fernández, T.M. Orlando*, Georgia Institute of Technology

Microplasma ionization sources have been shown to be simple, effective tools for ambient mass spectrometry. Microplasmas have the advantages of being cheap to operate and manufacture, and require only modest gas flows and power sources. One of the challenges in ambient mass spectrometry is to produce sample ions from a wide variety of sample molecules without excessive fragmentation. Due to the chemically-specific nature of ionization, this remains a challenge for any new source. In this work we attempt to mitigate both of these problems by using high energy photons to ionize our samples. We have created a microplasma source that employs a mixture of neon and hydrogen to produce vacuum ultraviolet (VUV) light which can ionize samples at atmospheric pressure. Traditionally, VUV light has been both difficult and expensive to produce, which limits its use for applications like ambient mass spectrometry. With the development of our microplasma VUV source, we are able to take advantage of the VUV photon's capability as a broadly-applicable, low-fragmentation photoionization source, while retaining the low cost and simple operation which makes ambient mass spectrometry so appealing. By combining this ionization technique with laser desorption, we investigate the use of this source for mass spectrometric imaging.

This work was supported by the National Science Foundation under award number 0923179.

9:20am **AS+BI+IS-WeM5 Advances in Pulsed-Plasma Sources for Surface Analysis by Ambient Mass Spectrometry**, ***J.W. Bradley***, *K. McKay, A. Bowfield,* University of Liverpool, UK, *T.L. Salter,* National Physical Laboratory, UK, *J.W. Walsh,* University of Liverpool, UK, *M.R. Alexander, D.A. Barrett,* University of Nottingham, UK, *I.S. Gilmore*, National Physical Laboratory, UK

The potential benefits of using atmospheric pressure "cold" plasma sources as a means of both desorption and ionisation of material in ambient mass spectrometric analysis of surfaces has been recognized by a number of researchers worldwide. Plasma sources include dielectric barrier jets (PADI [1] and LTP [2]) operating at mid-frequency and also RF corona needle discharges.

Here we develop further strategies to pulse modulate such sources (jet and needle) and investigate the influence of duty cycle on the production of chemical species in the source plasma and the composition of the ionised desorbed species from a range of test surfaces (polymeric, pharmaceutical and biological). For the plasma plume study we use a time resolved (5 μs) Hiden Analytical molecular beam MS (HPR-60) unit, while detailed information on the spatial distribution of surface species from the chosen material samples was done using a Thermo Velos LTQ Orbitrap MS.

The influence of source-sample and sample-instrument distances on the signal intensities is investigated for both sources. We observe that as the duty cycle of the pulse is decreased the positive ion yield shifted towards higher mass clusters, due to a decrease in gas temperature enabling increased hydration reactions. The negative ions also display similar trends with the yield of larger negative ions increasing with shorter duty cycles. From time-resolved ion intensities it is clearly seen that positive ions are produced in the on-phase of the discharge, and decay in the off-phase. Negative ions, in contrast, are produced mainly in the off-phase of the discharge and decay during the on-phase. With increased distance between source and instrument we observe that the yield of large positive ions increases, at the expense of smaller positive ions which are lost before they reach the orifice. Negative ions, on the other hand, show an increase in yield as distance is increased.

Preliminary analysis of common pharmaceutical products suggest that a decreased duty cycle gives improved identification of negative ion surface compounds however, where surface compounds undergo ionisation to form positive ions, larger duty cycles allowed for better identification. The gas-phase plasma chemistry for different arrangments will be discussed.

1] Ratcliffe LV, Rutten FJ, Barrett DA, Whitmore T, Seymour D, Greenwood C, Aranda-Gonzalvo Y, Robinson S, McCoustra M, Anal Chem. (2007) 79 (16) 6094

2] Zhang, JI, Costa, AB,Tao, WA, Cooks, RG, Analyst, (2011), 136, 15, 3091

9:40am **AS+BI+IS-WeM6 Comparison of Ambient Pressure Ionization Sources by Determining Useful Yields of Forensic Compounds of Interest**, ***T. Brewer***, *C. Szakal, E. Sisco, S. Muramoto, T. Forbes, G. Gillen*, NIST

The detection of illicit drugs and trace explosives represents one of the most significant challenges for law enforcement and forensic communities. Of particular interest to the forensic analyst is the ability to rapidly identify suspected illicit drug materials and explosives residues in their native state (powder, tablet or liquid form), under atmospheric conditions and with a high level of specificity and sensitivity. To that end there are numerous ambient pressure ionization techniques such as atmospheric pressure glow discharge (APGD), low temperature plasma (LTP), and desorption electrospray ionization (DESI) that can be used to interrogate forensic compounds. However, a method of comparing between the different ambient ionization sources does not exist. Here, useful yields are determined for a series of forensic compounds using different ambient pressure ionization sources as a means of comparison. Using a precision inkjet deposition system a well-defined array of microdrops is produced with each deposit containing a known number of analyte molecules. The individual deposits were removed or desorbed until consumed while monitoring the integrated characteristic molecular secondary ions for each analyte. The ratio of integrated counts to the number of molecules in the deposit defines the useful yield of the experiments. The results here highlight a way to compare the different ambient ionization sources for the analysis of forensic compounds of interest.

10:40am **AS+BI+IS-WeM9 Atmospheric Pressure Ionization Mass Spectrometry: Fundamentals, Simulations, and Applications**, ***Th. Benter***, University of Wuppertal, Germany **INVITED**

Almost for a century now, mass spectrometric instrumentation is generally designed to establish linear analyte concentration – ion signal responses. Deviations from linear relationships are tolerated to a certain extent but such observations usually raises doubts on the performance of the method applied. Surprisingly, Atmospheric Pressure Ionization (API) techniques have swiftly led to the frequent usage of terms such as "matrix effects", "ion suppression", or "non-linear response". This is particularly true for ambient ionization methods. In fact, the various API methods not only target different analyte properties, e.g. gas phase acidities, they also frequently generate new ion signals which are then somehow related to the neutral analyte precursor. On the other hand API mass spectra may also show unexpected fragmentation patterns – despite the often claimed "soft" nature of the ionization processes involved.

In this contribution we are attempting to highlight some of the key processes operating on the primarily generated analyte ion population en route from the origin of ion formation to the collision free analyzer region. For this purpose, we are defining *chemical domains* such as the initial reagent ion generation domain (in ambient ionization often plasmas), the chemical ionization domain, or the thermal ion transport domain, among others. These domains exhibit distinct features, which are significantly changing the chemical matrix in which ions and neutrals are moving towards the collision free - and thus chemically non-reactive - analyzer region.

Primary ionization pathways, subsequent thermal ion molecule chemistry, and electrical fields are discussed as potential drivers of chemical transformation processes, which may render the interpretation of API mass spectra quite difficult. This is particularly true for the analysis of complex mixtures using API MS without chromatographic pre-separation of the neutrals. Ambient ionization methods are generally designed to do exactly that: Analyze samples (e.g., human urine, drug tablets, surface contaminations, to name but a few) without sample preparation and preferentially in real time.

Examples are given to illustrate the extent of selected transformation processes. Among other issues it is discussed why the generation of Helium metastable atoms (He^M) results in protonation in API MS, or why aromatic hydrocarbons ionized with the exact same primary excitation scheme yield almost exclusively radical cations in classical mass spectrometers but often deprotonated molecules in API systems.

11:20am **AS+BI+IS-WeM11 Ambient Mass Spectrometry for Structural Analysis of Organic Monolayers**, ***H. Zuilhof***, Wageningen University, Netherlands

For the analysis of covalently bound organic monolayers a variety of surface-sensitive techniques has been developed, including XPS, AES, IR, contact angle measurements and X-ray reflectivity. While each of these has its own merits, none of them provide **structural** information. In addition, via e.g. XPS it is sometimes possible to follow A -> B reactions on a surface, but A -> x% B + y% C is already nearly impossible to properly analyze. Similar restrictions apply to the study of diluted monolayers (e.g. 10% of a bioactive compound surrounded by 90% inert surface-covering monolayer), while dilution may actually be essential for the proper biological functioning of the monolayer! Therefore novel analysis techniques are still in demand, and here we present the application of DART ambient mass spectrometry as a generic and highly powerful technique for the analysis of such monolayers. Using a variety of tailor-made, covalently attached organic monolayers on silicon nitride and other substrates we show that MS can be used to study: 1) the progress of four sequential surface-bound organic reactions, 2) surfaces with a mixture of halogens on them, 3) the progress of incomplete reactions, and 4) the stability of biofunctional groups. In the current presentation we summarize our recently published work in this area (ChemComm 2013, 922) and present new, as of yet unpublished data that outline the tremendous potential of this novel analysis technique!

11:40am **AS+BI+IS-WeM12 Differentiation of Microbial Species & Strains in Coculture Biofilms by Multivariate Analysis of Laser Desorption Postionization Mass Spectra**, *C. Bhardwaj, Y. Cui,* University of Illinois at Chicago, *H.C. Bernstein, R.P. Carlson,* Montana State University, ***L. Hanley***, University of Illinois at Chicago

The metabolic states of microbial biofilms vary with growth conditions such as host surface, culture media, or antibiotic concentration. 7.87 and 10.5 eV vacuum ultraviolet (VUV) photon energies were used in laser desorption postionization mass spectrometry (LDPI-MS) to analyze microbial biofilms comprised of binary cultures of interacting microorganisms grown on polymer membranes. Principal components analysis (PCA) was applied to the MS data to differentiate species in *Escherichia coli-Saccharomyces cerevisiae* coculture biofilms. PCA of LDPI-MS also differentiated individual *E. coli* strains in a biofilm comprised of two interacting gene deletion strains, even though these strains differed from the wild type K-12 strain by no more than four gene deletions each out of approximately 2000 genes. PCA treatment of 7.87 eV LDPI-MS data separated the *E. coli* strains into two "pure" groups and a distinct mixed region. Furthermore, the "pure" regions of the *E. coli* cocultures showed greater variance by PCA when analyzed by 7.87 eV photon energies than by 10.5 eV radiation. Comparison of the 7.87 and 10.5 eV data is consistent with the expectation that the lower photon energy selects a subset of low ionization energy analytes while 10.5 eV is more inclusive, detecting a wider range of analytes. These two VUV photon energies therefore give different spreads via PCA and their respective use in LDPI-MS constitute an additional experimental parameter to differentiate the metabolite states of microbial biofilms growing on different surfaces.

In Situ Spectroscopy and Microscopy Focus Topic
Room: 203 B - Session IS+AS+SS-ThM

Ambient Pressure XPS from Sophistication to Reality

Moderator: A. Thissen, SPECS Surface Nano Analysis GmbH

8:40am **IS+AS+SS-ThM3 Ambient Pressure XPS Observation of Electrode Surfaces during Electrochemical Reactions**, *H. Sanchez Casalongue, S. Kaya, D.J. Miller, D. Friebel, A. Nilsson,* ***H. Ogasawara***, SLAC National Accelerator Laboratory **INVITED**

The sluggish kinetics in oxygen reduction reaction (ORR) is one of key challenges in polymer electrolyte membrane fuel cells (PEMFCs). Understanding the ORR mechanism under operating conditions is essential to isolate parameters that allow for high PEMFC efficiencies. Through the use of ambient pressure photoemission spectroscopy (APXPS) at Stanford Synchrotron Radiation Lightsource (SSRL) [1], we identified the surface speciation of the fuel cell Pt cathode under different operating conditions. We also established that the species on the electrode change drastically depending on the oxygen pressures. We used this knowledge to clarify that the favored ORR pathway is dependent on the operating conditions, thus identifying a key parameter to be controlled in high efficiency fuel cells [2].

1. S. Kaya, H. Ogasawara, L.-A. Nasdslund, J.-O. Forsell, H. Sanchez Casalongue, D.J. Miller, A. Nilsson, Ambient-pressure photoelectron spectroscopy for heterogeneous catalysis and electrochemistry, Catalysis Today 205 (2013) 101.

2. H.S. Casalongue, S. Kaya, V. Viswanathan, D. Miller, D. Friebel, J.K. Noskov, A. Nilsson, H. Ogasawara, Direct observation of the oxygenated species during oxygen reduction reaction on a Pt fuel cell cathode, submitted.

9:20am **IS+AS+SS-ThM5 Ambient Pressure Photoelectron and Electron Spectro-Microscopy Using Electron Transparent Membranes**, *A. Yulaev,* Southern Illinois University Carbondale, *M. Amati, L. Gregoratti,* Sincrotrone Trieste, Italy, *S. Guenther,* Technical University Muenchen, Germany, *M. Kiskinova,* Sincrotrone Trieste, Italy, *I. Sgura, B. Bozzini,* University of Salento, Italy, ***A. Kolmakov***, Southern Illinois University Carbondale

Truly *in situ* (photo-) electron spectroscopy and microscopy under ambient pressure conditions in different environments such as electrolytes, water, reactive liquids and gases would provide a nanoscopic access to processes taking place at solid-liquid-gas interfaces. However this exciting line of research still remains a challenging experimental task but is strongly demanded by a variety of active research directions *i.e.* in fuel cells, batteries, catalysis, (bio-) medical, automotive, geological, forensic *etc*. To address these needs a number of designs have been developed since nineties to probe the samples in liquid state or gases at sub-atmospheric pressure. In particular, the elevated pressure XPS at liquid solid and liquid-gas interfaces have been demonstrated via development of advanced differentially pumped lens systems for the electron energy analyzer or via liquid micro jets and droplet "trains" methods.

Novel quasi-2D materials such as graphene and its derivatives currently constitute the active source of innovations in electronics, optics, energy harvesting/storage, catalysis and bio-medical applications. When isolated as ultrathin (~0.3-1 nm) membranes, graphene sheets have thicknesses comparable to the effective attenuation length of 200-1000 eV electrons. In addition, these membranes are chemically stable, gas impermeable and mechanically robust. Based on this unique combination of properties and on recent developments in fabrication and transfer protocols we demonstrate the capability to perform XPS and electron microscopy studies of the processes taking place at liquid-solid interface through graphene-based membranes.

9:40am **IS+AS+SS-ThM6 Surface Chemistry over Inverse Model Catalysts under Near-Ambient Pressure**, ***A. Baber****, K. Mudiyenselage, S. Senanayake, J. Rodriguez, D. Stacchiola*, Brookhaven National Laboratory

The importance of metal–oxide interfaces has long been recognized, but the molecular determination of their properties and role is only now emerging. Atoms with properties ranging from metallic to ionic are available at the metal–oxide interface and create unique reaction sites. We have shown that the activation of an efficient associative mechanistic pathway for the water–gas shift reaction by an oxide–metal interface leads to an increase in the catalytic activity of ceria nanoparticles deposited on Cu(111) or Au(111) by more than an order of magnitude. *In situ* near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) experiments demonstrated that a carboxy species formed at the interface is the critical intermediate in the reaction. To obtain a complete picture of the morphological and chemical changes occurring during catalytic processes, we investigated the reduction of Cu_2O/Cu(111) under NAP of CO by a combination of *in situ* scanning tunneling microscopy (STM) and XPS to provide insight into the highly reducing environment of the water gas shift reaction on a model oxide surface. Systematic studies allow us to identify intermediate structures and determine how reaction fronts propagate across a surface with atomic scale resolution. Traditionally, STM is used to monitor surface structures and electronic properties, but here we show the surface oxide species can be identified with atomic-scale detail under near ambient pressures.

10:40am **IS+AS+SS-ThM9 Ambient Pressure Photoelectron Spectroscopy using Tender X-ray**, *S. Axnanda, E.J. Crumlin, R. Chang, B. Mao,* Lawrence Berkeley National Laboratory, *W. Stolte,* Lawrence Berkeley National La **INVITED**

The ambient pressure x-ray photoelectron spectroscopy (AP-XPS) endstations based on differentially pumped electron energy analyzers have been recognized by scientific communities as an important in-situ tool to study water, environmental science, catalysis and many other important fields.

Multiple new AP-XPS endstations are currently under planning or development at US and international synchrotron light sources. Recently we have installed a new hard x-ray AP-XPS endstation at ALS Beamline 9.3.1 (2.5keV- 5keV). By using tender X-ray up to 5KeV, we can perform AP-XPS at a pressure up to 110 torr. The probing depth of photoelectrons also increases to >10 nm, which will allow us to study not only the gas/solid interface but also the liquid/solid interface. In this meeting, we will present results of our in-situ study on the electrolyte/electrode interface of a working model electrochemical cell.

We believe the successful development of hard X-ray APXPS endstation will provide energy research community a powerful in-situ tool to directly study the electrolyte/electrode interface of many important electrochemical devices.

11:20am **IS+AS+SS-ThM11 Novel Developments in Near Ambient Pressure XPS – The Route Towards Standard Analysis Tools in Laboratory Environments**, *A. Thissen,* ***S. Bahr***, SPECS Surface Nano Analysis GmbH, Germany

Modern devices are often only functional in environments far away from ultrahigh vacuum, still being the standard operation conditions for all Surface Science techniques. In parallel the importance of surfaces for the correct device operation is continuously increasing due to miniaturiziation down to the nanoscale. To contribute to advanced materials analysis in future means using Photoelectron spectroscopy combined with Scanning Probe Microscopies and related techniques in the generic or near generic device environments. This means high, elevated or near ambient pressures of defined working gas mixtures, liquid media, potentials or magnetic fields applied. Also extremely low or high temperatures might be necessary. In past all standard Surface Science Techniques did not work under these extreme environments. As a route to in situ sample analysis Near Ambient Pressure XPS has already been used for a longer time with tremendous success. Nowadays steps are made to utilize this analysis technique not only at synchrotrons and in academic environments, but also as standard analysis tools in user friendly laboratory systems. This work summarizes and presents existing solutions nowadays and future development routes to new instruments and materials analysis methods being functional under these working conditions. Opportunities and limits will be discussed. from the perspective of a supplier of scientific instruments. Finally applications, examples and results from existing In situ methods like high pressure treatments cells, complete High Pressure or Near Ambient Pressure Photoelectron Spectroscopy or Scanning Probe Microscopy Systems (NAP-PES or NAP-SPM), liquid and electrochemical cells, Liquid sample "manipulators", and concepts and status of equipment working in highest or lowest temperatures, high magnetic fields and static or dynamic potentials will be demonstrated.

In Situ Spectroscopy and Microscopy Focus Topic
Room: 203 B - Session IS+EN+SP+SS-ThA

In Situ Studies of Electrochemical Interfaces and Processes

Moderator: A. Kolmakov, Southern Illinois University Carbondale

2:00pm **IS+EN+SP+SS-ThA1 Direct *In Situ* Probe of Electrochemical Processes in Operating Fuel Cells**, ***S.S. Nonnenmann***, *R. Kungas, J.M. Vohs, D.A. Bonnell*, University of Pennsylvania

Many strategies for advancing energy related processes involve high temperatures and reactive environments. Fuel cell operation, chemical catalysis, and certain approaches to energy harvesting are examples. Scanning probe microscopy boasts a versatile toolbox of local and often atomic resolution measurements of phenomena at a scale that enables understanding of complex processes involved in many systems. Applying these techniques to the realistic conditions under which these processes operate inherently poses significant experimental design challenges. To overcome this, we have developed a system allowing SPM at temperatures to 600°C in reactive gas environments. Here the characterization of an operating fuel cell serves as the first demonstration. Solid oxide fuel cells (SOFCs) offer the highest conversion efficiencies with operating temperatures ranging from 400°C - 1000°C and operate under variable gaseous fuel environments – H_2-based environments (anode side) and O_2-based environments (cathode side). Topography and the influence of the local ionic chemical potential on the surface potential are observed along the electrode/electrolyte interface while under operation. While not (yet) at atomic levels of spatial resolution, these probes are at the scale to examine local interface properties.

2:20pm **IS+EN+SP+SS-ThA2 *Ex Situ* Lift-Out of Specimens for *In Situ* TEM Studies**, ***L.A. Giannuzzi***, L.A. Giannuzzi & Associates LLC, *Z. Yu, M.P. Harmer*, Lehigh University

In-situ transmission electron microscopy (TEM) of grain boundaries at elevated temperature requires accurate manipulation of electron transparent specimens to site-specific carbon films patterned on heating membranes measuring only ~5-10 micrometers in diameter. Ex-situ lift-out (EXLO) of focused ion beam (FIB) prepared or other electron transparent specimens (e.g., fibers, particles, platelet precipitates) is advantageous for accurate manipulation of specimens to these membranes because it is fast, reproducible, and avoids deleterious ion implantation into the specimens while FIB imaging during the in-situ lift-out method. The ex-situ lift-out technique for this application will be described and in-situ TEM results will be presented.

2:40pm **IS+EN+SP+SS-ThA3 *In Situ* Characterization of Thermal Degradation of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ Cathode Materials for Lithium Ion Batteries: Insights from Combined Synchrotron XRD, XAS and Environmental Microscopy Studies**, ***E. Stach***, *S. Hwang, S.-M. Bak, K.-W. Nam,* Brookhaven National Laboratory, *W. Chang,* Korean Institute of Science and Technology, *X. Yu, E. Hu, K.-B. Kim,* Brookhaven National Laboratory, *K.-Y. Chung,* Korean Institute for Science and Technology, *X.-Q. Yang*, Brookhaven National Laboratory **INVITED**

Li-ion batteries have seen widespread application as secondary batteries in numerous applications in consumer electronics, and have attracted recent attention for various forms of electric vehicles. One particularly attractive material for the cathode is the Ni-rich system of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$. These materials are being explored as a replacement to $LiCoO_2$, as they offer several performance improvements, including higher energy density and lower cost. However, these materials have demonstrated a significant increase in impedance and capacity fade during aging, or upon cycling at elevated temperatures. Additionally, when in highly delithiated states, the reduction of Ni ions during thermal cycling releases oxygen from the crystal structure, which can lead to both thermal runaway and violent reactions with the flammable electrolyte.

We have utilized a variety of in-situ characterization methods to understand the mechanisms associated with the thermal degradation of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$materials, as a function of their delithiation / charge state. By combining time-resolved synchrotron x-ray diffraction and mass spectrometry, we have directly shown that these materials undergo a specific sequence of phase transformations - from layered to disordered spinel to rock salt - as a function of temperature, and directly correlate these phase transformations with the evolution of oxygen from the microstructure. In-situ observations in an environmental transmission electron microscope confirm these global average measurements on the nanoscale, and allow us to kinetically track the evolution of oxygen from the surfaces of the nanoparticles into their bulk. In-situ spectroscopic results - from XAS and EELS - allow correlation between electronic structure changes and the resulting phase transformations. Finally by performing these same thermal treatments in-situ to the TEM and in the presence of excess oxygen, we show that it is possible to suppress these phase transformations to significantly higher temperatures, thereby suggesting that methods to protect the surfaces from oxygen evolution could lead to significant enhancements in the safety performance of these materials. Throughout the presentation, the insights gained from complementary in-situ techniques will be highlighted.

3:40pm **IS+EN+SP+SS-ThA6 *In Situ* Measurement and Control of Interaction Forces at Electrified Softmatter | Metal Interfaces**, ***M. Valtiner***, Max Planck Institut fur Eisenforschung GmbH, Germany, *S.H. Donaldson, K. Kristiansen, M.A. Gebbie, J.N. Israelachvili*, University of California, Santa Barbara

Redox-active interfaces are ubiquitous in the realms of natural and technological systems. For instance, prevention of corrosive delamination at metal|oxide|paint interfaces, or bio-mimicry of adhesive bonding in natural systems (e.g. mussel glues) rely on a fundamental understanding of interaction forces at electrified and/ or redox-active solid|liquid|softmatter interfaces. Recently, we developed a newly designed electrochemical surface forces apparatus setup (EC-SFA) that allows control and measurement of both surface potentials and interfacial electrochemical reactions with simultaneous measurement of normal interaction forces and the absolute distances between (similar or dissimilar) apposing surfaces [1], [2].

To quantify both oxide growth and interaction forces between asymmetric apposing softmatter and metal surfaces we performed normal force measurements across atomically smooth polarized gold electrodes facing PEGolated lipid bilayers with different head-group chemistries. Switching electrochemical potentials allowed us to quantitatively and qualitatively identify, rationalize, and therefore control, which interaction forces dominated between the electrode surfaces and a surface coated with differently end-functionalized polyethylene glycol (PEG) polymers. In particular, the manipulation of *surface potentials and the oxidation of the gold have profound and very strong influences on the measured interaction forces*. Moreover, our measurements allowed us to *in-situ quantify the Au-oxide thickness with Ångstrom accuracy*. Here, we will discuss in detail, how (1) electric double layer potentials, (2) change of surface chemistry (e.g. oxide growth, oxide thickness) as well as (3) polymer chemistry (functional groups and backbone chemistry) influence specific and non-specific interaction forces (electrostatic, hydrophobic and Van der Waals forces, see also [3]) across electrified softmatter|metal interfaces.

[1] Valtiner, M., Kristiansen, K., Greene, G. W. et al. in Advanced Materials 23, 2294 (2011).

[2] Valtiner, M., Banquy, X., Kristiansen et al. in Langmuir 28, 13080-13093 (2012).

[3] Valtiner, M., Donaldson, S. H., Jr., Gebbie, M. A. et al. in Journal of the American Chemical Society 134, 1746-1753 (2012).

4:00pm **IS+EN+SP+SS-ThA7 *In Situ* Studies of Strain Evolution in Graphene on Ir(111) and Interplay with Magnetic Few Layer Cobalt Films**, ***A. N'Diaye***, Lawrence Berkeley National Laboratory **INVITED**

Graphene's transport properties make it a promising component of spintronic applications and logic circuitry operating at gigahertz frequencies or as a support for nanocatalysts. Understanding graphene's interplay with the substrate is key to understanding and tailoring its properties. Here we show how thermal compression leads to few nanometer wide and micrometer long elongated wrinkles on singe layer epitaxial graphene on Ir(111) to partially relieve compressive strain in the graphene layer. The strain relief process can be followed in-situ with spot profile analysis low energy electron diffraction (SPA-LEED) and low energy electron microscopy (LEEM). We show that micrometer wide regions of graphene slide over substrate and that the residual strain is spatially inhomogeneous. An other example for the interplay of graphene with its support is the enhancement of the perpendicular magnetic anisotropy in thin Cobalt films intercalated between graphene and Ir(111). We use spin-polarized LEEM (SPLEEM) to study the thickness induced spin reorientation transition in the graphene/Co/Ir(111) system and produce a phase diagram of an in-plane state, an out of-plane state, and a partially canted state. This work was supported by the U.S. Department of Energy under Contract No. DE-AC02-

05CH11231, by the French ANR contract ANR-2010-BLAN-1019-NMGEM and by the Alexander von Humboldt Foundation.

4:40pm **IS+EN+SP+SS-ThA9 The Lithium-Induced Conversion Reaction of CoO Thin Film Battery Materials in Ultra-High Vacuum**, ***R. Thorpe***, *S. Rangan, M. Sina, F. Cosandey, R.A. Bartynski*, Rutgers University

Lithium-ion conversion batteries can store 2-3 times more charge than intercalation batteries by utilizing the full range of oxidation states of their constituent divalent or trivalent transition metal compounds during discharge. A prototypical conversion compound is CoO, which follows the reaction

$2Li^{+} + 2e^{-} + Co^{(2+)}O \rightarrow Li_2O + Co^{(0)}$.

Cobalt oxide and other transition metal oxides are attractive for use as Li-ion anodes in portable electronics due to their high charge storage capacity and moderate voltage versus Li^{+}/Li^{0}. However, the cycling stability of conversion electrodes is poor, and capacity losses have thus far prevented their implementation.

In order to understand phase progression during the conversion reaction of CoO, high-purity CoO thin films grown in UHV were sequentially exposed to atomic lithium. The electronic structure of the pristine films and of the products of lithiation was studied using x-ray photoemission spectroscopy (XPS), UV photoemission spectroscopy, and inverse photoemission spectroscopy. The crystal structure and film reorganization were probed in parallel with transmission electron microscopy (TEM) and scanning tunneling microscopy.

The amount of CoO reduction for a given Li dose was observed to be highly dependent upon the temperature at which lithiation was performed. At 150^{o}C, Li mobility in the active material was sufficient to allow full reduction of the CoO film as confirmed by XPS. Consistent with electrochemically lithiated CoO electrodes, precipitation of Co nanoparticles in a Li_2O matrix was observed in TEM images. However, at room temperature, the Li-rich overlayers that formed on the CoO film after initial lithiations inhibited further Li diffusion. This could be due to the intrinsically poor kinetic properties of Li_2O or to the formation of Li_2O_2 and/or LiOH passivating films.

The reactivity of CoO films was also found to depend on the orientation of the film. CoO(100) films exhibited a higher degree of conversion for a given Li exposure than polycrystalline films. STM and angle-resolved XPS of these films have been used to investigate the differences between these two film morphologies upon exposure to Li.

In Situ Spectroscopy and Microscopy Focus Topic
Room: Hall B - Session IS-ThP

In Situ Microscopy and Spectroscopy Poster session

IS-ThP1 Scanning Tunneling Microscopy of the Topological Crystalline Insulator SnTe, ***D. Zhang***, *J. Ha*, NIST and University of Maryland, *H. Baek*, NIST and Seoul National University, Republic of Korea, *Y. Kuk*, Seoul National University, Republic of Korea, *J.A. Stroscio*, Center for Nanoscale Science and Technology, NIST

Recently, the topological classification of electronics states has been extended to a new class of matter called topological crystalline insulators. In contrast to topological insulators characterized by time reversal symmetry protected surface states with an odd number of Dirac cones, topological crystalline insulators arise from crystal symmetry and are characterized by surface states with an even number of Dirac cones. Here, we report *in-situ* low temperature scanning tunneling microscopy study of SnTe (001) surfaces grown by molecular beam epitaxy. SnTe high symmetry surfaces have been recently predicted and experimentally confirmed as hosting topological crystalline insulator surface states [1-3]. The growth of SnTe on multilayer graphene/SiC substrates is shown to produce SnTe (001) nanoplates with varying densities of Sn vacancies. The topological surface states on the SnTe (001) surface in these nanoplates were probed by scanning tunneling spectroscopic mapping. In this poster we discuss the spectroscopic mapping results in terms of scattering in Fermi surface contours of the topological surface states.

[1] T. H. Hsieh, *et al*., *Nat. Comm*. 3, 982 (2012).

[2] Y. Tanaka, *et al*., *Nat. Phys*. 8, 800 (2012).

[3] S.-Y. Xu, *et al*., *Nat. Comm*. 3, 1192 (2012).

IS-ThP2 *In Situ* Electrostatic and Thermal Manipulation of Suspended Graphene Membranes, *W. Bao*, ***K. Myhro***, *Z. Zhao, Z. Chen, W. Jang, L. Jing, F. Miao, H. Zhang, C. Dames, C.N. Lau*, University of California, Riverside

Graphene is nature's thinnest elastic membrane, and its morphology has important impacts on its electrical, mechanical, and electromechanical properties. Here we report manipulation of the morphology of suspended graphene via electrostatic and thermal control. By measuring the out-of-plane deflection as a function of applied gate voltage and number of layers, we show that graphene adopts a parabolic profile at large gate voltages with inhomogeneous distribution of charge density and strain. Unclamped graphene sheets slide into the trench under tension; for doubly clamped devices, the results are well-accounted for by membrane deflection with effective Young's modulus E = 1.1 TPa. Upon cooling to 100 K, we observe buckling-induced ripples in the central portion and large upward buckling of the free edges, which arises from graphene's large negative thermal expansion coefficient.

In Situ Spectroscopy and Microscopy Focus Topic
Room: 203 B - Session IS+AS+SP-FrM

Evolving In Situ Microscopic and Spectroscopic Techniques and Applications

Moderator: G. Zhou, Binghamton University

8:20am **IS+AS+SP-FrM1 *In Situ* Atomic-Scale Observations of the Oxidation of Metals**, ***G. Zhou***, *L. Luo, L. Li,* State University of New York, Binghamton University, *J. Ciston,* Lawrence Berkeley National Laboratory, *E. Stach,* Brookhaven National Laboratory, *J. Yang*, University of Pittsburgh **INVITED**

Transmission electron microscopy (TEM) has evolved dramatically in recent years and allows for temperature-, time-, and pressure-resolved imaging of gas-surface reactions at the atomic scale. This is accomplished by differentially pumped environmental TEM (max pressures of several Torr) and the incorporation of aberration correction techniques. Here we describe how dynamic, atomic-scale TEM observations of terraces and steps during oxidation of Cu surfaces demands revisions in the current held oxidation mechanism. The canonical description of oxide formation in metals involves a solid-solid transformation proceeding with initial oxygen chemisorption induced reconstructions followed by oxygen subsurface incorporation. Such a mechanism has been inferred from idealized experiments that are primarily restricted to planar surfaces under ultrahigh vacuum conditions. In practice, however, metallic surfaces are seldom perfect. Rather, they contain a high density of low-coordinated surface sites. Thus, in order to gain a detailed understanding of the mechanism of oxide formation under *realistic* conditions, the role of surface defects during surface oxidation must be elucidated under practical environments. By observing the coordinated step retraction and oxide propagation on surface terraces in real time with in-situ TEM, we demonstrate that the oxide grows via an adatom process, in which Cu atoms detach from step edges and diffuse in along the surface terrace. This process involves neither reconstructive oxygen adsorption nor oxygen subsurface incorporation and is rather different from the mechanism of solid-solid transformation of bulk oxidation that is most commonly postulated. These results demonstrate that the presence of surface steps can promote the development of a flat metal-oxide interface by kinetically suppressing subsurface oxide formation at the metal-oxide interface.

9:00am **IS+AS+SP-FrM3 X-ray Analysis of Ultrastructure of Vitrified Biological Objects**, ***A.R. Buck***, *T. Gorniak, T.M. Senkbeil,* Karlsruhe Institute of Technology, Germany, *V.M. Haramus,* Helmholtz-Zentrum Geethacht, Germany, *K. Hilpert,* University College London, UK, *A. Rosenhahn*, Ruhr-Universitat Bochum, Germany

Cryogenic sample environments allow investigations in the X-ray 'water window' of 284 – 540 eV which is of tremendous interest for microscopy and coherent scattering due to the high contrast of organic matter with respect to the aqueous background. In addition, no fixatives and stains are required and thus real in-situ analysis becomes possible. We present coherent diffractive imaging and X-ray micrographs of bacteria and compare the data against small angle X-ray scattering on large ensembles. Most measurements have been conducted at the synchrotron BESSY II, U49 PGM2 with our dedicated scattering chamber *HORST*. As example for the approach, ultrastructure changes in bacteria induced by stress conditions such as different environmental conditions and biocides. We show that imaging and scattering provide complementary results as latter provides information averaged over thousands of cells and can thus provide insights of a very high statistical quality.

9:20am **IS+AS+SP-FrM4 Recent Advances in the Electrochemical Surface Forces Apparatus**, ***K. Kristiansen***, University of California, Santa Barbara, *M. Valtiner,* Max Planck Institut fur Eisenforschung GmbH, Germany, *X. Banquy,* Universite de Montreal, Canada, *G.W. Greene,* University of Deakon, Australia, *J.N. Israelachvili*, University of California, Santa Barbara

We present a newly designed electrochemical Surface Forces Apparatus (EC-SFA) that allow control of surface potential and interfacial electrochemical reactions with simultaneous measurements distances between apposing surfaces (with 0.1 nm resolution), normal interaction forces (with nN resolution), and friction forces (with μN resolution). We will describe three applications of the EC-SFA:

(1) Oxide growth of a gold surface. Applying a high positive electrical potential on a metal surface will lead to an oxide growth. Using the EC-SFA we compared the measured thickness of the anodic gold oxide layer and the charge consumed for generating this layer which allowed the identification of its chemical structure as a hydrated $Au(OH)_3$ phase formed at the gold surface at high positive potentials.

(2) The evolution of the friction forces at a metal-ceramic contact as a function of the applied electrochemical potential.

(3) The phenomenon of "pressure solution". We have found an intimate relationship between dissolution rate and the surface potential difference across interfaces of dissimilar materials that are immersed in brine solution. For example, using the EC-SFA we have visualized and measured the dissolution of silica glass surfaces close to a gold electrode surface, which is on the order of 0.1 nm/hr. This is similar to geological samples of sandstones.

References:

Valtiner M, Banquy X, Kristiansen K, Greene GW, and Israelachvili JN, *Langmuir*, **28** (2012) 13080-13093.

Kristiansen K, Valtiner M, Greene GW, Boles JR, and Israelachvili JN, *Geochimica et Cosmochimica Acta*, **75** (2011) 6882-6892.

Valtiner M, Kristiansen K, Greene GW, and Israelachvili JN, *Advanced Materials*, **23** (2011) 2294-2299.

9:40am **IS+AS+SP-FrM5 Emerging Mesoscale Phenomena in Energy Conversion/Storage Characterized by *In Situ* Soft X-ray Spectroscopy**, ***J.-H. Guo***, Lawrence Berkeley National Laboratory **INVITED**

Advanced technology arises from the understanding in basic science, and both rest in large on in-situ/operando characterization tools for observing related physical and chemical processes directly at the places where and while reactions occur. In energy science, experimental insight into physical and chemical processes has been largely limited to information obtain with in a framework of thermodynamic and kinetic concepts or atomic and nanoscale. In many important energy systems such as energy conversion, energy storage and catalysis, advanced materials and fundamental phenomena play crucial roles in device performance and functionality due to the complexity of material architecture, chemistry and interactions among constituents within. To understand and ultimately control the interfaces in energy conversion and energy storage application calls for in-situ/operando characterization tools. Soft x-ray spectroscopy may offer some unique features. This presentation reports the development of in-situ reaction cells for soft x-ray spectroscopic towards the studies of photosynthesis and catalytic reactions in recent years. The challenge has been that soft x-rays cannot easily peek into a high-pressure catalytic cell or a liquid photoelectrochemical cell (PEC). The unique design of the in-situ cell has overcome the burden. Some of the instrumentation design and fabrication principle are to be presented, and a number of experimental studies of nanocatalysts are given as the examples, also the recent experiment performed for studying the hole generation in a specifically designed photoelectrochemical cell under operando conditions.

10:20am **IS+AS+SP-FrM7 Changes to the Microstructure of Fibrous Collagen Hydrogels formed under Different Physicochemical Parameters and Upon Cross-Linking with Non-Toxic Reagents are Detected with *In Situ* Multiphoton Microscopy Imaging**, *Y.J. Hwang, X. Lang,* ***J.G. Lyubovitsky***, University of California, Riverside

This presentation will highlight the knowledge developed by our laboratory regarding the microstructure of 3D collagen hydrogels detected in situ with multi-photon imaging while employing second harmonic generation (SHG) and two-photon fluorescence (TPF) contrasts. The materials were prepared under different physicochemical parameters and independently stabilized with non toxic cross-linkers. The effects of collagen solid content, incubation temperature and ionic strength as well as cross-linking with genipin and carbodiimide (EDC) on 3D collagen hydrogel microstructure will be addressed. Second Harmonic generation (SHG) contrast was employed to follow modifications and/or evolutions of the hydrogels' microstructure in real time and two-photon fluorescence (TPF) was beneficial in monitoring the extent of the chemical reaction between collagen and genipin as well as spatial locations of the newly induced fluorescent fibers. The induced microstructures differ dramatically upon changing collagen solid content, incubation temperature or ionic strength. For example, short lag time, fast assembly rates and short, tightly connected fibers were detected upon assembly from 30 mM phosphate buffer. In 0.9 M NaCl adjusted 30 mM phosphate buffer only unconnected one micron fiber nuclei with low second harmonic generation contrast formed. Fiber width and length was somewhat similar upon assembly of collagen fibers from 30 mM phosphate buffer adjusted with 0.3 M or 0.6 M NaCl while pore structure depended on the polymerization temperature. Non-zero-length cross-linker genipin induced formation of long aggregated

fluorescent strands throughout hydrogels. The SHG imaging suggested that modification with genipin partially disaggregated initial collagen microstructure within hydrogels at the expense of forming these new fluorescent fibers. On the other hand, zero-length cross-linker EDC, even with an addition of N-Hydroxysuccinimide (NHS), does not affect micro-structures. Imaging of the interactions of these important materials with embryonic stem cells induced to differentiate into a neural lineage and implication for tissue engineering will be discussed as well.

10:40am **IS+AS+SP-FrM8 *In Situ* Atomic Scale Observation of Catalyst Surface and Carbon Nanotube Cap Interplay during the Lift-Off**, *M. Picher, PA. Lin,* University of Maryland, College park, *J. Winterstein,* FEI Co, ***R. Sharma***, National Institute of Standards and Technology

Catalytic chemical vapor deposition (C-CVD), using a transition metal catalyst (Ni, Fe, Co, etc.) on an SiO_2, Al_2O_3, or MgO support and a carbon-containing precursor (C_2H_2, C_2H_4, CH_4, CO, etc.), is commonly employed for large-scale synthesis of carbon nanotubes (CNTs). However, synthesis of CNTs with the desired structure and morphology for a specific application has still not been demonstrated. Understanding the atomic-scale interplay between catalyst structure and CNT nucleation will aid us in determining the reaction conditions suitable for selective synthesis, especially for single walled CNTs (SWCNTs). During the last decade, the environmental scanning transmission electron microscope (ESTEM) has been successfully employed to reveal the structural, chemical and morphological changes occurring in catalyst nanoparticles during CNT growth. However, the mechanisms of CNT cap formation are yet to be revealed under normal growth conditions: the SWCNT nucleation and growth process is too fast to be captured at currently available video frame rates (30 s^{-1}). We have successfully addressed this problem by slowing the kinetics of the process using a Co-Mo/MgO catalyst system and low pressures of acetylene (C_2H_2) and ethanol (C_2H_5OH) as carbon precursors. Our direct observations show that the CNT cap preferentially nucleates on certain surfaces and first finds two surfaces as suitable anchor points before lift-off. The detailed interplay of catalyst surface structure, cap formation, incubation period, and lift-off will be presented using atomic-resolution videos recorded under these novel CVD conditions. Our observations provide direct insight into the mechanisms of SWCNT growth and open up possibilities for diameter and chirality control.

11:00am **IS+AS+SP-FrM9 *Operando* FTIR-MS Studies of Methanol on WO3/SBA-15: How Stable Are Methanol Species on Oxide?**, ***Y. Yang***, Pacific Northwest National Laboratory, *C. Mims,* University of Toronto, Canada, *C. Peden*, Pacific Northwest National Laboratory, *J. Kwak*, Ulsan National Institute of Science and Technology, Korea

Methanol adsorption and desorption are important on many oxide surfaces, for instance, as probe molecules of surface active sites. In this study, atomic layer deposited (ALD) tungsten oxide on silica was used as oxide sample and dimethyl ethylene (DME) synthesis was observed by operando FTIR-mass spectroscopy (IR-MS). Methanol adlayer, which contains both methanol and methoxy, was formed by exposing the sample with methanol at low partial pressure (~1 torr) with carrier inert gas at ~ 1 bar. The stability of the adlayer molecules was observed under two conditions: a) exposed to pure argon purging at different temperatures up to 300 C overnight; b) with constant methanol partial pressure (1 torr) in ambient flow while DME synthesis processed. The kinetics study here requires isotopic deuterated methanol exchange(CD_3OH/CH_3OH). Operando IR results shows under condition a), the majority of the adlayer, both methanol ad methoxy species, remained on the surface overnight after the highest temperature treatment. Methanol stability is even stronger than methoxy. Temperature dependent IR results show an isosbestic point between the surface water and Methanol species which is direct evidence of water replacement by methanol adsorption. These results further confirms other earlier studies reported. However, under condition b), both replacements transient of surface methanol and methoxy species by deuterated flow are by far much faster. As expected, only CD3/CH3 group exchange was observed upon isotope switch in IR and MS results. Measured replacement time constant for Methoxy was ~1000 s and that for methanol was ~2000 s. These surface species transients are compared with simultaneous MS data of gas products with the similar scale of the surface species. These preliminary results indicate that the methanol and methoxy are by far more active on a crowdie surface with gas phase methanol exposing comparing a surface with slightly lower coverage and no gas phase exposure. This is a good example of reactivity strong dependence on the surface coverage.

11:20am **IS+AS+SP-FrM10 Coupling Environmental High Resolution Transmission Electronic Microscopy and Raman Spectroscopy: Toward a More Comprehensive *In Situ* Characterization**, ***M. Picher***, *R. Blankensihp, S. Mazzuco, R. Sharma*, National Institute of Standards and Technology

In situ imaging, using an environmental scanning transmission electron microscope (ESTEM), has been successfully used to reveal and better understand the crucial chemical and physical processes occurring at the nanoscale, e.g. oxidation/reduction, coalescence, Ostwald ripening, surface reconstruction, substrate/catalyst interaction… However, the relevance of such ETEM studies can be diminished if the following two questions cannot be satisfactorily answered: i) Do high energy electrons affect the reaction mechanism? In other words: is the probed area representative of what is happening on the whole sample? ii) What is the sample temperature in the gaseous environment? Here, we present unique instrumentation that helps to solve these two issues by collecting Raman data during ETEM observation. We can now combine and compare the structural information and kinetics obtained from large (micrometer-scale) areas by the Raman spectrometer with the local information collected by the ETEM at the nanoscale. This system also enables us to simultaneously monitor the actual temperature of the probed material by analyzing shifts in Raman peak frequency. Moreover, this versatile optical setup can be used i) to investigate light/matter interactions (the current 532 nm laser can be easily replaced by any IR/Vis/UV wavelength) ii) as a heating source: the sample can be heated up to 1000°C at 15 mW with a 532 nm laser, iii) for general spectroscopy (absorption, photoluminescence, cathodoluminescence…).

This combined approach is made possible by the insertion of a parabolic mirror in between the sample holder and the lower pole piece of the microscope (Fig1. in Supp Info). It focuses a laser on the sample and collects the scattered Raman photons. A set of optics then carries the Raman signal to the spectrometer.

11:40am **IS+AS+SP-FrM11 New Tools for *In Situ* Chemical and Structural Analysis: Raman and Photoluminescence Go Inside the Vacuum Chamber**, ***A.J. King***, Renishaw Inc.

Micro-Raman systems have become very popular tools for analysing novel materials in a wide variety of application areas. Their ease of use has driven them to be employed routinely with carbon materials (graphene, carbon nanotubes, diamond, diamond-like-carbon (DLC)); semiconductors (silicon, germanium, III-V and II-VI materials); photovoltaics (silicon, CIGS, CdTe, CZTS); Chalcogenides (MoS_2, Bi_2Te_3, Bi_2Se_3); as well as oxides, nitrides and carbides. This technology enables researches to probe the molecular structure for phase identification, stress and crystal quality. It can also be used for reaction and catalysis monitoring.

New demands are now being made that require the use of in-situ techniques with very high sensitivity. The ability to conduct measurements inside the vacuum chamber has been enabled with highly efficient optical probes and spectrometer technology to give the required performance in these demanding applications. This talk will cover the basic concepts of Raman spectroscopy, the instrumentation required for these measurements, and highlight some of the applications where in-situ Raman and photoluminescence can increase the understanding of vacuum processes and how they can be optimised to improve quality and yield.

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Baran, N.: BI+AS+IS+NL-MoM3, 2
Barlow, D.E.: BI+AI+BA+IS-MoA3, 4
Barrett, D.A.: AS+BI+IS-WeM5, 7
Bartynski, R.A.: IS+EN+SP+SS-ThA9, 11
Bauer, S.: BI+AI+BA+IS-MoA2, **4**
Benter, Th.: AS+BI+IS-WeM9, **8**
Bernstein, H.C.: AS+BI+IS-WeM12, 8
Bhardwaj, C.: AS+BI+IS-WeM12, 8
Biffinger, J.C.: BI+AI+BA+IS-MoA3, 4
Blankensihp, R.: IS+AS+SP-FrM10, 14
Bluhm, H.: IA+AI+BI+IS+NL+SS-MoA10, 6
Bonn, M.: BA+AI+AS+BI+IS+NL-MoM10, 1; BA+AI+AS+BI+IS+NL-MoM5, 1; IA+AI+BI+IS+NL+SS-MoA3, **5**
Bonnell, D.A.: IS+EN+SP+SS-ThA1, 10
Bowfield, A.: AS+BI+IS-WeM5, 7
Bozzini, B.: IS+AS+SS-ThM5, 9
Bradley, J.W.: AS+BI+IS-WeM5, **7**
Brewer, T.: AS+BI+IS-WeM6, **7**
Buck, A.R.: IS+AS+SP-FrM3, **13**
Buttery, L.: BI+AS+IS+NL-MoM2, 2

— C —

Cai, X.: BA+AI+AS+BI+IS+NL-MoM8, 1
Callow, J.A.: BI+AI+BA+IS-MoA2, 4
Callow, M.E.: BI+AI+BA+IS-MoA2, 4
Carlson, R.P.: AS+BI+IS-WeM12, 8
Chang, C.: BI+AS+IS+NL-MoM8, 3
Chang, R.: IS+AS+SS-ThM9, 9
Chang, W.: IS+EN+SP+SS-ThA3, 10
Chen, Z.: IS-ThP2, 12
Christophis, C.: BI+AS+IS+NL-MoM3, 2
Chung, K.-Y.: IS+EN+SP+SS-ThA3, 10
Ciston, J.: IS+AS+SP-FrM1, 13
Corkery, R.: IA+AI+BI+IS+NL+SS-MoA7, 5
Cosandey, F.: IS+EN+SP+SS-ThA9, 11
Crookes-Goodson, W.J.: BI+AI+BA+IS-MoA3, **4**
Crumlin, E.J.: IS+AS+SS-ThM9, 9
Cui, Y.: AS+BI+IS-WeM12, 8

— D —

Dames, C.: IS-ThP2, 12
Davies, M.C.: BI+AS+IS+NL-MoM10, 3; BI+AS+IS+NL-MoM8, 3
Denning, C.: BI+AS+IS+NL-MoM10, 3
Donaldson, S.H.: IS+EN+SP+SS-ThA6, 10
Doughty, B.: BA+AI+AS+BI+IS+NL-MoM1, 1
Drake, C.N.: BI+AI+BA+IS-MoA3, 4
Dufresne, C.: BI+AS+IS+NL-MoM4, **2**
Dunn, M.: BI+AI+BA+IS-MoA11, 5

— E —

Eisenthal, K.B.: BA+AI+AS+BI+IS+NL-MoM1, **1**
Epa, V.C.: BI+AS+IS+NL-MoM8, **3**

— F —

Faubel, M.: IA+AI+BI+IS+NL+SS-MoA10, 6
Fernández, F.: AS+BI+IS-WeM4, 7
Finlay, J.: BI+AI+BA+IS-MoA2, 4
Forbes, T.: AS+BI+IS-WeM6, 7
Friebel, D.: IS+AS+SS-ThM3, 9
Fröhlich, J.: BA+AI+AS+BI+IS+NL-MoM10, 1

— G —

Gann, R.D.: AS+BI+IS-WeM4, 7
Gebbie, M.A.: IS+EN+SP+SS-ThA6, 10
Geiger, F.: BA+AI+AS+BI+IS+NL-MoM3, **1**
Giannuzzi, L.A.: IS+EN+SP+SS-ThA2, **10**
Gibbs-Davis, J.M.: IA+AI+BI+IS+NL+SS-MoA6, **5**
Gillen, G.: AS+BI+IS-WeM6, 7
Gilmore, I.S.: AS+BI+IS-WeM5, 7
Gorniak, T.: IS+AS+SP-FrM3, 13
Greene, G.W.: IS+AS+SP-FrM4, 13
Gregoratti, L.: IS+AS+SS-ThM5, 9
Guenther, S.: IS+AS+SS-ThM5, 9
Guo, J.-H.: IS+AS+SP-FrM5, **13**
Gupta, S.: BI+AS+IS+NL-MoM11, 3

— H —

Ha, J.: IS-ThP1, 12
Hanke, M.: BI+AS+IS+NL-MoM3, 2
Hanley, L.: AS+BI+IS-WeM12, **8**
Haramus, V.M.: IS+AS+SP-FrM3, 13
Harmer, M.P.: IS+EN+SP+SS-ThA2, 10
Hemminger, J.C.: IA+AI+BI+IS+NL+SS-MoA10, 6
Hilpert, K.: IS+AS+SP-FrM3, 13
Hlaing, M.M.: BI+AI+BA+IS-MoA11, **5**
Ho, A.D.: BI+AS+IS+NL-MoM3, 2
Hook, A.L.: BI+AS+IS+NL-MoM8, 3
Hu, E.: IS+EN+SP+SS-ThA3, 10
Hussain, Z.: IS+AS+SS-ThM9, 9
Hwang, S.: IS+EN+SP+SS-ThA3, 10
Hwang, Y.J.: IS+AS+SP-FrM7, 13

— I —

Israelachvili, J.N.: IS+AS+SP-FrM4, 13; IS+EN+SP+SS-ThA6, 10

— J —

Jang, W.: IS-ThP2, 12
Javed, M.A.: BI+AI+BA+IS-MoA1, 4
Jing, L.: IS-ThP2, 12

— K —

Kaya, S.: IS+AS+SS-ThM3, 9
Kazer, S.M.: BA+AI+AS+BI+IS+NL-MoM1, 1
Kim, K.-B.: IS+EN+SP+SS-ThA3, 10
King, A.J.: IS+AS+SP-FrM11, **14**
Kingshott, P.: BI+AS+IS+NL-MoM1, 2
Kiskinova, M.: IS+AS+SS-ThM5, 9
Kolmakov, A.: IS+AS+SS-ThM5, **9**
Kristiansen, K.: IS+AS+SP-FrM4, **13**; IS+EN+SP+SS-ThA6, 10
Kuk, Y.: IS-ThP1, 12
Kungas, R.: IS+EN+SP+SS-ThA1, 10
Kwak, J.: IS+AS+SP-FrM9, 14
Kwok, S.J.J.: BA+AI+AS+BI+IS+NL-MoM1, 1

— L —

Lang, X.: BA+AI+AS+BI+IS+NL-MoM6, **1**; IS+AS+SP-FrM7, 13
Langer, R.: BI+AS+IS+NL-MoM10, 3; BI+AS+IS+NL-MoM8, 3
Lau, C.N.: IS-ThP2, 12
Li, L.: IS+AS+SP-FrM1, 13
Lin, PA.: IS+AS+SP-FrM8, 14
Liu, Z.: IS+AS+SS-ThM9, **9**
López, G.P.: BI+AI+BA+IS-MoA6, **4**
Luo, L.: IS+AS+SP-FrM1, 13
Lyubovitsky, J.G.: BA+AI+AS+BI+IS+NL-MoM6, 1; IS+AS+SP-FrM7, **13**

— M —

Mantovani, G.: BI+AS+IS+NL-MoM2, 2
Mao, B.: IS+AS+SS-ThM9, 9
Margarella, A.M.: IA+AI+BI+IS+NL+SS-MoA10, 6
Mazzuco, S.: IS+AS+SP-FrM10, 14
McArthur, S.M.: BI+AI+BA+IS-MoA1, 4; BI+AI+BA+IS-MoA11, 5
McKay, K.: AS+BI+IS-WeM5, 7
Miao, F.: IS-ThP2, 12
Miller, D.J.: IS+AS+SS-ThM3, 9
Mims, C.: IS+AS+SP-FrM9, 14
Mudiyenselage, K.: IS+AS+SS-ThM6, 9
Muramoto, S.: AS+BI+IS-WeM6, 7
Myhro, K.: IS-ThP2, **12**

— N —

Nadeau, L.J.: BI+AI+BA+IS-MoA3, 4
Nam, K.-W.: IS+EN+SP+SS-ThA3, 10
N'Diaye, A.: IS+EN+SP+SS-ThA7, **10**
Netz, R.: IA+AI+BI+IS+NL+SS-MoA8, **5**
Nilsson, A.: IS+AS+SS-ThM3, 9
Nonnenmann, S.S.: IS+EN+SP+SS-ThA1, **10**

— O —

Ogasawara, H.: IS+AS+SS-ThM3, **9**
Orlando, T.M.: AS+BI+IS-WeM4, 7

— P —

Pandey, R.: BA+AI+AS+BI+IS+NL-MoM10, 1
Patel, A.K.: BI+AS+IS+NL-MoM10, **3**
Peden, C.: IS+AS+SP-FrM9, 14
Perrine, K.A.: IA+AI+BI+IS+NL+SS-MoA10, **6**
Piatkowski, L.: IA+AI+BI+IS+NL+SS-MoA3, 5
Picher, M.: IS+AS+SP-FrM10, **14**; IS+AS+SP-FrM8, 14
Pirlo, R.K.: BI+AI+BA+IS-MoA3, 4
Pöschl, U.: BA+AI+AS+BI+IS+NL-MoM10, 1

— R —

Rangan, S.: IS+EN+SP+SS-ThA9, 11
Rao, Y.: BA+AI+AS+BI+IS+NL-MoM1, 1
Reviakine, I.: BI+AS+IS+NL-MoM11, **3**
Rodriguez, J.: IS+AS+SS-ThM6, 9
Rosenhahn, A.: BI+AI+BA+IS-MoA2, 4; BI+AS+IS+NL-MoM3, **2**; IS+AS+SP-FrM3, 13
Ross, P.: IS+AS+SS-ThM9, 9
Russell, Jr., J.N.: BI+AI+BA+IS-MoA3, 4

— S —

Salter, T.L.: AS+BI+IS-WeM5, 7
Sanchez Casalongue, H.: IS+AS+SS-ThM3, 9
Senanayake, S.: IS+AS+SS-ThM6, 9
Senkbeil, T.M.: IS+AS+SP-FrM3, 13
Sgura, I.: IS+AS+SS-ThM5, 9
Sharma, R.: IS+AS+SP-FrM10, 14; IS+AS+SP-FrM8, **14**
Shen, Y.R.: IA+AI+BI+IS+NL+SS-MoA1, **5**
Simoes, F.A.: BI+AS+IS+NL-MoM2, **2**
Sina, M.: IS+EN+SP+SS-ThA9, 11
Sisco, E.: AS+BI+IS-WeM6, 7
Somorjai, G.A.: BA+AI+AS+BI+IS+NL-MoM8, **1**
Stacchiola, D.: IS+AS+SS-ThM6, 9
Stach, E.: IS+AS+SP-FrM1, 13; IS+EN+SP+SS-ThA3, **10**
Stamps, B.W.: BI+AI+BA+IS-MoA3, 4
Stevenson, B.S.: BI+AI+BA+IS-MoA3, 4
Stoddart, P.R.: BI+AI+BA+IS-MoA1, 4; BI+AI+BA+IS-MoA11, 5
Stolte, W.: IS+AS+SS-ThM9, 9
Stroscio, J.A.: IS-ThP1, 12
Symonds, J.M.: AS+BI+IS-WeM4, **7**
Szakal, C.: AS+BI+IS-WeM6, 7

— T —

Takats, Z.: AS+BI+IS-WeM2, 7
Taubert, I.: BI+AS+IS+NL-MoM3, 2

Thissen, A.: IS+AS+SS-ThM11, 9
Thorpe, R.: IS+EN+SP+SS-ThA9, **11**
Turro, N.T.: BA+AI+AS+BI+IS+NL-MoM1, 1
Tyrode, E.C.: IA+AI+BI+IS+NL+SS-MoA7, **5**

— V —

Valtiner, M.: IA+AI+BI+IS+NL+SS-MoA11, 6; IS+AS+SP-FrM4, 13; IS+EN+SP+SS-ThA6, **10**
Van Spyk, M.H.C.: IA+AI+BI+IS+NL+SS-MoA10, 6
Vohs, J.M.: IS+EN+SP+SS-ThA1, 10

— W —

Wade, S.A.: BI+AI+BA+IS-MoA1, **4**
Walsh, J.W.: AS+BI+IS-WeM5, 7
Wang, P.Y.: BI+AS+IS+NL-MoM1, **2**
Weidner, T.: BA+AI+AS+BI+IS+NL-MoM10, **1**; BA+AI+AS+BI+IS+NL-MoM5, 1
Weitz, D.A.: BI+AS+IS+NL-MoM5, **2**
Whitchurch, C.B.: BI+AI+BA+IS-MoA9, **4**
Williams, P.: BI+AS+IS+NL-MoM8, 3
Winkler, D.A.: BI+AS+IS+NL-MoM8, 3
Winter, B.: IA+AI+BI+IS+NL+SS-MoA10, 6
Winterstein, J.: IS+AS+SP-FrM8, 14
Wuchter, P.: BI+AS+IS+NL-MoM3, 2

— Y —

Yang, J.: BI+AS+IS+NL-MoM8, 3; IS+AS+SP-FrM1, 13
Yang, X.-Q.: IS+EN+SP+SS-ThA3, 10
Yang, Y.: IS+AS+SP-FrM9, **14**
Yousaf, M.N.: BI+AS+IS+NL-MoM9, **3**
Yu, X.: IS+EN+SP+SS-ThA3, 10
Yu, Z.: IS+EN+SP+SS-ThA2, 10
Yulaev, A.: IS+AS+SS-ThM5, 9

— Z —

Zhang, D.: IS-ThP1, **12**
Zhang, H.: IS-ThP2, 12
Zhang, Z.: IA+AI+BI+IS+NL+SS-MoA3, 5
Zhao, Z.: IS-ThP2, 12
Zhou, G.: IS+AS+SP-FrM1, **13**
Zingarelli, S.: BI+AI+BA+IS-MoA3, 4
Zuilhof, H.: AS+BI+IS-WeM11, **8**