Applied Surface Science Division
Room: 13 - Session AS+BI+MI-MoM

Practical Surface Analysis: Getting the Most Out of Your Analysis using Complementary Techniques

Moderators: Mark Engelhard, EMSL, Pacific Northwest National Laboratory, Michaeleen Pacholski, The Dow Chemical Company

8:20am **AS+BI+MI-MoM1 Obtaining Complete Characterisation of Core-shell Nanoparticle Structure and Composition *via* the use of Complementary Techniques**, ***David Cant***, *C. Minelli*, National Physical Laboratory, UK, *K. Sparnacci*, Università degli Studi del Piemonte Orientale, Italy, *W. Unger*, Bundesanstalt für Materialforschung und -prüfung (BAM), Germany, *A. Hermanns*, Bundesanstalt für Materialforschung und -prüfung (BAM), *W.S.M. Werner*, *H. Kalbe*, TU Wien, Austria, *R. Garcia-Diez*, *C. Gollwitzer*, *M. Krumrey*, Physikalisch-Technische Bundesanstalt, Germany, *A.G. Shard*, National Physical Laboratory, UK

Core-shell nanoparticles are commonly used in a variety of applications, including medicine, catalysis, optoelectronics, and others. Accurate identification of core-shell nanoparticle structure and morphology is an important challenge to overcome before such nanoparticles can be effectively utilised. This is not necessarily a trivial obstacle, as no single characterisation technique can accurately identify every possible peculiarity of structure or composition that may exist.

For example, characterisation methods that observe bulk properties, such as differential centrifugal sedimentation (DCS), thermogravimetric analysis (TGA), or techniques based on observation of Brownian motion such as dynamic light scattering (DLS) may be unable to distinguish particles with a standard core-shell morphology from those with the same core and shell masses, but with an uneven shell, or where the core and shell have merged to form a homogenous particle.

Similarly, surface sensitive techniques which analyse a population of particles, such as x-ray photoelectron spectroscopy (XPS) or small angle x-ray scattering (SAXS), may be able to provide information on shell thicknesses in standard core-shell particles and distinguish them from particles with an uneven shell or a homogenous particle, but may have difficulty distinguishing homogeneity from an uneven shell or off-centred core.

Techniques that allow observation of individual particles, such as electron microscopy, may be able to clearly show the structure, but are rarely able to provide any in-depth quantification of the composition. As such it is necessary to use a careful selection of appropriate techniques to fully characterise any given nanoparticle system. To illustrate these issues, two polymeric core-shell nanoparticle systems have been characterised, both consisting of a Hyflon® core coated in varying thicknesses of either PMMA or polystyrene. These systems are nominally very similar, but differ notably in structure. The results from several different characterisation techniques (XPS, SAXS, DCS, TGA, DLS, and SEM.) were compared in order to demonstrate the difference in information provided by each and obtain a full understanding of both types of nanoparticle.

9:00am **AS+BI+MI-MoM3 Correlative Microscopy based on Secondary Ion Mass Spectrometry for High-Resolution High-Sensitivity Nano-Analytics**, ***Tom Wirtz***, *J.-N. Audinot*, *D.M.F. Dowsett*, *S. Eswara*, Luxembourg Institute of Science and Technology (LIST), Luxembourg **INVITED**

Development of innovative characterization tools is of paramount importance to advance the frontiers of science and technology in nearly all areas of research. In order to overcome the limitations of individual techniques, correlative microscopy has been recognized as a powerful approach to obtain complementary information about the investigated materials. High-resolution imaging techniques such as Transmission Electron Microscopy (TEM) or Helium Ion Microscopy (HIM) offer excellent spatial resolution. However, the analytical techniques associated with TEM such as Energy Dispersive X-ray spectroscopy (EDX) or Electron Energy-Loss Spectroscopy (EELS) are inadequate for the analysis of (i) isotopes, (ii) trace concentrations (< 0.1 at. % or < 1000 ppm) and (iii) light elements (H, Li, B). Likewise, for the case of HIM, until recently there was no direct possibility to perform elemental mapping because sub-30 keV He^+ or Ne^+ ion irradiation do not excite X-ray emission. Secondary Ion Mass Spectrometry (SIMS), on the other hand, is an extremely powerful technique for analysing surfaces owing in particular to its excellent sensitivity (detection limits down to the ppb are possible, so that SIMS can be used to detect both major and trace elements), high dynamic range (a same signal can be followed over several orders of magnitude), high mass resolution and ability to differentiate between isotopes.

In order to combine the high spatial resolution of TEM and HIM with the analytical sensitivity of SIMS, we developed integrated TEM-SIMS [1,2] and HIM-SIMS [2-4] instruments. The main advantage of this in-situ correlative approach is its capability to analyse the same area of interest of any sample without need of transferring the sample from one instrument to another one, which would result in a number of artefacts ranging from surface contamination to issues with localizing exactly the same ROIs. Moreover, the integrated approach allows fast and multiple interlacing between the different imaging and analysis modes.

In this talk, we will first introduce the TEM-SIMS and HIM-SIMS instruments and discuss their performance characteristics. We will then present a number of examples taken from various fields of materials science and life science to show the powerful correlative microscopy possibilities enabled by these new in-situ methods.

[1] L. Yedra et al., Sci. Rep. 6, 28705, 2016

[2] T. Wirtz et al., Nanotechnology 26 (2015) 434001

[3] T. Wirtz et al., Helium Ion Microscopy, ed. G. Hlawacek, A. Gölzhäuser, Springer, 2017

[4] P. Gratia et al, J. Am. Chem. Soc. 138 (49) 15821–15824, 2016

9:40am **AS+BI+MI-MoM5 New Insights on Layered Polymer Systems, Polymer Networks and Polymerization in Defined Geometries by Combining Surface Analysis with Depth Profiling using ToF-SIMS and XPS as Analytical Tools**, ***Sven Steinmüller***, Institute for Applied Materials, Karlsruhe Institute of Technology, Germany, *A. Llevot*, Institute of Organic Chemistry, Karlsruhe Institute of Technology, Germany, *D. Moock*, Institute for Applied Materials, Karlsruhe Institute of Technology, Germany, *B. Bitterer*, Institute of Organic Chemistry, Karlsruhe Institute of Technology, Germany, *F. Cavalli*, Institute for Biological Interfaces, Karlsruhe Institute of Technology, Germany, *S. Hurrle*, Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology, Germany, *M. Bruns*, Institute for Applied Materials, Karlsruhe Institute of Technology, Germany

Surface analytical characterization of polymers is still a tough topic if precise information are favored. Especially for characterization of stepwise layered systems and for studying reaction rates and composition of network formation or to confirm polymerization within defined geometries a lot of techniques are not sensitive enough to fulfill the desired degree of precision and resolution. Within the recently installed Cooperate Research Center “SFB 1176” at KIT (Molecular Structuring of Soft Matter), a high degree of precision is necessary to qualitatively and quantitatively confirm the defined structures achieved during the polymer syntheses. Here a new surface analysis approach combining X-ray Photoelectron Spectroscopy (XPS) and Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) including Ar cluster ion sputter depth profiling for three dimensional systems is utilized to prove every reaction step of polymer syntheses and to evidence three-dimensional structures at high lateral resolution. By using different marker molecules as well as specific molecule ion fragments, the combination of these two methods enables to obtain the precise characterization and evaluation of the different polymeric systems.

We present our results on the implementation of new methods for precise surface analysis of polymers. Starting with the investigation of molecular layered systems prepared via electrografting of surfaces followed by successive thiol-yne or thiol-ene reactions, we show controlled functionalization on silicon as well as on highly oriented pyrrolytic graphit substrates. Finally the developed strategy will be transferred to real graphite electrodes. This is an important step to design and tailor the properties of artificial solid electrolyte interfaces (SEI) for lithium ion batteries.

From the characterization of these two dimensional systems (according to the surface analytical tasks), we follow up with polymer systems with three dimensional analysis questions. We present analytical results of network formation using the *Para*-fluoro-thiol reaction and strategies for the confirmation of polymer position after polymerization within defined geometries. Surface analytical recipes to confirm synthesis routes were established. The analytical results of the three dimensional chemical picture are taken to further optimize the synthesis routes and network properties.

We kindly acknowledge the SFB 1176, funded by the German Research Council (DFG), in the context of projects B2, C1, C4 and Z1 for funding. The K-Alpha+ instrument was financially supported by the Federal Ministry of Economics and Technology on the basis of a decision by the German Bundestag.

10:00am **AS+BI+MI-MoM6 Combining Monoatomic- and Cluster Ion Sputtering in ToF-SIMS and XPS Depth Profiling of Organic-inorganic Multilayer Structures**, ***Eric Langer***, *J.-P. Barnes, O.J. Renault, T. Maindron*, CEA-Leti, France, *L. Houssiau*, University of Namur, Belgium

Organic electronics have risen to great importance in the world of consumer electronics. Especially organic light emitting diode (OLED) displays have brought new possibilities to the market. However, organic materials are more susceptible to electrical dysfunctions than conventionally used inorganic materials. This leads to a shortened lifetime for those materials. Environmental impacts like humidity or ultraviolet irradiation can create chemical reactions that lead to dark spots and device failures. Additionally, the flow of current through the device can further promote device degradation and can even induce migration and diffusion of dopants and small molecules. Precise chemical depth profiling is therefore essential to identify sources of failure and improve the device lifetime of organic electronics. Surface analysis techniques such as time-of-flight secondary ion mass spectrometry (ToF-SIMS) and x-ray photoelectron spectroscopy (XPS) are efficient tools to characterize the chemical composition in depth. With the recent introduction of gas cluster ion beam (GCIB) sources, it is possible to sputter through organic materials without inducing a significant amount of damage to the sample [1]. Typically, argon clusters (1000 – 5000 atoms per cluster) with low energy per atom ratios (1 – 5 eV/atom) are used for gentle sputtering. However, these low energies are not sufficient to break the atomic bonds in inorganic materials. This poses a major problem in the characterization of hybrid inorganic-organic devices.

In this work, we present an approach to overcome the difficulties in depth profiling of inorganic-organic interfaces. Green OLED devices are characterized by ToF-SIMS depth profiling using GCIB as well as monoatomic sources for sputtering. This allows for precise tracking of characteristic chemical species in both the inorganic and the organic parts of the multilayer structures. Additionally, XPS depth profiling is used to measure the sputter induced damage during analysis [2]. We show, that by optimizing the sputter parameters, the sputter induced damage can be minimized and precise and reliable chemical information of hybrid inorganic-organic devices can be gained by combining ToF-SIMS and XPS analysis.

This work was carried out on the Platform for Nanocharacterization (PFNC) at the CEA Grenoble.

[1] Ninomiya, S ; Ichiki, K ; Yamada, H ; Nakata, Y ; Seki, T ; Aoki, T ; Matsuo, J Rapid Comm. Mass Spec. **23** 20 (2009) 3264.

[2] Miyayama, T ; Sanada, N ; Bryan, SR ; Hammond, JS ; Suzuki, M ; Surf. Interface Anal. **42** 9 (2010) 1453

10:40am **AS+BI+MI-MoM8 Ultra High Surface Sensitivity – Elemental Analysis of the Outer Layer**, ***Thomas Grehl***, *P. Brüner, H.H. Brongersma*, ION-TOF GmbH, Germany

In materials science and applications, the outer surface plays a vital role for a range of properties and in general for the interaction of a solid with its surroundings. The chemical properties of the surface govern macroscopic properties like wettability/contact angle, but also the chemical interactions as in catalysis, corrosion or thin film growth. The outer surface and its understanding is crucial for catalysis, fuel cells, thin film formation, nanoparticles and a wide range of other processes.

The analysis of the outer surface is frequently hampered by the fact that the origin of the signal is not completely limited to the first atomic layer, but bulk and surface signals are mixed. This issue is avoided in the case of Low Energy Ion Scattering (LEIS). The elemental composition of the outer atomic layer is determined quantitatively and separately from deeper layers. We will demonstrate a number of cases where this is essential to draw the relevant conclusions and reveal surface properties that would not be detected by other surface analytical techniques.

Nevertheless, the combination of complementary techniques is always required to address complex problems. We will demonstrate how the combination of LEIS with other established analytical techniques is beneficial for a comprehensive analysis.

One of these cases is the interaction of Ar cluster ions with a solid sample: it is well known that the sputtering yield of massive argon clusters is some orders of magnitude larger for organic than for inorganic materials. Therefore, Ar cluster beams have been discussed as a means of removing atmospheric adsorbents from surfaces prior to analysis. Using thin film samples, we have evaluated this approach applying LEIS in order to detect the removal of the organic material and the influence on the underlying inorganic surface. Despite the low sputtering yield for the inorganic material, a complete removal of the organic material will lead to a significant modification of the inorganic surface even when the actual erosion is limited.

Other examples from nanoparticles, catalysis and thin films will support the importance of outer layer surface analysis for materials research and other applications.

11:00am **AS+BI+MI-MoM9 Towards Predictive Understanding of Li-S Battery Materials through Multimodal Analysis**, ***Vijayakumar Murugesan***, *K. Han, M.I. Nandasiri, V. Shutthanandan, S. Thevuthasan, K.T. Mueller*, Pacific Northwest National Laboratory

Comprehensive understanding about the interfacial reactions between electrode and electrolyte is the major knowledge gap which inhibit the development of the lithium sulfur (Li-S) batteries. Despite numerous studies, the interfacial reaction mechanism such as SEI layer evolution and polysulfides dissolution process is still unclear. Hence, it is critical to develop a multi-modal approach that can provide unprecedented chemical imaging of complex interfaces in wide lateral (ranging from subatomic to micron) and temporal scales (few ns to seconds). Herein, we report an *in-situ* X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS) and nuclear magnetic resonance (NMR) combined with ab initio molecular dynamics (AIMD) computational modelling to gain fundamental understanding about the complex interfacial interactions in Li-S batteries. A multi-modal approach involving AIMD modelling and in situ XPS and NMR characterization uniquely reveals the chemical identity and distribution of active participants of interfacial reactions as well as the -battery capacity fading mechanism.

11:20am **AS+BI+MI-MoM10 Combined use of Back Side SIMS and FIB Sample Preparation**, ***Mikhail Klimov***, University of Central Florida

When profiling multilayered samples or even a homogeneous samples with rough surface SIMS depth resolution can suffer a rapid deterioration, particularly when polycrystalline metal layers are concerned. The back side SIMS was traditionally used to alleviate a loss of depth resolution during front side depth profiling. The traditional back side SIMS sample preparation involves painstaking polishing or/and ion milling, that requires considerable skills to produce a high quality finish surface that is parallel to front surface and terminated not too far from the interface of interest. Also, because the traditionally prepared sample is relatively large, the precise site specificity is, in general, unattainable.

I offer a relatively expedient FIB sample preparation (~2hrs.) for back side SIMS analysis at precise location and at exact distance from the front surface. The FIB sample extracted from the bulk has a typical lateral dimensions of 10 µ by 10 µ or less. In order to analyze such a small area, even smaller ion beam is required with diameter of 1µ or less to provide good depth resolution and high sensitivity. Also, it's very much desirable that the ion beam was Oxygen or Cesium to achieve a secondary ion yield enhancement, particularly important for small area analysis. In my case, micron and sub-micron beam of O_2^+ ions was produced by RF Plasma source by Oregon Physics that replaced, for the first time, Duoplasmatron on ADEPT1010 Dynamic SIMS System by Physical Electronics.

The FIB sample preparation procedure is discussed in detail and the first back side SIMS results compared to the front side depth profiles.

11:40am **AS+BI+MI-MoM11 Phase Quantification of Mixed TiO_2 Powders by X-ray Photoemission Valence Band Analysis and Raman Spectroscopy**, ***Paul Mack***, *T.S. Nunney*, Thermo Fisher Scientific, UK, *R.G. Palgrave*, University College London, United Kingdom of Great Britain and Northern Ireland

Titanium dioxide is one of the most studied materials in surface science. It has applications in heterogeneous catalysis, dye-sensitised solar cells, bone implants and self-cleaning windows. Many polymorphs of TiO_2 are known to exist but only two occur naturally in abundance: rutile and anatase. Rutile is the more thermodynamically stable form but anatase is more energetically favourable when forming nanoparticles at atmospheric temperature and pressure. The anatase polymorph has been recognised as more photoactive than rutile, although recent research indicates that the greatest photovoltaic efficiencies are achieved in devices that contain a mixture of anatase and rutile. The degree of mixing between two polymorphs influences other material properties, such as catalytic activity. This raises the question: how can one determine the polymorph ratio in a sample that contains a mixture of anatase and rutile?

Quantitative phase analysis of anatase-rutile mixtures by two experimental methods is presented in this work. Spectra of pure reference anatase and rutile were acquired X-ray Photoelectron Spectroscopy (XPS) and Raman spectroscopy. These spectral shapes were then used to fit similar data from mixed phase samples. XPS and Raman spectroscopy give information from different depth regions in a sample. The surface sensitive character of XPS yields a surface phase fraction of anatase and rutile. Mixed phase samples were prepared from high and low surface area anatase and rutile powders. In this work, the surface phase fraction of anatase was found to be linearly correlated with photocatalytic activity of the mixed phase samples, even for samples with very different anatase and rutile surface areas.

Biomaterial Interfaces Division
Room: 12 - Session BI-MoM

Engineering a Paradigm Shift in Control of Microbes and Fouling

Moderators: Joe Baio, Oregon State University, Daniel Barlow, US Naval Research Laboratory

8:20am **BI-MoM1 Characterization of Adult Barnacle Adhesion Upon Reattachment to Hydrophobic Surfaces**, ***Manuel Figueroa***, *G. Dickinson*, The College of New Jersey

Although a wide range of environmentally friendly surface coatings can reduce biofouling on marine structures, there is still not a fundamental understanding of barnacle adhesion upon reattachment. This study assessed the effect of hydrophobicity on adhesion in the barnacle *Amphibalanus amphitrite*, an abundant and widespread biofouler. Self-assembled monolayers were made on glass slides from alkyl silanes with methylated and fluorinated terminal groups to produce hydrophobic surfaces. Coated and uncoated glass slides underwent a 2-week barnacle reattachment assay. Barnacles were removed using a force gauge and critical shear stress was calculated for each substrate. Following reattachment assays, a Coomassie Blue G250 protein stain was used to quantify the amount of glue remaining on substrates by measuring pixel density with ImageJ software on glue scans.

Critical shear stress was found to be significantly higher for both hydrophobic surfaces as compared to the hydrophilic uncoated glass, and correspondingly the density of residual glue was higher on hydrophobic surfaces. Given that hydrophobic substrates can exclude water from the surface, they may provide a protected environment for glue release that is favorable for adhesive bond formation with the substrate as well as inter and intramolecular bonding within the glue layer. Critical shear stress showed a strong positive correlation with residual glue density, suggesting barnacle release occurs primarily via cohesive failure. Scanning electron microscope micrographs depicted a diverse mixture of features in the glue remnants depending on the coating and its location under the base plate. These features, which included a sponge-like matrix, globular structures, viscous fingering and nanoscale fibers contribute to adhesion strength. The design of marine coatings must continue to consider the nanoscale topography as an essential attribute to reducing biofouling as well as the ability of a coating to exclude water from the surface.

8:40am **BI-MoM2 Constructing and Deconstructing the Barnacle Adhesive Interface**, *C.R. So, K.P. Fears*, US Naval Research Laboratory, *H. Ryou*, ASEE Research Fellow at US Naval Research Laboratory, *D.E. Barlow, D.H. Leary, J.A. Wollmershauser, C.M. Spillmann*, ***Kathryn Wahl***, US Naval Research Laboratory

Barnacles are sessile marine arthropods that live and reproduce on nearly any available surface in the ocean. They adhere via a thin adhesive layer developed through a multistep secretory process synchronized with growth via molting. Unlike other arthropods, the combination of expansion, molting and protein secretion within the narrow adhesion interface leads to a nanofibrillar protein layer manipulated by shear stresses, protected by calcite, and containing a cocktail of chemically active molecules and proteins. Here we use *in vivo* imaging, mechanics, and spectroscopy of barnacle growth and development, coupled with mass spectrometry and proteomics to reveal much about the biophysics and biochemistry of barnacle adhesion. We will discuss the role of interfacial processes, self-assembly, amino acid composition, and chemical manipulation in the construction and function of the adhesive.

9:00am **BI-MoM3 Live Confocal Microscopy of *Balanus Amphitrite* Reveals Anti-Fouling Strategy of a Marine Fouler**, ***Kenan Fears***, US Naval Research Laboratory, *B. Orihuela, D. Rittschof*, Duke University Marine Laboratory, *K.J. Wahl*, US Naval Research Laboratory

The adhesion of hard foulers (e.g., barnacles and tubeworms) has plagued the maritime community for as long as mankind has been setting sail. Since the biological processes responsible for adhesion occur at buried interfaces, elucidating the mechanisms by which foulers adhere is challenging. Through the use of multiple fluorescent probes, peptides, and antibodies, we have been able to discern an unprecedented level of detail about biological processes that occur at the interface between acorn barnacles (Balanus Amphitrite) and the underlying substratum during the barnacle growth cycle. Barnacles secrete a lipidaceous substance around the outside of their shell, prior to expansion that dislodges microorganisms and biofilms to present a cleaned surface. During molting, epithelia cells build a new interfacial cuticular layer, which becomes autofluorescent as it is sclerotized, above the existing cuticle whose degradation coincides with the exuviation of the main body's cuticle. Rather than being directly secreted onto the substrate, nanostructured barnacle cement accumulates in the space in between the new and old cuticle. As the barnacle expands, the cuticular layers are stretched and pulled around the outside of the side plate. The strain causes the old cuticle to randomly tear, allowing the new cuticle to deposit cement into the interface as it is dragged across the substrate. Furthermore, antibody staining allowed us to spatially and temporally identify where different cement proteins are presenet. These results illustrate that the methodologies we have developed to break down and analyze barnacle cement collection are yielding a more accurate representation of the proteins at the buried interface, and providing insight on their roles which will lead to improved strategies to both combat and mimic barnacle adhesives.

9:20am **BI-MoM4 Considering the Consequences of a Paradigm Shift in Biofouling Management**, ***Daniel Rittschof***, *B. Orihuela*, Duke University, *K. Efimenko, J. Genzer*, NC State University

Present Fouling Management Strategies that use long-lived, broad-spectrum biocides are not sustainable because they alter ecosystem services and threaten food security. As globalization continues, human populations increase and wild fisheries collapse there will be increasing pressure and genuine need for less environmentally damaging approaches. A question that should be asked up front for any new fouling management technology is what are the environmental, food security and human health consequences if a technology gains market share. Information on impacts of industrial grade components, acute and chronic toxicity, breakdown and non-toxic biological effects such as teratogenicity, carcinogenicity and environmental steroid activity should be evaluated. This presentation looks at a few of the details of basic silicone coatings which have had their components purified and then tested for acute toxicity, impacts on a hydrolytic enzyme and teratogenicity. Some components like catalysts and small cyclics are extremely toxic. Other components impact enzyme activity, some inhibit activity other potentiate activity. Terratogenicity assays are so sensitive that even effects of medical grade silicones can be demonstrated. This information needs to be taken as preliminary factual information that can be used by engineers in developing risk benefit analysis.

9:40am **BI-MoM5 Microbiological Fouling on Aircraft: Understanding the Mechanisms of Polyurethane Topcoat Deterioration by Fungal Isolates**, ***Daniel Barlow***, *J.C. Biffinger*, US Naval Research Laboratory, *C.-S. Hung*, Air Force Research Laboratory, *L.J. Nadeau*, Air Force Institute of Technology, *A.L. Crouch, T. Zicht*, Air Force Research Laboratory, *J.N. Russell, Jr.*, US Naval Research Laboratory, *W.J. Crookes-Goodson*, Air Force Research Laboratory

Fungal and bacterial fouling on military aircraft is a problem that can lead to polyurethane top coat deterioration and pose health hazards to personnel; the phasing out of hexavalent chromium in coatings is expected to worsen fouling problems. Thus, better understanding of the relevant microbiological interactions with polyurethanes is required to identify new ways to inhibit fouling and associated affects. We have screened over 400 aircraft isolates for polyurethane degradation, with Cryptococcus strains among the most aggressive polyurethane degraders. These strains were further characterized for their capability to metabolize and grow on expected hydrolysis products from polyester components of the polymers, showing that fungal growth occurs to varying degrees on the metabolites. Gas chromatography also showed that microbes metabolize polymers and hydrolysis products to CO_2. Polymer metabolization to CO_2 results in bulk polymer loss and optical profilometry confirmed that fungal cells steadily "eat" trenches into solid polyurethane films over time. Initial polyurethane film degradation processes at the micro and nano scales were analyzed by confocal Raman and AFM-IR (combined AFM and infrared spectroscopy). These results showed varying, non-uniform degradation events among cells, indicating that variations in single cell physiology play roles in early stage degradation. The spectroscopic results are consistent with lipase activity as the primary driver of degradation.

10:00am **BI-MoM6 Dynamic Accumulation Assays under Laminar Flow Conditions to Probe Attachment of Marine Biofilm Formers**, ***Kim Alexander Nolte***, *J. Schwarze, A. Rosenhahn*, Ruhr-University Bochum, Germany

Novel materials with environmentally benign fouling-release properties have been developed during the last years to substitute toxic coatings. Assessment of fouling-release coating's efficiency is of key relevance for the down selection of chemistries. Several techniques are accessible that quantify, how easy fouling organisms can be removed, including calibrated, turbulent flow channels, push-off tests, water jets, and microfluidic devices [1, 2]. We developed a laboratory assay based on a parallel plate flow chamber that allows testing of coating candidates against algal cell adhesion with precisely controlled flow rates and cell concentrations. Using self-assembled monolayers as model surfaces and diatoms as model organisms we were able to show that the adhesion strength [1] correlates with the accumulation dynamics if an appropriate wall shear stress is applied. Similar to the critical wall shear stress for removal assays, a range of wall shear stresses was

identified within which the discrimination potential was maximized [3]. The setup has been parallelized to increase throughput and to become able to test a large number of coating chemistries per day. Due to the modular assembly of our setups, not only model surfaces and thin organic films, but also practical coatings can be tested.

[1] M. Alles, A. Rosenhahn, *Biofouling.* **2015,** 31, 469–480.

[2] MP. Schultz, *et al*., *Biofouling.* **2000,** 15, 243-251.

[3] K. Nolte, J. Schwarze, A. Rosenhahn *Biofouling.* **2017,** in press

10:40am **BI-MoM8 Coatings with Amphiphilic Surfaces Via Self-Stratification for Marine Fouling-Release Applications**, ***Dean Webster***, *T. Galhenage, S. Stafslien, L. Vanderwal*, North Dakota State University

Due to the complexity of adhesion mechanisms of marine life to surfaces, it is becoming apparent that combating biofouling will require coatings having complex surfaces. Specifically, coatings having mixed hydrophobic and hydrophilic surface domains are being shown to be able to mitigate the adhesion of a broader variety of marine organisms than can the silicone elastomer fouling-release coatings. Since it is also desirable to have a coating that can adhere well to a variety of substrates and stand up to occasional cleaning, a tough coating system is needed.

The incorporation of a low surface energy polymer such as a siloxane into a robust coating system such as a polyurethane results in stratification of the low surface energy component to the surface. By chemically binding hydrophilic groups to the siloxane, both functional groups stratify leading to a polyurethane coating having amphiphilic character on the surface. By varying the molecular parameters of the hydrophobic and hydrophilic components, the surface composition can be tuned to achieve a range of fouling-release properties when characterized using a broad variety of marine organisms. Different architectures of the reactive amphiphilic component have been explored including block and graft copolymers as well as dual-functionalized prepolymers.

11:00am **BI-MoM9 Zero-Energy Flux Recovery in Biofouled Liquid Gated Membranes**, *J.C. Overton*, ***Caitlin Howell***, University of Maine

Membranes coated with antifouling immobilized liquid layers have been recently shown to permit filtration while reducing surface fouling. In this work, we test the ability of liquid gated membranes created with expanded polytetrafluoroethylene and perfluorinated liquids to reduce the buildup of internal pore fouling using whey protein, an extremely challenging biological foulant. We find no differences in the decrease of flux or rate of fouling between coated and uncoated membranes in a dead-end filtration setup. However, upon stopping flow for 15-30 minutes, up to 70% of the original flux can be recovered with no additional energy input. This cycle can be repeated multiple times, with approximately 5% decrease in flux recovery each time. We use standard fouling equations and light microscopy to demonstrate that this zero-energy recovery may occur within the pores of the membrane due to the refilling of the pore with lubricating liquid, pushing the proteins off the pore walls. This work could have important applications in filtration processes with high fouling rates, reducing costs associated with standard chemical or physical cleaning methods.

11:20am **BI-MoM10 Stimuli Responsive Polymers in Biofouling and Bioadhesion**, ***Gabriel Lopez***, University of New Mexico **INVITED**

This talk will review work by the Lopez lab and its collaborators on the role of stimuli-responsive polymers in processes associated with biopolymer adsorption, biofouling and bioadhesion. Wikipedia currently defines stimuli-responsive (or “smart”) polymers as those that change their shape or properties “according to the environment they are in.” From this perspective, almost any polymer in solution that adsorbs to an interface placed in its proximity can be thought of as a stimuli-responsive polymer. In the present context, a less trivial distinction includes polymeric systems that are sensitive to external fields (e.g., thermal, stress, optical, electric) in a way as to dramatically affect tendency for adsorption or adhesion. Such polymeric systems include synthetic polymers comprising engineered interfaces with biologically relevant aqueous phases (brushes, solution and vacuum deposited films, gels) and biopolymers (proteins) in aqueous phases. These systems and their ability to dramatically influence adsorption, attachment and adhesion are of potential use in a wide range of biotechnological, biomedical, aquatic, marine and food production applications including processes such as separations, assays, controlled delivery, cell culture, packaging, energy transfer and transportation.

MEMS and NEMS Group
Room: 24 - Session MN+BI+NS-MoM

Feature Session: Large Scale Integration of Nanosensors

Moderators: Wayne Hiebert, National Institute for Nanotechnology, Canada, Robert Davis, Brigham Young University

8:20am **MN+BI+NS-MoM1 Large Scale Integration: A Not-so-simple Cure for Loneliness of Silicon Nanoresonators**, ***Sébastien Hentz***, Cea Leti, France **INVITED**

After two decades of pioneering work, Nano Electro Mechanical Systems are only starting to fulfil (some) of their huge promises, in particular for sensing. A few start-up companies have been created in the last few years, but NEMS are still far from the industrial success of their micro- counterparts. Among others, one reason is the increasing difficulty to interface the "real-world" quantities to sense with the extremely small size of nanomechanical resonators. An easy to understand example of this is mass sensing: there is huge size mismatch between the NEMS capture cross section (in the μm^2 range) and an actual particle beam size that one can produce (in the mm to $10mm^2$ range). Most of the particles to detect are lost. Industrial applications may require the use of large arrays comprising from 10's to 10000's NEMS.

LETI has been working on nanomechanical resonators for a number of applications in the last ten years and have been pioneering their fabrication with Very Large Scale Integration processes. State of the art performance (signal to background ratio, signal to noise ratio, frequency stability...) has been reached with single silicon resonators and specific transduction means adapted to VLSI technologies. The real strength of VLSI though, as evidenced every day by microprocessor fabrication is the possibility to process a large number of devices operating in sync with great reproducibility and control.

We investigated several types of NEMS arrays in the past at LETI. Arrays comprising typically a few 1000 resonators all connected in parallel for gas sensing have been demonstrated. Smaller arrays with the ability to weigh and localize single particles via frequency addressing have been tested too for mass spectrometry applications. LETI has also been pioneering NEMS co-integration with CMOS in the last decade or so and several technologies have been explored. We took advantage of this know-how to fabricate large and dense arrays of NEMS-CMOS arrays for mass sensing applications.

9:00am **MN+BI+NS-MoM3 Nanomechanical Sensors (MSS, AMA) Toward IoT Olfactory Sensor System**, ***Genki Yoshikawa***, National Institute for Materials Science, Japan **INVITED**

Owing to their intrinsic versatility, nanomechanical sensors have potential to cover a wide range of olfactory sensing applications in various fields including food, agriculture, medicine, security, and environment. Based on the newly developed platform "Membrane-type Surface stress Sensor (MSS)," we are now trying to realize useful nanomechanical sensor systems which can fulfill the practical requirements, such as portability, low-cost, ease of use, in addition to the basic specifications, e.g. high sensitivity and selectivity. While the MSS provides a practical sensing element, a consumer mobile/IoT sensor system requires further optimization and integration of lots of components including receptor layers, hardware including electronics and sample handling, multidimensional data analysis, and precise calibration for high reproducibility. To establish a de facto standard for odor analysis and sensor systems employing the nanomechanical MSS technology, the "MSS Alliance" was launched jointly with companies and a university. In addition, "Aero-Thermo-Dynamic Mass Analysis (AMA)," which we have recently developed, will provide another approach to characterizing gases by directly measuring molecular weight in ambient condition without a vacuum or ionization. In this talk, the overview of the MSS, AMA, and the related technologies ranging from the optimization scheme of the sensor chip to system level developments will be presented.

9:40am **MN+BI+NS-MoM5 Micro-Gas Chromatography Linked with Nano-optomechanical Systems for Breath Analysis**, ***Khulud Almutairi***, University of Alberta, Canada, *W.K. Hiebert*, National Institute for Nanotechnology, Canada

One of the applications of microfabrication and nanofabrication technologies is fabricating a micro-Gas Chromatography (GC) on a chip. The miniaturized GC system is designed for the rapid determination of volatile organic compounds (VOCs) that can be used in remote locations with low consumptions and cost of utilization. It was reported that specific VOCs can be found in exhaled breath sample from patients suffering from lung cancer [1]. Therefore, designing a μGC device can help in separating and analyzing VOCs that comes from exhaled breath samples, such as acetone, benzene and toluene.

Our group has reported that connecting Nano-optomechanical systems (NOMS) to Gas Chromatography can enhance the detection sensitivity limit of VOCs up to 1 ppb [2]. This presentation will feature our first efforts in connecting μGC with NOMS for higher sensitivity and responsivity. In particular, we will discuss our NOMS sensor chips with microheaters for localized control of sensor temperature. One of our goals is to move toward large scale integration of GC analysis by simultaneously sensing at multiple temperatures.

REFERENCES:

[1] Mazzone, Peter J. "Exhaled breath volatile organic compound biomarkers in lung cancer." *Journal of breath research* 6, no. 2 (2012): 027106.

[2] Venkatasubramanian, Anandram, Vincent TK Sauer, Swapan K. Roy, Mike Xia, David S. Wishart, and Wayne K. Hiebert. "Nano-optomechanical systems for gas chromatography." *Nano Letters* 16, no. 11 (2016): 6975-6981.

10:00am **MN+BI+NS-MoM6 Micro Chladni Figures and Multimode Manipulation of Breast Cancer Cells in Liquid**, ***Hao Jia***, *H. Tang*, Case Western Reserve University, *X. Liu, H. Liu*, Northwestern University, *P.X.-L. Feng*, Case Western Reserve University

Non-invasive, microscale positioning of delicate biological cells can foster fundamental research involving probing cellular properties and controlling cellular behaviors and interactions [1-3], which lead to a multitude of applications, such as disease screening, tissue engineering, *etc.*

Here we demonstrate that microscale manipulation of breast cancer cells can be achieved in a fast and non-invasive manner through exploiting multimode micromechanical systems. We design edge-clamped diaphragm resonators (~300μm in length scale) and piezoelectrically excite their mechanical resonances (within 50–500 kHz) in fluidic environment. The transverse vibrations induce localized, microscale hydrodynamic flow that can aggregate microbeads (3.6μm-diameter) on device surfaces into a variety of one- and two-dimensional (1D and 2D) 'Chladni figures' [4] (optical images in Fig.1a & b). This phenomenon allows us to further manipulate single or a group of breast cancer cells (MDA-MB-231, 15μm-diameter), in both 1D and 2D fashions, at a speed of ~4μm/s (fluorescent images in Fig. 1a & b). By simply programming the piezoelectric excitation frequency, we achieve dynamic control of cancer cell spatial distributions, switching between mode patterns.

We further demonstrate that such multimode resonator platform can facilitate cellular-level biological studies, such as evaluating cellular adhesive interactions and its connection with cancer biomarker (*e.g.*, CD44). As shown in Fig.2, by exploiting the 'Chladni figure' phenomenon, and carefully selecting 2 resonance modes of a square diaphragm, *e.g.*, Mode (1,1) and Mode (3,3), a controlled number of MDA-MB-231 cells can be quickly manipulated into single cluster and then forced to break as the excitation voltage of Mode (3,3) gradually increases. Cancer cells with CD44 gene knocked out by CRYSPR technology are named as $CD44^-$ cells, while those with CD44 gene maintained named as $CD44^+$ (control) cells. The break of $CD44^-$ cell cluster after $0.8V_{pp}$ in Fig. 2 indicates that they form much weaker adhesive interactions than $CD44^+$ cells do, which indicates that CD44 plays a significant role in the metastatic breast cancer cell clustering.

[1] E.E. Hui, *et al.*, PNAS **104**, 2007.

[2] H. Zhang, *et al.*, J. R. Soc. Interface **5**, 2008.

[3] X. Ding, *et al.*, PNAS**109**, 2012.

[4] E.F.F. Chladni, *Entdeckungen über die Theory des Klanges*,1787.

10:40am **MN+BI+NS-MoM8 Microfabrication and Assembly Processes for Integrating Microelectrode Arrays into Tissue-Engineered Scaffolds for Novel Nerve Interfaces**, ***Jack Judy***, *C. Kuliasha, P. Rustogi, S. Natt, B. Spearman, S. Mohini, J.B. Graham, E.W. Atkinson, E.A. Nunamaker, K.J. Otto, C.E. Schmidt*, University of Florida **INVITED**

To advance fundamental understanding and develop therapies for neurological disease or injury, microfabricated implantable electrode arrays have been designed and manufactured to stimulate and record neural activity. The materials in these implants, as well as the processes used to integrate them together, must be carefully selected to maximize biocompatibility, device performance, and overall reliability. For upper-limb amputees, nerves are a promising neural-interface target to control sophisticated robotic limbs. Recent advances have shown that nerve stimulation can provide natural sensory feedback. In contrast, it is currently not possible to extract large-scale, high-resolution, and reliable movement-intent signals from nerves. To provide rapid and precise limb control and elicit high-resolution sensory percepts, a nerve interface needs many independent motor and sensory channels. Unfortunately, all existing non-invasive and non-regenerative nerve interfaces grossly under-sample the heterogeneous population of efferent and afferent axons. Although tissue engineering, nerve regeneration, and implantable neural-electronic interfaces are individually well-established fields, the concept of merging these fields to create scalable, and high-performance neural interfaces has not been extensively explored. To overcome the scalability challenge, we present a novel approach. Specifically, we describe a hybrid tissue-engineered electronic nerve interface (TEENI), which consists of multi-electrode polyimide-based "threads" embedded into a biodegradable hydrogel composite scaffold that is sutured to the ends of a transected nerve. Single or multiple thread sets can be incorporated in the hydrogel to enable the TEENI implant to comprehensively engage with the nerve. These polyimide threads will be fully enveloped and held precisely in position during implantation by the hydrogel scaffold, which has properties optimized to reduce foreign-body response. Eventually, the hydrogel will degrade and be replaced with regrown and maturing axons. Since the TEENI approach is scalable to high channel counts over the nerve volume, we believe TEENI nerve interfaces are well positioned to comprehensively capture movement-intent information and impart sensory-feedback information so that upper-limb amputees can get the most out of their prosthetic limbs.

11:20am **MN+BI+NS-MoM10 Magnetically Actuated Synthetic Cilia for Microfluidics**, ***Peter Hesketh***, *S.K.G. Hanasoge, M. Ballard*, Georgia Institute of Technology, *M. Erickson*, University of Georgia, *A. Alexeev*, Georgia Institute of Technology **INVITED**

Many bacteria use cilia for swimming, sensing and signal transduction. These functions are achieved by manipulating the fluid around the cilia with continuous and synchronised asymmetric beating patterns . We have fabricated arrays of synthetic cilia using thin film deposition of NiFe thin films. The cilia are able to manipulate fluid in these creeping flow regimes by creating an asymmetry in the forward and recovery strokes. We propose to use artificial cilia in microfluidic devices to perform different functions including mixing, fluid transport, and particle capture.

We use a simple rotating magnet to actuate the cilia array and observe a large asymmetry in the bending pattern of these cilia in the oscillation cycle. We analyze the asymmetric strokes of the cilia by imaging from the side view and quantify the asymmetry between forward and recovery strokes as a function of drive frequency. These asymmetric oscillations are important in creating any microfluidic transport phenomenon such as pumping, mixing and capture in a microchannel as demonstrated in this work. Computational modeling was also used to simulate the motion of the cilia over a broader range of design parameters. We show the dependence of the ciliary performance on several non-dimensional numbers based on the balance of magnetic, viscous and elastic forces acting on the cilia.

The motivation for this work is to improve the quality of sampling for the detection of bacteria and virus in food. Detecting low concentrations of bacteria in food samples is a challenge. The pre-concentration and separation of the target bacteria from the food matrix can be enhanced using improved fluid handling. We demonstrate particle capture with cilia, by functionalizing the surface of the cilia with streptavidin protein and capturing biotin labelled particles on its surface. The functionalized cilia are incorporated inside a microchannel and biotin labelled particles are introduced into array of the cilia. Likewise, these artificial cilia find varied application in many lab on a chip devices where active fluid transport is needed.

Applied Surface Science Division
Room: 13 - Session AS+BI-MoA

Practical Surface Analysis: Complex, Organic and Bio-systems

Moderators: Scott Lea, Pacific Northwest National Laboratory, Paulina Rakowska, National Physical Laboratory, UK

2:00pm **AS+BI-MoA2 Environmental Charge Compensation - Near Ambient Pressure XPS as a Tool for Surface Chemical Analysis of Iinsulators without Charging Effects**, ***Paul Dietrich***, *A. Thissen*, SPECS Surface Nano Analysis GmbH, Germany, *S. Bahr*, Enviro Analytical Instruments GmbH, Germany

Since many decades XPS (or ESCA) is the well-accepted standard method for

non-destructive chemical analysis of solid surfaces. To fulfill this task existing ESCA tools

combine reliable quantitative chemical analysis with comfortable sample handling concepts,

integrated into fully automated compact designs.

Generically insulators will positively charge in XPS due to the irradiation with X-rays and

the emission of photoelectrons. Without compensation this effect leads to strong continuous

shifts and asymmetric line shapes of the emission lines in the spectra. To perform an exact

characterization and quantification of strongly insulating materials different concepts of

charge compensation or neutralization have been developed over the last decades. A short

overview is given starting from low energy electrons offered from so-called "flood guns" or

other sources, via compensation by a combination of electrons and ions to rare methods like

illumination with visible light during the analysis and compensation by the produced

electron-hole pairs. The opportunities and challenges of the different methods are compared.

The development of XPS method towards environmental or (near) ambient pressure

working conditions has revolutionized this method regarding applications. In-situ and

in-operando measurements in pressure of up to and above 25mbar are easily possible, even

with laboratory based systems and using EnviroESCA even in a standard analytical tool.

During the last months, measurements on insulators have shown, that they can be measured

with exception in surrounding pressures of a couple of mbar without any charging. This new

technique of charge neutralization is neamed Environmental Charge Compensation (ECC).

This presentation summarizes results of measurements on insulating polymer samples,

showing the resulting spectroscopic resolution for C1s and O1s emission lines. A

comparison for PET and PTFE to other neutralization techniques is given. In addition

measurements on bulk insulators from polymeric materials, ceramics, food samples,

aqueous solutions, stones, soil and even zeolites are shown, that cannot easily be obtained in

UHV based XPS systems.

Furthermore the effect is described in detail, including the influence of pressure and gas composition on the charge neutralization. An outlook is presented towards completely new

resulting fields of application of XPS, when combined with ECC.

2:20pm **AS+BI-MoA3 Does Time Play a Role in Glyoxal and Hydrogen Peroxide Photochemical Aging?**, ***Fei Zhang***, *X.F. Yu, X. Sui*, Pacific Northwest National Laboratory, *J.M. Chen*, Fudan University, *Z.H. Zhu, X.Y. Yu*, Pacific Northwest National Laboratory

Aqueous surfaces consisting of glyoxal and hydrogen peroxide (H_2O_2) after photochemical aging have been studied in a microfluidic reactor (System for Analysis at the Liquid Vacuum Interface, SALVI) by in situ liquid Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS). Positive and negative ion mode mass spectra provide complementary information of the surface reactions. Compared with previous results using bulk solutions, our unique liquid surface molecular imaging approach makes it possible to observe glyoxal hydration (i.e., first and secondary products, hydrates), oxidation products (i.e., glyoxylic acid, oxalic acid, formic acid, malonic acid, tartaric acid), oligomers (i.e., $C_7H_{11}O_9^+$, $C_6H_5O_{10}^-$), water clusters (i.e., $(H_2O)_nH^+$, n< 43, $(H_2O)_nOH^-$, n< 44), and cluster ions (i.e.,$C_6H_{17}O_{12}^+$, $C_7H_9O_{11}^-$) with submicrometer spatial resolution. Spectral principal component analysis (PCA) is used to determine similarities and differences among photochemical aging samples ranging from 15 minutes to 8 hours. The oxidation products such as glyoxylic acid, glycolic acid, and tartaric acid tend to peak at around between 30 min and 1 h. UV aging; while oligomers and large water clusters (i.e., $(H_2O)_{22}OH^-$, $(H_2O)_{23}OH^-$,$(H_2O)_{24}OH^-$) form significantly at about 3 h. The oligomer formation reaches its maximum at 4 h., and reduces afterwards. Large water clusters (n> 15) become more significant as photochemical aging progresses, indicating more hydrophobicity at the aqueous surface as predicted by molecular dynamic simulation in earlier works. SIMS three-dimensional (3D) chemical mapping enables visualization of the surface mixing state at the molecular level. We have presented the temporal progression of the 3D surface mixing state of various products from glyoxal and hydrogen peroxide oxidation for the first time. Such physical measurements pave a new way to investigate complex surface reaction mechanisms as an important source of aqueous secondary organic aerosol (SOA) formation in atmospheric chemistry.

2:40pm **AS+BI-MoA4 Study of Drug Uptake and Action on Metabolic Processes at the Single-Cell Level using the 3D OrbiSIMS**, ***Ian S. Gilmore***, *M.K. Passarelli, M. Lorenz*, National Physical Laboratory, UK, *C.F. Newman, P.S. Marshall, A. West*, GlaxoSmithKline, UK, *P.D. Rakowska, R. Havelund, C.T. Dollery*, National Physical Laboratory, UK

A major quest for the pharmaceutical industry is the reduction of late-stage drug failure. Measurements that can identify future failure at the early stages of drug development are therefore of great importance. This requires label-free imaging of the distribution of pharmaceutical compounds and metabolites with subcellular resolution. We have previously shown [1] that ToF-SIMS can provide useful sub-cellular resolution images but analysis is limited by insufficient mass accuracy, mass resolving power for accurate identification of metabolites and sensitivity.

We have recently led the development of a powerful new hybrid instrument, the 3D OrbiSIMS [2], combining an Orbitrap™-based Thermo Scientific™ Q Exactive™ HF instrument and a dedicated ToF-SIMS 5. The instrument is equipped with high-resolution ion beams including a new micrometre resolution argon cluster ion beam for biomolecular imaging and 3D analysis of organics and an ultra-high resolution Bi cluster focussed ion beam with < 200 nm resolution.

In this study, we demonstrate the unparalleled ability for 2D and 3D metabolite imaging with sub-cellular resolution. We show significant variability of drug uptake at the single cell level and demonstrate direct evidence of up regulation of metabolites. This can only be revealed with a single-cell study. Furthermore, we demonstrate a new method for in situ matrix deposition for 3D imaging that significantly increases sensitivity. This is especially important for current drug candidates with Log P values ≤ 3 (Lipinski rule of five), which are known to have low molecular secondary ion yields. [3]

[1] M.K. Passarelli et al, Analytical chemistry 87 (13), 2015, 6696

[2] M.K. Passarelli et al, submitted, 2017

[3] J.L. Vorng et al, Analytical Chemistry 88 (22), 2016, 11028

3:00pm **AS+BI-MoA5 TOF-SIMS Cluster Beam Depth Profiling and 3D Imaging of Oral Drug Delivery Films**, ***Greg Gillen***, *S. Muramoto, J. Staymates, E. Robinson*, NIST

Dissolvable oral thin film (OTF) drug delivery systems are gaining increased interest as convenient alternatives to more conventional tablets and capsules

for drug delivery applications. The OTF's are typically made by mixing an active pharmaceutical ingredient (API) into a dissolvable polymer that is administered to the patient by placing under the tongue or against the inside of the cheek. Direct adsorption of the API into the systemic circulation bypasses gastrointestinal delivery and can provide higher levels of bioavailability and a more rapid release profile in appropriate medications. One critical challenge with further development of OTF drug delivery systems is the lack of appropriate measurement tools for the characterization of API concentration, phase and dose uniformity throughout the depth of the polymer film (typically ~100 um in thickness). Furthermore, OTF's are currently manufactured as bulk sheets with fixed levels of API. This is a significant roadblock to realization of OTF's for personalized medicine where there is a growing interest in manufacturing of OTF's with individualized and patient-specific API dosages. One promising method of production of such films that is currently being explored in our laboratory is the used of drop on demand inkjet printing to precisely deposit individualized API doses onto prefabricated films.

In this work, we explore the utility of Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS) using gaseous cluster ion beam (GCIB) depth profiling for the characterization of the lateral and in-depth distribution of API's in model OTF films. Three types of films were examined; (1) model thin films of pullulan, (2) model thin films of pullulan that had been dosed using drop on demand inkjet printing with various concentrations of relevant API's and (3), commercially available OTF films (single and multilayer films) containing the anti-opioid medications buprenorphine and naloxone which are widely used medications for treatment of opioid dependency. Cluster SIMS depth profiling was able to resolve compositional differences throughout the depth of each of these films (>70 um in thickness) and localize the individual API's. Furthermore, the ability to characterize the lateral and in depth distribution of API's in individual inkjet droplets will be demonstrated as well as the use of inkjet printing to prepare in situ concentration standards for evaluation of dosage variability. Finally, we also demonstrate the use THz Raman imaging for chemical identification of the API and possible phase changes due to the use of inkjet-printed formulations.

3:20pm **AS+BI-MoA6 Characterisation of Bioelectronic Material Surfaces using Surface Spectroscopies**, ***Sarah Coultas***, Kratos Analytical Limited, UK, *W. Boxford*, Kratos Analytical Ltd, UK, *C.J. Blomfield*, Kratos Analytical Limited, UK, *M. Firlak, J. Hardy*, Lancaster University, UK

Electromagnetic fields affect a variety of tissues (e.g. bone, muscle, nerve and skin) and play important roles in a multitude of biological processes. This has inspired the development of electrically conducting devices for biomedical applications, including: biosensors, drug delivery devices, cardiac/neural electrodes, and tissue scaffolds. It is noteworthy that there are a number of clinically approved devices capable of electrical stimulation of the body, all of which are designed for long term implantation. The first examples were developed in Sweden and include bionic eyes, ears and electrodes for deep brain stimulation (DBS). Recently there has been considerable industrial interest in the development and commercialisation of bioelectronic medicines. Bioelectronics is an emerging area of technology that promises broad impact in healthcare.

The detailed analysis of biomaterials and biomedical devices offers valuable insight into the underlying function of the products. The materials are composites of electroactive polymers (e.g. polypyrrole) and biopolymers (e.g. polysaccharides and proteins) that can be used for various applications (e.g. drug delivery, tissue scaffolds).

Here we demonstrate the application of surface spectroscopies, including XPS and UPS, to characterise bioelectronic materials in various morphologies (e.g. films and foams). We utilise a range of approaches to fully characterise the materials, including investigating any variations in composition either laterally or with depth. We also explore the usefulness of surface cleaning using Argon clusters.

References:

J. Rivnay, et al. Review on bioelectronics: Chem. Mater. 2014, 26, 679−685

G. G. Wallace, et al. Review on bioelectronics: Nanoscale. 2012, 4, 4327–4347

J. G. Hardy, et al. Article on bioelectronic drug delivery devices: J. Mater. Chem. B, 2014, 2(39), 6809-6822.

J. G. Hardy, et al. Article on instructive bioelectronic tissue scaffolds: Macromol. Biosci., 2015, 15, 1490-1496.

4:00pm **AS+BI-MoA8 High-resolution SIMS Imaging of Subcellular Structures**, ***Mary Kraft***, *A.N. Yeager*, University of Illinois at Urbana-Champaign, *P.K. Weber*, Lawrence Livermore National Laboratory **INVITED**

In mammalian cells, lipids and cholesterol form the selectively permeable plasma membrane that separates the cell from its surroundings, and the intracellular membranes that delineate the boundaries of organelles and transport vesicles. The distributions of cholesterol and each lipid species between these organelles is correlated with health and disease. The accumulation of cholesterol and certain lipid species within lysosomes and endosomes causes defects in intracellular trafficking that can be fatal if left untreated. The ability to image the relative abundances of cholesterol and distinct lipid species within intracellular compartments could lead to a better understanding of the biological mechanisms that regulate subcellular lipid distribution. For this purpose, we have combined metabolic stable isotope incorporation with secondary ion mass spectrometry (SIMS), which is performed on a Cameca NanoSIMS 50, to image the intracellular distributions of cholesterol and sphingolipids. By using depth profiling SIMS to image the distributions of ^{18}O-cholesterol and ^{15}N-sphingolipids within a portion of a Madin-Darby Canine Kidney (MDCK) cell, we determined that these two components are enriched within separate intracellular compartments. The sizes and relative positions of the ^{15}N- and ^{18}O- enriched intracellular features that are visible in the 3-D representations of the SIMS images suggest that the ^{15}N-sphingolipids are located within transport vesicles, whereas the ^{18}O-cholesterol seem to be concentrated within lipid droplets.

4:40pm **AS+BI-MoA10 EnviroESCA – Routine Surface Chemical Analysis under Environmental Conditions For Biological Samples**, ***Andreas Thissen***, *P. Dietrich*, SPECS Surface Nano Analysis GmbH, Germany, *S. Bahr*, Enviro Analytical Instruments GmbH, Germany, *M. Kjaervik, W. Unger*, Bundesanstalt für Materialforschung und -prüfung (BAM), Germany

Since many decades XPS (or ESCA) is the well-accepted standard method for

non-destructive chemical analysis of solid surfaces. To fulfill this task existing ESCA tools

combine reliable quantitative chemical analysis with comfortable sample handling concepts,

integrated into fully automated compact designs.

Over the last years it has been possible to develop XPS systems, that can work far beyond

the standard conditions of high or ultrahigh vacuum. Near Ambient Pressure (NAP) XPS has

become a fastly growing field in research inspiring many scientist to transfer the method to

completely new fields of application. Thus, by crossing the pressure gap, new insights in

complicated materials systems have become possible using either synchrotron radiation or

laboratory X-ray monochromators as excitation sources under NAP condtions.

Based on this experience SPECS Surface Nano Analysis GmbH has developed a

revolutionary tool to realize the long existing dream in many analytical laboratories:

reproducible chemical surface analysis under any environmental condition. EnviroESCA

allows for different applications, like extremely fast solid surface analysis of degassing (but

also non-degassing) samples, ESCA analysis of liquids or liquid-solid interfaces, chemical

analysis of biological samples, materials and device analysis under working conditions.

After introduction of the technological realization a comprehensive survey of results will be

given starting from standard solid conductive samples under different pressure conditions,

bulk insulators with environmental charge compensation applied, high throughput analysis

of batches of similar objects, geological samples, chemical analysis of pharmaceuticals to

the comparative analysis of ultrapure liquid water with different aqueous solutions.

The application of Near Ambient Pressure XPS to biological specimen from plants and

animals, biofilms and bacteria, as well as food samples is a completely new field for

electron spectroscopic studies of the surface chemical composition.

An outlook is presented on the application to electrochemical and other in-operando devices.

Finally the influence of the ambient conditions on quantification in XPS will be

demonstrated and discussed.

This project has received funding from the EMPIR programme co-financed by the Participating

States and from the European Union's Horizon 2020 research and innovation programme.

Magnetic Interfaces and Nanostructures Division
Room: 11 - Session MI+BI+EM+SA-MoA

Role of Chirality in Spin Transport and Magnetism

Moderators: Greg Szulczewski, The University of Alabama, Hendrik Ohldag, SLAC National Accelerator Laboratory

1:40pm **MI+BI+EM+SA-MoA1 Spin Transport and Polarization in Chiral Molecules: Theory and Possible Applications**, ***Karen Michaeli***, Weizmann Institute of Science, Israel **INVITED**

The functionality of many biological systems depends on reliable electron transfer. Unlike artificial electric circuits, electron transport in nature is realized via insulating chiral (i.e., parity-symmetry breaking) molecules. Recent experiments have revealed that transport through such molecules strongly depends on the electron's spin relative to the propagation direction. In the talk I will introduce the mechanism behind this phenomenon, which has been dubbed chiral induced spin selectivity (CISS). The discovery of the CISS effect has raised important questions about the role of spin in biological processes more generally, and suggests the possibility of a new class of organic-based nanoscale devices. I will discuss some of the key developments regarding spin selectivity; I will present new questions that arise from these results and offer ideas for their resolution.

2:20pm **MI+BI+EM+SA-MoA3 Enantio-sensitive Charge Transfer in Adsorbed Chiral Molecules Probed with X Ray Circular Dichroism**, *F.J. Luque*, Universidad Autónoma de Madrid, Spain, *I.A. Kowalik*, Polish Academy of Sciences, Poland, *M.Á. Niño*, IMDEA-Nanoscience, Spain, *D. Arvanitis*, Uppsala University, Sweden, ***Juan José de Miguel***, Universidad Autónoma de Madrid, Spain

Recent studies have shown how layers of purely organic, chiral molecules can induce the appearance of strong spin polarization in initially unpolarized electron currents. [1] Furthermore, spin-polarized photoemission experiments comparing adsorbed films of opposite enantiomers of the same chiral molecule have revealed that they can display different behavior, producing spin polarization along different directions in space instead of simply changing its sign. [2]

In this study enantio-pure ultrathin films of chiral 1,2-diphenyl-1,2-ethanediol (DPED) have been deposited on Cu(100) at 100 K and studied at the MAX-lab synchrotron in Lund, Sweden, using circularly polarized x ray absorption (XAS) at the carbon K edge. XAS excites element-specific core electrons to empty levels in the ground state thus probing the molecule's electronic configuration. The different features present in the absorption spectra have been identified and assigned to specific electronic transitions. The comparison of absorption spectra taken with photons of opposite helicity shows a surprisingly strong dichroism localized at transitions into empty molecular orbitals with π character. Theoretical modeling of the spectra reveals that this response is associated to the charge transferred between the Cu substrate and the adsorbed molecules. This charge is found to be polarized in orbital momentum, and the direction of the polarization is different for the two enantiomers studied: (R,R)–DPED and (S,S)–DPED. These findings indicate that chiral organic layers can play an important role in the emerging field of molecular orbitronics.

[1] B. Göhler V. Hamelbeck, T. Z. Markus, M. Kettner, G. F. Hanne, Z. Vager, R. Naaman, and H. Zacharias, Science **331**, 894 (2011).

[2] M. Á. Niño, I. A. Kowalik, F. J. Luque, D. Arvanitis, R. Miranda, and J. J. de Miguel, Adv. Mater. **26**, 7474 (2014).

2:40pm **MI+BI+EM+SA-MoA4 Evolving of Soliton Phase in Exfoliated 2D $Cr_{1/3}NbS_2$ Nanolayers**, *S. Tang*, Oak Ridge National Laboratory and Central South University, China, *J. Yi, R. Fishman, S. Okamoto, Q. Zou*, Oak Ridge National Laboratory, *D.G. Mandrus*, University of Tennessee, ***Zheng Gai***, Oak Ridge National Laboratory

Cr1/3NbS2 is an emergent quasi-2D material that has recently been attracting wide attentions. Cr1/3NbS2 has both chiral helimagnetic behavior and broken inversion symmetry of Cr atoms, the two necessary conditions for creating Dzyaloshinskii–Moriya interaction in skyrmion. Bulk studies show that a nonlinear periodic magnetic state called a soliton lattice exists in the material. By applying microexfoliation techniques, we successfully prepared thin layers of Cr1/3NbS2 with various thickness from single crystal. When the thickness of Cr1/3NbS2 layer falls into the range around the pitch of its helimagnetic state, kinks of field dependent magnetization start to evolve. The new phase is studied experimentally and theoretically. This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

3:00pm **MI+BI+EM+SA-MoA5 Tailoring the Chirality of Domain Walls via Interface Modification**, ***Arantzazu Mascaraque***, *S. Ruiz-Gomez, M.A. Gonzalez Barrio, L. Perez*, Universidad Complutense de Madrid, Spain, *G. Chen, A.K. Schmid*, Lawrence Berkeley National Laboratory, *E.G. Michel*, Universidad Autonoma de Madrid, Spain

The possibility of manipulating magnetic domain walls (DWs) without the intervention of magnetic fields has interest for a wide variety of applications, such as spintronic devices [1]. Applying an electric current to a ferromagnet creates a force that drives the DWs in the direction of the electron motion, the so-called Spin Transfer Torque. However, this effect is weak and high current densities are needed. Recently, it has been discovered that spin accumulation at the edges of a current-carrying non-magnetic material due to the Spin Hall Effect (SHE), can exert a torque on the magnetization of a neighboring magnetic layer [2]. The torque induced by SHE depends on the chirality of the DW and, as most ferromagnetic materials lack a well-defined chirality, the device applications are limited. However, the presence of surfaces and interfaces removes the point-inversion symmetry, giving rise to an additional interaction, the Dzyaloshinskii–Moriya interaction (DMI) that lifts the left-right degeneracy through spin-orbit coupling [3].

In this work, we have modified the interface between the substrate and a non-chiral magnetic layer, in order to investigate in which way DW chirality can be induced and stabilized in the magnetic layer. The experiments were done using the SPLEEM instrument of the Lawrence Berkeley National Laboratory. This microscope can map independently and in real space the three magnetic components of the spin structures. The magnetic system was a (Ni/Co)n multilayer epitaxially grown on Cu(111). It is well known that magnetic films grown on Cu(111) do not exhibit homo-chiral DWs [4]. We have found that this behavior can be changed by modifying the interface. After introducing a thin metal layer (suitable to induce a high DMI) between the substrate and the magnetic layer, we have found relevant changes in the chirality of the DWs of the magnetic layer. Our results demonstrate that the buffer layer influences the spin texture, which evolves from non-chiral Bloch to homo-chiral Néel DWs.

[1] S. S. P. Parkin et al, Science 320, pp190 (2008); D. A. Allwood et al , Science 309 , pp1688 (2005)

[2] I. M. Miron Nat. Mat 9 pp230 (2010)

[3] I. E. Dzyaloshinskii , J. Exp. Theor. Phys. 5, pp1259 (2007),; T. Moriya , Phys. Rev. 120 , pp91 (1960).

[4] G. Chen, et al., Ap. Phys. Lett. 106, 062402 (2015)

3:20pm **MI+BI+EM+SA-MoA6 Spin Transport in an Electron Conducting Polymer**, ***Greg Szulczewski***, *T. Sutch, M. Lockart, H. Chen, P. Rupar, M. Bowman*, The University of Alabama

We report results from an electron spin resonance (ESR) study to probe the spin-dynamics in the conducting polymer poly {[N, N9 -bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5 9 -(2,2 9 -bithiophene)} or P(NDI2OD-T2). Chemical reduction of the polymer was achieved by using cobaltacene, which introduces unpaired electrons into the polymer. Continuous wave ESR measurements were done on frozen solutions and thin films over the temperature range of 77 to 300 K. Narrow ESR peaks with broad tails were observed, suggesting strong one-dimensional anisotropic conduction. Electron nuclear double resonance spectroscopy was used to analyze the hyperfine coupling of the frozen solutions. The results indicate a proton hyperfine coupling of 1.5 MHz, which suggests the spins are delocalized over several monomer units. Electron spin echo envelope modulation spectroscopy was measured from 6 to 90 K to investigate the spatial distribution of nuclear spins in the environment of the unpaired electrons spins. The measurements show that spin relaxation increases rapidly when the temperature in increases from 6 to 90 K. A kinetic model that accounts for the spin-dynamics will be presented.

4:00pm **MI+BI+EM+SA-MoA8 Utilizing the Chiral induced Spin Selectivity Effect to Achieve Simple Spintronics Devices**, ***Yossi Paltiel***, The Hebrew University of Jerusalem, Israel **INVITED**

With the increasing demand for miniaturization, nano-structures are likely to become the primary components of future integrated circuits. Different approaches are being pursued towards achieving efficient electronics, among which are spin electronics devices (spintronics) [1]. In principle, the application of spintronics should result in reducing the power consumption of electronic devices.

A new, promising, effective approach for spintronics has emerged using spin selectivity in electron transport through chiral molecules, termed Chiral-Induced Spin Selectivity (CISS) [2]. Recently, by utilizing this effect we demonstrated a magnet-less magnetic memory [3,4]. Also we achieve local spin-based magnetization generated optically at ambient temperatures [5,6]. The locality is realized by selective adsorption of the organic molecules and the nano particles [7]. Lastly we have been able to show chiral proximity induced magnetization on the surface of ferromagnetic and superconducting materials. The magnetization is generated without driving current or optically exciting the system [8,9].

In the talk I will give a short introduction about spintronics and the CISS effect. Then I will present ways achieve simple spintronics devices utilizing the effect.

[1] S. A. Wolf, D. D. Awschalom, R. A. Buhrman, J. M. Daughton, S. von Molnar, M. L. Roukes, A. Y. Chtchelkanova, D. M. Treger; *Science* **294** 1488 (2001).

[2] B. Göhler,V. Hamelbeck, T.Z. Markus, M. Kettner, G.F. Hanne, Z. Vager, R. Naaman, H. Zacharias; *Science* **331,** 894-897 (2011).

[3] O. Ben Dor, S. Yochelis, S. P. Mathew, R. Naaman, and Y. Paltiel *Nature Communications* **4**, 2256 (2013).

[4] G. Koplovitz, D. Primc, O. Ben Dor, S. Yochelis, D. Rotem, D. Porath, and Y. Paltiel; Advanced Materials (2017).

[5] O. Ben Dor, N. Morali, S. Yochelis, and Y. Paltiel; *Nano letters* 14 6042 (2014).

[6] M. Eckshtain-Levi, E. Capua, S. Refaely-Abramson, S. Sarkar, Y. Gavrilov, S. P. Mathew, Y. Paltiel, Y.V Levy, L. Kronik, R. Naaman; *Nature Communications*. **7**, 10744 (2016).

7] O. Koslovsky, S. Yochelis, N. Livneh, M. Harats, R. Rapaport, and Y. Paltiel, *Journal of Nanomaterials* 938495 **2012** (2012).

[8] H. Alpern, E. Katzir, S. Yochelis, Y. Paltiel, and O. Millo; New J. Phys. 18 113048 (2016).

[9] O. Ben Dor, S. Yochelis, A. Radko, K. Vankayala, E. Capua, A. Capua, S.-H. Yang, L. T. Baczewski, S. S. P. Parkin, R. Naaman, and Y. Paltiel; *Nature Communications*, **8** 14567 (2017).

4:40pm **MI+BI+EM+SA-MoA10 Magnetic Nano Platelets based Spin Memory Device Operating at Ambient Temperatures**, ***Guy Koplovitz***, The Hebrew University of Jerusalem, *Y. Paltiel*, The Hebrew University of Jerusalem, Israel

There is an increasing demand for realizing a simple Si based universal memory device working at ambient temperatures. In principle non-volatile magnetic memory could operate at low power consumption and high frequencies. However, in order to compete with existing memory technology, size reduction and simplification of the used material systems are essential. In our work we use the Chiral Induced Spin Selectivity (CISS) effect along with 30-50nm Ferro-Magnetic Nano Platelets (FMNPs) in order to realize a simple magnetic memory device. The vertical memory is Si compatible, easy to fabricate and in principle can be scaled down to a single nano particle size. Results show clear dual magnetization behavior with threefold enhancement between the one and zero states. The magnetization of the device is accompanied with large avalanche like noise that we ascribe to the redistribution of current densities due to spin accumulation inducing coupling effects between the different nano platelets.

5:00pm **MI+BI+EM+SA-MoA11 Magnetization Switching in Ferromagnets by Adsorbed Chiral Molecules without Current or External Magnetic Field**, ***Oren Ben Dor****, The Hebrew University of Jerusalem, Israel

Ferromagnets are commonly magnetized by either external magnetic fields or spin polarized currents. The manipulation of magnetization by spin-current occurs through the spin-transfer-torque effect, which is applied, for example, in modern magnetoresistive random access memory. However, the current density required for the spin-transfer torque is of the order of 1×10^{6} $A\cdot cm^{-2}$, or about 1×10^{25} $electrons\cdot sec^{-1}\cdot cm^{-2}$. This relatively high current density significantly affects the devices' structure and performance. Here, we present a new effect – that of magnetization switching of ferromagnetic thin layers that is induced solely by adsorption of chiral molecules. In this case, about 10^{13} electrons per cm^2 are sufficient to induce magnetization reversal. The direction of the magnetization depends on the handedness of the adsorbed chiral molecules. Local magnetization switching is achieved by adsorbing a chiral self-assembled molecular monolayer on a gold-coated ferromagnetic layer with perpendicular magnetic anisotropy. These results present a simple low power magnetization mechanism when operating at ambient conditions.

Plasma Processing for Biomedical Applications Focus Topic
Room: 12 - Session PB+BI+PS-MoA

Plasma Agriculture & Processing of Biomaterials
Moderator: Kristian Wende, INP Greifswald

1:40pm **PB+BI+PS-MoA1 Control for Plant Disease and Development by Atmospheric Pressure Plasma**, ***Gyungsoon Park***, Kwangwoon University, Republic of Korea **INVITED**

Previously, we observed that seeds contaminated with *Fusarium fujikuroi* (a fungus causing rice bakanae disease) were more effectively disinfected in water by arc discharge plasma than ozone. Efficiency of disinfection was decreased when the distance between seeds and electrodes becomes greater. This indicates that shockwave from arc plasma may play an important role in seed sterilization, and we measured about 50-60 atm shockwave pressure. In addition, seed surface became more hydrophillic after plasma than ozone treatment indicating that water containing ROS and RNS can more easily get inside hull. Ozone level in water was decreased when seeds were present. This is probably due to the chemical reaction of ozone with seed surface molecules and will eventually cause the decrease in efficiency of seed disinfection. We also analyzed the effect of water and buffer treated with microwave plasma generated gas containing nitric oxide (PGNO) on development of spinach. The real time level of nitric oxide in water and phosphate buffer was increased to about 100 μM after treatment with PGNO for 50 min. Spinach treated with PGNO water seems to become more tolerant to drought stress. Our work was supported by the National Research Foundation of Korea (NRF) grant (No. 2010-0027963), Rural Development Administration (RDA) grant (No. PJ009891) and National Fusion Research Institute (NFRI) grant.

2:20pm **PB+BI+PS-MoA3 Biomass Pyrolysis Using Low Temperature Plasma**, *Y. Gao, N.B. Uner, J. Meyer, M. Foston*, ***Elijah Thimsen***, Washington University in St. Louis

Low temperature plasmas (LTP) are recently being used for processes involving complicated heterogeneous chemistry. Due to their unique non-equilibrium environment and the abundance of reactive radicals, LTPs are expected to bring selectivities and reactivities that are difficult to obtain in systems governed by local thermal equilibrium. In this study, we utilize low temperature plasmas for converting biomass into more valuable chemicals.

Biomass is an abundant and renewable source of carbon. It is recently reported that biomass can be supplied and processed at a scale large enough that is comparable to petroleum [1]. Current research efforts are focused on upgrading biomass into hydrocarbons and valuable aromatic compounds. One common method is to pyrolyze biomass into oils at high pressure. However, the product distribution usually turns out to be very broad, therefore the yields of the desired components are often low. Another common method is to gasify the biomass into syngas, a mixture of CO and H_2. Both pyrolysis and gasification are indirect routes of converting biomass into valuable chemicals. Complicated additional steps are usually required, as in the case of hydrodeoxygenation of pyrolysis oil or production of various paraffins/olefins via Fischer-Tropsch synthesis from biomass-derived syngas. Furthermore, a common drawback for both pyrolysis and gasification methods is the deactivation of catalysts due to coke formation.

In this study, we demonstrate a single-step process without catalysts that generates oxygen-free hydrocarbons with high yield. We will report low temperature plasma conversion of lignocellulosic biomass in a gram-scale radio frequency reactor. Preliminary work shows that the plasma rapidly converts solid feedstock into primarily small chain hydrocarbons. Effects of process parameters such as plasma power, plasma gas composition, operating pressure and biomass feedstock will be presented, along with a techno-economic analysis of the process.

*** Falicov Student Award Finalist**

[1] U.S. Department of Energy, "2016 Billion-Ton Report: Advancing Domestic Resources for a Thriving Bioeconomy," Oak Ridge National Laboratory, Volume 1, 2016.

2:40pm **PB+BI+PS-MoA4 Growth of Plasma-Treated Corn Seeds under Realistic Conditions**, ***Chisung Ahn***, *I.A. Shchelkanov*, University of Illinois at Urbana-Champaign, *J. Gill*, AgReliant Genetics, LLC, *D.N. Ruzic*, University of Illinois at Urbana-Champaign

Plasma treatments of agricultural seeds have been proposed to enhance germination and improve growth rate by elimination of unwanted microbes, water absorption control, introducing functional groups or other effects. In particular, making a plasma-activated medium which has nitrogen as its main component can affect the efficiency of water use in the germination phase. There is also a remarkable complementary effect between plasma treatments and biological pre-treatment. To confirm the plasma effects seen in the lab scale, this work seeks to investigate a variety of seed treatments on an industrial agriculture scale.

In this study, various kinds of plasma were introduced for mass treatment of corn seeds to investigate the germination and growth effect. The seed utilized for the experiment is an elite 111 days yellow dent corn hybrid adapted to the US Midwest. Seven experimental treatments were evaluated: Control, Biological treatment only, Plasma Activated Water (PAW) treatment, Atmospheric Pressure DBD Plasma, Microwave Atmospheric Plasma, Vacuum Plasma and Just Vacuum. The corn seeds were treated uniformly by one-layer arrangement on each stage without burning or blackening by the plasma. Each treatment was performed on a total of 1800 corn seeds. Seed of each experimental condition were treated with the recommended rate of Poncho Votivo with Acceleron, a commercial biological seed treatment that helps protect the seeds from fungus, insects, and nematodes after planting. The 1800 seeds were divided evenly into three replications with 100 seeds planted for each replication at six unique locations across central Illinois. The results of germination, growth, and product yield over the 2017 growing season will be presented.

3:00pm **PB+BI+PS-MoA5 Advanced Control of Plasma Medical Devices**, ***David Graves***, University of California, Berkeley, *A. Mesbah*, *D. Gidon*, University of California at Berkeley

Atmospheric pressure plasma jets (APPJs) have widespread use in plasma medicine. This presentation aims to demonstrate the importance of using advanced control strategies for safe, reproducible, and therapeutically effective application of APPJs for dose delivery to a target substrate. Key challenges in advanced control of APPJs arise from: (i) the multivariable, nonlinear nature of system dynamics, (ii) the need to constrain the system operation within an operating region that ensures safe plasma treatment, and (iii) the cumulative, non-decreasing nature of dose metrics. To systematically address these challenges, we propose a model predictive control (MPC) strategy for real-time control of a radio-frequency APPJ in argon. To this end, a lumped-parameter, physics-based model is developed for describing the jet dynamics, and cumulative dose metrics are defined for quantifying the thermal and non-thermal energy effects of the plasma on substrate. The closed-loop performance of the MPC strategy is compared to that of basic proportional-integral control. Simulation results indicate that MPC provides a versatile framework for dose delivery in the presence of system disturbances, while fulfilling the safety and practical constraints of APPJ operation. In addition, we demonstrate the use of advanced control in experimental APPJ systems. Advanced control can lead to unprecedented opportunities for effective dose delivery in plasma medicine.

3:20pm **PB+BI+PS-MoA6 Fingerprinting Different Plasma Sources for Biomedical Applications**, ***Katharina Stapelmann***, North Carolina State University, *K. Wende*, INP Greifswald, Germany, *B. Offerhaus*, Ruhr University Bochum, Germany, *C. Verlackt*, University of Antwerp, Belgium, *C. Klinkhammer*, *F. Kogelheide*, *M. Havenith*, Ruhr University Bochum, Germany, *A. Bogaerts*, University of Antwerp, Belgium, *P. Awakowicz*, *J-W. Lackmann*, Ruhr University Bochum, Germany

Cold technical plasmas (CAPs) are under investigation in various fields of industry and medicine. First clinical trials using CAPs for wound healing show promising results. Preliminary results in other fields of plasma medicine, such as cancer treatment, offer promising findings as well. However, the interactions of technical plasmas with biological samples on a molecular level are only partly understood. CAPs generate complex chemical cocktails, having an impact on various biological structures [1]. The impact can vary betweeen different sources, e.g. by employing a DBD in air or a noble gas driven jet. A better understanding of the chemical reactions occuring would allow to tune and adapt plasmas for specific tasks. One prevalent impact of plasma on biological targets has been the chemical modification of thiol groups, which carry out various important tasks in the human body, such as cell signaling and protein structure formation. As thiols are involved in many regulatory and functional processes in tissues, an in-depth understanding of the impact of plasma treatment on thiols is highly relevant for a safe application of plasmas in medicine.

In order to get insight into these interactions, various thiol-containing model substrates, such as the amino acid cysteine and larger target substrates, were investigated with different plasma sources [2,3]. By using a standard target substrate, the impact of various plasma sources can be compared not by means of a physical characterization but by their chemical impact. Stepwise increase of sample complexity allows monitoring how thiols are affected by plasma treatment in an ever more complex environment. The combination of experimental evidence and MD simulations permit a comprehensive overview of chemical processes induced by plasma treatment. This combined approach allows a more throughout investigation of modifications on a molecular level and helps to understand fundamental plasma chemistry processes. Furthermore, knowledge about the substrate chemistry enables the use of test substrates as bio-probes for the investigation of plasma chemistry in other industrial fields [4].

[1] Lackmann J-W and Bandow J E 2014 *Appl. Microbiol. Biotechnol.* **98** 6205-13

[2] Kogelheide F *et al* 2016 *J. Phys. D: Appl. Phys.***49** 084004

[3] Lackmann J-W *et al*. 2015 *J. Phys. D: Appl. Phys*. **48** 494003

[4] Offerhaus B *et al*. 2017, accepted in *Plasma Process Polym.*

4:00pm **PB+BI+PS-MoA8 Exploring Plasma Coatings Comprising Vertical Chemical Gradients and Multilayers for Biomedical Applications**, ***Dirk Hegemann***, *M. Vandenbossche*, *M. Heuberger*, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland **INVITED**

The common definition of "surface" includes surface atoms and molecules, practically extending at the most some three layers – typically one nanometer. This definition is justified by the fact that many surface properties related to symmetry breaking, such as chemistry, wettability or surface charge are determined by the top most surface layer. The common understanding is that this thin surface region also determines how molecules adsorb onto it. Far less explored are effects due to interactions with deeper subsurface layers, i.e. the region extending over several nanometers underneath the "surface". This subsurface region, however, might significantly contribute to molecular adsorption via long-range (i.e. few nm) interaction forces; mainly interactions with fixed dipoles, water structuring and Van der Waals interactions. A key factor to make use of these interaction forces thus lies in the hydration of the subsurface region.

Therefore, stable plasma polymer films made of siloxanes were designed that contain a hydrophilic nanoporous base layer terminated by a hydrophobic top coating, nominally 2-12 nm thick. As a model molecule, bovine serum albumin (BSA) was selected and its adsorption was studied on gradient coatings as well as reference coatings immersed in water or phosphate buffered saline (PBS). As a result, protein adsorption was reduced on hydrated hydrophobic/hydrophilic gradient coatings, while dry or dehydrated films show the same adsorption as the reference hydrophobic plasma polymer film.

Furthermore, double layers made of a terminal a-C:H:O plasma polymer layer (1-5 nm thick) on a-C:H:N base layers were investigated comprising a gradient in carboxylic-to-amino groups. Again conditions were selected to obtain stable plasma polymer films when immersed in aqueous environments. Adsorption using the green fluorescent protein (GFP) on different double layers and reference layers were examined. Enhanced protein adsorption was observed for the 1 nm thick terminal layer of a-C:H:O on a-C:H:N as compared to each reference layer.

Hence the vertical nanostructure of a functional surface implies an additional factor to control adsorption processes. Protein adsorption, selectivity and bioactivity can thus be controlled by using subsurface effects being an important finding for biomedical applications such as e.g. tissue engineering.

MEMS and NEMS Group
Room: 24 - Session MN+BI+EM+SS+TR-TuM

Microelectromechanics: Relays to RF/Surfaces in Micro- and Nano- Systems

Moderators: Sushma Kotru, The University of Alabama, Roya Maboudian, University of California at Berkeley

8:00am **MN+BI+EM+SS+TR-TuM1 The Industrialization of MEMS through Materials Innovations**, ***Chris Keimel***, Menlo Micro **INVITED**

For the past 150 years, the mechanical relay was one of the original building blocks of electrical systems, for power electronics, controls, and even computing. With the introduction of the transistor in the middle of the 20th century, many industries were transformed with the introduction of ubiquitous, low-cost switches (solid-state) that could be manufactured by the billions with highly advanced equipment and manufacturing processes. Still today, many industries, especially power distribution and controls, are still not able to live with the tradeoffs of solid-state technologies (leakages, losses, lack of air-gap, thermal) and continue to employ large, slow, and costly mechanical relays which have evolved only slightly over the past 50+ years. The miniaturization of the mechanical relay through MEMS technology, coupled with materials innovations, will enable a new class of devices capable of connecting (wireless control) and controlling (distributed power) today's and the futures billions of automated electrical nodes.

We have developed electrostatically actuated MEMS relays capable of switching in ~3usec, sustaining more than 400V across its open contacts and controlling loads of 10s of watts to a few kilowatts. Ohmic MEMS switch with creep resistant metal alloy beams, and a highly reliable ruthenium contact has been developed based on methodical failure mode analysis taking into account material, mechanical and electrical constraints. The ohmic relays, when applied to RF applications, deliver multi throw configurations capable of <0.3dB insertion loss from DC to 3GHz combined with the ability to handle 25W of RF power.

A metal MEMS switch technology has been developed from the ground up through material, process, device, package and electronic integration innovations. The combination of fast microsecond switching speed and broadband (DC to RF) signal operation along with the ability to control amperes of current and sustain hundreds of volts across micron sized air gaps has enabled the miniaturization of the mechanical relay for broad ranging applications from wireless infrastructure to the Industrial IOT.

8:40am **MN+BI+EM+SS+TR-TuM3 Electron-Phonon Waltz: Acoustoelectrics in MEMS**, ***Dana Weinstein***, Purdue University **INVITED**

The Acoustoelectric (AE) effect is a result of the interaction between free charge carriers and the electrical deformation potential produced by a propagating elastic wave in the piezoelectric. When an external DC electric field is applied across the semiconductor in the direction of the propagating wave, a drift velocity (v_d) is imparted to the free carriers. If the drift velocity is slower than (or opposite to) the acoustic wave velocity (v_s), the electrical deformation potential lags behind the strain wave. This phase lag not only decreases the acoustic wave velocity, but also transfers energy from the acoustic wave to the electrons, increasing the acoustic losses. When a sufficient DC field is applied to cause the drift velocity to exceed the acoustic wave velocity, the electrical deformation potential now leads the strain wave. This transfers energy from the electrons to the acoustic wave, resulting in an increased acoustic velocity and net acoustic gain [1,2,3,4].

A large body of work based on AE was established in the 1960s and 70s, resulting in a range of devices from phase shifters to correlators. With the development of new materials and new processing needs, there has been a recent resurgence of interest in this field, particularly for its amplifying and inherently non-reciprocal properties. Here, we discuss the implications of the AE effect for GHz frequency electromechanical signal processing. RF applications, linearity, and noise of the AE effect will be examined. Finally, benefits and limitations of prospective semiconductor/piezoelectric material systems will be discussed.

[1] J. H. McFee, "Transmission and Amplification of Acoustic Waves in Piezoelectric Semiconductors," Phys. Acous. A, vol. 4, 1-45 (1966).

[2] D. L. White, "Amplification of Ultrasonic Waves in Piezoelectric Semiconductors," Journal of Applied Physics, vol. 33, no. 8, pp. 2547-2554, Aug. 1962.

[3] B. K. Ridley, "Space charge waves and the piezo-electric interaction in 2D semiconducting structures," Semiconductor Science and Technology, vol. 3, no. 6, p. 542, 1988.

[4] G. S. Kino and T. M. Reeder, "A normal mode theory for the Rayleigh wave amplifier," in IEEE Transactions on Electronic Devices, vol. 18, no. 10, pp. 909-920, Oct. 1971.

9:20am **MN+BI+EM+SS+TR-TuM5 Autonomous Oscillations of a MEMS Resonator**, ***David Czaplewski***, Center for Nanoscale Materials, Argonne National Laboratory, *C. Chen, D. Lopez*, Argonne National Laboratory, *D.H. Zanette*, Centro Atomico Bariloche and Instituto Balseiro, *S.W. Shaw*, Florida Institute of Technology

Resonant MEMS and NEMS structures are used in a wide variety of applications including mass and force sensing, time keeping, and quantum information. For all MEMS and NEMS resonators, energy is lost every cycle of oscillation to the environment (modeled as a coupled bath). If this energy is not restored by an external source, the amplitude of the resonant motion will decrease toward zero. This well-known effect is commonly referred to as "ring-down". For linear resonators, the frequency of the resonator will remain constant and the amplitude will decreases exponentially while for non-linear resonators, the amplitude will decrease exponentially and the frequency will simultaneously decrease toward the linear response due to the amplitude-frequency (a-f) effect. However, we demonstrate a non-linear resonator that has constant frequency and an amplitude that does not decay for a given period of time (~ 0.1 s) after discontinuing the restoring energy to the system. We call this time "coherence time" because the amplitude and frequency of the oscillation does not decay when the restoring energy is removed. In essence, the resonator is autonomous during coherence time. Unfortunately or fortunately, this behavior does not violate the second law of thermodynamics. The behavior can be explained by looking at the entire system. We drive a non-linear MEMS resonator to a frequency where the primary mode couples with another internal mode. When the resonator is actively driven, the higher order mode receives energy from the primary mode. When the external energy is discontinued, this energy is restored back to the primary mode allowing the primary mode to continue to oscillate. However, once the energy stored in the higher order mode is depleted (its amplitude is near zero), the behavior of the primary mode begins to "ring-down". During this talk, I will show characteristics of the coupled modes including operation with constant frequency and a non-decaying amplitude for a period of time with no drive.

9:40am **MN+BI+EM+SS+TR-TuM6 Metallic Glass for MEMS Microphone Device**, ***MaiPhuong Nguyen***, WPI-Advanced Institute for Materials Research (WPI-AIMR)/ Micro System Integration Center (μSIC), Tohoku University, Japan, *J. Froemel*, WPI-Advanced Institute for Materials Research (WPI-AIMR), Tohoku University, Japan, *S. Tanaka*, Graduate School of Engineering/ Micro System Integration Center (μSIC), Tohoku University, Japan

Micro Electro-Mechanical Systems (MEMS) microphones have been extensively developed and introduce into mobile phones market with high performance such as high signal to noise ratio, good sensitivity, and power consumption and good reliability in term of packages. Up to now, most studies have been focused on the improvement of sensitivity of microphone which is proportional to the compliance of the membrane. However, no significant progress has been achieved due to the limitation of material itself. Generally, single crystal and polycrystalline silicon based devices are brittle and fracture causing the interior defects during the fabrication processes. Therefore, the research of new materials to substitute polycrystalline silicon is necessary. Amorphous metals exhibit no grain boundaries, crystal defects and excellent mechanical properties such as fatigue free, large elastic limit, high strength, corrosion resistance which has been promising materials for MEMS devices such as micro-scanner, RF MEMS varactor, capacitive switch ... Metallic glasses are a kind of amorphous alloy exhibiting viscous flow at a certain temperature range so-called "supercooled liquid region". In the supercooled liquid region, metallic glasses can be easily produced through a variety of fast-cooling methods and have excellent mechanical formability. In addition, metallic glass thin films are easily prepared on Si or SiO_2 substrates by sputtering technique which is compatible with MEMS processes such as photolithography, dry or wet etching and lift off processing. Therefore, characterization and fabrication of metallic glasses films deposited by sputtering for MEMS microphone will be studied.

The CoTaB films with thicknesses in the range of 100 nm to several micrometers have been successful deposited on thermal SiO2 substrates by rf-sputter technique. The amorphous structure with smooth surface and negligible magnetic property was confirmed by TEM, AFM, XRD and SQUIDS measurement, respectively. The metallic glass behavior was investigated by DSC analysis which shows the glass transition and crystalline

temperature of 700 and 720.9 C, respectively. In addition, the mechanical properties such as stress, stress gradient and Young modulus have been studied by using pointer and cantilever structure. Co-based metallic glass exhibited tensile and compressive stress depending on sputter conditions, thicknesses as well as further treatment process. Additional results will be presented in detail at the conference with an emphasis on the dependence of the process conditions.

11:00am **MN+BI+EM+SS+TR-TuM10 Role of Surfaces in Assembly of Ceria Nanostructures**, ***Sudipta Seal***, University of Central Florida **INVITED**

Cerium is a rare earth element of the lanthanide series with a fluorite lattice structure. The cerium atom can exist in either 3+ or 4+ states, and may alternate between the two in a redox reaction that is more pronounced in nanoparticles. However, the physicochemical properties of a nanocrystal assembly can be different from the properties of both the individual nanoparticles and the bulk phase. We have synthesized ceria nanoparticles in various medium and studied the self-assembly of particles to octahedral and star shaped nanostructure assembly. It was further identified that the concentration of Ce4+ in nanoceria decreases over time, further controlling the surface chemistry. We will also highlight some of the key aspects of self-assembly of CeO_2 into nanorods. The surface area available and the orientation of crystallographic planes in ceria nanostructures highly regulate the catalytic property at nanoscale as evident by high resolution TEM. Further we discuss the role of Madelung energy and its relation to the catalytic activity, which is important in sensing and other analyte interactions. The surface chemistry or the ratio of Ce^{3+}/Ce^{4+} can be extensively modulated by the assembly process. At the end we report, the feasibility of a novel H_2O_2 based electrochemical sensor that directly measures the current response of multivalent ceria in presence of H_2O_2. The fabricated sensor showed a picomolar range limit of detection while remaining insensitive to interfering species. Peroxide sensing is very important in biologically relevant oxidative stress in cells. It was observed that a lower ratio of Ce^{3+}:Ce^{4+} redox states elicits a greater current response towards H_2O_2 The detection of such electroactive analytes make it easier to detect using normal nanoparticle modified electrodes, thereby eliminating the use of organic mediators.

11:40am **MN+BI+EM+SS+TR-TuM12 Optimization and Nano-characterization of Electrostrictive Response of Gd-doped Ceria Actuators**, ***Sidney Cohen***, *E. Mishuk, E. Makagon, E. Wachtel, K. Rechav, R. Popovitz-Biro, I. Lubomirsky*, Weizmann Institute of Science, Israel

Gd-doped ceria (GDC) recently attracted great interest due to its non-classical (non-Newnham) electrostrictive behavior. Although the material is well-known for its ionic conduction properties and use in solid-oxide fuel-cells, it also holds great promise for incorporation into MEMS devices because it is completely inert with respect to silicon compounds. The fact that GDC is lead-free is particularly appealing.

Here, we demonstrate fabrication and testing of membrane actuators formed with near 100% yield by a relatively simple, low temperature process. Preparation of these devices involves magnetron-sputtering of a thin film of GDC onto Si, and further processing using standard micromachining, resulting in free-standing membranes. Bridge and cantilever structures have been fabricated as well, to explore the possibility for diverse functional devices. The films were structurally characterized by electron microscopy and by x-ray diffraction, whereas electrical characterization was performed using impedance spectroscopy and cyclic voltammetry. These electrical tests revealed details of the conduction mechanism, role of the contacts, and charge-trapping.

Scanning probe microscopy was applied to quantitatively characterize the energetics and mechanics of the electromechanical response: Displacement of a circular membrane was measured by recording displacement of the cantilever probe under feedback as a function of frequency and applied voltage, and temporal Joule heating recorded using a scanning thermal probe. These measurements support calculations of heat-induced strain at high frequencies. These measurements showed that displacements obtained are sufficient for practical applications and provided insights on the factors controlling performance.

12:00pm **MN+BI+EM+SS+TR-TuM13 Sustainable Thermoregeneration of Plastrons on Superhydrophobic Surfaces**, ***Tomer Simovich***, Ruhr-University Bochum, Germany, *J. Arnott*, The University of Melbourne, Australia, *A. Rosenhahn*, Ruhr-University Bochum, Germany, *R.N. Lamb*, Canadian Light Source, Canada

A popular and desirable function of superhydrophobic coatings is their remarkable ability to retain an entrapped layer of air, called a plastron, when submerged underwater. The drawback is that the air layer is short lived due to solvation into the surrounding liquid. Liquid gas extraction has been explored for the purpose of respiration through oxygen filtering or generation via chemical reaction. Manipulating solubility through temperature has been attempted but due to its inefficiencies has not been developed further into functioning technologies. This paper introduces a novel method of extracting gas from water to generate enough air to permanently stabilize a plastron on superhydrophobic surfaces for sustained anti-fouling, rust resistance and drag reduction abilities. This method involves locally heating the liquid surrounding a superhydrophobic coating, reducing gas solubility causing the gas to migrate to the liquid-air interface. Due to the low surface energy of superhydrophobic coatings, nucleation of supersaturated gasses occurs preferentially at the coating interface, thereby replenishing the plastron. This requires a relatively low energy input, due to the small volume of water required to be locally heated combined with the small temperature differential induced between substrate and liquid. This process may be more environmentally sustainable in comparison to competing methods. With a constant supply of equilibrated water and minimal energy input, the plastron can survive indefinitely without need for the mechanical application of additional gas.

Plasma Processing for Biomedical Applications Focus Topic
Room: 12 - Session PB+BI+PS-TuM

Plasma Medicine
Moderator: Katharina Stapelmann, Ruhr-University Bochum, Germany

8:00am **PB+BI+PS-TuM1 Spatial Distribution of Biological Effects Induced by Plasma Reactive Species**, ***Sylwia Ptasinska***, University of Notre Dame **INVITED**

Several *in vitro* and *in vivo* studies have been conducted in a variety of cancer cell lines that demonstrate the efficacy of cold plasmas in causing cell death since the advent of this new research area in the plasma physics community in 2010. Due to the complexity of both the plasma and biological systems, many questions must be answered to sharply improve our understanding of the physical, chemical, and biological processes underlying their interactions. However, since cold plasmas produce a cocktail of reactive oxygen species (ROS) and reactive nitrogen species (RNS), these species are believed to be key agents that can induce a number of biological effects, including impairment of cell substructures and even cell death. Moreover, cancer cells have proven to be more susceptible to damage by these reactive species than normal cells subjected to plasma exposure. The outcome of cell responses to plasma treatment has inspired the potential application of plasma as an effective and safe tool for novel cancer therapy. Our research focuses on investigations of nucleus DNA damage in cancer cells and bacterial inactivation caused by exposure to plasma reactive species. Initially, to detect ROS and RNS that reached the targeted biological systems we used semi-quantitative test strips, while to investigate biological effects in cells we used digital imaging or immunofluorescence microscopy. Recently, to obtain the high-resolved spatial distribution of DNA strand breaks we developed a workflow with algorithms for image analysis using CellProfiler and MATLAB, including background correction, cell segmentation, feature extraction, cell classification, and data visualization. This method well preserves the essential spatial information about cell distribution, which is critical because of the localized nature of the plasma jet treatment. By applying both supervised and unsupervised machine learning techniques to the images, we were also able to classify the cells according to different cell cycle phases, and thus obtain spatial information regarding plasma jet effects on cell cycle progression.

8:40am **PB+BI+PS-TuM3 Mechanisms of Cell Death in Prostate Epithelial Cells after Treatment with Low Temperature Plasma**, *J. Packer, A.M. Hirst, F.M. Frame*, ***Deborah O'Connell***, *N.J. Maitland*, University of York, UK

Low-temperature plasma (LTP) treatment of cancer cells have been explored for a variety of malignancies. These plasmas, operated at atmospheric pressure and close to room temperature, are efficient sources of reactive oxygen and nitrogen species (RONS), electric fields and photons, and can induce a variety of biological responses. There is an increasing clinical move towards focal therapy for more conservative management of prostate cancer, with reduced levels of common side effects such as incontinence and impotence compared with radical treatments, and promising outcomes. Low-temperature plasmas may offer such potential.

A dielectric barrier discharge jet, created within a glass tube surrounded by two electrodes (~ 6 kV applied sinusoidal voltage), with a helium plus 0.3% oxygen gas flow is used for these investigations. We have employed both purified tumour cells freshly extracted from prostate cancer patients, and matching, non-tumour cells from a distant region of the same prostate.

Freshly isolated primary tumour cells acts as a near patient model, which has recently confirmed differences in pharmacological susceptibility as compared with 30 year old established cell lines.

Treatment of primary prostate epithelial cells with LTP resulted in sigificant cell death in both normal and cancer cells; and no significant selectivity observed, as commonly reported. In addition, most cells appeared to die via a necrotic mechanism, rather than apoptosis, maybe as a result of the mitochondrial toxicities of the LTP-activated reactive oxygen species (ROS). However, some autophagy was also detected, which has been shown to act as a salvage pathway for sub-lethally damaged cells.

To determine which of the multiple plasma activated bio-reactive species are responsible for the cytotoxicity, we have explored immediate and longer-term effects on gene expression, with a particular focus on oxidative responses, in multiple patient samples. Comparative studies in the established cell lines indicated a delayed and different response, highlighting that cell lines don't always reflect the response of primary cells. Expression of 84 genes (mRNA by RT^2 arrays from Qiagen) was assessed at multiple time points, after a 3 minute LTP treatment, and candidate genes/response pathways were identified. Immunofluorescence and western blotting were used to verify changes in protein expression. The response varied according to the clinical grade of the tumour (including a remarkable downregulation of 18 factors only seen in the highest grade tumours). All epithelial cells showed a stimulation of transcription factor-driven anti-oxidative response, as a potential resistance mechanism.

9:00am **PB+BI+PS-TuM4 Selective Antitumor Effect of the Plasma-Activated Medium Produced by Atmospheric Pressure Plasma with High Plasma Density**, ***Yohei Takahashi***, *Y. Taki*, Nikon Corporation, Japan, *K. Takeda*, Meijo University, Japan, *H. Hashizume, H. Tanaka, M. Hori*, Nagoya University, Japan

Recently, atmospheric pressure plasma has been widely developed for the applications on various fields, such as synthesis approaches, surface modification, sterilization, etc. Especially, cancer therapy using atmospheric pressure plasma is one of the most attractive applications. The culture medium irradiated with the atmospheric pressure plasma was called Plasma-Activated Medium (PAM), which exhibited the selective apoptotic cell death of cancer cells. In this study, we have demonstrated the antitumor effect of medium induced by irradiation of atmospheric pressure plasma with high plasma density and compared the cell survival between cancer and normal cells, which showed that the selective apoptotic cell death was achieved. Additionally, the basic diagnostics of the plasma and the analysis of the PAM were performed and the relation with the antitumor effects was discussed. The emission peak of OH radical ($A^2\Sigma$-$X^2\Pi$) was observed in the atmospheric pressure plasma. This transition is the intense systems emitted by low temperature plasmas containing even a small amount of H_2O. The selective apoptotic cell death effect by treatment with PAM produced by atmospheric pressure plasma irradiation was confirmed. The survival of cancer cell after incubation in PAM was greatly lower than that of normal cell was. The productions of H_2O_2 and NO_2^- by irradiation of high density plasma were detected by the colorimetric assay. The synergistic effect of H_2O_2 and NO_2^- in PAM is considered to affect the proliferation of cancer cells.

9:20am **PB+BI+PS-TuM5 Multiplex Coherent Anti-Stokes Raman Scattering (CARS) Observations of HeLa Cells Cultured in Non-equilibrium Atmospheric Pressure-Plasma-Activated Medium (PAM)**, ***Kenji Ishikawa***, *R. Furuta*, Nagoya University, Japan, *K. Takeda, T. Ohta, M. Ito*, Meijo University, Japan, *H. Hashizume, H. Tanaka, H. Kondo, M. Sekine, M. Hori*, Nagoya University, Japan

Non-equilibrium atmospheric-pressure plasma (NEAPP) affects cancer cells not only directly[1] but also indirectly through exposure of cells to medium irradiated beforehand with NEAPP (i.e., plasma-activated medium [PAM]).[2] Recent studies have revealed that NEAPP irradiation generates reactive oxygen and nitrogen species (RONS) in the gas phase and relatively long-lived RONS such as hydrogen peroxide, nitrites and nitrates in the aqueous phase.[3] To further elucidate a cell-death mechanism in more detail, the present study focused on the direct analysis of PAM-induced intracellular molecules such as lipids, acylglycerol, triglyceride, adiposome in HeLa cells as cervical cancer cells. Lipid droplets (LDs) are dynamic organelles with complex and interesting biological functions that go beyond mere energy storage and are important in lipid homeostasis and metabolism. To evaluate LDs, coherent anti-Stokes Raman scattering (CARS) microscopy was used. The observation-results by multiplex coherent anti-Stokes Raman scattering (CARS) microscopy elucidated the mechanism underlying the apoptosis of HeLa cells in cultivating in PAM, leading to be simultaneously occurred the exhaustion of LDs in the cells in contrast to the accumulation, while the activation of caspase-3/7 was induced, though accumulation in lipid droplets (LDs) and lipid metabolism in the normal apoptosis of HeLa cells with activation of caspase-3/7 was previously reported.

Acknowledgement: This study was supported in part by the JSPS-KAKENHI (No. 24108002).

1 S. Iseki et al., Appl. Phys. Lett. **100**, 113702 (2012); 2 H. Tanaka et al., Plasma Med. **2**, 207 (2012); 3 N. Kurake et al., Arch. Biochem. Biophys. **605**, 102 (2016).

9:40am **PB+BI+PS-TuM6 Plasma Medicine - From Bench to Bedside**, ***Kai Masur***, *T. von Woedtke, K.D. Weltmann*, Leibniz Institute for Plasma Research and Technology, Germany

During the last decade it became possible to stimulate eukaryotic cells by applying non-thermal plasma. The same plasmas can be used to kill micororganisms - both in vitro and in vivo. However, there is the need to understand the processes of how electrical fields, ROS /RNS and UV generation influence the cellular activities in order to find the balance between stimulating or killing biological matter. Therefore, much effort had been done by in order to control the plasma components and finally modulate biological activities. It was shown before that argon plasma treatment leads in a time dependent manner to an activation of cell proliferation in human skin samples. Furthermore, it is known that non-thermal plasma is able to diminish bacterial load of cultured microorganisms *in vitro* independent of the strain. Even more, plasma reduces the amount of antibiotic resistant bacteria in the same manner as their non-resistant strains.

In 2013, new developed plasma sources were certified as medical products and since than those devises are in clinical application. Here we report on our findings on plasma treated chronic wounds and the efficacy of non-thermal plasma. There is a very promising rate of healed and improved wounds, which demonstrate that plasma indeed can help patients with chronic wounds. However, there are some discrepancies between *in vitro* findings and results from patient treatment. The bacterial reduction is lower than in *in vitro* studies, but skin regeneration seems not to be dependent on complete bacterial removal. On the other hand, patient treatment reveals new facts about the positive effects of plasma treatment of persisting wounds. Here we summarize the positive results of plasma mediated stimulation of patients with chronic wounds.

11:00am **PB+BI+PS-TuM10 Plasma Medicine, RONS, Tissue and Cell Models**, ***Rob Short***, University of Lancaster, UK, *E. Szili*, University of South Australia, Australia **INVITED**

Electrically-generated cold plasma gas discharges are being intensively researched for novel applications in medicine and biology. Significant attention is being given to the reactive oxygen and nitrogen species (RONS), initially generated upon plasma-air interactions that are delivered to biological systems. The effects of plasma exposure are observed deep within tissue, to millimetre depths and within cells. However, very little is known about the exact nature of the initial plasma-tissue interactions, including RONS speciation and delivery depth, or how plasma RONS intervene in biological processes. In this presentation I will focus on current research using tissue and cell models to learn more about the plasma delivery and transport of RONS into tissue and cells. I will argue this research is vital to establishing an underpinning knowledge that is needed to realise the full potential of plasma in medicine and biology.

11:40am **PB+BI+PS-TuM12 Non-thermal Plasmas in Biomedical Applications– Beyond the Long Lived Species**, ***Kristian Wende***, *J. Volzke*, INP Greifswald, Germany, *J-W. Lackmann*, Ruhr University Bochum, Germany, *H. Jablonowski, S. Bekeschus*, INP Greifswald, Germany, *K. Stapelmann*, Ruhr-University Bochum, Germany, *S. Hasse*, INP Greifswald, Germany, *P.J. Bruggeman*, University of Minnesota, *K.D. Weltmann*, INP Greifswald, Germany

Non-thermal plasmas have reached evidence level 2 regarding acceleration of wound healing and in certain aspects of cancer treatment, with a growing community of physicians successfully using it (plasma medicine). Key players in such biomedical applications are reactive oxygen or nitrogen species (ROS/RNS), which are deposited in either tissue (in vivo) or liquid (in vitro) and subsequently influence cellular redox signaling. A huge variety of plasma sources for potential application has been developed and comparing these sources in respect of safety and efficacy remains challenging but desirable.

One aspect can be the identification and quantification of the sources ROS/RNS deposition in liquids. However, due to the short lifetime of many ROS/RNS and limited specificity of available probes their detection is demanding. To meet this challenge, we applied a variety of analytical techniques including high-resolution mass spectrometry of small molecules (cysteine, tyrosine), ion chromatography (RNS detection), electron paramagnetic resonance spectroscopy (O, O_3, $^1O_2$, O_2^-, OH), and colorimetric assays to infer on dominant active species. Two argon plasma jets (MHz jet kinpen, RF jet) and a helium based RF jet (COST jet) were investigated. In addition, cell biology experiments allowed a first estimation of the biological impact of plasma treated small molecules.

A large number of covalent modifications have been detected and in part identified. The majority of changes to the chemical structure of cysteine was found in the vicinity of the thiol group, while in tyrosine the aromatic ring was targeted. The resulting products also occur in physiological situations in vivo, allowing to conclude that the covalent modification of small organic molecules is part of the mechanism of direct plasma-cell interaction. Predominantly short-lived oxygen species were found to be of relevance regarding the chemical and biological impact of plasma, challenging the popular concept of remote treatment (e.g. plasma treated buffers).

12:00pm **PB+BI+PS-TuM13 Effects of Oxygen or Water in Plasma Jet Environment and Feed Gas on DNA Damage**, ***Ek Adhikari***, *V. Samara, S. Ptasinska*, University of Notre Dame

Atmospheric pressure plasma jet (APPJ) sources have been explored for applications in industry and medicine. Since environmental conditions such as room temperature and humidity fluctuate, two identical APPJ sources operating at various places and time might perform differently. An APPJ operating in a controlled environment may be able to overcome that issue. Moreover, the interaction of plasma components (e.g., ions, electrons, UV light) with the air in the atmosphere generates the reactive oxygen species (ROS) and reactive nitrogen species (RNS) in the plasma jet [1]. These reactive species can be controlled by adjusting a fraction of oxygen and water vapor in the plasma jet environment and the feed gas. To create a controlled environment for a plasma source, a helium APPJ source was operated in a cylindrical glass chamber with an ambient pressure and filled with pure nitrogen gas along with a fraction of oxygen and water vapor. This APPJ source was used to induce damage in aqueous DNA. The fraction of different types of damaged DNA such as single strand breaks (SSBs) and double strand breaks (DSBs), which were induced due to plasma irradiation, and undamaged DNA were quantified by using agarose gel electrophoresis. We observed that a moderate amount of oxygen and water vapor in the environment, as well as in the feed gas, increases the level of DNA damage.

1. K. Arjunan, V. Sharma, and S. Ptasinska, Int. J. Mol. Sci. **16**, 2971 (2015).

2D Materials Focus Topic
Room: 16 - Session 2D+BI+MN+SS-TuA

Surface Chemistry, Functionalization, Bio and Sensor Applications
Moderator: Matthias Batzill, University of South Florida

2:20pm **2D+BI+MN+SS-TuA1 Preserving Chemically Modified Graphene from Thermal and Chemical Loss of Functionality**, ***Keith Whitener***, *W.-K. Lee*, Naval Research Laboratory, *R. Stine*, NOVA Research, *J.T. Robinson, D. Kidwell, C. Tamanaha, P.E. Sheehan*, Naval Research Laboratory

Chemical functionalization can dramatically alter graphene's properties, enabling one to tune its chemical and physical properties for a wide range of applications. To be useful, these modifications must be stable; however, some of these chemical modifications can be unstable, allowing the material to partially revert to unfunctionalized graphene over time. In this talk, we present our detailed studies of the kinetics of graphene hydrogenation and dehydrogenation. Single layer hydrogenated graphene can be dehydrogenated via thermal, mechanical, and chemical routes. Interestingly, bilayer graphene is much more robust to both chemical and thermal dehydrogenation than is single layer graphene. Possible mechanisms for this difference in reactivity will be discussed. Finally, we leverage the insights from these studies to first fabricate functional chemistries and electronic devices on graphene and then to transfer the devices *in toto* onto arbitrary substrates including biological ones. This enables graphene to act like a chemical "sticky note", transferring chemical and physical properties from one surface to another.

2:40pm **2D+BI+MN+SS-TuA2 Chemical Vapor Sensing with 1T/2H Phase Engineered MoX_2 Films**, ***Adam Friedman***, *A.T. Hanbicki, F.K. Perkins, G.G. Jernigan, J.C. Culbertson, P.M. Campbell*, Naval Research Laboratory

Transition metal dichalcogenides (TMDs) show remarkable potential for use in chemical vapor sensor devices. They are inexpensive, inherently flexible, low-power, can be grown in large areas, and have shown high sensitivity and selectivity to electron donor analyte molecules. However, for most devices the conductance response is dominated by Schottky contacts, to the detriment of the sensitivity and obscuring the intrinsic sensing capability of the devices. We use contact engineering to transition the contacts in a MoS_2 FET-based chemical vapor sensor to the 1T conducting phase, leaving the channel in the 2H semiconducting state, thus providing functional Ohmic contacts to the device. We show that the resultant sensors have greatly improved electrical characteristics, are more selective, and recover fully after chemical vapor exposure—all major improvements to previous MoS_2 sensor devices. We study the dynamics of the sensing reactions identifying two possible models for the chemical sensing reaction with physisorption likely dominant. Additionally, we present both conductance and optical evidence that the phase transition can be induced in MoX_2 films by a saturating dose of strong electron donor vapor. We find that the conductance response to strong electron donors in both monolayer MoS_2 and $MoSe_2$ FET devices ceases after moderate exposure, with final value of the conductance being on order of that expected for the 1T phase. We also examine chemically exposed TMD films intermittently interrogated with Raman and photoluminescence spectroscopy. We observe the appearance of weak characteristic 1T phase Raman features for MoS_2 and we observed a quenching of the photoluminescence of both TMD films that is recoverable with annealing. The data cannot by explained solely by doping mechanisms. Our results suggest a mechanism for a new type of passive chemical vapor sensor.

[1] F.K. Perkins, A.L. Friedman, et al., *Nano Lett*. **13**, 668-673 (2013).

[2] A.L. Friedman, F.K. Perkins, et al., *Sol. St. Elec*. **101**, 2-7 (2014).

[3] A.L. Friedman, F.K. Perkins, et al., *Nanoscale***8**, 11445 (2016).

3:00pm **2D+BI+MN+SS-TuA3 Nanopores in 2D Materials**, ***Aleksandra Radenovic***, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland **INVITED**

Atomically thin nanopore membranes are considered to be a promising approach to achieve single base resolution with the ultimate aim of rapid and cheap DNA sequencing. Recently, we made advances in using nanopore platform for its integration with 2 D materials such as graphene or MoS2. Translocation of various types of DNA exhibits a signal amplitude that is five times higher than in the case of solid-state Si3N4 membranes and a SNR of more than 10. These features are highly desirable for event detection and we take advantage of them by showing the electric-field induced unfolding of a 48 kbp long DNA molecule within the nanopore which manifests itself in the quantization of the current drop. Although single nucleotide identification and DNA sequencing using biological pores have already been demonstrated their fragility, difficulties related to measuring pA-range ionic currents together with their dependence on biochemical reagents, make solid state nanopores an attractive alternative. In this talk I will address novel applications that address identification of single nucleotides but as well go beyond DNA sequencing. We use novel solid state nanopore platform based on atomically thin nanopore membranes in 2D materials such as graphene or molybdenum disulfide for DNA detection, sequencing, water desalination and osmotic power generation.

4:20pm **2D+BI+MN+SS-TuA7 Spectroscopic Observation of Oxygen Dissociation on Nitrogen-Doped Graphene**, ***Mattia Scardamaglia***, University of Mons, Belgium, *T. Susi*, University of Vienna, Austria, *C. Struzzi*, Unviersity of Mons, Belgium, *R. Snyders*, University of Mons, Belgium, *G. Di Santo, L. Petaccia*, Elettra-Sincrotrone Trieste, Italy, *C. Bittencourt*, University of Mons, Belgium

The reactivity of carbon nanomaterials towards oxygen is very poor, limiting their potential applications as low-cost, high-yield catalysts. However, nitrogen doping is an established way to introduce active sites that facilitate interaction with gases [1,2]. This boosts the materials' reactivity for gas/bio sensing and enhances their catalytic activity for the oxygen reduction reaction, promising to substitute expensive metals in fuel cell cathodes. Despite this interest, the role of differently bonded nitrogen dopants in the interaction with molecular oxygen is obscured by experimental challenges and has so far resisted clear conclusions. We study the interaction of molecular oxygen with graphene doped via nitro-gen plasma by in situ high-resolution synchrotron techniques, supported by density functional theory core level simulations [3,4]. The interaction with oxygen gas leads to the dissociation of the molecule and the formation of carbon-oxygen single bonds on the graphene surface, along with a band gap opening and a rounding of the Dirac cone. The change of the N 1s core level signal indicates that graphitic nitrogen is responsible for the observed mechanism: it catalyses the dissociation of an absorbed oxygen molecule, after which the two O atoms chemisorb with epoxy bonds to the nearest and next-nearest carbon neighbours of the graphitic nitrogen. Our findings help resolve existing controversies and offer compelling new evidence of the ORR pathway.

1. Liu, X., Dai, L. (2016) Carbon-Based Metal-Free Catalysts. Nat. Rev. Mater., 1, 16064.

2. Ni, S., Li, Z., Yang, J. (2012) Oxygen Molecule Dissociation on Carbon Nanostructures with Different Types of Nitrogen Doping. Nanoscale, 4, 1184-1189.

3. Scardamaglia, M. et al., (2016) Tuning Nitrogen Species to Control the Charge Carrier Concentration in Highly Doped Graphene. 2D Mater., 3, 11001.

4. Scardamaglia, M. et al., (2017) Spectroscopic observation of oxygen dissociation on nitrogen-doped graphene. Submitted

4:40pm **2D+BI+MN+SS-TuA8 Back to Black: Can Molecular Networks Preserve the Surface of Black Phosphorus?**, ***Vladimir Korolkov***, The University of Nottingham, UK, *I.G. Timokhin, R. Haubrichs*, CristalTech Sàrl, Switzerland, *S. Yang, M. Schröder*, University of Manchester, UK, *P.H. Beton*, The University of Nottingham, UK

Black phosphorus (BP), one of several allotropic forms of phosphorus, has a layered structure and is a narrow gap semiconductor with a bulk band gap of ~0.3 eV. Similar to other layered materials it can be exfoliated with scotch tape to form a single layer of black phosphorus known as phosphorene. Unlike gapless graphene, phosphorene has a band-gap which was predicted, and later confirmed to be ~2 eV. The band gap is thickness dependent and thus can be easily tuned. Since the first reports of exfoliation of BP, and some 100 years after the first high-pressure synthesis of black phosphorus crystals by Bridgman in 1914, phosphorene or few layered BP has been widely used to construct transistors, including flexible devices.

One of the biggest challenges in BP and phosphorene research remains its stability under atmospheric conditions.

In this work we explore a new route to the solution of this problem through an investigation of the compatibility of BP with the formation of supramolecular networks which have monolayer thickness and are stabilised by non-covalent in-plane interactions, specifically hydrogen bonding. We find that supramolecular networks can be formed on BP and demonstrate this for a mono-component nanoporous array of trimesic acid (TMA) and the bimolecular network formed by cyanuric acid (CA) and melamine (M). While the more open TMA array does not passivate the BP surface, the hexagonal melamine cyanurate (CA.M) array is highly effective and provides

protection under ambient conditions over a period of more than three months. In addition, we identify the orientation of the CA.M relative to the rows of phosphorus atoms at the surface and, normal to the rows, observe moiré effects which are characteristic of a well-ordered interfacial structure. We have further demonstrated that CA.M monolayers on BP provide a stable platform for the sequential growth of additional molecular layers, for example, 1,2,4,5-tetrakis(4-carboxyphenyl)benzene (TCPB), leading to the formation of a supramolecular heterostructure and demonstrating the facility for further functionalisation of the BP substrate.

Our work demonstrates that a single layer of CA.M can successfully passivate the surface of BP and preserve it intact for at least 3 months. We believe that this facile approach of depositing a passivating organic monolayer stabilised by in-plane non-covalent bonding could be extended to the protection of other two-dimensional materials with air sensitive atomically flat surfaces, and is likely compatible with other solvents and molecules.

The work also presents outstanding examples of high resolution AFM imaging achieved under ambient conditions.

5:00pm **2D+BI+MN+SS-TuA9 Defect-mediated Properties of Single-layer $MoSe_2$**, ***Sara Barja***, Materials Physics Center, San Sebastián, Spain, *S. Wickenburg, Z.-F. Liu, Y. Zhang*, Molecular Foundry, Lawrence Berkeley Lab, *A. Pulkin*, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland, *S. Refaely-Abramson, B. Schuler*, Molecular Foundry, Lawrence Berkeley Lab, *H. Ryu*, Lawrence Berkeley National Laboratory, *D. Qiu*, University of California at Berkeley, *M. M. Ugeda*, CIC nanoGUNE, Spain, *Z.-X. Shen*, Stanford Institute of Materials and Energy Sciences, *S.-K. Mo, M.B. Salmeron*, Lawrence Berkeley National Laboratory, *M.F. Crommie*, University of California at Berkeley, *D.F. Ogletree*, Molecular Foundry, Lawrence Berkeley Lab, *O.V. Yazyev*, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland, *J.B. Neaton, A. Weber-Bargioni*, Molecular Foundry, Lawrence Berkeley Lab **INVITED**

Properties of two-dimensional transition metal dichalcogenides are highly sensitive to the presence of defects in the crystal structure. A detailed understanding of the defect electronic structure may lead not only to the control of the material's properties through defect engineering towards a particular device application, but also may lead the emergence of novel physico-chemical functionalities. We show how linear mirror twin boundaries and individual atomic defects in single-layer $MoSe_2$ alter the electronic structure of the pristine semiconductor. Such linear and point defects tend to be highly localized in the plane, which imposes the need of experimental and theoretical characterization of the defects at the atomic level. Using non-contact atomic force microscopy and scanning tunneling spectroscopy, we directly correlate the morphology and electronic properties of structural defects in $MoSe_2$ at the defect-length scale. We provide direct evidence for the existence of isolated, one-dimensional charge density waves at mirror twin boundaries in single-layer $MoSe_2$. We also determine the local density of states of Se vacancies in monolayer $MoSe_2$ and discuss the correlation to density functional theory calculations, studying the role of the GW approximation to reproduce the energetics of the valence and conduction band as measured in the experimental dI/dV spectra.

5:40pm **2D+BI+MN+SS-TuA11 Scalable Flexible Graphene Gate TMD Biosensors**, ***RamSurya Gona***, *C.H. Naylor, A.T. Johnson*, University of Pennsylvania

Two dimensional transition metal dichalcogenides, such as MoS_2 and WS_2, have been shown to be promising materials for use in bio-sensing. I will present our work on the fabrication of scalable flexible MoS_2 field effect transistors with patterned graphene back-gate. Flexible devices were fabricated on a Kapton substrate and incorporating graphene as the back-gate material due to its biocompatibility and its favorable physical properties. Monolayer MoS_2 single-crystal flakes were grown over large area by chemical vapor deposition, and then transferred onto a pre-patterned electrode array, resulting in a device yield > 70% and an average mobility of 1.0 $cm^2V^{-1}s^{-1}$. To create nano-biosensors, the surface of the MoS_2 was functionalized via a reengineered mu-opioid receptor and the devices were tested against opioid solutions of various concentrations. This work provides a pathway for the integration of MoS_2 and other TMDs onto flexible/wearable/implantable devices that for trace detection of opioids or other chemicals. This work was supported by the National Science Foundation through EFRI 2DARE ENG-1542879

6:00pm **2D+BI+MN+SS-TuA12 Development and Validation of Polarized Models for Peptide-Graphene Interactions**, ***Amanda Garley***, University of Colorado Boulder, *N. Saikia*, Michigan Technological University, *R. Berry*, Air Force Research Laboratory, *H. Heinz*, University of Colorado Boulder

Biosensor technologies require the understanding of interactions between organic and inorganic materials to tune electric response functions, such as peptide assembly on graphitic substrates. Laboratory characterization of specific interactions and molecular assembly can be complemented by atomistic molecular simulations, as well as by quantum-mechanical analysis of band gaps and expected conductivity.

As a first step, we improved common dispersive interatomic potentials for graphite to include pi electron density at virtual sites. The new model reproduces experimental cation-pi energy, X-ray structure, density, cleavage energy, hydration energy, contact angle and elastic constants. As a result we have improved existing models which gave the wrong sign of hydration energies and deviations up to 1000% in these properties from experiment. The parameters are embedded in CHARMM, CVFF, TEAM-AMBER, and other common force fields as part of the INTERFACE force field. An analysis of binding residues, binding energies, conformations, and dynamic information of molecular mobility on the surfaces will be presented.

Biomaterial Interfaces Division
Room: 12 - Session BI+AS+MI+SA-TuA

Bio from 2D to 3D: Challenges in Fabrication and Characterization & Flash Presentations

Moderators: Lara Gamble, University of Washington, Anna Belu, Medtronic

2:20pm **BI+AS+MI+SA-TuA1 Cell-instructive Polymer Matrices for Therapies and Tissue Models**, ***Carsten Werner***, Leibniz Institute of Polymer Research Dresden and TU Dresden, Deutschland **INVITED**

Sulphated and non-sulphated glycosaminoglycans (GAGs) can be instrumental in biomedical technologies beyond. In particular, incorporation of GAGs into biomaterials has been demonstrated to allow for the biomimetic modulation of growth factor signaling, providing control over therapeutically relevant cell fate decisions in various different settings. In an attempt to systematically explore the related options, we have introduced a rational design strategy for biology-inspired hydrogels based on multi-armed poly(ethylene glycol), GAGs and peptides (1,2,3). The theoretically predicted decoupling of biochemical and mechanical gel properties was confirmed experimentally and applied for implementing GAG-based biofunctionalization schemes to afford cell adhesiveness and morphogen presentation. A number of applications of customized GAG-based materials will be given, including inflammation-modulating wound dressings (3), cryogel particles to support cell replacement in Parkinson's disease (4) and gel matrices to enable tissue and disease *in vitro* models for cancer biology (5,6) and nephrotoxicity studies. In sum, our reported approach demonstrates the power of joint theoretical and experimental efforts in creating bioactive materials with specifically and independently controllable characteristics (7).

References

(1) U. Freudenberg, J.-U. Sommer, K. Levental, P. Welzel, A. Zieris, K. Chwalek, , K. Schneider, S. Prokoph, M. Prewitz, R. Dockhorn, C. Werner (2012) Adv Funct Mater 22:1391

(2) M. Tsurkan, K. Chwalek, S. Prokoph, A. Zieris, K. Levental, U. Freudenberg, C. Werner (2013) Adv Mater 25:2606

(3) U. Freudenberg, A. Zieris, K. Chwalek, M.V. Tsurkan, M.F. Maitz, P. Atallah, K.R. Levental, S.A. Eming, C.Werner (2015) J Control Release 220:79

(4) B. Newland, P.B. Welzel, H. Newland, C. Renneberg, P. Kolar, M. Tsurkan, A. Rosser, U. Freudenberg, C. Werner (2015) Small 11:5047

(5) K. Chwalek, M.V. Tsurkan, U. Freudenberg, C. Werner (2014) Sci Rep 4:4414

(6) L.J. Bray, M. Binner, A. Holzheu, J. Friedrichs, U. Freudenberg, D.W. Hutmacher, C. Werner (2015) Biomaterials 53:609

(7) U. Freudenberg, Y. Liang, K.L. Kiick, C. Werner (2016) Adv Mater 10.1002/adma.201601908

3:00pm **BI+AS+MI+SA-TuA3 Plant Virus Particles for 2D and 3D Architectures on Surfaces**, *V. Rink*, University of Kaiserslautern, Germany, *M. Braun*, RLP Agroscience GmbH, Germany, *M. Ani*, University of Kaiserslautern, Germany, *K. Boonrood*, RLP Agroscience GmbH, Germany, *C. Müller-Renno*, University of Kaiserslautern, Germany, *G. Krczal-Gehring*, RLP Agroscience GmbH, Germany, ***Christiane Ziegler***, University of Kaiserslautern, Germany

Biohybrid materials consist of biological entities and artificial, often inorganic materials. These biohybrids may be used in many fields of applications, ranging from biosensors to implant materials. In this context, bottom-up approaches, in which small elementary building blocks of matter

are used to form larger elements through self-assembly have gained a lot of interest.

Plant viruses are promising candidates for such building blocks. Because of their simple structure and pre-defined size and form they have a high potential for self-assembly. Furthermore they can be genetically manipulated to create new functionalities by extending the capsid with different side chains.

We could show that unspecific electrostatic interactions govern the formation of large ordered 2D structures of self-assembled icosahedral tomato bushy stunt virus (TBSV) particles. By adding amino acid side chains to the capsid subunit the isoelectric point of the virus is changed. Thus by the right combination of virus modification, substrate and pH (and as a minor effect ionic strength) one can control the dimensions of 2D virus islands which may form layers with macroscopic dimensions. Specific structures in these 2D layers may be introduced by substrates which are pre-structured, e.g. by nano imprint lithography.

In addition to the electrostatic control the amino acid side chains allow also more specific interactions. Examples are histidine side chains interacting with Ni ions or gold binding peptide side chains with Au. With these specific interactions, also the third dimension is accessible. This opens the possibility to play with viruses in a kind of nano Lego which will soon become reality.

In this contribution we will show a scanning force and scanning electron microscopy study of the self-assembly of 2D and 3D structures of TBSV on Si and mica surfaces. The three dimensional structure is based on a homogeneous layer consisting of virus-particles carrying additional 4xAsp6xHis side chains (lowest stack). For the following second stack the chemical selectivity of these side chains to Ni ions (here: Ni-nitrilotriacetic acid (Ni-NTA) carrying a 5 nm Au nanoparticle was utilized. Au-binding virus-particles interact with these Au particles and create the third stack of this 3D virus architecture. The success of this strategy could be proven by SFM height measurements which reveal a height in the range of 66 nm, which corresponds to two layers of virus particles (30 nm each) coupled by Ni-NTA.

Lüders et al. (2012). Tomato bushy stunt viruses (TBSV) in nanotechnology investigated by scanning force and scanning electron microscopy. *Colloids Surf. B91*, 154

3:20pm **BI+AS+MI+SA-TuA4 Designing Thermo-responsive Nanocomposites that Provides Multiple Defense Mechanisms against Fouling**, ***Ya Liu***, University of Pittsburgh, *C. Zhang, S. Kolle, J. Aizenberg*, Harvard University, *A.C. Balazs*, University of Pittsburgh

We use computational modeling to design synthetic gel-based composite coatings that provide multiple defense mechanism against the fouling of the underlying substrate. The system encompasses rigid posts embedded in a lower critical solution temperature (LCST) thermo-responsive gel, which swells at lower temperatures and collapses at higher temperatures. By developing new dissipative particle dynamics (DPD) simulationd that capture the cell-surface interactions , we exam the biofilm growth and structure development on the substrates and pinpoint the parameter space that yields the optimal antifouling behavior for this system. The advantage of our approach relies on physical mechanisms and doesn't have unwanted environmental consequences.

4:20pm **BI+AS+MI+SA-TuA7 3D Ink-jet Printing for Tissue Engineering**, ***Thomas Boland***, The University of Texas at El Paso **INVITED**

An inkjet application is described, where biologically active ink, which may include drugs and living cells as well as non-active can be deposited alongside scaffolding materials to build two- and three-dimensional constructs for medical treatment. The technology faces several limitations that present interesting engineering opportunities. The nature and scope of the problems will be discussed in the context of the fabrication of microvasculature. The current tissue engineering paradigm is that successfully engineered thick tissues must include vasculature. As biological approaches alone such as growth factors have fallen short of their promises, one may look for an engineering approach to build microvasculature. Layer-by-layer approaches for customized fabrication of cell/scaffold constructs have shown some potential in building complex 3D structures and with the advent of cell printing, one may be able to build precise human microvasculature. Several research projects will be presented. The fabrication of microvsculatures for skin and adipose tissue engineering and current studies to characterize the biology and functionality of these engineered structures will be presented. These data suggests that a combined simultaneous cell and scaffold printing can promote microvasculature formation and improve current tissue engineering technology.

5:00pm **BI+AS+MI+SA-TuA9 Digging for Answers: Challenges in ToF-SIMS Tissue Depth Profiling**, ***Daniel Graham***, *T.B. Angerer, L.J. Gamble*, University of Washington, Seattle

The advent of cluster ion beams for time-of-flight secondary ion mass spectrometry (ToF-SIMS) instrumentation has opened up many opportunities for depth profiling organic samples. Combined with its high lateral resolution imaging capabilities, SIMS can provide 3D imaging information from a wide range of organic materials including cells and tissues. The ability to track chemical changes both across and throughout tissue sections could help identify molecular changes related to targeted drug delivery or disease states in the cellular micro-environment. While there have been many studies showing the utility of ToF-SIMS depth profiling for polymer materials, similar studies with cells and tissues have been limited. This has likely been due to the challenges encountered when working with biological samples. It has been shown that one can depth profile cells as long as the levels of buffer salts and other inorganic components is minimized. Similar work with depth profiling tissues has been limited. Herein we will present our findings on the challenges of depth profiling tissues and discuss ways these challenges may be avoided. Examples will be shown using both single beam argon cluster depth profiling and dual beam depth profiling using Bi3+ for analysis and argon clusters for sputtering. In general a significant loss in signal is seen after the first few layers of a tissue depth profile. This could be due to migration of components to the surface, ion beam damage, or ion suppression due to salts. In spite of these issues, tissue depth profiles can be acquired in most cases. The challenge then becomes processing and interpreting these large data sets. Ideas on how to overcome these challenges will be presented.

5:20pm **BI+AS+MI+SA-TuA10 Cryo-SIMS – Metrology of Biological Sample Preparation Methods for Preservation of Cell Ultrastructure and Chemistry**, ***Paulina Rakowska***, *J.-L. Vorng, I.S. Gilmore*, National Physical Laboratory, UK

With the potential of high-throughput, high-resolution and high-sensitivity label-free imaging in 3D, secondary ion mass spectrometry imaging methods are, arguably, ones of the most powerful techniques for high-resolution chemical imaging of biological samples. However, there are some critical limitations for these analyses. As the high-performance SIMS instruments require high vacuum, a careful consideration of sample preparations is often needed. For example, advanced methods are necessary to prepare and measure complex hydrated bacterial biofilm structures. Also, in the pharmacological imaging of potential drug candidates at their targets, the positioning of water soluble drug compounds within cells or tissues can be altered by pre-treatment processes such as drying, resin-embedding or histological fixation. Advanced cryo-preparation methods are necessary for immobilisation of water in these samples to prevent the ultrastructural reorganisation and the loss or translocation of water-soluble molecules, to circumvent the use of chemical fixation and to enable their analysis in high-vacuum of mass spectrometry instruments.

The UK's National Centre of Excellence in Mass Spectrometry Imaging (NiCE MSI) at NPL has a special focus on the development of advanced solutions to challenging measurements. Our recently innovated 3D OrbiSIMS instrument has the capability to handle and measure cryogenically-prepared samples. The instrument is equipped with a vacuum cryo transfer system that is compatible with cryo-SEM and cryo-TEM. A shuttle chamber allows the interchange of samples, in vacuum and cryogenically, between cryo-preparative equipment and the 3D OrbiSIMS instrument.

This presentation will show our recent developments of the cryo-SIMS methodologies. Different sample cryo-preparation techniques will be compared, such as the analysis performed on frozen-hydrated vs. frozen-dehydrated mammalian cells. The application of cryo-SIMS to a range of biological samples including cells, bacteria, biofilms and organic reference samples will be presented. Focus will be given to the use of different types of cryo-protectants, often required for the vitrification of thicker samples such as biofilms, by high-pressure freezing and their effects on SIMS analysis.

5:40pm **BI+AS+MI+SA-TuA11 Towards Cryogenic 3D Nano-XRF Imaging of Biological Samples**, ***Axel Rosenhahn***, *S. Stuhr, C. Rumancev, T. Senkbeil, T. Gorniak, A. von Gundlach, J. Reinhardt*, Ruhr-University Bochum, Germany, *Y. Yang, P. Cloetens*, ESRF, France, *M. Grunze*, Karlsruhe Institute of Technology (KIT), Germany, *J. Garrevoet, G. Falkenberg, W. Schröder*, DESY, Germany

Nanoprobe X-ray fluorescence (nano-XRF) analysis allows spatially resolved imaging with chemical sensitivity. Approaching the diffraction limit at the next generation of storage rings, both, spatial resolution and brilliance are going to be strongly enhanced for nano-XRF experiments. For biological samples, the combination of nano-XRF with cryogenic sample environments allows to understand elemental distributions in cells with minimum preparation artefacts. In addition, the cryo-protected samples provide enhanced resistance against radiation damage, which is particularly important

for the high photon densities at modern synchrotron sources. Three different applications of cryo-nano-XRF will be presented. For single melanosomes, the technique enabled us to prove the core-shell organization of the organelles using metals as surrogate markers. As second application, the distribution of metals in single, adherent cells was directly imaged without the requirement of additional markers. Finally, marine adhesives of diatoms were analyzed and the occurrence of metals are linked with the known organic constituents in the EPS of diatoms. In all three cases, the detection of metal distribution has provided a new view on the investigated samples. The cryogenic sample environments proved to be the key to apply synchrotron radiation to all three types of biological samples. The data will also be discussed in relation to the perspectives of new implementations that will enable fast cryo-3D imaging in the future.

Biomaterial Interfaces Division
Room: Central Hall - Session BI-TuP

Biomaterial Interfaces Poster Session with Flash presentations

BI-TuP1 Optimizing Micropost Arrays to Break Up Biofilms, ***James Waters***, *A.C. Balazs*, University of Pittsburgh

Surfaces covered with periodic arrays of microposts represent an appealing avenue of fouling mitigation, as they rely on a physical mechanism without unintended environmental consequences. In addition to reducing the area for contaminant cells to bind to the surface, the flow field generated by specific configurations of posts under shear may help push particles away from the surface, or break up biofilms as they form. We represent such a system computationally using a hybrid of bulk fluid simulated via the lattice Boltzmann method, and deformable vesicles, representing cells, simulated via that lattice spring method. This simulation methodology allows us to rapidly implement and test different surface structures, and explore how the parameters of post shape and arrangement can most effectively deter the accumulation of biofilms.

BI-TuP2 Dynamic Field Testing of Fouling Release Coatings by a Rotating Disk System, ***Julian Koc***, *K.A. Nolte*, Ruhr-University Bochum, Germany, *A. Stephens*, Florida Institute of Technology, *M.P. Schultz*, United States Naval Academy, *G. Swain*, *K. Hunsucker*, Florida Institute of Technology, *A. Rosenhahn*, Ruhr-University Bochum, Germany

The development of materials with the capability to resist the accumulation of biomass on surfaces in contact with seawater (marine fouling) is both, economically and ecologically desired. To rank the performance of novel coating technologies, different lab and field screening methods have been established. While technical coatings are tested over several months, methods for short-term testing of thin film chemistries are missing. We developed a setup for dynamic, short term field testing of coatings. To obtain a constant shear stress during colonization, a rotating disc was used. The rotating disc was designed to be easily transported and installed at various marine testing sites. The shear situation above the disk was theoretically simulated and adjusted to shear ranges identified in recent laboratory experiments to be suited to distinguish the fouling-release potential of surfaces [1]. To validate the setup, self-assembled monolayers with well characterized physicochemical properties were tested under similar shear conditions, as in our recently reported laminar flow lab assay. The same discriminations with the same trends as in the lab assay were obtained for a mixed population of marine diatoms in the ocean. In the future, the setup will be used to compare the results of lab tests of new promising coating chemistries with short term dynamic field exposure.

[1] K. Nolte, J. Schwarze, A. Rosenhahn, *Biofouling* **2017**, in press

BI-TuP3 Bioinspired Vascularized Polymers for Controlled Drug Delivery, ***Kayla Marquis***, *A. Webber*, *C. Howell*, University of Maine

Nearly all methods that deliver bioactive compounds to the surface of a substrate rely on application from above or fail over time due to depletion of compounds. Here we explore the use of natural vascular channels embedded within polymeric matrices to allow for continuous, targeted, low concentration delivery of bioactive compounds to the surface from below. To achieve this, networks of empty 3D printed vascular channels are continuously filled with bioactive compounds. The compounds flow through the vascular network and diffuse through the polymer, eventually reaching the substrate surface of the matrix. By varying the locations and depths of these vascular channels we demonstrate that the amount of material and duration over which it is delivered to the surface can be controlled. The ability to control the diffusion of compounds both spatially and temporally is key in developing assays that test the effects of chemical gradients on various systems at both the cellular and organismal levels. This approach may prove useful in applications such as toxicity and wound healing assessment and targeted antifouling surfaces.

BI-TuP4 Measuring the Mechanical Properties of Hydrophobic Anti-Fouling Surfaces, ***Samantha Zanetti***, *S. Moorzitz*, *G. Dickinson*, *M. Figueroa*, The College of New Jersey

Biofouling by marine organisms causes damage to ships and underwater structures. Some anti-fouling coatings reduce adhesion by small marine organisms but are not as effective in deterring adhesion from barnacles. To develop a surface capable of further reducing barnacle adhesion, it is important to understand the chemical and mechanical interactions in the formation of bonds between the glue and surface. While some experiments have studied the mechanical properties of the cyprids and barnacles, their adhesion is complex and still not fully understood. Furthermore, there are only a few studies that have measured the adhesive properties of reattached barnacles. To study the adhesive properties of the glue, adult barnacles were removed from hydrophobic surfaces and the glue residue was characterized by atomic force microscopy (AFM).

Assessments were conducted on methylated and fluorinated self-assembled monolayer substrates. Substrates were prepared on glass slides that were cleaned with Piranha solution prior to use. Barnacles were reattached to the substrates in artificial seawater for two weeks. They were then removed via shear force following ASTM D5618-94. Separately, a mechanical testing frame was used to remove another set of reattached barnacles in a controlled manner. Force required to displace the barnacle was recorded and compared to the ASTM standard.

To determine the glue's viscoelastic properties and Young's Modulus, an AFM was used to collect force curves and images of the barnacle glue residue. The mechanical properties of the glue were recorded for each type of coating following an indentation procedure using an intermittent contact mode. Adhesion data and the deflection of the tip was used to plot applied force vs. vertical displacement. A contact model was applied to the approach and retraction curves to gather the viscoelastic properties of the samples.

The poster will present summer 2017 research results. This will include the measured mechanical properties of glue from reattached barnacles, retrieved from the AFM analysis and mechanical test strain data.

BI-TuP5 *In Vitro* Degradation Performance and Increased Biological Response of a Surface Modified Mg-Al-Zn Alloy, ***Michael Melia***, *D.C. Florian*, *J.R. Scully*, *J.M. Fitz-Gerald*, University of Virginia

As a lightweight metal with mechanical properties similar to natural bone, Mg and its alloys are great prospects for biodegradable, load bearing implants. However, the United States has yet to clear Mg for any substantial role in the body due to the concerns of electrochemically derived hydrogen gas and unpredictable loss of structural integrity as a result of a dynamic corrosion resistance varying with time. This research investigates how the chemical homogenizing effects of laser processing and the application of a corrosion resistant coating impacts the corrosion resistance, cell viability, and cell adhesion of the AZ31B (3 wt. % Al, 1 wt. % Zn, 0.3 wt. % Mn, and 95.7 wt% Mg) alloy in a physiological solution.

Cell viability and adherence measurements were carried out utilizing the osteosarcoma (MG63) cell line and were plated on the AZ31B specimens in the as-received, laser processed, and coated conditions. In vitro cell viability assays show improved cytocompatibility for both the laser processed and coated specimens over the as-received AZ31B alloy. The coated specimen performed the best with a 5 fold improvement in cell viability over the as-received alloy. Cell adhesion was further investigated by fixation of the MG63 cells and imaging using scanning electron microscopy (SEM). Electron micrographs revealed significant adhesion of cells to the coated specimen with limited adhesion for specimen in the as-received and laser processed condition.

Laser processing utilized a KrF pulsed excimer laser ($\lambda = 248$ nm and FWHM = 25 ns) which has been shown to reduce the corrosion rate of Mg alloys by an order of magnitude in NaCl containing solutions. Corrosion experimentation was performed under full immersion in a minimal essential media (MEM). Time dependent corrosion rates and electrochemical kinetics were analyzed using open circuit potential, electrochemical impedance spectroscopy, and potentiodynamic polarization measurements. The corrosion product morphology was investigated using SEM, energy dispersive spectroscopy, and x-ray diffraction. The coated specimens exhibited an order of magnitude reduction in cathodic kinetics after 24 hours of immersion in MEM compared to the as-received AZ31B alloy. The laser processed condition exhibited a 5 fold reduction in cathodic kinetics to the as-received alloy as well as maintaining an open circuit potential 150 mV lower than the coated and as-received specimen. The passivate nature of all three specimen conditions was similar.

BI-TuP6 Interactions between Single Molecules and Surfaces, *C. Klinger*, TU Bergakademie Freiberg, Germany, ***Laila Moreno-Ostertag***, MPI for Iron Research, Germany, *C. Weber*, *P. Schiller*, *M. Valtiner*, TU Bergakademie Freiberg, Germany

Unraveling the complexity of the macroscopic world relies on understanding single molecule interactions and their scaling towards integral interactions at the meso- and macroscopic scale [1]. Here, I will discuss how one can measure the interaction free energy of single interacting functional groups at various solid/liquid interfaces. The adhesion between single molecules and surfaces in electrolytes is a central point regarding many biological systems and the delamination of coatings.

Single molecule force spectroscopy with an AFM is a suitable tool for measuring the work and force needed to unbind single molecules. The relation between the work of non-equilibrium trajectories and the free energy of interaction can be described by Jarzynskis equation [2]. So the surface-to-molecule bond rupture can in principle be characterized fully, but systematic errors arises. First, we will discuss how the effect of contour length of typically utilized molecular linkers such as PEG potentially adds a systematic bias on the free energy determined from AFM experiments. Secondly, also experiments with varying speed of the force runs were realized and the bias due to increasing rates (i.e. further shift from the equilibrium situation), which will be discussed in this contribution.

Finally, we will discuss in detail how single molecule unbinding energy landscapes can be utilized to predict scenarios where a large number of molecules simultaneously interact, giving rise to adhesive failure under corrosive and wet conditions. As such, our experimental strategy provides a unique framework for the molecular design of novel functional coatings through predicting of large-scale properties such as adhesion and molecular interactions in various systems based on experimentally determined single molecule energy landscapes.

[1] T. Utzig, S. Raman, and M. Valtiner, Langmuir 31, 2722-2729 (2015)

[2] S. Raman, T. Utzig, T. Baimpos, B. R. Shrestha, and M. Valtiner, Nat. Commun. 5, 5539 (2014)

BI-TuP7 Proton Transfers Involved in Melanin Biosynthesis: Binding of Cysteine to Dopaquinone Investigated by Density Functional Theory based Calculation, ***Ryo Kishida***, Osaka University, Japan

Melanin is a natural pigment present in many types of living organisms. The color of the skin, hair, and eyes is a manifestation of melanin biosynthesis (melanogenesis). Melanogenesis is initiated by oxidation of tyrosine to form reactive dopaquinones. The formed dopaquionone rapidly reacts with cellular cysteine, resulting in the generation of yellow to reddish brown pheomelanin. At lower concentration of cysteine, dopaquionone undergoes intramolecular cyclization, resulting in the generation of brown to black eumelanin. Thus, the reactions of dopaquinone (cyclization and cysteine binding) affect the pheomelanin/eumelanin ratio, determining the body color. The color of eumelanin is further controlled by its monomer ratio. Eumelanin monomers are formed from dopachrome, which is a molecule generated after the stage of dopaquinone.

We have investigated the reactions of dopaquinone and dopachrome [1-4]. In this symposium, we present our recent mechanistic study on reactions of dopaquinone with a focus on the cysteine binding. Using density functional theory based calculation, we computed the energy profiles for the approaching of cysteine to dopaquinone and obtained stable cysteine-bound structures. We found that the cysteine-bound structures can undergo intramolecular proton transfer for further stabilization with fairly small activation energy.

[1] R. Kishida et al., Pigment Cell Melanoma Res. 27 (2014) 734.

[2] R. Kishida et al., Biochim. Biophys. Acta 1850 (2015) 281.

[3] R. Kishida et al., J. Electron. Mater. (2017) doi:10.1007/s11664-017-5299-x.

[4] R. Kishida et al., Biochim. Biophys. Acta (to be submitted).

BI-TuP10 Interferometry: A New Way to Study Corrosion at Confined Interfaces, ***Claudia Merola***, *H.-W. Cheng*, Max Planck Institute for Iron Research, Germany, *M. Valtiner*, University of Freiberg, Germany

Understanding marine corrosion and biofouling is of central importance for designing materials for marine use that last longer and protect more effectively from biofouling. Many different types of destructive attack can occur to structures, ships and other equipment used in sea water service.

Crevice corrosion (CC), which is corrosion at an interface, still remains one of the most difficult types of corrosion to detect and to prevent. Most often CC occurs in narrow fissures where oxygen access is poor and a stagnant electrolyte solution is present. Experimentally it is a challenge to obtain in-situ information of processes in confined geometries and to establish well defined confined situations in the first place.

Here, we show how white light interferometry[1] can be utilized, for the first time, to study and monitor in situ the initial stages of the crevice corrosion process of thin layers of different metals[2] (e.g. Ni, Al, Au..) in different concentrations of NaCl solutions. Using Mica as a crevice former in an electrochemical surface apparatus allowed us to provide a deeper understanding of the initiation of the corrosion process, which also occurs at the adhesive interface of bio organism such as barnacles or mussels.

Our new approach provides a real-time view of the initial corrosion of confined surfaces, and hence may contribute to a deeper general understanding, and ultimately prevention, of localized corrosion and corrosion underneath biofoulers.

[1]J. Israelachvili *et al.*, Recent advances in the surface forces apparatus (SFA) technique. *Reports on Progress in Physics* **73**, 036601 (2010).

[2] B. R. Shrestha *et al.*, Real-Time Monitoring of Aluminum Crevice Corrosion and Its Inhibition by Vanadates with Multiple Beam Interferometry in a Surface Forces Apparatus. *Journal of the Electrochemical Society* **162**, C327 (2015, 2015).

BI-TuP11 Stimuli-responsive Thin Films made from the Mucilage of *Opuntia Ficus-indica* Cactus, ***Zeinab Veisi***, University of South Florida, *M. Cardenas, A. Cardenas-Valencia*, SRI International, *R. Toomey, N. Alcantar*, University of South Florida

We have used the mucilage of *Opuntia ficus-indica* cactus to fabricate ultra-thin films of surface-attached networks. The gelling properties and swelling behavior of these thin films were studied as a function of various stimuli to determine the main factors affecting the responsiveness of such layers.

Opuntia ficus-indica belongs to the cactaceae family, and is grown in dry regions. Its abundance makes it a promising commercial source of industrial pectin. Mucilage extracted from *Opuntia ficus-indica* is a heteropolysaccharide composed of a backbone chain structure of α-D-galacturonic acid and β-L-rhamnose interrupted by different neutral sugars. The carboxyl groups present in a polygalacturonic acid chain can be cross-linked in the presence of divalent ions to render hydrogel networks with conformations responsive to internal and external variables. The presence of a considerable amount of water within the polysaccharide matrices renders unique hydrophilic gels suitable to be used in a wide range of applications.

Thin films of surface-attached polysaccharide networks were fabricated by spin-casting solutions of mucilage. Ca^{2+} ions were then introduced to obtain cross-linked networks with adjustable extent of crosslinking. The fabricated surface-attached thin films of cross-linked polysaccharide were then characterized by Attenuated Total Reflection-Fourier Transform Infrared (ATR-FTIR) Spectroscopy and ellipsometry. Swelling behavior of the confined surfaces was studied as a function of temperature in contact with aqueous solutions, and their response was perturbed by different stimuli. Moreover, surface-attached networks were exposed to buffer solutions of pH of 9 and 2 to investigate the effect of charge concentrations on the response of networks.

The average water content in the networks as a function of temperature and the extent of crosslinking was precisely measured using ellipsometry. The results revealed that the extent of equilibrium water content and release profiles of thin films strongly depend on the degree of crosslinking. Moreover, the extent of equilibrium water uptake is affected by the values of pH of the media.

Our findings provide an improved understanding of the chemical properties, functionalities and the gelling behavior of thin films of surface-attached naturally occurring polysaccharides which can be employed for establishing responsive surfaces with tunable response suitable for the pharmaceutical and biotechnology industries.

BI-TuP13 Effect of Topography on Retinal Stem Cell Viability and Regrowth, ***Aleksandr Filippov***, *Y. Tian, Y. Xie*, SUNY Polytechnic Institute

Age-related macular degeneration is a devastation eye condition that inflicts damage to the retina and leads to irreversible vision loss. The retina is made up of several layers of light-sensing cells, which are supported and nourished by the retinal pigmented epithelial (RPE) layer. The RPE cells sit atop the Bruch's Membrane and form a highly-selective blood-retinal-barrier that is critical for retinal homeostasis. In this project, we attempt to recreate the barrier in vitro using elestrospun nanofibers. Human RPE cells were cultured on nanofibers made from natural and synthetic polymers, such as chitosan and polycaprolactone, with Synthemax and gelatin as controls. We found that human RPE cells demonstrated proper morphology and protein expression when cultured on the chitosan substrate.

BI-TuP14 DNA Interactions with Elastin like Polypeptide Coacervates, ***Telmo Díez***, *P.A.H. Nguyen, N. Carroll, J. Satterfield, G.P. Lopez*, University of New Mexico

Intrinsically disordered proteins (IDPs) are dynamic biomaterials used by mammalian cells in cell signaling, transcription, and chromatin remodeling functions. In native cells, they are frequently used in packaging and un-packaging of nucleic acids (NAs), making them promising biomaterials for drug delivery and gene delivery. Elastin Like Polypeptides (ELPs) are synthetic biopolymers that have similar structural features to natural IDPs with many similar associated functions. In this research, we focus on replicating IDPs' ability to assemble into hierarchal phase-separated granular structures and interact with nucleic acids using cationic ELPs. Importantly, ELPs condense to form coacervates above a lower critical solution temperature (LCST). Below this temperature, ELPs exist as a fully soluble random coil polymer. In this study, we use an ELP comprising 8 positive charges due the presence of 8 lysines interspersed within the chain. We

demonstrate that condensed ELP coacervates provide the necessary charge density to attract and encapsulate nucleic acids. Here, ELP coacervates are incubated with fluorescently labeled DNA containing a Cy3 fluorophore on its 5' end. We characterize the amount of DNA captured by fluorescence intensity measurements that are taken prior to and following formation of a phase-separated ELP coacervate in aqueous solution. Furthermore, we use microfluidics to form aqueous microdroplets comprising ELP and fluorescent DNA to visualize DNA capture within ELP coacervate spheres via fluorescence microscopy. ELP coacervates formed by heating the microdrops above the ELP transition temperature are shown to electrostatically complex with- and capture DNA. We characterize the thermodynamic binodal boundary (i.e. temperature-dependent phase boundary) of the ELP to resolve the ELP volume fraction within the coacervate to determine the optimal temperature to maximize DNA capture. These initial studies will inform our future work to engineer smart, programmable nanoparticles for the delivery of nucleic acids for gene therapy applications.

BI-TuP15 Bovine Aortical Endothelial Cell Encapsulation with Elastin-like polypeptides (ELP) and bis(sulfosuccinimidyl)suberate (BS3)., ***Phuong Anh Nguyen***, *T. Diez Perez, H.E. Canavan,* University of New Mexico, *N.J. Carroll,* Universiity of New Mexico

Chronic wounds do not adequately recover through the healing process and have become a major challenge to healthcare systems worldwide. In the U.S., chronic wounds affect an estimated 6 million people per year, costing more than $25 billion annually due to complications and over $18.5 billion in associated care. Current biomaterials for wound healing scaffolds including aglinate, hydrofibers, foam, hydrogels, cadaver skins, fetal cow skin, skin grafts or fish skin to wounds to encourage healing. However, common drawbacks include poor biocompatibility, risk of disease transmission and host rejection. Bioprinting of hydrogel materials has emerged as a flexible tool with potential to obviate these problems. For example, tissue engineering by extrusion bioprinting uses robotic deposition to print cells encapsulated in hydrogel scaffolds to form new organs or tissues. However, biocompatible and biofunctional materials for printable hydrogels are lacking. We propose to encapsulate cells in novel microgel materials, elastin-like-polypeptides (ELP), to create printable bioinks that are biocompatible, bioinert, and recapitulate physicochemical cues of natural extracellular matrices. In our study, ELP hydrogels are formed by crosslinking ELPs with bis(sulfosuccinimidyl)sulfate (BS3), an amine-reactive crosslinker, to encapsulate bovine aortic endothelial cells within the formed hydrogels. Initial testing via live/dead assays shows cells are able to survive in the hydrogel scaffold for many days. Hydrogel stiffness can easily be controlled via temperature, pH, and crosslinker concentrations. Future work leveraged from these assays will be encapsulation and differentiation of mesenchymal stem cells (MCMs) for programmable wound healing.

BI-TuP16 Direct Electron Beam Imaging of Proteinaceous Fibrils, *T.M. Thieu*, KRISS, Republic of Korea, *T.H. Ha,* KRIBB, ***SangJung Ahn***, KRISS, Korea, Republic of Korea

Direct electron beam imaging method was investigated with abnormal protein assembly of amyloid fibrils. Without and with metal coating, the fast electron beam methods such like scanning electron microscope (SEM) and transmission electron microscope (TEM) were used to observe in nanoscale and compared with slow tip-probing method, atomic force microscope (AFM). As a model protein for amyloid fibril, insulin protein (15 kDa) was chosen, whose aggregation has been believed to have a relation with type II diabetes in human. The insulin amyloid fibrils have grown under several effector molecules such as treholose, ectoines, and citrulline in order to discriminate the morphology differences in various conditions. The direct imaging of proteinaceous fibrils with electron beam was possible only in narrow windows of imaging conditions due to the facilitation of electrostatic charging effect, which is dependent on the underlying substrate. The comparisons of images with electron beams and physical tip-contact were conducted and analyzed in terms of measurement speed, charging, and mechanical damages.

BI-TuP17 Textured TNZT Foams for Bone Implant Applications, ***Elizabeth Blackert***, *S. Murguia, M. Kramer, M. Young, S.M. Aouadi*, University of North Texas

TNZT alloys with compositions of Ti-35Nb-7Zr-5Ta are materials that are more biocompatible than the more widely used Ti-6Al-4V alloy since each of its constituent elements is biocompatible. In addition, it has the lowest Young's modulus of all the titanium-based alloys created so far (50-60 GPa). This property allows for a greater transfer of functional loads, which ultimately leads to bone growth stimulation. TNZT alloys were produced by arc melting of pure elements and were forged into rods. Oxide nano-scaffolds were grown on TNZT samples to investgate the potential of these nanostructures surfaces to improve osseointegration. These nanoscaffolds were grown using the hydrothermal method to create an oxide film. The alloys with and without nano-scaffolds were characterized using top-view and cross-sectional scanning electron microscopy equipped with an energy dispersive x-ray spetrometer to investigate the structure, morphology and chemistry of the resulting nanostructures. Finally, the formation of hydroxyapatitite on the modified surfaces was investigated upon immersion in simulated body fluid (SBF).

BI-TuP18 Synthesis and Immobilization of Silver Nanoparticles in Natural Hydrogels by Directed Liquid-plasma Nanosynthesis, ***Camilo Jaramillo***, *A.R. Shetty, A.F. Civantos, S.L. Arias, J.C. Devorkin,* University of Illinois at Urbana-Champaign, *S. Chang,* Nanjing University of Aeronautics and Astronautics, China, *J.P. Allain*, University of Illinois at Urbana-Champaign

Plasma technology has seen an increased demand in nanotechnology, because of the changes in chemistry and morphology it can induce. These capabilities enable novel applications in a wide range of areas from advanced optical components to biomaterials [1]. Traditional plasma-based techniques work in low-pressure controlled environments. Compared to vacuum-based systems, atmospheric-pressure plasma (APP) systems offer reduced costs (e.g. no vacuum needed), higher reaction rates due to their high neutral-particle component and low-temperature treatment of polymer-based materials [2]. In addition, for specialized applications such as biology or catalysis, APP can offer treatment under gaseous or aqueous environments. One weakness of APP is the difficulty in controlling the coupled ion-neutral species and in turn high-fidelity modification of materials. One alternative to APP is the ability to tailor surface properties by careful control of species in the liquid plasma-material interface resulting in manipulation of nanostructured surface properties. Directed liquid-plasma nano-synthesis (DLPNS) is used in this work as the basis for systematic studies on the synthesis of silver nanoparticles (Ag NPs) in aqueous solution with DLPNS compared to in-vacuum directed plasma nanosynthesis (DPNS) on natural hydrogel matrices. Silver NPs are important for antimicrobial applications due to their unique antibacterial properties [3], but they also possess cytotoxic properties, making them harmful to human tissues [4]. Chitosan (CS) is a biodegradable, biocompatible and non-toxic natural biopolymer, which has been studied due to its antimicrobial properties [5]. DLPNS was used to treat Ag and Ag/CS solutions, driving NPs synthesis and surface nanopatterning. Surface morphology and composition were studied with SEM and EDS, respectively. Ambient-pressure *in-situ* XPS was used to measure irradiation-induced chemistry changes of CS. The antimicrobial properties of synthesized Ag NPs and nanostructured CS was systematically studied with control parameters such as energy and fluence. Notable transformation of the hydrogels was achieved, with self-organized pillar structures and porous structures produced on CS.

[1] J.P. Allain, A. Shetty, J. Phys. D Appl. Phys 50 (2017).

[2] R. Foest, E. Kindel, A. Ohl, M. Stieber, K.-D. Weltmann, Plasma Phys. Control. Fusion 47 (2005) B525–B536.

[3] B. Le Ouay, F. Stellacci, Nano Today 10 (2015) 339–354.

[4] P. Dubey, I. Matai, S.U. Kumar, A. Sachdev, B. Bhushan, P. Gopinath, Adv. Colloid Interface Sci. 221 (2015) 4–21.

[5] I. Bano, M. Arshad, T. Yasin, M.A. Ghauri, M. Younus, Int. J. Biol. Macromol. 102 (2017) 380–383.

Applied Surface Science Division
Room: 13 - Session AS+BI+MI+NS+SA+SS-WeM

Beyond Traditional Surface Analysis: Pushing the Limits
Moderators: Svitlana Pylypenko, Colorado School of Mines, Paul Vlasak, The Dow Chemical Company

8:00am **AS+BI+MI+NS+SA+SS-WeM1 Photolysis of Pyruvic Acid in Aqueous Solution as a Source of Aqueous Secondary Organic Aerosol**, ***Yao Fu***, *X.F. Yu*, *F. Zhang*, *Z.H. Zhu*, Pacific Northwest National Laboratory, *J.M. Chen*, Fudan University, *X.Y. Yu*, Pacific Northwest National Laboratory

Pyruvic acid are found in fogs, aerosols and clouds. The sunlight driven reaction pathways of pyruvic acid in the aqueous phase are more elusive compared to its well-known gas phase chemistry. Aqueous solutions containing pyruvic acid in a microchannel after different UV photolysis times up to 8 hours have been studied by in situ liquid time-of-flight secondary ion mass spectrometry (ToF-SIMS) for the first time. Both positive and negative ion mode mass spectra provided complementary information of the photochemical aging products at the solution surface. Compared with previous results using bulk approaches (i.e., NMR, ESI-MS), our unique liquid surface molecular imaging enables the observation of photochemical products of pyruvic acid at the aqueous solution surface including oxidation products (i.e., acetic acid, oxalic acid, formic acid, lactic acid), oligomers (i.e., dimethyltartaric acid), and water clusters (i.e., $(H_2O)_nH^+$, $(H_2O)_nOH^-$) with submicrometer spatial resolution. Spectral principal component analysis is used to determine similarities and differences among various photochemical aging samples. SIMS three-dimensional chemical mapping permits visualization of the surface mixing state at the molecular level. For example, oligomers and oxidation products become more significant shown in the chemical spatial mapping with increased photolysis time. In situ molecular imaging of the pyruvic acid aqueous solution surface provides new understanding of complex photochemical reactions as an important source of aqueous secondary organic aerosol (SOA) formation in atmospheric chemistry.

8:20am **AS+BI+MI+NS+SA+SS-WeM2 XPS Depth Profiling of $SrTiO_3$ and HfO_2 with Small Argon Clusters**, ***Christopher Deeks***, Thermo Fisher Scientific, UK, *M. Baker*, University of Surrey, UK, *P. Mack*, Thermo Fisher Scientific, UK

Metal oxides are employed in a wide variety of functional applications. There is currently strong technological interest in strontium titanate ($SrTiO_3$) and hafnium oxide (HfO_2) due to their specific band gaps and high dielectric constants. $SrTiO_3$ is being studied for use in photocatalysis, energy storage and electronic sensors, whilst HfO_2 is widely employed for optical coatings and optoelectronic device applications. Both materials are regularly deposited as thin films and doped to optimise their properties for the application. An accurate determination of thin film composition is paramount to the understanding and optimisation of device performance.

In this work, thin films of $SrTiO_3$ and HfO_2 have been deposited onto silicon substrates and XPS depth profiles have been performed through the thin films using both monatomic and cluster argon ion bombardment. The monatomic Ar^+ profiles were performed using an incident ion energy of 500 eV and the gas cluster ion beam (MAGCIS) profiles were recorded using8 keV Ar_{1000}^+ and 8 keV Ar_{150}^+ for $SrTiO_3$ and HfO_2 respectively. For HfO_2 the optimum results were found when the MAGCIS ion beam was incident upon the sample at a glancing angle. These MAGCIS conditions yielded excellent retention of the original $SrTiO_3$ and HfO_2 stoichiometry during the profile, with no evidence of preferential sputtering or ion beam induced reduction. Using 500 eV Ar^+,however, resulted in the preferential sputtering of oxygen leading to the presence of sub-oxide states in the XPS spectra of Ti in $SrTiO_3$ and Hf and HfO_2. The depth resolution was similar between the monatomic and cluster ion depth profiles for both thin film materials. Using the same incident ion beam angle, the etch rate for 8 keV Ar_{1000}^+ was only 2.5 times lower than that for 500 eV Ar^+. The results will be discussed in the light of known ion beam effects when sputtering metal oxide materials.

8:40am **AS+BI+MI+NS+SA+SS-WeM3 Surface Analysis of Intact Biomolecules: the Bigger They Are the Harder They Fly**, ***Nina Ogrinc Potocnik***, *R. Heeren*, Maastricht University, The Netherlands **INVITED**

Secondary ion mass spectrometry (SIMS), as the oldest MSI techniques, gained popularity for analysis of biological samples due to its ability to obtain chemical and spatial information at unmatched lateral resolutions. The use of focused ion beams for desorption and ionization of surface molecules in SIMS affords for this notable spatial resolution over, for example, laser-based MS approaches such as Matrix Assisted Laser Desorption Ionisation (MALDI). However, the excessive energy of the primary ions limits the method to the detection of elements, fragmented molecules and small intact molecular species. This consequently points at the method's major drawback, which is the difficulty to ionize and detect larger, intact molecular species such as peptides and proteins with great sensitivity. Over the last years, SIMS has been pushing the boundaries by redirecting focus into biomedical applications. Tissue sections and cell imaging has become common practice in research labs all over the world. Now, abundant lipids and small peptides can be studied with different sample surface modifications, where the upper most layer of the surface is sputter coated with a thin layer of metal ((MetA) SIMS – metal –assisted SIMS) or covered with the matrix (ME-SIMS). In both cases the sputtering efficiency and the secondary molecular yield have increased. Here, we studied how ME-SIMS can influence the ionization efficiency of desorbed intact molecules in comparison to MALDI.

First, we imaged mammalian tissue sections that were subjected to a variety of different matrices using a home-built sublimation chamber. Matrix sublimation produces small, homogenous crystal sizes, without the need for solvents that delocalize molecular species. The same or consecutive sections were subsequently analyzed by FTICR-SIMS, to accurately identify the enhanced molecular species of interest specifically intact lipids and metabolites, and by the PHI nano-TOF II for high lateral resolution images and confident identification of said species with tandem MS.Second, *de-novo* peptide sequencing was performed on endogenous neuropeptides directly from a pituitary gland. Careful sample preparation and the capability of using a 1 Da mass isolation window of the precursor ion followed by a collision-induced dissociation (CID) at 1.5 keV in an activation cell with argon gas enables the molecules to be fragmented in a specific pattern. Neuropeptides up to *m/z* 2000 were detected and sequenced from the posterior lobe. Further on, we applied it for the characterization of tryptically digested peptides from a variety of tissue sections investigating the applicability to bottom-up proteomics.

9:20am **AS+BI+MI+NS+SA+SS-WeM5 Hydrogen/Deuterium Exchange Using Vapor Phase D_2O to Enhance SIMS Characterizations**, ***Paul Vlasak***, The Dow Chemical Company

Hydrogen/Deuterium exchange of labile hydrogens is a well-known water solution-based phenomenon that has in recent years seen extensive use in the area of protein characterization. This presentation will demonstrate a method to accomplish vapor phase hydrogen/deuterium exchange of solid sample surfaces prior to analysis by SIMS. In many cases, it is not desirable to expose the sample to liquid solvent due to the possibility of dissolving and rearranging or removing surface species of interest. In contrast, the effect of vapor phase D_2O exposure is similar to typical exposures of the sample to humid room air.

The described method is simple and inexpensive in comparison with synthetic isotopic labeling studies. However, it is expected that only the sufficiently labile and sterically accessible H atoms can be tagged, typically those bound to N, O, or S. Possible benefits of this method include isomer differentiation, elucidation of fragmentation pathways, fundamental studies of ionization, differentiation of sterically or otherwise protected vs. unprotected functional groups, and determination of water diffusion or permeability in solid materials.

9:40am **AS+BI+MI+NS+SA+SS-WeM6 Fragmentation and Backscattering of Large Ar_n^+ Clusters as a Probe of Polymer Glass Transition**, *C. Poleunis*, Université Catholique de Louvain, Belgium, *V. Cristaudo*, Université Catholique de Louvain, Belguim, ***Arnaud Delcorte***, Université Catholique de Louvain, Belgium

Gas cluster ion beams (GCIB) have become the standard sources for molecular depth-profiling of organic materials with secondary ion mass spectrometry (SIMS) [1] and X-ray photoelectron spectroscopy (XPS). Since 2009, a number of experimental and theoretical studies were devoted to the investigation of the effects of energy, nuclearity and incidence angle of the Ar clusters on the energy deposition, fragmentation and molecular emission induced in organic solids [2-4]. Recently, Mochiji et al. reported that the backscattered Ar_n^+ clusters observed in the SIMS spectra of pure metal surfaces provide information on the mechanical properties of the surfaces analysed by GCIB [5]. They correlated the ratio of Ar_2^+ to the sum of Ar_n^+ clusters intensities with the impulsive stress caused by the impact, a parameter directly linked to the elastic modulus of the material.

Here, the intensity variations of the backscattered Ar_n^+ clusters are studied as a function of temperature for a series of thermoplastic polymers: high molecular weight polydisperse polyisobutylene and polybutadiene, polystyrene (Standard; $M_w = 4000$) and polymethyl methacrylate (Standards; $M_w = 2000$ and 150000). For all these polymers, our results show a transition of the intensity ratio $Ar_2^+/(Ar_2^+ + Ar_3^+)$ when the temperature is scanned from

-120 °C to +125 °C. This transition generally spans over a few tens of degrees and the temperature of the inflexion point of each curve is very close to the glass transition temperature (T_g) reported for the considered polymer. Due to the surface sensitivity of the cluster backscattering process (a few nanometers as indicated by molecular dynamics simulations [4]), the presented analysis could provide a new method to specifically evaluate the surface T_g of polymers, with the same lateral resolution as the gas cluster beam. The results are discussed from the point of view of the structure and mechanics of polymers.

[1] S. Ninomiya, K. Ichiki, H. Yamada, Y. Nakata, T. Seki, T. Aoki, J. Matsuo, Rapid Commun. Mass Spectrom. 23, 2009, 1601.

[2] M. P. Seah, The Journal of Physical Chemistry C 117(24), 2013, 12622.

[3] B. Czerwinski, L. Rzeznik, R. Paruch, B. J. Garrison, Z. Postawa, Nucl. Instrum. Meth. Phys. Res. Sect. B 269, 2011, 1578.

[4] A. Delcorte, M. Debongnie, J. Phys. Chem. C 119, 2015, 25868.

[5] K. Mochiji, N. Se, N. Inui, K. Moritani, Rapid Commun. Mass Spectrom. 28, 2014, 2141.

11:00am **AS+BI+MI+NS+SA+SS-WeM10 Evolution of the Bi Cluster LMIS as a Universal Source for High Performance SIMS Analysis**, ***Felix Kollmer****, ION-TOF GmbH, Germany **INVITED**

In 1987 Appelhans and co-workers performed a groundbreaking experiment. They bombarded a polymer surface with a neutral SF6 beam in order to avoid charging effects on insulators. By coincidence they discovered that "the SF_6 beam is doing an excellent job of producing secondary ions ... it is unexpectedly efficient at sputtering secondary ions from these polymer surfaces "[1].

In the following years the bombardment of organic surfaces with clusters was investigated by many research groups. The lateral resolution of the applied beams was rather low since the focus at this time was clearly on the fundamentals of the ion solid interaction and the secondary ion generation. However, as early as 1991 Benguerba applied an Au cluster liquid metal ion source (LMIS) for a fundamental study of phenylalanine [2].

At the beginning of the millennium Au cluster LMIS became commercially available for TOF-SIMS instrumentation. This led to a wider application in the SIMS community and to a further improved performance. However, the cluster sources remained an additional option for the SIMS instruments especially since the low cluster currents did not allow the replacement of the reference Ga LMIS for many applications.

With the introduction of a LMIS operated with Bi this changed fundamentally [3]. Roughly 50% of the beam consists of clusters and 50% are emitted as mono-atomic Bi species. This ensures a large flexibility for the analysis of inorganic as well as organic surfaces. Moreover, an uncompromised performance in terms of lateral and mass resolution is achieved, even with cluster beams, and a lateral resolution in the sub 20 nm range has been demonstrated with Bi_3^{++} species [4].

Today, the Bi LMIS is used as the standard analysis source on more than 250 TOF-SIMS instruments for all kinds of applications. In combination with a massive cluster beam that is applied for the erosion of the sample (e.g. Ar_n) even depth profiling or 3D analysis of organic samples is possible.

In this contribution, we will have a retrospective look at the development of high performancecluster SIMS. Besides fundamental capabilities of the Bi LMIS and the secondary ion generation we will discuss milestones of the application as well.

[1] A.D. Appelhans, et. al., Anal. Chem. 59 (13) (1987) 1685–1691

[2] M. Benguerba, et. al. Nucl. Instrum. Meth. B 62 (1991) pp. 8-22.

[3] Kollmer, F. (2004): Applied Surface Science 231-232, pp. 153–158

[4] Kollmer, F. et. al. (2013) Surface and Interface Analysis 45 (1), pp. 312–314

11:40am **AS+BI+MI+NS+SA+SS-WeM12 Evaluating the Benefits of Cs Cluster Analysis in ToF-SIMS and Cs/Xe Co-sputtering for Depth Profiling Layered Thin Films**, ***James Ohlhausen***, *P.T. Vianco, M.T. Brumbach, R. Chow*, Sandia National Laboratories

Depth profiling with Cs to create MCs^+ clusters can produce semi-quantitative results by greatly reducing the matrix effects observed in common M^+ analysis. Additionally, alkali metal clusters enhance negative ion detection in the form of positive Cs clusters, such as MCs^+ and MCs_2^+. In his review article, Wittmaack[1] discussed the many ways that Cs is used in SIMS analyses to provide this enhancement which includes using Cs as the sputtering species and/or analytical probe and using directed Cs vapor. Unfortunately, high Cs surface concentrations can lead to suppression of Cs cluster formation. Xenon and Cs can be co-sputtered in a ToF-SIMS system to adjust the relative amounts of Cs and Xe in the co-sputtered beam to control Cs surface concentration and optimize Cs cluster formation[2]. Cs/Xe co-sputtered depth profiling has been shown to work well in materials systems such as Au thin film on Si[3] and Pd-Rh thin film[4].

The present paper discusses the use of Cs/Xe co-sputtering to investigate an Au/Pd/Ni electroplated layered system. Gold and to some extent Pd have low positive ionization yields, so typical ToF-SIMS data from these metals can be difficult to interpret. However, Cs/Xe co-sputtering has been found to generate high yield MCs^+ clusters in Au and Pd, thus enabling this analysis. This Au/Pd/Ni metal stack were analyzed in a pristine (as received) condition, after accelerated aging and after exposure to a (very high temperature) solder reflow process. The elemental and molecular sensitivities as well as quantitative results stemming from this analysis will be investigated. The manner whereby these results support the use of Au/Pd/Ni stack in an engineering application will be shown. In particular, interlayer diffusion, trace contaminants and interfacial contamination will be examined. Comparisons will be made to Auger and XRF to assess quantitation and sensitivity and to illustrate the advantage of this SIMS technique.

1) K. Wittmaack, *Surface Science Reports*, 68 (2013) 108-230.

2) E. Niehus, T. Grehl, in: J.C. Vickerman, D. Briggs (Eds.), ToF-SIMS, IMPublications, Chichester, West Sussex, UK, 2001, p. 753.

3) J. Brison and L. Houssiau, *Surf. Interface Anal*. 2006; 38: 1715-1719.

4) J. Brison, R. Hubert, S. Lucas and L. Houssiau, *Surf. Interface Anal*. 2006; 38: 1654-1657.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525.

12:00pm **AS+BI+MI+NS+SA+SS-WeM13 Real-Time Monitoring Electrochemical Reaction Intermediates using *In Situ* Time-of-Flight Secondary Ion Mass Spectrometry**, ***Jun-Gang Wang***, East China University of Science and Technology; Pacific Northwest National Laboratory (PNNL), *Y. Zhang, X.Y. Yu, Z.H. Zhu*, PNNL

In situ monitoring of electrochemical reactions is traditionally performed by cyclic voltammetry[1], plasmonic spectroelectrochemistry[2, 3], and surface probing techniques such as scanning electrochemical microscopy and scanning ion conductive microscope.[4] However, it has been extremely difficult to obtain direct molecular evidence of the electrochemical reaction intermediates using these traditional techniques. Thus, the debate of rection machnisms has long been an issue. Recently, mass spectrometric techniques have been coupled with electrochemistry to provide the molecular information of intermediates of redox reactions.[5] The advantage of mass spctetrometric techniques is that capture of molecular ions can provide direct molecular information of key chemical species, such as rection intermediates. A novel approach, based on coupling of time-of-flight secondary ion mass spectrometry (ToF-SIMS) and electrochemistry has been developed in Pacific Northwest National Laboratory and it has been used for in situ analysis of reaction intermediates in electro-oxidation of ascorbic acid at the electrode–electrolyte interface.[6] Herein, the electrochemical oxidation of acetaminophen was chosen as a model system, which simulated the function of oxidase enzymes cytochrome P-450 to catalyze the oxidation of acetaminophen.[7] This reaction was real-time monitored using in situ ToF-SIMS. The highly reactive N-acetyl-p-benzoquinone-imine (NAPQI) was captured. The NAPQI subsequently conjuated with glutathione and cysteine was molecularly confirmed. We demonstrated the proof of principle for the use of ToF-SIMS for real-time monitoring of electrochemical reaction with high chemical specificity. Our results demonstrate that the coupling of ToF-SIMS and electrochemistry has great potential to molecularly elucidate reaction machnisms in the oxidative metabolism, pharmaceutical intoxification, and cell toxicology.

References

[1] J.-G. Wang, X. Cao, X. Wang, S. Yang, R. Wang, Electrochim. Acta 2014, 138, 174.

[2] J.-G. Wang, J. S. Fossey, M. Li, D.-W. Li, W. Ma, Y.-L. Ying, R.-C. Qian, C. Cao, Y.-T. Long, J. Electroanal. Chem. 2016, 781, 257.

[3] J.-G. Wang, C. Jing, Y.-T. Long, in Frontiers of Plasmon Enhanced Spectroscopy Volume 2, Vol. 1246, American Chemical Society, 2016, pp. 57.

[4] J. T. Cox, B. Zhang, Annu. Rev. Anal. Chem. 2012, 5, 253.

[5] T. A. Brown, H. Chen, R. N. Zare, J. Am. Chem. Soc. 2015, 137, 7274.

*** ASSD Peter Sherwood Award**

[6] Z. Wang, Y. Zhang, B. Liu, K. Wu, S. Thevuthasan, D. R. Baer, Z. Zhu, X.-Y. Yu, F. Wang, Anal. Chem. 2017, 89, 960.

[7] D. C. Dahlin, G. T. Miwa, A. Y. Lu, S. D. Nelson, Proc. Natl. Acad. Sci. 1984, 81, 1327.

Biomaterial Interfaces Division
Room: 12 - Session BI+NS-WeM

Biomaterials and Nanomaterials Fabrication & In Honor of Dave Castner's 65th Birthday: Multitechnique Bio-Surface Characterization I

Moderator: Caitlin Howell, University of Maine

8:00am **BI+NS-WeM1 Plasma-Enhanced Chemical Vapor Deposition of an Antibacterial Coating from an Essential Oil-Derived Precursor**, ***Michelle Mann***, *E.R. Fisher*, Colorado State University

Polymeric constructs, such as filtration membranes for water treatment and nanocomposite scaffolds for wound healing and drug release, are often chosen for their ideal bulk properties (e.g., porosity, mechanical strength, and chemical inertness). Challenges faced when using such materials in aqueous settings, however, include their hydrophobicity and propensity for bacterial attachment, leading to biofilm formation and degradation of material performance. Modifying the surface of the constructs while simultaneously maintaining the bulk properties offers both the possibility of addressing these limitations and the potential for creating new advanced materials. Plasma processing is a valuable tool often used to improve material wettability and deposit antifouling coatings. Here, plasma-enhanced chemical vapor deposition is used to deposit films from eucalyptol (1,8-cineole), an antibacterial precursor derived from tea tree oil. Although the antibacterial properties of eucalyptol are supported by numerous clinical trials, it is unknown to what extent the monomer structure and biocidal capabilities are maintained in plasma polymerized films. Thus, we have explored the properties of the eucalyptol-based films as a function of plasma parameters (e.g., power, pressure). Surface analyses (contact angle goniometry, X-ray photoelectron spectroscopy, scanning electron microscopy, and optical profilometry) reveal film wettability directly correlates to precursor pressure, with water contact angles ranging from ~50° to 85°. To further improve wettability of these materials, they were subjected to H_2O (v) plasma modification, an approach that has been successful in past studies to improve polymer biocompatibility. After plasma treatment, wettability increased, with water contact angles of ~20-35°, and the films exhibited a significant enhancement in oxygen content (40-150%), while remaining stable in aqueous solutions. Attachment and biofilm formation assays allowed for assessment of bacterial interactions at 1 and 5 days after exposure, respectively, with gram-negative *E. coli* and gram-positive *S. aureus*. Using microscopy techniques, we observed attachment and growth are substantially diminished for as-deposited and H_2O (v) plasma treated films. Moreover, performance data (i.e., flux of coated ultrafiltration membranes) are presented. Surface analysis and performance testing results, combined with information about gas phase excited state species observed using optical emission spectroscopy, guide our development of additional antibacterial essential oil-based films for 2D and 3D constructs used in environmental and biomedical applications.

8:20am **BI+NS-WeM2 Transition Metal Nanoparticles and Quantum Dots with Tunable Electronic Properties by Bacterial Precipitation: Synthesis and Applications**, *K.E. Marusak, Y. Feng, E. Ngaboyamahina, Y. Cao, J.T. Glass, L. You*, ***Stefan Zauscher***, Duke University

We present a new method for the fabrication of semiconducting, transition metal nanoparticles (NPs) with tunable bandgap and useful photoelectric properties, through bacterial precipitation. *Escherichia coli* bacteria have been genetically engineered, by overexpression of a cysteine desulfhydrase gene, to precipitate transition metal NPs from solution, here more specifically, cadmium sulfide (CdS). Transmission electron microscopy (TEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) revealed that the bacterially precipitated NPs are agglomerates of mostly quantum dots (QDs), with a diameter of 4-5 nm, in a carbon-rich matrix. We discovered that the precipitation conditions of the bacteria can be tuned to produce NPs with bandgaps that range from quantum-confined to bulk CdS. Furthermore, we determined their photoelectrochemical (PEC) properties and their energy band structure by electrochemical measurements. In addition, by taking advantage of the organic matrix, which is residual from the biosynthesis process, we fabricated a prototype photocharged capacitor electrode by incorporating the bacterially precipitated CdS with a reduced graphene oxide (RGO) sheet. Our results show that bacterially precipitated CdS NPs are potentially useful components for PEC devices with applications for energy conversion and storage.

References:

1) Katherine E. Marusak, Yaying Feng, Cooper F. Eben, Stephen T. Payne, Yangxiaolu Cao, Lingchong You, Zauscher, S. “Cadmium sulphide quantum dots with tunable electronic properties by bacterial precipitation,” RSC Advances, **2016**,6, 76158-76166.

2) Yaying Feng, Edgard Ngaboyamahina, Katherine E. Marusak, Yangxiaolu Cao, Lingchong You, Jeffrey T. Glass, and Stefan Zauscher, "Hybrid (Organic/Inorganic) Electrodes from Bacterially Precipitated CdS for PEC/Storage Applications," The Journal of Physical Chemistry C **2017***121* (7), 3734-3743

8:40am **BI+NS-WeM3 Plasma Surface Modification of 2D and 3D Constructs: Creating and Evaluating New Materials for Biomedical Applications**, ***Ellen Fisher***, Colorado State University **INVITED**

Plasma processing represents a powerful approach to modification of 2D and 3D substrates with an array of chemistries appropriate for use in biomedical applications. It is an attractive methodology because of its versatility, low waste, and scalability. The three major plasma surface modification classifications are deposition (film formation, polymerization), etching (removal of material) and functional group implantation (covalent bonding of chemical functional groups), which collectively provide a large landscape for creating materials with specific properties tailored for particular applications. Combining a range of spectroscopic techniques, materials characterization tools, and basic biological interaction studies provides a platform for deeper insight into these underlying mechanisms than just one approach alone. Yet, this can also lead to a range of obstacles, especially when seeking to apply traditional diagnostic methodologies to new systems and materials. For example, data on the surface chemistry of 3D constructs coated with thin films having a range of film chemistries (via utilization of allylamine/allylalcohol mixed gas plasmas) combined with an understanding of the gas-phase chemistry in these systems and cell-surfaces interaction studies highlights key properties required to tune the surface chemistries that can promote or deter cell viability and proliferation. Thus, this presentation will highlight a few key examples, including inherent challenges, where such a unified, comprehensive approach has been fruitful for 2D and 3D materials intended for use as antimicrobial materials, in separations, and for tissue engineering applications.

9:20am **BI+NS-WeM5 The Ins and Outs of Functionalized Natural Materials for Applications in Drug Delivery and Separations**, ***Norma Alcantar***, *R. Toomey, Z. Veisi*, University of South Florida, *A. Cardenas-Valencia, M. Cardenas*, SRI International, *R. Falahat*, Moffitt Cancer Center, *T. Peng, F. Guo*, University of South Florida **INVITED**

In the last decade, numerous natural materials have been investigated as platforms in functionalized surfaces. In our case, we have studied the structure and properties of two natural materials, chitosan from crustaceous shells and cactus mucilage from cactus plants. Those two natural materials have been used as building blocks in drug delivery systems, and as flocculants or adsorbent materials to remove contaminants from water. In the drug delivery systems, the natural material is used as surface membranes capable to respond to external stimuli. Our team has discovered that chitosan has a specific bond with the MUC1 enzyme found in epithelial-type cancers, which can enhance its specificity towards cancer cells when used in drug delivery systems. The results of our research have also shown that depending on the biophysical conditions surrounding the natural materials, their response to hydrophilic and hydrophobic interactions to separate organic and inorganic contaminants are controlled by their structure, which can then be finely tuned to enhance their performance. The use of natural materials for functional applications is an area of study that could lead to discoveries in microfluidic devices, health applications, cosmetics, coatings and paintings, and water purification systems.

11:00am **BI+NS-WeM10 Combinatorial Material Chemistry-Topography Screening: The ChemoTopo Chip**, ***Britta Koch****, University of Nottingham, UK, *A. Vasilevich, N. Beijer, J. de Boer*, Maastricht University, The Netherlands, *M.R. Alexander*, The University of Nottingham, UK

The interaction of cells with their culture substrate is critical to their fate, having a profound impact on cell response and viability. However, complex cell-cell as well as cell-matrix interactions in native tissue make it challenging to emulate *in vivo* cell behavior in the lab. The design of man-made, biomimetic cell environments hold great potential for biomedical

*** BID Early Career Researchers Award**

applications like tissue engineering, disease modeling and drug screening. Therefore, suitable biomaterials are sought that can interface with cells and provide adequate physical, chemical and biological characteristics to elicit the desired cell response in a well-defined *in vitro* environment.

In recent years, microarray technology in combination with high-throughput surface characterization methods has proven to be a valuable tool for the cost-efficient and rapid screening of large libraries of biomaterial candidates. However, until now screening has been performed either on planar samples, focusing on optimizing sample chemistry rather than topography [1] or on topography with no chemical variation [2]. Here we propose a novel platform that augments the chemical screening approach with deterministic control of the topography. This new platform called the 'ChemoTopo Chip' allows the systematic investigation of combinatorial effects of well-defined surface chemistry and topography and moves closer to recapitulating the range of 3D cues at play *in vivo* within an *in vitro* screen. The first results on the identification of hit combinations supporting mesenchymal stem cell growth are presented and future steps aiming at enhancing our global understanding of the context-dependent cell response are outlined. The ChemoTopo Chip platform contributes to the discovery of novel substrates with the potential to ultimately translate these into biomedical applications. Also, the gathering of data allows to develop surface structure-property relationships from which understanding can be generated to support rational design of the *in vitro* cell environment.

[1]. Y. Mei, K. Saha, S. R. Bogatyrev, J. Yang, A. L. Hook, Z. I. Kalcioglu, S.-W. Cho, M. Mitalipova, N. Pyzocha, F. Rojas, K. J. Van Vliet, M. C. Davies, M. R. Alexander, R. Langer, R. Jaenisch, D. G. Anderson. *Nature Materials* 9, 768-778 (2010).

[2]. H. V . Unadkat, M. Hulsman, K. Cornelissen, B. J. Papenburg, R. K. Truckenmüller, A. E. Carpenter, M. Wessling, G. F. Post, M. Netz, M. J. T. Reinders, D. Stamatialis, C. A. Bitterswijk, J. de Boer. *PNAS* 108, 16565-16570 (2011).

11:20am **BI+NS-WeM11 Combining Surface Analytical and Computational Techniques to Investigate Orientation Effects of Immobilized Proteins**, ***Elisa Harrison***, *G. Interlandi, D.G. Castner*, University of Washington, Seattle

Controlling how proteins are immobilized (e.g. controlling their orientation and conformation) is essential for developing and optimizing the performance of *in vitro* binding protein devices, such as enzyme-linked immunosorbent assays. The objective of this work is to develop new methodologies to study proteins and complex mixtures of proteins immobilized onto surfaces.

The focus of this study was to control and characterize the orientation of protein G B1, an IgG antibody-binding domain of protein G, on well-defined surfaces as well as measure the effect of protein G B1 orientation on IgG antibody binding using a variety of surface analytical and computational techniques. The goal was to immobilize protein G B1 into well-ordered films with different orientations that control the accessibility of antibody binding sites.

The surface sensitivity of time-of-flight secondary ion mass spectrometry (ToF-SIMS) was used to distinguish between different proteins and their orientation by monitoring the changes in intensity of characteristic amino acid mass fragments. Amino acids with asymmetric distributions (Asn, Trp, Gly, Ala, and Thr) were used to calculate peak intensity ratios from ToF-SIMS data in the C- and N-terminus of protein G B1 to determine the orientation of five different cysteine mutants of protein G B1 covalently attached to a maleimide surface.

To study the effect of protein orientation on antibody binding, we formed multilayer protein films. Quartz crystal microbalance with dissipation monitoring (QCM-D) detected protein coverages of 69 - 130 ng/cm^2. QCM-D and X-ray photoelectron spectroscopy (XPS) analysis revealed that packing density along with orientation affected the antibody binding process. Spectra from ToF-SIMS using large Ar gas cluster ion sources distinguished between different proteins in multilayer protein systems.

Additionally, development of computational methods to study proteins on surfaces can complement surface analytical data. A Monte Carlo algorithm was developed to predict protein orientation on surfaces. Two distinct orientations of protein G B1 adsorbed onto a hydrophobic surface were found and characterized as two mutually exclusive sets of amino acids on the outermost β-sheets contacting the surface. This prediction was consistent with sum frequency generation (SFG) vibrational spectroscopy results. In fact, theoretical SFG spectra calculated from an equal combination of the two predicted orientations exhibited reasonable agreement with measured spectra of protein G B1 on polystyrene surfaces. This method has been expanded to predict protein G B1 orientations on more complex surfaces, such as self-assembled monolayers.

11:40am **BI+NS-WeM12 Characterizing the Tumor Microenvironment and Tumor Progression**, ***Blake Bluestein***, University of Washington, *F. Morrish, D. Hockenbery*, Fred Hutchinson Cancer Research Center, *L.J. Gamble*, University of Washington

Solid tumors are not simply masses of malignant cells but are a structurally complex system, composed of a myriad of cells. The interactions between malignant cells and non-transformed cells form the tumor microenvironment. The tumor microenvironment has been associated with regulating tumor cell growth, metastatic potential, and drug resistance. Here, a combination of techniques including imaging time-of-flight secondary ion mass spectrometry (ToF-SIMS), H&E staining, and second harmonic generation (SHG) microscopy are used to analyze pancreatic biopsies from a mouse model with Myc-dependent inducible pancreatic β-cell neoplasia to relate changes in the composition and distribution of metabolic related molecules with tumor development. Myc, one of the most frequently deregulated oncogenes in human cancers, contributes to tumorigenesis through various mechanisms, including the deregulation of cell proliferation and metabolic alterations.

Pancreatic tissues were harvested and frozen in optimal cutting temperature (OCT) at 6 days post Myc induction and without any Myc induction (control). Cryosections (4 µm thickness) were serially cut, with one used for H&E staining and SHG microscopy, and one for ToF-SIMS analysis. ToF-SIMS data was acquired using an IONTOF TOF.SIMS 5. Regions identified by analysis and principal components analysis (PCA) were cross-referenced against immunohistochemical, H&E, and SHG images to differentiate the tumor areas from the surrounding tissue.

PCA analysis of ToF-SIMS image data separate tumor from surrounding tissue and reveal the differences in chemistries between the two regions. The Myc-induced islet tumors exhibit a signal of C14:0, a likely product of *de novo* fatty acid synthesis within the islet tumor. Image data shows higher signal regions within the interior of the tumor. These regions exhibit an increased, localized signal of CN^-, CNO^-, Fe^+, and characteristic histidine fragments, $C_5H_8N_3^+$ and $C_6H_5N_2O^+$. SHG images showed that there were no organized structures in these higher signal regions and immunohistochemistry showed no signs of angiogenic processes, confirming that these areas are blood pools resulting from vascular hemorrhaging. Further metabolic analyses showed that when compared to control islets, Myc-induced tumor islets exhibited increased intensities of amino acids and phosphatidylcholine lipids (30:0, 32:1, 32:2), which are known to be related to tumor growth. Tissue surrounding the Myc islet tumors exhibited lower intensities of serine, glycine, and arginine when compared to the tissue surrounding the control islets, which suggests tumor uptake or an increased catabolism induced by the adjacent tumor.

12:00pm **BI+NS-WeM13 Observing the Molecular Mechanisms of Insect Adhesion by Sum Frequency Generation Spectroscopy**, *J.E. Fowler*, Oregon State University, *S.N. Gorb*, Kiel University, Germany, *T. Weidner*, Aarhus University, Denmark, ***Joe Baio***, Oregon State University

Many insects can walk on a range of natural surfaces through an adhesion process that combines an expansive array of hairy contacts on their feet, known as setae, and an adhesive fluid, forming contact between the setae and a substrate. Previous studies of this adhesion system have focused almost exclusively on the mechanical and kinematic aspects of adhesion, while ignoring the molecular interactions at the fluid – substrate interface. However, recent experiments illustrate that substrate chemistry does influence the adhesive forces produced by this fluid. Additionally, mass spectrometry results demonstrate that this adhesive fluid is a complex mixture containing both hydrophobic (*i.e.* fatty acids and lipids) and hydrophilic (*i.e.* sugars, alcohols, and carbohydrates) compounds. We hypothesize that the molecular structure at the adhesive fluid-substrate interface is dynamic, with different molecules within the fluid selectively organizing at the interface as a function of substrate hydrophobicity. In the work presented here we probe the molecular interactions between the adhesive fluid taken from lady bugs (*Cocinella septempunctata*) and three model substrates, polyethylene oxide, polystyrene and CaF_2 with vibrational sum frequency generation (SFG) spectroscopy and scanning electron microscopy (SEM). The observed water contact angles for the polyethylene oxide, polystyrene and CaF_2 substrates were 66^o, 92^o and 106^o, respectively. High-resolution SEM images of individual seta-fluid footprints on the surfaces indicate localized "water in oil" emulsion de-wetting with no sign of distinct patterning. SFG spectra collected, from the three substrates, at the C-H (2800-3100 cm^{-1}) contain peaks at 2850 cm^{-1} and 2870 cm^{-1}, characteristic of symmetric CH_2 and CH_3 stretches, respectively. The presence of these peaks suggests an ordered hydrocarbon monolayer at the interface. However, subtle changes in ordering of these molecular groups at the interface were observed across substrates by comparing the ratio of the intensities of observed vibrational modes related to the CH_2 and CH_3 modes. Across the three different substrates this ratio increased with surface hydrophobicity suggesting that the fluid-surface interactions adapt to different substrate chemistries.

Biomaterial Interfaces Division
Room: 12 - Session BI+AS-WeA

In Honor of Dave Castner's 65th Birthday: Multitechnique Bio-Surface Characterization II

Moderators: Lara Gamble, University of Washington, Daniel Graham, University of Washington

2:20pm **BI+AS-WeA1 Contributions Advancing Surface Technologies: NEXAFS, ESCA, Rhodium (and More)**, ***Buddy D. Ratner***, University of Washington, Seattle **INVITED**

The broad impact that surface science has had on so many technologies is mirrored by the contributions of Professor David Castner to many sub-fields dependent upon surface science. Dave's earliest contributions to the scientific literature were associated with the surface science of rhodium, iron and cobalt catalysts. Papers were published addressing CO hydrogenation, Fischer-Tropsch polymerization and related topics with relevance to energy consumption and chemical production. With Dave's arrival at the University of Washington in 1986, the subjects of his research shifted from catalysis to biomedical surfaces. Dave and I have always shared a common interest (maybe passion). That is, generating quality data and extracting maximum information from that data. We both had extensive experience with early HP5950 electron spectroscopy for chemical analysis (ESCA) instruments. These monochromatized instruments generated exceptionally high resolution spectra for that era, and the instruments had effective charge compensation for insulators. This allowed us to make great strides in highlighting the use of ESCA for bio-relevant surfaces and biological materials. The theme of data quality has persisted into the present with newer ESCA instruments and then SIMS instrumentation. Dave Castner has taken surface analysis into the 21st century with studies on cells, proteins, novel polymer surfaces and nano-materials. This talk will highlight Dave Castner's remarkable contributions to surface science with particular emphasis on his contributions to the evolution of methods available to analyze complex surfaces and morphologies.

3:00pm **BI+AS-WeA3 Characterization of Bio-Molecules with GCIB-SIMS equipped with MS/MS Spectrometer**, ***Jiro Matsuo***, *T. Seki*, *T. Aoki*, Kyoto University, SENTA, JST, Japan

Secondary ion mass spectrometry (SIMS) is now widely used for chemical analysis of polymers and biological materials that have a rather complicated molecular structure. Various types of primary ion beams and mass spectrometers have been developed and used in an attempt to improve sensitivity, as well as lateral and mass resolution. Large gas cluster ion beams (GCIB) have been commercialized for surface analysis techniques, such as SIMS and XPS. Molecular depth profiling and three-dimensional analysis have been applied on organic devices and biological materials. A large cluster ion beam could overcome the limitation of ion dose, which is the biggest obstacle for obtaining more signals in static SIMS.

To expand the applications of the SIMS technique, we have developed a finely focused large cluster ion beam (~1mm) for the primary ion beam for use in SIMS [1] and combined it with mass spectrometers of the quadrupole time-of-flight mass spectrometry (Q-TOF) type without pulsing primary ions. This mass spectrometer is equipped with MS/MS capability and allows to determine the structure of the secondary ion by using the collision-induced dissociation (CID) technique. This is a new SIMS instrument that helps in the characterization of biomolecules in cells, tissue and medicine. For instance, the detection limit of a drug molecule is improved by using the MS/MS technique, because of a much-reduced background.

In this paper, we demonstrate the capability of SIMS with the MS/MS spectrometer to determine the structure of molecular-related ions and discuss the benefits and drawbacks of this technique.

[1] J. Matsuo, S. Torii, K. Yamauchi, K. Wakamoto, M. Kusakari, S. Nakagawa, M. Fujii, T. Aoki, and T. Seki, *Appl. Phys. Express*, ***7*** (2014), 056602

3:20pm **BI+AS-WeA4 Linking Nanosilver (AgNP) Toxicity to the Physicochemical Properties of the Particles which can Change as a Function of Experimental and Biological Conditions**, ***Donald Baer***, Pacific Northwest National Laboratory, *J.M. Brown*, University of Colorado at Denver, *A. Porter*, Imperial College London, UK, *B.D. Thrall*, Pacific Northwest National Laboratory, *T.D. Tetley*, Imperial College London, UK, *L.S. Van Winkle*, University of California at Davis, *T. Xia*, University of California at Los Angeles

Although colloidal Ag is generally considered safe for humans, use of nanosilver in consumer products has dramatically increased both the amount of Ag exposure and possible exposure pathways. To fill knowledge gaps for nano-Ag safety assessment, the National Institute of Environmental Health Sciences supported a consortium of investigators to examine how physical and chemical characteristics of AgNPs can lead to adverse health outcomes. Here we report a consortium perspective linking physicochemical properties of the particles to Ag biodistribution and toxicity. It is necessary to recognize the dynamic nature of AgNPs. They can change in response to handling and variations in their environment and such changes can influence Ag biodistribution and biological responses. Consortium studies identified the critical relationships among AgNP properties, environmental effects, and the biodistribution and fate of Ag associated with the particles. Three critical regions of interactions were identified: i) effect of exposure medium and biological environment on particle properties and transformations; ii) processes occurring at the cellular surface impacting particle attachment, uptake, accumulation and clearance; and iii) particle fate and transformations within a cell. The nature of AgNPs during biological exposure is influenced by the initial characteristics of the particles including size, structure and the presence of designed or inadvertent coatings. These initial properties are usually altered by exposure to artificial or natural media. These physicochemical properties are often time dependent and such changes, including often ignored effects due to handling or storage, can influence biological outcomes. Ag can be transported into cells as both ions and particles. While ions are known to impact cytotoxicity, AgNPs within cells often have greater toxicity. Intercellular processes are similar to those in extracellular media except that the Ag is located within specific microenvironments within a cell. It appears that intracellular dissolution of Ag is a major cause of toxicity.

4:20pm **BI+AS-WeA7 Protein Imaging from the Subcellular Level to the Single Protein Level**, ***DaeWon Moon***, DGIST, Republic of Korea

Most of biological story tellings are mainly based on proteins and their interactions. Therefore protein imaging and their interaction studies have been the key interest in bio imaging. Most of protein bioimaging have been based on confocal fluorescence microscopy for 2 or 3 proteins. We have developed a new multiplex protein imaging method for TOF-SIMS with metal oxide nanoparticle (MONP) conjugated with proteins up to 9 proteins, in theory, several tens, and a single protein imaging technique based on He Ion Microscopy (HIM)

In SIMS analysis, MONPs provide high secondary ionization yield and amplification of ion yields. We systhesized 9 MONPs working right such as CoO, CdO, Fe3O4, TiO2, PbO, In2O3, SiO2, Al2O3, La2O3. In addition to protein imaging, SIMS intrinsically provides tens of bio-molecular imaging including lipids and metabolites, and metals with a TOF mass analyzer, which makes this new methodology to be an omni-molecular mass spectrometric imaging technique. Sliced and cultured mouse hippocampal tissues were imaged with typical spatial resolution of 2 μm, which can be improved down to 300 nm for 9 neuronal proteins. Proteins chosen to image mouse hippocampal tissues are NeuN for all nuclei, Cav1,3 for neuron cells, Iba1 for microglia cells, GFAP for astrocytes, AMPA receptor, phosphorylated Tau, amyloid beta (Aß) 1-42, amyloid precursor protein, and APOE, which were selected to visualize important proteins as landmarks of Alzheimer Disease (AD). With multiplex proteins imaging, we could estimate the proximity of associated proteins in mouse hippocampal tissues, which changes with aging and AD progression.

Since HIM has a spatial resolution of 0.5 nm, HIM can observe single proteins in theory but in practice, it may be very dfficult to observe a single protein molecule due to the similar secondary electron yields of proteins compared to other proteins or extracellular matrix molecules. We demonstrated that HIM can image each MONP conjugated with proteins from a mouse hippocampal tissue revealing the distribution of single proteins in synapses, neuronal soma, amyloid plaques, and neurofibrillary tangels with their changes along aging and AD.

With the co-development of multiplex protein SIMS imaging and single protein HIM imaging technology, I expect we can improve our understanding on the role of proteins and their interactions in biology, biomaterials, and medicine.

4:40pm **BI+AS-WeA8 Integrating Biological and Surface Chemical Characterisation to Probe Bacterial and Lipid Vessicle Interactions at Surfaces**, ***Sally McArthur***, Swinburne University of Technology and CSIRO, Australia, *M. Abrigo, H. Askew, K.L. Jarvis*, Swinburne University of Technology, Australia

Control and the ability to elicit specific responses from a biological system lies at the heart of most bioengineering. We want to immobilize proteins on biosensors but ask them to behave as they would in the body, stimulate cells to assemble tissues, form new blood vessels and replicate structures in the lab just as well as they can in our bodies. We want methods that prevent bacteria forming biofilms and better still we would like them to stop attaching to surfaces full stop. We have an armada of techniques at our disposal, surface engineering, macro, micro and nanomaterials, drugs and biomolecules, light, electricity and a plethora of analysis tools to give us new insight into how the systems we build behave. But as we increase the complexity of the system, we need to be able to match this with combinations of characterisation techniques that probe both the biological and physicochemical processes occurring at the biointerface.

This talk will explore how we utilise QCM, XPS, ToF-SIMS, florescence imaging and biological assays to investigate the influence of surface chemistry and micro and nanoscale topography on interactions with lipid vesicles and bacteria.

5:00pm **BI+AS-WeA9 A Physical Chemist and a Chemical Engineer Walk into a Bar… Reflections on Surface and Interface Analysis**, ***Matthew Wagner***, The Procter & Gamble Company **INVITED**

Surface and interface science is critical to many applications across many industries, spanning from advanced technologies in microelectronics and biomaterials to everyday household goods such as laundry detergents and shampoos. Micro and nanoscale phenomena at surfaces and interfaces, including adsorption, wetting, self-assembly, and many others, drive macroscale performance, resulting in significant benefits when done well and significant failures when poorly understood or controlled. At all scales, measurement science specific to surfaces and interfaces is critical to understanding these phenomena.

In the field of biomaterials science (and beyond), protein adsorption is a foundational step in all interactions between biological systems and synthetic materials. Many surface analysis techniques have been applied to the characterization of adsorbed protein films, including understanding the amount, composition, spatial distribution, and orientation of adsorbed proteins. In this special session in honor of Dave Castner, this presentation will review key contributions from the Castner group on the application of multi-technique surface analysis techniques to adsorbed protein films. In particular, the use of ToF-SIMS and multivariate data analysis techniques in conjunction with complementary surface spectroscopies including XPS, NEXAFS, SPR, and others, will be reviewed. The broader impact of these developments in surface analysis methodologies on the fields of surface and interface science across industries will be discussed.

5:40pm **BI+AS-WeA11 Investigating the Cytotoxicity of Commercially Available Poly(*N*-isopropyl Acrylamide)-coated Surfaces**, *L. Stapleton, M.A. Cooperstein, P.A.H. Nguyen,* ***Heather Canavan***, University of New Mexico

Poly (*N*-isopropyl acrylamide) (pNIPAM) is a thermoresponsive polymer that undergoes a phase change at a physiologically relevant temperature range, which leads to mammalian cell release. Below its lower critical solution temperature (LCST ~32° C), pNIPAM becomes hydrated and is hydrophilic. In this state, its chains become extended and cells detach as intact cell sheets. Before the detached cell sheets can be used on humans, the cytotoxicity of the surfaces must be accessed. In previous studies, we found that although most techniques for polymerizing NIPAM (e.g., plasma polymerization, ppNIPAM; and sol-gel preparations of NIPAM, spNIPAM) yielded biocompatible films, those from commercially available NIPAM (cpNIPAM) were relatively cytotoxic. In this work, we investigate the reasons behind this anomaly. The cpNIPAM-coated surfaces were evaluated for their thermoresponse and surface chemistry using standard surface science techniques (e.g., goniometry, X-ray photoelectron spectroscopy). The relative biocompatibility of the substrates with cultured bovine aortic endothelial cells (BAECs) and monkey kidney epithelial cells exposed to extracts from the cpNIPAM, spNIPAM, and ppNIPAM films was assessed using pop off experiments and Live/Dead assays. In addition, the extract solutions themselves were analyzed by NMR and mass spectroscopy. We find that the diminished cell viability of BAECs exposed to cpNIPAM substrates is due to a combination of factors, including the inclusion of short chain length polymers and the presence of unreacted catalyst. This work will have valuable insights into the cytotoxicity of cpNIPAM-coated surfaces, and therefore, into the applicability of cells grown on this surface for human subjects.

6:00pm **BI+AS-WeA12 Development of Surface Analysis Methods for Characterizing Immobilized Proteins**, ***David Castner***, University of Washington

One of the first events that occurs when a biomedical device is placed in the biological environment is the interactions of proteins with the surface region of the biomedical device. How the proteins interact with the surface can have a significant impact on further biological responses in both *in vivo* and *in vitro* applications. Thus, it is essential to understand how proteins interact with surfaces and any structural modifications they undergo as a result of these interactions. Key objectives for characterizing surface-bound proteins are (1) identifying the type of proteins bound to the surface, (2) determining the amount of each surface-bound protein, (3) determining the conformation and orientation of the bound proteins and (4) characterizing the spatial distributions of surface-bound proteins. There are many bonding mechanisms for attaching proteins to surfaces (charge-charge, coordination complexes, covalent bond formation, ligand interactions, etc.). Each method has its advantages and disadvantages. How the protein structure, especially its conformation and orientation, is affected by surface attachment will be a function of the surface structure and composition of the biomaterial as well as properties of the protein. There are often time-dependent changes in the composition, conformation, orientation, and distribution of the complex, multi-component protein films deposited from the biological environment. So the structural determinations for surface bound proteins need to be related not only to the properties of the biomaterial surface and protein, but also to the experimental conditions used to attach the protein to the surface. Results using experimental methods (XPS, ToF-SIMS, SFG, SPR, QCM-D, etc.) combined with computation methods (e.g., MD simulations) provide important information about the attachment, specificity, orientation, conformation and spatial distribution of surface immobilized proteins. This talk will discuss the significant progress has been made in developing surface analysis methods for characterizing the structure of surface immobilized proteins as well as the current challenges. Future protein characterization studies need to be extended to more complex samples as well as more tightly integrating complementary techniques that can be used to directly study immobilized proteins in the presence of the biological environment. In addition, further advances in computational methods for predicting protein-surface interactions and structures as well as providing structural information at the atomic level for large biomolecules is needed.

Applied Surface Science Division
Room: 13 - Session AS+BI+SA+SS-ThM

Spectroscopy of the Changing Surface

Moderators: Timothy Nunney, Thermo Fisher Scientific, UK, Tony Ohlhausen, Sandia National Laboratory

8:00am **AS+BI+SA+SS-ThM1 In Situ Investigation of the Dynamic Transformations of Model Catalyst Surfaces using Ambient Pressure XPS**, ***Iradwikanari Waluyo***, Brookhaven National Laboratory **INVITED**

In heterogeneous catalysis, the interaction between reactant molecules and the surface of the catalyst often causes changes in the surface composition and chemical state of the catalyst, which may result in changes in the reactivity of the catalyst. Using ambient pressure x-ray photoelectron spectroscopy (AP-XPS), these changes can be monitored in situ under close-to-realistic conditions. Unlike conventional XPS, which requires UHV conditions, AP-XPS measurements can be performed in the presence of gases at pressures of up to 100 Torr through the use differentially pumped analyzer, small analyzer entrance aperture, and x-ray transparent windows. Although AP-XPS measurements using lab x-ray sources are possible and becoming more common, experiments at modern synchrotron light sources have distinct and significant advantages including tunable photon energy, tightly focused beam, and better resolution. A general overview of the technique as well as recent experimental results will be presented. Examples shown include (1) the potassium-promoted reduction of $Cu_2O/Cu(111)$ by CO, in which the reduction of Cu^+ to Cu is accelerated by the presence of K through the formation of surface carbonate species, (2) the surface segregation of Pt/Cu(111) model bimetallic catalyst in the presence of various reactant gases, and (3) the reduction of $Cu_2O/Pt/Cu(111)$ by H_2.

8:40am **AS+BI+SA+SS-ThM3 Observation of Oxygen Binding on PGM-free Electrocatalysts by Ambient Pressure XPS and XAS**, ***Kateryna Artyushkova***, University of New Mexico, *M.J. Dzara*, *S. Pylypenko*, Colorado School of Mines, *P. Atanassov*, University of New Mexico

The most promising class of PGM-free materials for oxygen reduction reaction (ORR) is based on graphene-like carbon containing nitrogen and transition metal (MNC). They show promise as replacement of Pt in two different technological platforms - alkaline exchange membrane fuel cells (AEMFCs) and proton exchange membrane fuel cells (PEMFC). It is well established that nitrogen coordination with metal in the carbon network of MNC materials is directly related to ORR activity; however, the ***exact nature of the active sites*** is still debated even after over 50 years of research. Understanding the specific roles of nitrogen and metal in the properties/activity/stability/durability of MNC-based catalytic materials is a prerequisite for the rational design of ORR electrocatalysts with improved performance.

The key component in elucidating the relationship between the chemistry of active sites and activity is a better understanding of the formation of adsorbates, intermediates, and products during reactions occurring within the fuel cell.

In situ monitoring reaction steps under realistic conditions in metal-free and metal-containing building blocks will shed light onto the reaction mechanism that is essential for developing active and durable PGM-free catalyst for ORR.

We will report on AP-XPS analysis for series of electrocatalysts belonging to Fe-N-carbon families based on sacrificial support method (SSM) and Metal-organic frameworks (MOF). The effect the nitrogen chemistry and the type of iron have on the oxygen binding was investigated by ambient pressure X-ray Photoelectron Spectroscopy (XPS) and X-ray Adsorption Spectroscopy (XAS) under an O_2 environment at operating temperature of the fuel cell. The effect of the relative abundance of different types of nitrogens, such as pyridinic, coordinated to iron and hydrogenated nitrogens (pyrrolic and hydrogenated pyridine) on the preference of oxygen binding is studied by high-resolution nitrogen photoelectron spectra. The role of metallic and atomically dispersed iron will be investigated by a combination of XAS and XPS. Linking differences in oxygen binding to the differences in the chemistry of the electrocatalysts are of ultimate importance for elucidating the oxygen reduction reaction mechanism.

1. Artyushkova, K., et al., *Oxygen Binding to Active Sites of Fe–N–C ORR Electrocatalysts Observed by Ambient-Pressure XPS.* The Journal of Physical Chemistry C, 2017. **121**(5): p. 2836-2843.

9:00am **AS+BI+SA+SS-ThM4 In situ Monitoring of Electrochemically Generated Carbene by XPS**, ***Pinar Aydogan Gokturk****, *S.E. Donmez, Y.E. Turkmen, B. Ulgut, S. Suzer*, Bilkent University, Turkey

Ionic liquids provide a platform for fundamental electrochemical studies in vacuum. In this present work, we report an in-situ X-ray photoelectron spectroscopic (XPS) investigation of N-heterocyclic carbene(NHC) generation from the electrochemical reduction of imidazolium based ionic liquids (ILs) through changes in oxidation state of nitrogen atoms. The IL serves as an electroactive material as well as the electrolyte in the cell between a Si substrate which is connected to the instrument ground and a gold wire connected to the sample holder for electrical connection. Through the course of the electrochemical reaction, the positive charge on imidazolium cation is neutralized to give free NHC as reflected by the distinct shifts in the N 1s and C 1s binding energies. The observations are further supported by colorful adduct formation of carbenes with CS_2, reversible redox peaks in the voltammogram and the density functional theory calculations. The presented structure and XPS measurements can lead on understanding of the mechanism for various electrochemical reactions.

9:20am **AS+BI+SA+SS-ThM5 The Influence of Water on the Ionic Liquid-Vapor Interface**, ***John Newberg***, University of Delaware, *M.B. Shiflett*, University of Kansas, *A. Broderick, Y. Khalifa*, University of Delaware

Ionic liquids (ILs) have a wide array of applications in biotechnology, coatings, synthesis, separations, and energy sciences. Many of these processes involve either IL-solid or IL-vapor interactions and it is important we understand the fundamental interfacial properties of ILs on a molecular level. Due to the ubiquity of water and the hydrophilic nature of ILs, water can either be unintentionally present or often intentionally added to alter IL properties including density, viscosity, friction and electrochemical window. In this talk we will highlight our recent efforts examining the IL-water vapor interface utilizing ambient pressure X-ray photoelectron spectroscopy (APXPS). APXPS allows for a molecular level assessment of the IL-vapor interface including a quantitative assessment of interfacial water concentration, moiety specific electronic environment changes, structural changes and obtaining adsorbate energetics.

9:40am **AS+BI+SA+SS-ThM6 Ambient Pressure XPS Studies of Model N-C and Fe-N-C Catalysts Under Oxygen Environment**, ***Michael Dzara***, Colorado School of Mines, *K. Artyushkova*, University of New Mexico, *C. Ngo, M.B. Strand, J. Hagen, S. Pylypenko*, Colorado School of Mines

Producing inexpensive polymer electrolyte membrane fuel cells requires significant reduction in the amount of platinum group metal (PGM) oxygen reduction reaction (ORR) catalyst used. High surface area iron- and nitrogen-functionalized carbon (Fe-N-C) materials are a promising PGM-free replacement. These catalysts are very heterogeneous, leading to difficulties in discerning contributions from various potential active sites and identifying the most active species.[1] Techniques such as scanning transmission electron microscopy (STEM), energy dispersive x-ray spectroscopy (EDS), and x-ray photoelectron spectroscopy (XPS) provide structural and chemical information that can be correlated to ORR activity measured with electrochemical methods. Ambient pressure XPS (AP-XPS) and x-ray absorption spectroscopy (XAS) conducted in a humidified O_2 environment, at an elevated temperature, and with applied potential offer opportunities to study materials under *in situ* conditions to determine adsorbates, intermediates, and products during ORR steps.[2,3]

In this work, model Fe-N-C catalysts are studied along with reference nitrogen-doped carbon (N-C) materials. Development of model catalyst materials with controlled morphology and speciation can simplify the elucidation of active sites. Micro-porous N-C nanospheres with high graphitic content were synthesized by a solvothermal treatment of resorcinol, formaldehyde, and ethylenediamine, and a subsequent pyrolysis in N_2.[4] Incorporation of Fe into the N-C nanospheres was carried out by wet-impregnation of various Fe precursors followed by a second N_2 pyrolysis. By varying synthetic parameters, a set of N-C and Fe-N-C nanospheres with diverse compositions and properties were produced. Differences in composition and structure were evaluated using STEM-EDS and XPS, demonstrating control over N and Fe quantity and speciation. Select N-C and Fe-N-C nanospheres were then characterized with *in situ* AP-XPS, and in the case of Fe-N-C nanospheres, *in situ* XAS. By understanding the ORR on

*** ASSD Student Award Finalist**

these model Fe-N-C nanospheres, synthesis-property-performance conclusions are drawn, guiding the development of highly active Fe-N-C catalysts.

[1] A. Serov, K. Artyushkova, E. Niangar, C. Wang, N. Dale, F. Jaouen, M.-T. Sougrati, Q. Jia, S. Mukerjee, and P. Atanassov, Nano Energy **16**, 293 (2015).

[2] K. Artyushkova, I. Matanovic, B. Halevi, and P. Atanassov, J. Phys. Chem. C **121**, 2836 (2017).

[3] Q. Jia, N. Ramaswamy, H. Hafiz, U. Tylus, K. Strickland, G. Wu, B. Barbiellini, A. Bansil, E.F. Holby, P. Zelenay, and S. Mukerjee, ACS Nano **9**, 12496 (2015).

[4] N.P. Wickramaratne, J. Xu, M. Wang, L. Zhu, L. Dai, and M. Jaroniec, Chem. Mater. **26**, 2820 (2014).

11:00am **AS+BI+SA+SS-ThM10 Real-time Photoelectron Spectroscopy Observation of Oxidation and Reduction Kinetics of Ni(111) Surface**, ***Ryo Taga***, *S. Ogawa, Y. Takakuwa*, Tohoku University, Japan

Nitrogen contained in the air is oxidized and then harmful nitrogen oxide (NO_X) is formed in the combustion chamber of engine. Accordingly, the exhaust gas which contains NO_X is purified by catalysts. However, platinum group metals, whose prices are likely to rise by the depletion of resources in the future, are used as the catalysts, so the reduction of the amount used is an important matter for industrial and environmental fields. On the other hand, it has been already known that Ni has an effect to NO_X reduction, but the its catalytic ability disappears when the Ni surface is oxidized. If O atoms on the Ni surface can be efficiently desorbed, Ni is expected as a catalyst for NO reduction. In the previous studies, some of researches have studied about reduction of oxidized Ni surfaces, but the relation between oxide reduction kinetics and behavior of O atoms has not yet been clarified. In this study, the oxidation and reduction kinetics on Ni(111) surfaces was investigated by real-time ultraviolet photoelectron spectroscopy (UPS). to investigate the amount of O atom adsorption and the changes of work function.

The experiments were performed using UPS apparatus with base pressure of ~3×10^{-8} Pa. The Ni(111) surface was firstly cleaned by the Ar^+ ion bombardment, and the annealed at 600℃. O_2 gas (1×10^{-5} Pa) was directly introduced to UPS apparatus at the sample temperature of 100℃. After the end of the introduction of O_2 gas, the sample heated up to and H_2 gas (1×10^{-5} Pa) was introduced in order to investigate the Ni oxide reduction process. The photoelectron spectra were measured repeatedly each 72 s during oxidation and reduction.

From the time evolution of O 2p photoelectron spectra, we obtained the O 2p uptake curve and the change in work function. When O_2 gas was introduced, O 2p intensity increases linearly, so it turned out that the oxidation of Ni(111) surfaces was a zero order reaction. After introduction of H_2 gas, O 2p intensity decreases gently for about 500 s and then decreased rapidly. On the other hand, the work function slightly increased and then rapidly decreased. The work function reaches the same value on the clean Ni(111) surface. Therefore, Ni oxide can be reduced completely using H_2 gas.

These changes after introduction of H_2 gas can be divided into two areas. In the first area, O atoms are drawing from subsurface because of slight increase of work function. In the second area, then, it is suggested that the reduction progresses and the clean Ni surface area enlarges as like to island growth. In the symposium, we will discuss the reduction process of the oxidized Ni surface by NO gas.

11:20am **AS+BI+SA+SS-ThM11 Comparison of Initial Oxidation Kinetics between p- and n-type Si(001) Surfaces Studied by Real-time Photoelectron Spectroscopy**, ***Yuki Sekihata***, *S. Ogawa*, Tohoku University, Japan, *A. Yoshigoe*, JAEA, Japan, *R. Taga*, Tohoku University, Japan, *S. Ishidzuka*, National Institute of Technology, Akita College, Japan, *Y. Takakuwa*, Tohoku University, Japan

An oxidation reaction is the "trade" of electrons between oxygen and other materials, therefore it is thought that there is a difference in the oxidation kinetics on between p-type and n-type Si substrates. In the previous researches about the kinetics of the thermal oxidation of Si, the oxidation rate have not taken account of the difference of conduction type because the thermal oxidation was performed in high temperature region above 600℃ named intrinsic region where the intrinsic carrier concentration becomes comparable to the donor or acceptor concentration. On the other hand, oxidation temperature becomes lower to form thin oxide films below 1nm. Therefore, we believe that the difference of conductivity affects an oxidation kinetics on the Si(001) surfaces, but there is no oxidation reaction models that takes into account the difference of conductivity. In this study, we investigated the oxidation reaction kinetics on p- and n-type Si surfaces using real-time ultraviolet photoelectron spectroscopy.

The samples for oxidation were p-Si(001) and n-Si(001) surfaces. The dopants were Boron and arsenic for p- and n-type substrates, respectively. Their density of dopants were approximately 10^{18} atoms/cm^3 so extrinsic region can be kept in the high temperature region even below 700℃. These samples were oxidized using O_2 gas at the pressure of 1.0×10^{-5} Pa. During the oxidation reaction, the photoelectron spectra were measured repeatedly, therefore time evolution of the amount of oxygen adsorption, work function, and band bending can be investigated.

In the room temperature oxidation, it is found that oxidation reaction coefficient on n-Si(001) is larger than that on p-Si(001). To clarify the reasons, we focus to the changes of work function due to the formation of dipole layer. The work function of the n-Si(001) surface shows negative value but p-Si(001) is positive value. From this result, we can estimate the adsorption positions of O atoms. O atoms have a negative charge in the bond of Si-O, so it can be assumed that oxygen is placed on the n-Si(001) surfaces, but it is subsurface in case of the p-Si(001) surface. In case of n-Si(001) substrates, the doped electrons spill out into the surface because many electrons exist in the substrate. As the result, oxidation reaction is promoted in the n-Si(001) surface. From these results, we found that there is a difference of oxidation kinetics depending on the conductivity. In the presentation, we will show also the difference of oxide states between them.

11:40am **AS+BI+SA+SS-ThM12 Co-Pyrphyrin on Cu_2O(111) and TiO_2(110): Properties and Stability under Near Operando Conditions**, ***Zbynek Novotny***, *W.-D. Zabka, M. Hotz, D. Leuenberger*, University of Zurich, Switzerland, *L. Artiglia, F. Orlando, M. Ammann*, Paul Scherrer Institut (PSI), Switzerland, *J. Osterwalder*, University of Zürich, Switzerland

The pyridine-based macrocycle Co-pyrphyrin (Co-Pyr) is a promising molecular water reduction catalyst recently synthesized at the University of Zurich [1]. We investigated Cu_2O(111) and TiO_2(110) substrates covered with a complete monolayer of Co-Pyr at pressures spanning from ultra-high vacuum (UHV) up to near ambient pressures of 1 mbar of water vapor. To study the surface photovoltage (SPV) effect, samples were illuminated with UV laser light through the electron spectrometer lens system. Both under UHV and water pressures up to 1 mbar, SPV-induced shifts of the order of ΔE_k = +120 meV were observed in case of Cu_2O(111), while for TiO_2(110), much smaller SPV shifts of -0.12 meV were observed. X-ray absorption spectroscopy (XAS) of the Co L3-edge in dependence of illumination and water exposure was used to monitor the electronic structure of the Co metal center of Co-Pyr molecules. Comparison to simulated XAS spectra reveals that on the TiO_2(110), the Co centers partially transform from a +2 to +1 oxidation state upon exposure to water, while on the Cu_2O(111), the Co remains in the +2 oxidation state irrespective of the water exposure. Our measurements provide insights into the stability and behavior of the Co-Pyr molecules studied under near operando conditions, further stimulating the use of these molecular catalysts in the next-generation of solar fuel cells.

[1] Joliat, E et al., *Dalton Transactions* **2016,***45* (4), 1737-1745.

Biomaterial Interfaces Division
Room: 12 - Session BI+AS+SA-ThM

Characterisation of Biological and Biomaterial Surfaces
Moderators: Daniel Graham, University of Washington, Tobias Weidner, Aarhus University, Denmark

8:00am **BI+AS+SA-ThM1 Lipid Involvement in the Regenerative Processes of *Dugesia dorotocephala* - A GCIB ToF-SIMS Imaging Study**, ***Tina Angerrer***, *M.J. Taylor, D.J. Graham, L.J. Gamble*, University of Washington

Dugesia dorotocephala are planaria belonging to the class of Turbellaria, or non-parasitic flat worms. They are best known for their fascinating regenerative abilities, which allow them to be cut into more than 200 pieces, each piece missing essential parts necessary for the worms' survival and each re-growing a new flatworm. This level of reorganization involves a complex interplay of a wide range of molecules that varies spatially and temporally but is still poorly understood.

Recently the involvement of peptides and proteins in the process of regrowing the head and developing a new central nervous system has been studied by Sweedler et al.[1] using MALDI imaging. MALDI, in contrast to TOF-SIMS imaging, is capable of studying the distributions of peptides in tissue but spatial resolution is limited and molecules of interest have to be partially predetermined by the choice of matrix.

Using the J105-3D Chemical Imager, (Ionoptika Ltd) equipped with a 40 keV gas cluster ion beam (GCIB), molecules with sizes up to 2000 Da can be localized at a cellular scale, with spatial resolutions better than 3 µm.[2] Since ToF-SIMS is a label free technique, it can be used in an untargeted discovery approach which, in biological samples, is mainly used to study lipid distributions.

Lipids are a diverse group of molecules fulfilling numerous functions such as energy storage and cell signaling, however lipid and fatty acid data for Dugesia in general is very limited and their localizations completely unknown.[3] Our studies were targeted at establishing a full body lipid profile for the different organ systems present in Dugesia as well as monitoring their changes due to stem cell migration during head regrowth and eye/CNS regeneration.

Dugesia flatworms were sectioned on a cryomicrotome at -20 °C and slices were placed on ITO coated glass. After preparation samples were immediately taken to the lab for analysis. Sample preparation and transport time was kept to less than 2 hours to minimize lipid degradation. After SIMS analysis, optical images were acquired in order to facilitate identification of structures seen within the worms. To deal with the increased spectral and spatial complexity provided by our improved instrumental capabilities, imaging PCA was used to "untangle" the data. In this presentation we will present the results of our studies showing the unique lipid distributions throughout Dugesia cross sections and discuss their relevance.

[1] T. H. Ong, *et al.*, J Biol Chem 2016, 291, 8109-8120.

[2] T. B. Angerer, *et al.*, Int J Mass Spectrom 2015, 377, 591-598.

[3] F. Meyer, *et al.*, Biochim Biophys Acta 1970, 210, 257-&.

8:20am **BI+AS+SA-ThM2 Can ToF-SIMS Imaging Explain Biology?**, ***Lara Gamble***, *D.J. Graham*, University of Washington

Imaging time-of-flight mass spectrometry (ToF-SIMS) can provide images of cells and tissues with chemical and molecular specificity. These chemically specific images could revolutionize our understanding of biological processes such as the role of changes in tumor metabolism affecting the response to chemotherapy is under scrutiny. Regions of interest (ROIs) of the tumor can be utilized to compare similar regions from different tissue samples. PCA analysis of ToF-SIMS image data reveals the differences in chemistries between the regions. These results help to identify links between the chemical composition within and around tumors and the changes of these tumors as a response to the treatment. However, often the presentation of ToF-SIMS results might not be in the best format to gain the interest of non-SIMS scientists. Different data processing and data presentation format from clinical trial tissue samples and other tissue samples analyzed with ToF-SIMS will be presented. Additional validation of data interpretation from different techniques will be discussed.

8:40am **BI+AS+SA-ThM3 Applications of XPS for Novel Biomaterial Systems**, ***Jonathan Counsell***, *S.J. Coultas, C.J. Blomfield*, Kratos Analytical Limited, UK, *C. Moffitt*, Kratos Analytical, *S.J. Hutton*, Kratos Analytical Limited, UK **INVITED**

XPS is widely used in the field of biomaterials yielding quantitative elemental and chemical state information [1]. It is possible to identify changes in functional groups present both on the surface and, combined with depth profiling, within the bulk of a biomaterial.

Here we will discuss the latest advancements in XPS as applied to a range of biomaterial systems and examine new possibilities beyond routine spectroscopic analysis. Non-destructive depth profiling of the near surface region is applied to ultra-thin films examining growth modes and film closure mechanisms. With the dual Al/Ag monochromated sources it is possible to vary information depth for relative comparisons on the nature of the uppermost layers. New developments in cluster ion sources now allow soft biomaterials to be depth profiled. Accurate analysis of interfacial chemistry is possible without ion beam damage. XP Imaging will also be discussed for systems exhibiting surface inhomogeneity. Quantitative images yield useful additional information over conventional microscopies. Discussions will concentrate on both model systems and real life applications highlighting the latest possibilities of XPS for this growing field.

[1] Donald R. Miller and Nikolaos A. Peppas, Journal of Macromolecular Science, Part C Vol. 26 , Iss. 1,1986

9:20am **BI+AS+SA-ThM5 Surface Characterization of Polymer Scaffolds: Understanding Surface Modification and Biological Interactions**, ***Michael Taylor***, University of Washington, *M.J. Hawker, M.N. Mann*, Colorado State University, *G.E. Hammer*, University of Washington, *E.R. Fisher*, Colorado State University, *D.J. Graham, L.J. Gamble*, University of Washington

Biopolymers show increasing usage in medical device technologies including joint replacement, stents and tissue engineered supports. (polymer scaffolds). Barriers to successful use of biopolymer usage for medical devices can include ineffective interaction of biological systems with the biopolymer and biofilm formation. Historically, developing medical devices with antibacterial properties have involved inclusion of silver or copper dopants as they facilitate bacterial membrane rupture. Bacterio-static coatings provide an alternative approach by generating a hydrophobic surface that prevents colonisation by reversible adhesion via van der Waals forces prior to anchoring strongly with adhesion structures such as pili. Plasma enhanced chemical vapor deposition (PECVD) is a cheap yet powerful method of introducing chemical functionalities to surfaces as the low temperature high energy process may be used to couple a variety of monomers to biomaterial surfaces. Previous evidence provided by Fisher and coworkers showed that PECVD may be utilised to produce antifouling coatings by modifying polycaprolactone (PCL) with fluorinated organic compounds[1], however the porous morphology of scaffolds required for vascularisation also provides multiple points of attachment for the critical first step in biofilm formation. It is therefore necessary determine the effectiveness of PECVD throughout the scaffold. For this we employ time-of-flight secondary ion mass spectrometry (ToF-SIMS) and X-ray photoelectron spectroscopy (XPS) to analyse the surface modification of porous polymer scaffolds.

ToF-SIMS imaging coupled with X-ray photoelectron spectroscopy (XPS) provides a powerful combination of high resolution imaging and elemental quantitative analysis that allows a detailed analysis of the surface. Herein we apply this combination of analysis methods for the determination and quantification of fluorocarbon distribution across a PCL scaffold modified with octafluoropropane by PECVD, determining that a treatment time of 20 minutes Introduces a homogeneous distribution of fluorocarbon film throughout the construct cross section whereas lower treatment times produces a gradient distribution of fluorocarbon, as measured via CF^+ and CF_3^+ signals

(1) Hawker, M. J.; Pegalajar-jurado, A.; Fisher, E. R. Conformal Encapsulation of Three-Dimensional, Bioresorbable Polymeric Sca Ff Olds Using Plasma-Enhanced Chemical Vapor Deposition. **2014**.

9:40am **BI+AS+SA-ThM6 Seawater Bacteria on Technical Surfaces: Lateral and Vertical Adhesion Forces and Nanomechanical Properties**, *N. Davoudi, K. Huttenlochner*, University of Kaiserslautern, Department of Physics and Research Center Optimas, Germany, *C. Schlegel, M. Huster*, University of Kaiserslautern, Institute of Bioprocess Engineering, Germany, ***Christine Müller-Renno***, University of Kaiserslautern, Department of Physics and Research Center Optimas, Germany, *R. Ulber*, University of Kaiserslautern, Institute of Bioprocess Engineering, Germany, *C. Ziegler*, University of Kaiserslautern, Department of Physics and Research Center Optimas, Germany, Germany

Biofilms are often unwanted, but can also be utilized in biofilm reactors. In such a reactor different forces act on the cells: lateral forces by flow, forces perpendicular to the interface which dominate the first contact and the biofilm formation, and forces on the cell-wall by turgor pressure which influence the viability of the cells. The interplay of these forces plays a major role in the establishment of a biofilm.

Here, we report on the seawater bacterium *Paracoccus seriniphilus* on titanium and glass. Microstructured titanium is our substrate of choice in the reactor. We hence have to understand the influence of wettability, roughness, defined structures, and environmental conditions such as pH and ionic strength on the viability as well as the bacterial attachment and detachment.

In a first set of experiments, the turgor pressure of the bacteria was determined as a function of pH and salinity by measuring force-distance curves with a scanning force microscope (SFM). As a seawater bacterium, *P. seriniphilus* can easily adapt to saline conditions and can survive at NaCl concentrations up to 100 gL^{-1}. Depending on the ionic strength the turgor pressure and thus the elasticity and size of the cell changes. *P. seriniphilus* has its optimum pH at 7, but at pH 4 the results point to an active adaption mechanism to acidic conditions. The results at pH 11 show that *P. seriniphilus* cannot adapt to alkaline conditions.

As next step the vertical adhesion forces of a single bacterium were measured as a function of pH, ionic strength, and substrate. The adhesion force of one single cell decreases from pH 4 to pH 9. As a function of the ionic strength, the adhesion forces increase with increasing salt concentration with a pronounced spike (higher adhesion forces) at 0.9 % NaCl. All adhesion force changes completely correlate with the electrostatics as determined by zetapotential measurements. A conditioning film of growth medium strongly decreases the attachment forces. Thus the first bacterial layer should grow without medium at pH 4.

In a last step, the lateral detachment forces of the bacteria were measured. There is a clear correlation between the applied force and the number of moved bacteria, but the detachment forces vary for the individual bacteria. For small lateral forces (0.5 nN), the wettability of the substrate seems to control the detachment process. For higher lateral forces (2-3 nN), the effect of the wettability gets lost and the roughness of the samples controls the cell detachment. These detachment forces are in the same range or higher than the shear forces applied by the fluid flow.

11:00am **BI+AS+SA-ThM10 AVS 2017 Peter Mark Memorial Award Lecture: A Combined Experimental–Simulation Approach for Unraveling Hydrophobic Interactions at the Molecular Scale**, *P. Stock*, MPI for Iron Research, Germany, *J.I. Monroe*, UC Santa Barbara, *T. Utzig*, MPI for Iron Research, Germany, *D.J. Smith*, *M.S. Shell*, UC Santa Barbara, ***Markus Valtiner****, TU Bergakademie Freiberg, Germany **INVITED**

Interactions between hydrophobic moieties steer ubiquitous processes in aqueous media, including the self-organization of biologic matter. Recent decades have seen tremendous progress in understanding these for macroscopic hydrophobic interfaces. Yet, it is still a challenge to experimentally measure hydrophobic interactions (HIs) at the single-molecule scale and thus to compare with theory.

Here, I will present a combined experimental–simulation approach to directly measure and quantify the sequence dependence and additivity of HIs in peptide systems at the single-molecule scale. We combined dynamic single-molecule force spectroscopy on model peptides with fully atomistic, both equilibrium and nonequilibrium, molecular dynamics (MD) simulations of the same systems. Specifically, we mutate a flexible $(GS)_5$ peptide scaffold with increasing numbers of hydrophobic leucine monomers and measure the peptides' desorption from hydrophobic self-assembled monolayer surfaces. Based on the analysis of nonequilibrium work-trajectories, we measure an interaction free energy that scales linearly with 3.0–3.4 k_BT per leucine. In good agreement, simulations indicate a similar trend with 2.1 k_BT per leucine, while also providing a detailed molecular view into HIs.

Our approach potentially provides a roadmap for directly extracting qualitative and quantitative single-molecule interactions at solid/liquid interfaces in a wide range of fields, including interactions at biointerfaces and adhesive interactions in industrial applications. In this context, I will finally discuss in detail how single molecule unbinding energy landscapes can be utilized to predict scenarios where a large number of molecules simultaneously interact, giving rise to adhesive failure under corrosive and wet conditions.

[1] S. Raman et al. *in Nature Communications***,** 5**(2014)**, 5539.

[2] T. Utzig et al. *in Langmuir*, 31(9) **(2015)**, 2722.

[3] T. Utzig, P. Stock et al. *in Angewandte Intl.***(2016)**.

[4] P. Stock et al. in *ACS Nano***(2017)**, 11 (3), 2586.

11:40am **BI+AS+SA-ThM12 Quantitative Characterization of Bacterial Cells in Solution and on Surfaces**, *C. Sousa*, *K. Jankowska*, *L. Parga Basanta*, *I.M. Pinto*, ***Dmitri Petrovykh***, International Iberian Nanotechnology Laboratory, Portugal

Physicochemical properties of bacterial cells make them challenging subjects for methods typically used to characterize micro- and nanoparticles. Even for conceptually simple parameters, such as size and concentration, direct characterization of live bacteria (and their agglomerates) in solution is far from trivial because bacterial cells are soft and often anisotropic particles with sizes of not more than a few microns. Low contrast, in terms of optical and electronic properties, between bacteria and their aqueous environment complicates any attempted direct measurements in solution. Comparing bacterial cells to non-biological micro- or nanoparticles, whether in the context of mixed samples or calibration measurements, further compounds the complexity of characterizing these systems.

We are using *Staphylococcus aureus* (*S. aureus*) bacteria as a model system for quantitative characterization of bacterial cells. For systematic measurements, *S. aureus* bacteria offer the advantages of nearly spherical shape and of robust viability under a wide range of experimental conditions and treatments. The approximately one micron diameter of live *S. aureus* cells also makes them representative of the sensitivity and resolution challenges encountered in the characterization of bacterial cells. In microscopy, for example, the apparent size of individual *S. aureus* bacteria changes dramatically as they are prepared for measurements with increased spatial resolution: from confocal optical microscopy, to environmental scanning electron microscopy (SEM), to SEM in vacuum.

The objective of our work is to develop and validate a set of complementary techniques that can be used to characterize live bacterial cells. We will describe the use of nanoporous membranes with *S. aureus* suspensions and commonly overlooked effects of centrifugation, mechanical agitation, and other typical sample preparation procedures on the apparent distribution and properties of particles in biological samples. The forced contact of bacteria with these membranes during filtering also suggests their use as model systems for investigating the interactions of bacteria with surfaces having different chemistries and/or morphological features.

12:00pm **BI+AS+SA-ThM13 *In Situ* Multimodal Imaging of Microbial Communities**, ***Xiao-Ying Yu***, Pacific Northwest National Laboratory

We developed a vacuum compatible microfluidic interface, System for Analysis at the Liquid Vacuum Interface (SALVI), to enable direct observations of liquid surfaces and liquid-solid interactions using time-of-flight secondary ion mass spectrometry (ToF-SIMS) and a variety of spectroscopy and microscopy characterization techniques. SALVI was recently applied to investigate biological interfaces in living biofilms and co-cultured microbial communities. In this talk, two case studies will be presented using in situ liquid ToF-SIMS, light microscopy, and fluorescence microscopy. In the first case study, *Shewanella* wild type and mutant were both exposed to environmental stressors such as toxic heavy metal ions (i.e., Cr (VI)) and silver nanoparticles. The response of biofilm and its extracellular polymeric substance (EPS) to the environmental perturbation was investigated using in situ liquid SIMS coupled with structured illumination microscopy (SIM). In the second case, a more complex microbial communities consisting of syntrophic *Geobacter metallireducens* and *Geobacter sulfurreducens* was investigated. Electron donor and electron acceptor in this co-cultured microbial system were characterized first using the more traditional SIMS dry biological sample preparation approach followed by in situ liquid SIMS and confocal laser scanning microscopy (CLSM). The electron transfer between the two species was probed dynamically using the electrochemical SALVI. Correlative imaging is employed to achieve a more holistic view of complexed microbial systems across different space scales. Our results demonstrate that interfacial chemistry involving living microbial systems can be studied from the bottom up based on microfluidics, potentially providing more important understanding in system biology.

Advanced Ion Microscopy Focus Topic
Room: 7 & 8 - Session HI+BI+NS+TR-ThM

Advanced Ion Microscopy Applications

Moderators: Armin Golzhauser, Bielefeld University, Germany, Olga Ovchinikova, Oak Ridge National Laboratory

8:00am **HI+BI+NS+TR-ThM1 Scanning Helium Atom Microscopy: Imaging with a Deft Touch**, ***Paul Dastoor***, University of Newcastle, Australia **INVITED**

Delicate structures (such as biological samples, organic films for polymer electronics and adsorbate layers) suffer degradation under the energetic probes of traditional microscopies. Furthermore, the charged nature of these probes presents difficulties when imaging with electric or magnetic fields, or for insulating materials where the addition of a conductive coating is not desirable. Scanning helium microscopy is able to image such structures completely non-destructively by taking advantage of a neutral helium beam as a chemically, electrically, and magnetically inert probe of the sample surface. Here, we present scanning helium micrographs demonstrating image contrast arising from a range of mechanisms including, for the first time, chemical contrast observed from a series of metal-semiconductor interfaces [1]. The ability of neutral helium microscopy to distinguish between materials without the risk of damage makes it ideal for investigating a wide range of systems.

1. M. Barr, A. Fahy, J. Martens, A.P. Jardine, D.J. Ward, J. Ellis, W. Allison & P.C. Dastoor, "Unlocking new contrast in a scanning helium microscope", *Nature Communications*, **7**, 10189, (2016).

8:40am **HI+BI+NS+TR-ThM3 Biofilm Structure of Geobacter Sulfurreducens by Helium Ion Microscopy**, ***Alex Belianinov***, Oak Ridge National Laboratory, *M. Halsted*, *M.J. Burch*, Oak Ridge National Laboratory, *S. Kim*, *S. Retterer*, Oak Ridge National Laboratory

Microbial communities form biofilms on material surfaces in a multitude of ecosystems, from the root hairs of a plant to the human gut. The hallmarks of an established biofilm include (1) the attachment of microbial cells to a surface, (2) production of extracellular polymeric substance, (EPS) (3) a complex structure or "architecture," and (4) the ability to exchange genetic information between cells. [1] Geobacter sulfurreducens forms unique, electrically conductive biofilms, a property that can be exploited in production and design of microbial fuel cells. In this work, examine biofilm formation, and biofilm properties of Geobacter sulfurreducens using a Scanning Electron Microscope (SEM) as well as a Helium Ion Microscope (HIM).

*** Peter Mark Memorial Award Winner**

SEM is a high-resolution imaging technique used for characterization of a broad variety of materials. However, in order to image highly insulating, soft biological materials, the samples must be coated for charge compensation. These (typically) metallic coatings create a homogenous surface and may cloak true biological behavior and material contrast in the micrograph. In the case of Geobacter sulfurreducens, metal coating precludes detailed investigation of microbial attachment, presence of EPS, and fine surface details that may elucidate the mechanisms behind architecture formation and genetic material exchange.

Recently introduced HIM, offers more flexibility in investigating biological samples, as highly insulating sample can be imaged sui generis, without the use of a conductive coating. [2] This opens new pathways to capturing high resolution spatial details of biofilm formation and biofilm properties. Furthermore, high-resolution HIM imaging reveals true surface details of Geobacter sulfurreducens, such as flagella or pilin typically inaccessible by SEM. Finally, the effects of different sample preparation strategies for SEM and HIM will be illustrated and discussed.

References:

[1] 1. Donlan, R. M. "Biofilms: Microbial Life on Surfaces." Emerging Infectious Diseases, 8(9), 881–890, 2002

[2] Joens, M. S., Huynh, C., Kasuboski, J. M., Ferranti et. al.. "Helium Ion Microscopy (HIM) for the imaging of biological samples at sub-nanometer resolution." Scientific Reports, 3(3514), 2013

Acknowledgements:

This research was supported by Oak Ridge National Laboratory's Center for Nanophase Materials Sciences (CNMS), which is sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy.

9:00am **HI+BI+NS+TR-ThM4 Channeling via Transmission He Ion Microscopy**, ***Christoph Herrmann***, Simon Fraser University, Canada, *S.A. Scott*, *M. Lagally*, University of Wisconsin-Madison, *K. Kavanagh*, Simon Fraser University, Canada

The spatial coherence of focussed helium (He) ion beams is significant. The He ion source is atomic size (W filament tip) and the resolution from scanning probe, ion-induced secondary electron images is sub 1 nm. Scanning transmission images with atomic resolution are theoretically predicted. We have been experimenting with a digital camera located underneath the sample stage and tilt cradle of our instrument (Zeiss Nanofab). The camera consists of an array of Si p-i-n diodes (55 μm square pixels) that allow direct detection of single He ions and atoms (20 keV - 40 keV). We have previously reported that the beam intensity profiles are uniformly distributed, as expected from the small de Broglie wavelength (80 fm), with a half angle convergence of 2 mrad.[1] At beam currents in the pA range the detector count rate was consistent with one count per He ion or atom. In this talk, we will present results that indicate planar channeling in single crystalline Si (100) membranes (25 nm - 75 nm thick). The transmission intensity as a function of position depends on the beam incidence angle, and beam energy, with random incidence profiles consistent with monte carlo scattering and range calculations (SRIM). The peak in transmission as a function of incidence angle has a half angle width of 1° at 25 kV. These results will be compared with theoretical calculations based on impact factors at low energies. Channeling experiments with other thin crystalline materials including graphite and MgO will be discussed. **Acknowledgements**: We thank Norcada Inc. (Edmonton) for supplying Si (100) 50 nm thick membranes; NSERC, CFI/BCKDF, 4DLABs for funding. [1] K.L. Kavanagh and C. Herrmann, Direct He Detection for Transmission Helium Ion Microscopy, Microsc. Microanal. submitted 2017.

9:20am **HI+BI+NS+TR-ThM5 Rapid Imaging of Nano-Porous Catalyst Particles Via Helium Ion Microscopy**, *M.J. Burch*, *A.V. Ievlev*, ***Holland Hysmith***, Oak Ridge National Laboratory, *K. Mahady*, *P.D. Rack*, University of Tennessee, *L. Luo*, ExxonMobil Chemical Company, *A. Belianinov*, Oak Ridge National Laboratory, *S. Yakovlev*, ExxonMobil Chemical Company, *O.S. Ovchinikova*, Oak Ridge National Laboratory

Porous materials are some of the most important modern day material systems, as the pore structure defines many materials applications and functionality. The pore structure of catalyst precursor particles, in particular, is of great importance to the catalyst community, as this pore structure dictates the efficiency and efficacy of grown polymers. However, despite the importance of these materials systems, there are few techniques to analyze pore size and structure. The most common technique is gas absorption, where the amount of gas absorbed and desorbed from a known amount of material is tracked and the average pore volume and size can be extracted. However, the technique is heavily dependent on sample quality and which fitting model is used to calculate volume and size. In addition, the technique is quite slow, where generally at most a single sample can be analyzed a day.

In this work, we demonstrate a novel technique to directly image and quantify pore size in nano-porous catalyst precursor particles via helium ion microscopy. We demonstrate the technique by directly imaging the surface pore structure of SiO_2 precursor catalyst particles with helium ion microscopy. Using modern day data analytics, we created an automated routine to extract pore size and distributions. We show that our HIM based technique shows comparable data to the industry standard gas absorption technique, within a 5 percent difference between the techniques of a known porous samples.

Further, to determine the effect of the helium beam on the surface of the SiO_2 particles, we simulate the beam interaction between porous SiO_2 particles and the helium beam. At low ion doses the surface modification by the ion beam is quite negligible, where at higher ion doses, significant surface modification is observed.

In conclusion, we've demonstrated a novel technique to directly visualize and quantify nano-pore size and structure in SiO_2 that yields complimentary data to gas absorption.

Acknowledgements

This work was conducted at the Center for Nanophase Materials Sciences, which is a Department of Energy (DOE) Office of Science User Facility. The users acknowledge the ExxonMobil Chemical Company for funding.

9:40am **HI+BI+NS+TR-ThM6 Ion Beam Induced Current Measurements of Solar Cells with Helium Ion Microscopy**, *A. Belianinov*, *S. Kim*, ***Ryan Cannon***, *M.J. Burch*, *S. Jesse*, *O.S. Ovchinnikova*, Oak Ridge National Laboratory

The scanning electron microscope (SEM) is a versatile high-resolution microscopy tool, and perhaps the most widely used imaging platform across many engineering and scientific fields [1]. Within the last decade, another microscopy technique based on a gaseous field ionization source, utilizing Helium and Neon ions has been introduced [2]. While the popularity of the SEM is hardly challenged by the Helium Ion Microscopy (HIM), there are instances when imaging with ions offers significant advantage as opposed to imaging with electrons. In principle, both HIM and the SEM share many similarities, for example, a HIM operating at 40 keV will generate ions with velocity comparable to SEM operating at 5 keV. However, due to much higher stopping power of ions, as compared to electrons, ion based secondary electron (iSE) will be higher. Also, as a result, there is little ion backscattering, and consequently, the concentration of the ion-generated iSE2 (additional secondary electron generated by SE interaction within the material) is usually insignificant.

In this work, we exploit small interaction volumes in the HIM, and take advantage of the lower iSE2 yield, and positively charged helium ions to map ion beam induced current (IBIC) in solar cell materials. Similar studies, using electrons, have visualized induced current profiles at grain profiles in polycrystalline solar cells, and in silicon [3, 4]. Furthermore, broad ion sources have been utilized in conjunction with scanning probe systems in the past to map out current changes in FinFETs [5]. We are interested in utilizing the HIM to map current at the nanoscale near p-n junctions in CdTe to elucidate differences in contrast captured by the ion beam induced current, as opposed to the electron beam induced current. These findings will illustrate the peculiarities of ionic transport in these solar cell materials, and will evaluate the HIM technology as a potential quality control tool.

References:

[1] David C Joy, Helium Ion Microscopy: Principles and Applications, First ed. Springer, New York USA, Heidelberg Germany, Dordrecht Netherlands, London United Kingdom, 2013.

[2] Gölzhäuser, A. and Hlawacek, G., Helium Ion Microscopy. Springer International Publishing. 2016

[3] Donolato, C., Journal of Applied Physics, 54 (3), 1314-1322, 1983

[4] Chen, J., et. al., Journal of Applied Physics, 96(10), 5490-5495, 2004

[5] Manfredotti, C., et.al., Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment, 380(1-2), 136-140, 1996

11:00am **HI+BI+NS+TR-ThM10 Writing Magnetic Domains with a Helium Ion Microscope**, ***Daniel Emmrich***, Bielefeld University, Germany, *A. Gaul*, *D. Holzinger*, *A. Ehresmann*, University of Kassel, Germany, *F. Karimian*, *M. Klug*, *J. McCord*, Kiel University, Germany, *A. Beyer*, *A. Gölzhäuser*, Bielefeld University, Germany

Microscopes based on gas field ion sources offer surface-sensitive, high resolution imaging and state of the art nano-machining.[1] It was further shown that light ions like helium or neon enable a modification of the magnetic properties, e.g., turning thin films from paramagnetic to ferromagnetic state, without significant sputtering.[2]

In this work, two-dimensional ion bombardment induced magnetic patterning (IBMP)[3] is demonstrated with a helium ion microscope to create magnetic domains in an exchange biased thin film system. Such a system consists of a thin ferromagnetic layer coupled to an underlying antiferromagnet. Low dose helium ion irradiation at an energy of 15 keV in an external magnetic field leads to a new, remanent magnetization direction, determined by the external magnetic field. By subsequently patterning the sample in differently orientated external magnetic fields, complex magnetic domain patterns such as chiral structures can be written. Based on magnetic force microscopy and optical Kerr microscopy, we will discuss the achievable resolution as well as the shapes of different artificial magnetic domains.

[1]G. Hlawacek and A. Gölzhäuser (eds),Helium Ion Microscopy (Springer International Publishing, Switzerland, 2016.).

[2]F. Roder, G. Hlawacek, S. Wintz, R. Hubner, L. Bischoff, H. Lichte, K. Potzger, J. Lindner, J. Fassbender, and R. Bali, Scientific reports 5, 16786 (2015).

[3]A. Gaul, S. Hankemeier, D. Holzinger, N.D. Müglich, P. Staeck, R. Frömter, H.P. Oepen, and A. Ehresmann, Journal of Applied Physics 120, 33902 (2016).

11:20am **HI+BI+NS+TR-ThM11 Characterisation of Nanomaterials on the Helium Ion Microscope using Correlative Secondary Electron and Mass Filtered Secondary Ion Imaging**, *J.-N. Audinot, D.M.F. Dowsett, F. Vollnhals, T. Wirtz*, Luxembourg Institute of Science and Technology (LIST), Luxembourg, ***John A. Notte***, Carl Zeiss Microscopy, LLC

In order to add nano-analytical capabilities to the Helium Ion Microscope, we have developed a Secondary Ion Mass Spectrometry (SIMS) system specifically designed for the Zeiss ORION NanoFab [1-3]. SIMS is based on the generation and identification of characteristic secondary ions by irradiation with a primary ion beam (in this case helium or neon). It is an extremely powerful technique for analysing surfaces owing in particular to its excellent sensitivity (detection limits down to the ppb are possible, so that SIMS can be used to detect both major and trace elements), high dynamic range (a same signal can be followed over several orders of magnitude), high mass resolution and ability to differentiate between isotopes.

In SIMS, the typical interaction volume between the impinging ion beam and the sample is around 10 nm in the lateral direction. As the probe size in the HIM is substantially smaller (both for He and Ne), the lateral resolution on the integrated HIM-SIMS is limited only by fundamental considerations and not, as is currently the case on commercial SIMS instruments, the probe size [4,5]. We have demonstrated that our instrument is capable of producing elemental SIMS maps with lateral resolutions down to 12 nm [3-5].

Furthermore, HIM-SIMS opens the way for in-situ correlative imaging combining high resolution SE images with elemental and isotopic ratio maps from SIMS [4,5]. This approach allows SE images of exactly the same zone analysed with SIMS to be acquired easily and rapidly, followed by a fusion between the SE and SIMS data sets.

In this talk, we will present a number of examples taken from various fields of materials science (battery materials, solar cells, micro-electronics, coatings) and life science (nanoparticles in creams and biological tissues) to show the powerful correlative microscopy possibilities enabled by the integrated HIM-SIMS instrument.

[1] T. Wirtz, N. Vanhove, L. Pillatsch, D. Dowsett, S. Sijbrandij, J. Notte, Appl. Phys. Lett. 101 (4) (2012) 041601-1-041601-5

[2] L. Pillatsch, N. Vanhove, D. Dowsett, S. Sijbrandij, J. Notte, T. Wirtz, Appl. Surf. Sci. 282 (2013) 908-913

[3] T. Wirtz, D. Dowsett, P. Philipp, Helium Ion Microscopy, edited by G. Hlawacek, A. Gölzhäuser, Springer, 2017

[4] T. Wirtz, P. Philipp, J.-N. Audinot, D. Dowsett, S. Eswara, Nanotechnology 26 (2015) 434001

[5] P. Gratia, G. Grancini, J.-N. Audinot, X. Jeanbourquin, E. Mosconi, I. Zimmermann, D. Dowsett, Y. Lee, M. Grätzel, F. De Angelis, K.Sivula, T. Wirtz, M. K. Nazeeruddin, J. Am. Chem. Soc. 138 (49) (2016) 15821–15824

Biomaterial Interfaces Division
Room: 12 - Session BI+AS-ThA

Biomolecules and Biophysics at Interfaces

Moderators: Stephanie Allen, The University of Nottingham, UK, Markus Valtiner, TU Bergakademie Freiberg

2:20pm **BI+AS-ThA1 Engineering and Imaging Excitons for Brain Imaging of Modulatory Neurotransmitters**, *M. Landry*, ***Abraham Beyene***, University of California at Berkeley **INVITED**

For over 60 years, drugs that alter, mimic, or block modulatory neurotransmitters have formed the core arsenal for the treatment of neurological disorders such as depression, addiction, schizophrenia, anxiety, and Parkinson's disease. However, methods to diagnose and validate drug efficacy have remained largely the same: questionnaires and behavioral observations. The archaic nature of neurological disorder diagnosis results from the lack of tools to detect the molecular 'key players' of neuronal communication – the three primary modulatory neurotransmitters dopamine, serotonin, and norepinephrine. In this talk, we describe the design, characterization, and implementation of near-infrared optical sensors to image neurotransmitter dopamine. We show direct visualization of endogenous dopamine release over multiple rounds of acute brain slice stimulation, for over 80 minutes. We next introduce a new form of fluorescence microscopy for deep-brain neurotransmitter imaging: double infrared excitation-emission imaging. We characterize our findings in the context of their utility for high spatial and temporal neurotransmitter imaging in the brain, describe nanosensor exciton behavior from a molecular dynamics (MD) perspective, validate nanosensor use in vitro, and for nanosensor use in vivo, to correlate external stimuli (experiences, behavior) to chemical output (neurotransmission).

3:00pm **BI+AS-ThA3 Neurotrophin-like Peptides at the Interface with Gold Nanoparticles As New Nanoplatform for CNS Disorders**, ***Cristina Satriano***, *P. Di Pietro, N. Caporarello, C.D. Anfuso, G. Lupo*, University of Catania, Italy, *A. Magrì*, National Council of Research (IBB-CNR), Italy, *D. La Mendola*, University of Pisa, Italy, *E. Rizzarelli*, University of Catania, Italy

Neurotrophins are vital proteins for neural developing and maintenance as well as promising drugs in several neurodegenerative disorders.

In the present work we propose a combined approach of peptidomimetic and nanomedicine to tackle their current limits in an effective clinical application. Specifically, neurotrophin-mimicking peptides may allow for reducing some adverse side effects shown by the whole protein [1]. Moreover, the immobilisation of these peptides on nanoparticles offers many advantages, such as the protection against degradation, an enhanced permeability of barrier membranes and, if any, intrinsic nanomaterial therapeutic properties (for example, the anti-angiogenic and plasmonic features of gold nanoparticles, AuNPs) [2].

The functionalisation of spherical AuNPs of 12 nm of diameter by peptides owing respectively to the N-terminal domains of nerve growth factor, NGF1-14, and brain derived neurotrophic factor, BDNF1-12, were scrutinised both in the direct physisorption and in the lipid bilayer-mediated adsorption processes. UV-visible and X-ray photoelectron spectroscopies, QCM-D, dynamic light scattering, zeta potential analyses and atomic force microscopy were used to investigate the hybrid nano-biointerface. Both peptide- and lipid-dependant features were identified, in order to have a modulation in the nanoparticles peptide coverage as well as in the cellular uptake of NGF and BDNF peptides, as investigated by confocal microscopy. The promising potentialities in the capability to cross the blood brain barrier (BBB) were demonstrated with Human Brain Microvascular Endothelial Cells, a cell model representative of human brain endothelium that exhibits barrier properties comparable to other BBB models.

[1] Pandini, G., Satriano, C., Pietropaolo, A., Gianì, F., Travaglia, A., La Mendola, D., Nicoletti, V.G. and Rizzarelli, E. (2016). The Inorganic Side of NGF: Copper (II) and Zinc (II) Affect the NGF Mimicking Signaling of the N-Terminus Peptides Encompassing the Recognition Domain of TrkA Receptor. *Frontiers in Neuroscience*, *10*.

[2] Di Pietro, P., Strano, G., Zuccarello, L. and Satriano, C. (2016). Gold and silver nanoparticles for applications in theranostics. *Current Topics in Medicinal Chemistry*, *16*(27), 3069-3102.

4:00pm **BI+AS-ThA6 Controlling and Probing the Orientation of Immobilized Protein G B1 on Gold Nanoparticles Using Time of Flight Secondary Ion Mass Spectrometry and X-ray Photoelectron Spectroscopy**, ***Yung-Chen Wang***, *D.G. Castner*, University of Washington, Seattle

Nanoparticles (NPs) have been widely used in many fields of science due to their unique physical properties. While many applications of NPs such as imaging probes or drug carriers often require the conjugation of proteins or biomolecules, the surface interactions between NPs and biomolecules remains underexplored. For example, the immobilization of immunoglobulin G (IgG) onto nanoparticle surfaces is critical for the development of many immunosensors and drug delivery nanocarriers. Notably, the orientation of the immobilized IgG can have significant impact on the clinical outcomes of these carriers by impacting its biostability and efficacy.

In this work, Protein G B1, a protein that can selectively bind to the Fc tail of IgG, was immobilized onto gold NPs (AuNPs) functionalized with maleimide and oligo-(ethylene glycol)(OEG) self-assembled monolayers (SAMs). Protein G B1 was immobilized onto AuNPs through specific maleimide-cysteine interaction. As the wild type Protein G B1 does not contain a cysteine, we can strategically introduce cysteine mutants on Protein G B1 to control the location of the maleimide-cysteine bonding. We used the surface sensitive analysis techniques of x-ray photoelectron spectroscopy (XPS) and time of flight-secondary ion mass spectrometry (ToF-SIMS) to characterize the surface elemental composition, coverage, and orientation of the protein G B1 immobilization process.

XPS analysis confirmed the AuNP functionalization with the maleimide SAMs. After incubation with protein containing cysteine mutant, the immobilization of the protein was demonstrated by the increased nitrogen signal on the surface of the AuNP. Wild type Protein G B1 cannot form the maleimid-cysteine bond and was effectively removed through conventional centrifugation-resuspension washes and dialysis cleaning.

ToF-SIMS analysis also confirmed the successful functionalization and protein immobilization on the AuNPs by identifying signature secondary ions of the maleimide functional group and amino acids. Utilizing the small sampling depth (~2nm) of ToF-SIMS relative to the size of Protein G B1 (~3nm), the orientation of immobilized protein G B1 was determined by comparing the ratio of secondary ion intensity originating from the opposite regions of the protein. Overall, site-specific maleimide-cysteine interaction and systematic surface characterizations enabled us to both control and probe the orientation of immobilized proteins on AuNPs. The systematic characterization of this study provided detailed information about protein-NP interactions and a platform for controlled immobilization for IgGs on NPs.

4:20pm **BI+AS-ThA7 Angiogenin Peptides and Gold Nanoparticles for Modulated Angiogenesis Processes**, *L.M. Cucci, C. Satriano, E. Rizzarelli*, University of Catania, Italy, ***Diego La Mendola***, University of Pisa, Italy

Angiogenin (Ang) is a physiological constituent of the human plasma and is a protein overexpressed in different types of tumours [1]. Gold nanoparticles (AuNPs) exhibit anti-angiogenic activity [2] and inhibit growth factor-mediated signalling *in vitro* as well as vascular endothelial growth factor (VEGF)-induced angiogenesis *in vivo* [3].

Herein, the fragment Ang60-68, including the putative cellular binding site of the protein Ang, has been synthesized and used to functionalize spherical AuNPs of 12 nm of diameter. The Ang mimicking activity of the peptide was evaluated by the staining of actin, a key target of the entire Ang, in terms of cell cytoskeleton reorganisation.

The hybrid peptide-nanoparticle assembly was obtained by physical adsorption of the peptides at the surface of AuNPs and was analysed by UV-visible spectroscopy, in order to characterise, with titration experiments, the variations of the plasmonic properties of AuNPs as well as the peptide spectral features. Another hybrid nanosystem was prepared by the immobilisation on AuNPs of the fluorescent analogous, Fam-Ang59-68, synthetized through an amidic bond which involved the N-terminal residue with the carboxyfluorescein (Fam) moiety.

The hydrodynamic size of the peptide-Au nanosystems was determined by dynamic light scattering (DLS) analysis.

Proof-of-work experiments with human neuroblastoma cells line were carried out to prove the non-toxicity of Ang-mimicking peptide functionalised gold nanoparticles. Furthermore, laser scanning confocal microscopy (LSM) images showed the localization of the peptide-nanoparticles at the cell membrane and their sub-cellular distribution. These data reveal an auspicious new platform for imaging and therapeutic activities in angiogenesis-involved diseases.

[1] D.J. Strydom, *Cellular and Molecular Life Science*, **1998**, 54:811–824.

[2] P. Mukherjee, R. Bhattacharya, P. Wang, L. Wang, S. Basu, J.A. Nagy, A. Atala, D. Mukhopadhyay, S. Soker, *Clinical Cancer Research*, **2005**,11(9), 3530-4.

[3] S. Basu, J.A. Nagy, S. Pal, E. Vasile, I.A Eckelhoefer, V.S. Bliss, E.J. Manseau, P.S. Dasgupta, H.F. Dvorak, D. Mukhopadhyay, *Nature Medicine*, **2001**, 7, 569-574.

5:00pm **BI+AS-ThA9 Exploiting Protein-Polyelectrolyte Interactions to Control and Tune Protein Immobilization at Interfaces. Applications in Biocatalysis and Separation Technology**, *C. Dupont-Gillain, A. Bratek-Skicki*, ***Aurélien vander Straeten***, UC Louvain, Belgium

INTRODUCTION: For many applications in biomedical science and biotechnology, it is challenging to control and tune the nature, amount, and activity of proteins at interfaces. Since proteins are polyampholytes, they do interact with polyelectrolytes (PE), in a way which strongly depends on the pH and ionic strength of the medium. It is usually considered that PE provide a mild environment to proteins, which may help keeping their activity unaffected by surface immobilization. Here, we explore two different approaches to take advantage of the PE-protein interactions for the controlled and tunable surface immobilization of proteins.

STRATEGY: In a first approach, mixed brushes of poly(ethylene oxide) (PEO), a protein-repellent polymer, and of a negatively- or positively-charged PE, respectively poly(acrylic acid) (PAA) and poly(2-(dimethylamine)ethylmethacrylate) (PDMAEMA), were prepared by the "grafting to" approach. These stimuli-responsive mixed brushes were used to selectively adsorb/desorb a given protein from a mixture of several proteins. In a second approach, PE-protein complexes were prepared then immobilized at interfaces within layer-by-layer (LbL) assemblies. This was in particular performed for PE-enzyme complexes, including PE-lysozyme and PE-glucose oxidase complexes. Systems including several enzymes were designed, with a view to further enable enzymatic cascades. Polymer brush formation and protein immobilization were monitored using quartz crystal microbalance, X-ray photoelectron spectroscopy and time-of-flight secondary ions mass spectrometry. Gel electrophoresis was used to determine the nature of proteins collected from the interface. PE-protein complex formation was assessed based on turbidimetry and dynamic light scattering measurements. Enzyme activity was measured based on standard assays.

RESULTS: (i) *Mixed polymer brushes-protein interactions*: From adsorption experiments with single and mixed solutions of albumin, lysozyme and fibrinogen on PAA/PEO and PDMAEMA/PEO brushes, it was demonstrated that the selective adsorption of one protein could be achieved, as well as the sequential desorption of these proteins when the three of them were adsorbed initially, by means of appropriate pH and I triggers. (ii) *PE-enzyme complexes as building blocks for LbL assembly*: PE-enzyme complexes were successfully built and characterized, then incorporated into LbL assemblies. The specific activity of lysozyme was higher when immobilized as a complex rather than in its native form.

CONCLUSION:The developed systems may find direct applications in separation technology, on the one hand, and in biocatalysis, on the other hand.

5:20pm **BI+AS-ThA10 Determination of Confined Molecular Structure by using X-ray-Surface Force Apparatus (XSFA) Study in Bio-interface Application**, ***Hsiu-Wei Cheng***, *M. Valtiner*, Technical University Freiberg, Germany, *C. Merola*, Max-Planck Institute for Iron Research, Germany, *K. Schwenzfeier*, Technical University Freiberg, Germany, *M. Mezger*, *H. Weiss*, Max-Planck Institute for Polymer Research, Germany

In biology system, understanding of molecular dynamics at confined interface such as medicine diffusion across inter-cellular channel, lubrication at joints and electric signal transmission from nerves to nerves is boosting the modern medical and biomaterial study. To study the behavior of confined molecules in detail, a home-build X-ray surface force apparatus (XSFA) which combines a synchrotron X-ray with white light interferometry is used. In our first step, an imidazolium chloride based ionic liquid, which consists of a clear water induced phase change, was used as a modeling system to test the detection limit of XSFA. The result shows that the liquid phase change from liquid to liquid crystal can be clearly distinguished within a 50 to 100 nm confinement. Meanwhile, the application of X-ray reflectivity (XRR) reveal furthermore in-plane ordering information of the liquid crystal structure. Secondly, shear force were applied to study how confined liquids react to the friction to mimic the motion of joint. We found that friction behavior and molecular dynamics are strongly related to the gap size of the confinement, which is a useful information for artificial joint design. The combination of SFA and synchrotron X-ray has shown a great analytical potential to solve the interfacial molecular dynamic, which provides scientists another powerful tool to peer the world of molecule.

6:00pm **BI+AS-ThA12 Direct Quantification of the Hydrophobic-to-Hydrophilic Transition of Interaction Forces**, ***Laila Moreno Ostertag***, *T. Utzig*, *P. Stock*, Max Planck Institute for Iron Research, Germany, *M. Valtiner*, TU Bergakademie Freiberg, Germany

When two surfaces come in close contact, several forces arise and, depending on the nature of the surfaces, these forces will show different magnitude. This principle may also be applied to diverse biological systems. Van der Waals forces have been on the radar for a century or so, and the identification of electrostatic interactions can be traced back to ancient times. It has also been clear that the behavior of such surfaces in terms of their polarity is associated to another type of force, called hydrophobic interactions.[1,2] The combination of these contributions leads to a better understanding of the interactions as the surfaces get closer together.

In this regard, we have revisited the hydrophobic interactions theory by studying the interaction forces between apposing symmetric surfaces of varying hydrophobicity via Atomic Force Microscopy and correlating them to the behavior of water at the interface. Short hydrophobic chains ending in either non-polar, hydrophobic groups or in charged heads and combinations of them were attached to smooth surfaces and tested under constant ionic force conditions. Mathematical modeling of the interactions was applied to the experimental results in order to obtain numerical parameters that are associated to the surface properties. Interesting results that are in apparent contradiction with the expected trend of the hydration parameters were found but can be explained by what we suggest is a breakdown of the water structure at the interface, which in turn can contribute to the understanding of attraction or repulsion between certain biological systems in aqueous media.

1. Hammer, M. U.; Anderson, T. H.; Chaimovich, A.; Shell, M. S.; Israelachvili, J., The search for the hydrophobic force law. *Faraday Discussions* **2010,***146* (0), 299-308.

2. Donaldson, S. H.; Røyne, A.; Kristiansen, K.; Rapp, M. V.; Das, S.; Gebbie, M. A.; Lee, D. W.; Stock, P.; Valtiner, M.; Israelachvili, J., Developing a General Interaction Potential for Hydrophobic and Hydrophilic Interactions. *Langmuir* **2015,***31* (7), 2051-2064.

Authors Index

Bold page numbers indicate the presenter

— T —

— U —

— V —

— W —

— X —

— Y —

— Z —