Industrial Physics Forum
Room 101B - Session IPF+AS+BI+NS-MoM

Biofabrication: From Tissue to Organ

Moderators: Jason Bardi, American Institute of Physics, Jim Hollenhorst, Agilent Technologies

8:20am **IPF+AS+BI+NS-MoM1 Strategic Thinking on the Architecture and Design of Scaffolds for Regenerative Medicine*, Buddy D. Ratner,*** University of Washington, Seattle **INVITED**

Scaffolds for use in medicine and biology might be traced back to the 1940's when parachute cloth was first used for vascular prostheses. However, in the mid-1980's scaffolds took off as an essential tool in tissue engineering. This talk will explore some of the basic biology of porosities, roughness and textures on cell responses in vitro and tissue responses in vivo. University of Washington studies will be presented demonstrating enhanced healing and regeneration with precision control of pore structures for in vivo applications. The use of surface techniques and tools will be addressed for decorating the surfaces of scaffolds with biological molecules. Finally, the potential of secondary ion mass spectrometry (SIMS) for analyzing and imaging pore structure will be addressed.

9:00am **IPF+AS+BI+NS-MoM3 Sequential Bottom-up Assembly of Synthetic Cells*, Joachim Spatz,*** Max Planck Institute for Medical Research, Germany **INVITED**

The evolution of cellular compartments for spatially and temporally controlled assembly of biological processes became an essential step in developing life. Synthetic approaches towards cellular-like compartments are still lacking well-controlled functionalities as would be needed for more complex synthetic cells. In part, this is due to the mechanical and chemical instabilities of the lipid-based protocells and a lack of technical means for their well-controlled manipulation. We developed droplet supported lipid bilayer vesicles by microfluidics to generate mechanically and chemically stable and, therefore, manipulable cell-like compartments with a well-defined chemical and biophysical microenvironment. The enhanced stability enabled the sequential loading of such compartments with biomolecules by pico-injection microfluidics without compromising their functionality as synthetic cells. We demonstrate a successful sequential bottom-up assembly of a compartment with lipids, transmembrane proteins (integrin, F_oF_1-ATP synthase) and cytoskeleton proteins which would not assemble in a fully functional way by mixing and including them in one pot at once

9:40am **IPF+AS+BI+NS-MoM5 Activation of Inkjet Printed Cells Enhances Microvasculature Formation in Host Tissues*, Thomas Boland,*** *B. Oropeza, L.H. Solis,* University of Texas at El Paso*; M. Yanez,* University of South Carolina **INVITED**

Bioprinting refers to the co-deposition of cells alongside scaffolding materials to build two- and three-dimensional constructs for tissue engineering applications. 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. Studies of membrane properties of thermal inkjet printed cells by evaluating showed normal electrophysiology, but short-term membrane disruptions, which allow small molecular weight molecules to enter. Cell viability was high and apoptotic behavior was not upregulated. Alginate (1%) and gelatin type B (2.5%) constructs or scaffolds were prepared by bioprinting of a crosslinker with endothelial and endothelial / β cells. Control scaffolds were manually pipetted with the same cells and without any cells.Upon implantation the bioprinted endothelial cell constructs showed a nearly ten-fold increase in blood vessels was observed (p= 0.009), a dose response was observed but the β cells seemed to inhibit vessel formation. The explanted implants show large complete vascular features on the H&E and CD31 stains; Immunohistochemistry showed the tissue were regenerated with the human cells that made up a large part of the vasculature. Further insights into how the inkjet printing process activated endothelial cells will be presented. Understanding these processes will improve bioprinting and may eventually lead to creating fully vascularized large soft tissues, which have not been successfully grown thus far.

10:40am **IPF+AS+BI+NS-MoM8 Challenges in Organ-specific Vascular Engineering and Tissue Assembly*, Ying Zheng,*** University of Washington **INVITED**

Engineered tissues have emerged as promising new approaches to repair damaged tissues as well as to provide useful platforms for drug testing and disease modeling. Outstanding challenges remain in 1) the lack of well-defined and mature cell sources to facilitate translational outcomes and 2) the lack of control over vascular structure and perfusion efficiency in engineered 3D tissue constructs, preventing large-scale tissue fabrication, and leading to insufficient perfusion after implantation in vivo. In this talk, I will present recent progress in my lab in engineering microvasculature from human pluripotent stem cell derived endothelial cells, and their anastomosis *in vitro* and infarcted heart *in vivo*. The eventual goal of this drive is to use the single cell source to derive organ-specific vascular cells and tissue for regeneration. Next I will discuss our work in understanding the human microvascular endothelial cell heterogeneity from four major organs, heart, lung, liver and kidney and describe their distinct structure and function. I will show an example of using human kidney-specific microvascular cells to model kidney specific injury. Finally I will discuss challenges and future perspectives towards engineering human organ-specific tissue models.

11:20am **IPF+AS+BI+NS-MoM10 Bioprinting for Translational Applications: *The Quest for Whole Organ Fabrication*, *James J. Yoo,*** Wake Forest School of Medicine **INVITED**

Tissue engineering and regenerative medicine has emerged as an innovative scientific field that focuses on developing new approaches to repairing cells, tissues and organs. Over the years, various engineering strategies have been developed to build functional tissues and organs for clinical applications. However, challenges still exist in developing complex tissue systems. In recent years, 3D bioprinting has emerged as an innovative tool that enables rapid construction of complex 3D tissue structures with precision and reproducibility. This developing field promises to revolutionize the field of medicine addressing the dire need for tissues and organs suitable for surgical reconstruction. In this session novel and versatile approaches to building tissue structures using 3D printing technology will be discussed. Clinical perspectives unique to 3D printed structures will also be discussed.

Biomaterial Interfaces Division
Room 101B - Session BI+AS+IPF+MN-MoA

Advanced Imaging and Structure Determination of Biomaterials Research

Moderators: Dan Graham, University of Washington, Axel Rosenhahn, Ruhr-University Bochum, Germany

1:20pm **BI+AS+IPF+MN-MoA1 NMR Relaxometry as a Medical Diagnostic***, **Michael J. Cima,*** Massachusetts Institute of Technology **INVITED**

This talk will describe the diagnostic capabilities of magnetic resonance imaging (MRI) when brought to the patient bedside. Rather than imaging, NMR can be used for important chemical/physiologic diagnostic endpoints. Two will be discussed here; quantifying fluid overload and measurement of hypoxia within tumors. Assessment of intra- and extra-vascular volume is integral in managing patients with heart, liver, and kidney disease as volume status is closely linked to mortality. Commonly used determinants of volume status, such as physical exam and ultrasonography, lack sensitivity and specificity and require expertise in clinical practice. This talk reports on nuclear magnetic resonance (NMR) methods to a portable and clinically useful device. A clinical study with hemodialysis patients and age-matched healthy controls was performed at MGH. The T2 relaxation times of study participants' legs were quantified at multiple time points with both a 1.5T clinical MRI scanner and a custom 0.27T single-voxel MR sensor. The results showed that first sign of fluid overload is an increase in the relative fraction of extracellular fluid in the muscle. The relaxation time of the extracellular fluid in the muscle eventually increases after more fluid is accumulated. Importantly, these MR findings occur before signs of edema are detectable on physical exam. Solid tumors are often hypoxic and characterized by an extreme lack of oxygen. Tumor hypoxia imparts significant negative outcomes for patients but is highly variable within cancer types and patient populations. Many of these poor clinical outcomes can be tied to hypoxic-induced radiotherapy resistance. Resistance to radiotherapy in hypoxic regions can be overcome by increasing the dose delivered but exposure limitations of healthy tissue and organs must be considered. The lack of a viable quantitative clinical oxygen measurement method prevents safe dose escalation in these patient populations. Here we report on a silicone-based quantitative oxygen sensor. The MRI contrast of this material depends on dissolved oxygen. Thus, the material functions as a first of its kind solid-state contrast agent. The sensor leverages the existing MRI hardware, which is part of the current clinical work flow, to map tumor oxygen content. This information can then be integrated into the dose planning process clinicians currently conduct to selectively and safely boost dose to low oxygen tumor subvolumes. This sensor is approved by the institutional review board at Dana Farber Cancer Center for a clinical trial in patients locally advanced cervical cancer.

2:00pm **BI+AS+IPF+MN-MoA3 Direct Observation of Cell Signaling Proteins Interacting with a Model Cell Membrane by Sum Frequency Generation Vibrational Spectroscopy***, T.W. Golbek,* Oregon State University*; T. Weidner,* Aarhus University, Denmark*; C.P. Johnson, **Joe Baio**,* Oregon State University

Proteins that contain C2 domains are involved in a variety of biological processes including encoding of sound, cell signaling, and cell membrane repair. Of particular importance is the interface activity of the C-terminal C2F domain of otoferlin due to the pathological mutations known to significantly disrupt the protein's lipid membrane interface binding activity, resulting in hearing loss. Therefore, there is a critical need to define the geometry and positions of functionally important sites and structures at the otoferlin-lipid membrane interface. Here we describe the first *in situ* probe of the protein structure of otoferlin's C2F domain interacting with a cell membrane surface. To identify this protein's structure at the lipid interface we applied sum frequency generation (SFG) vibrational spectroscopy and coupled it with simulated SFG spectra to observe and quantify the otoferlin C2F domain interacting with model lipid membranes. A model cell membrane was built with equal amounts of phosphoserine (PS) and phosphocholine (PC). SFG studies that examined the ordering of the lipids that make up the model membrane, demonstrate that lipid fusion occurs after docking of the otoferlin C2F domain via the observation of a 62% increase in amplitude from the SFG signal near 2075 cm^{-1} assigned to specific groups within the model membrane. This increase is related to lipid ordering caused by the docking interaction of the otoferlin C2F domain. SFG spectra taken from the amide I region contain peaks near 1621 cm^{-1} and 1672 cm^{-1} related to the C2F domains beta-sandwich secondary structure, thus, indicating that the domain binds in a specific orientation. By mapping the simulated SFG spectra to the experimentally collect SFG spectra, we found the C2F domain of otoferlin orients 32° normal to the lipid surface. This information allows us to map what portion of the domain directly interacts with the lipid membrane. Furthermore, we show first experimental view of any C2 domain of otoferlin docked at the membrane interface, thereby, validating SFG as a method to probe C2 domain-membrane interfaces.

2:20pm **BI+AS+IPF+MN-MoA4 Vibrational Sum-frequency Scattering Spectroscopy for the Characterization of Protein Fiber Structures and their Surface Interactions in Biological Environments***, **Patrik K. Johansson**, D.G. Castner,* University of Washington

Biological processes are typically regulated by interactions at the interface of 3D structures, such as the membrane of cells or protein fiber surfaces. Collagen (the most common protein in mammals) forms large fibers that are responsible for the structural integrity of tissues. The structure, organization and interactions of these fibers are furthermore important for the survival, communication, migration, and proliferation of cells.

Investigating protein fiber interactions is challenging, particularly under biological conditions where the fibers exist in a 3D aqueous environment. Many techniques cannot interrogate interfaces buried in the bulk of a solvent and therefore require 2D surface models, while others need extensive purification and sample preparation. These approaches may not capture all key characteristics of the fiber surface structure and interactions in the real sample. However, vibrational sum-frequency scattering (SFS) spectroscopy, with inherent contrast for local molecular ordering, can be utilized towards these important goals.

As a first demonstration, we have applied SFS to protein fibers in aqueous environments, self-assembled from collagen type I. We detected signals from the amide I band and the N-H stretching vibrations, both of which are related to the specific protein backbone structure. Signals from the C-H stretching and bending vibrations were also identified, which are more associated with the side-chains in the fibers. The angular scattering patterns for the backbone (amide I) and side-chain (C-H stretches and bends) signals are different, making the spectra dependent on the angle of detection. While the backbone signals are dominant in the phase-matched direction, the side-chain signals remain high also at large scattering angles. Distinctions in the organizational symmetry and the relative fiber surface contribution to the overall signal are hypothesized as reasons for this observation.

Finally, we are investigating the impact of changes to the environment (e.g. ionic strength, pH, surfactants) on the shape of spectra and scattering patterns for the detected SFS signals. This could yield new insights to the structure and dynamics of collagen fibers in biological settings. The relevance of such investigations is enhanced by the fact that detection of vibrations from the surrounding molecules is a direct observation of their interactions with the collagen fiber surface, which thus can be correlated with the fiber structure. The relative orientations for the detected groups can also be obtained via vibrational SFS polarization analysis, for a deeper understanding of biomolecular interactions in biological processes.

2:40pm **BI+AS+IPF+MN-MoA5 How Proteins Grow Calcium Carbonates – The Mechanism of Vaterite Bioprecipitation Studied at the Molecular Level by Sum Frequency Generation Spectroscopy***, H. Lu,* Max Planck Institute for Polymer Research, Germany*; S. Roeters,* Aarhus University, Denmark*; H. Lutz, M. Hood, A. Schäfer,* Max Planck Institute for Polymer Research, Germany*; R. Muñoz-Espí,* Universidad de Valencia, Spain*; M. Bonn,* Max Planck Institute for Polymer Research, Germany*; **Tobias Weidner**,* Aarhus University, Denmark

Proteins can act as Nature's engineers at interfaces and manipulate hard tissue growths. Specialized peptides can bind and release specific mineral facets and grow the intricate mineral morphologies found in diatom cell walls, mollusk nacre, but also human teeth and bone. Taking clues from Nature we aim at understanding the mineralization processes at the molecular level and to develop design rules for biogenic nanophase materials. Mineral proteins control the biogenesis of $CaCO_3$ by selectively triggering the growth of calcite, aragonite or vaterite phases. The templating of $CaCO_3$ by proteins must occur predominantly at the protein/$CaCO_3$ interface. Surprisingly, molecular-level insights into the interface during active mineralization have been lacking. Here, we investigate the role of peptide folding and structural flexibility on the mineralization of $CaCO_3$. We discuss the mineral activity of amphiphilic

peptides based on glutamic acid and leucine with *ß*-sheet and *α*-helical secondary structures. While both sequences lead to vaterite structures, the *ß*sheets yield free-standing vaterite nanosheet with superior stability and purity. Surface-specific spectroscopy studies and molecular dynamics simulations reveal that the interaction of calcium ions with the peptide monolayer restructures both the peptide backbone and side chains. This restructuring enables effective templating of vaterite by mimicry of the vaterite (001) crystal plane. The approach is universally applicable to mineral peptide engineering. We will discuss how analogous peptide designs can be used to steer the growth not only of calcium carbonates but also calcium oxalates.

3:00pm **BI+AS+IPF+MN-MoA6 ToF-SIMS Imaging of Chemical Modifications in Topographically Challenging Materials***, **Michael Taylor**, D.J. Graham, L.J. Gamble,* University of Washington

Three-dimensional (3D) porous materials are applied in a variety of areas within materials science[1]. Pores in catalysts provide a high surface reaction area, pores in biofilters facilitate fluid movement for biomolecule capture, and pores in tissue engineered constructs allow for cellular ingress and vascularization. These applications require surface modifications to add specific functionality to their surfaces. The successful functionality of these materials is related to the ability of these modifications to reach all surfaces of the pores. However, it is challenging to characterize these complicated materials and verify the presence and distribution of these surface modifications. Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is a powerful label-free surface analysis tool that can be used to image the molecular composition of cells, tissues and polymers. Porous 3D materials however, are non-ideal for ToF-SIMS analysis as the technique is highly surface-sensitive, topography on the order of microns can inhibit the ability to produce secondary ions related to surface modifications. To solve this problem we have developed a methodology for filling voids in porous materials to produce a surface where ToF-SIMS imaging may be performed. A embedding process for porous materials with poly(vinyl alcohol)(PVA) is detailed followed by freezing and cryo-sectioning to expose the modified scaffold interior. Here, we demonstrate the versatility of this method by high spatial resolution 3D imaging of a number of surface modifications in PCL poly(caprolactone) scaffolds[2]. Characterisation of fluorocarbon (FC) films deposited using octofluoropropane (C3F8) plasma enhanced chemical vapor deposition (PECVD) will be demonstrated, showing that increased treatment times deposits uniform coatings while shorter treatment results in a gradient distribution of FC throughout the PCL scaffold. Additionally we show data on imaging immobilized/adsorbed proteins within PCL scaffolds. Using this methodology we demonstrate that high spatial resolution label-free 3D imaging of chemical modifications in materials with complex geometries is now possible with ToF-SIMS.

Refs:

(1) Yang, X.-Y.; Chen, L.-H.; Li, Y.; Rooke, J. C.; Sanchez, C.; Su, B.-L. Hierarchically Porous Materials: Synthesis Strategies and Structure Design. *Chem. Soc. Rev.***2017**, *46* (2), 481–558 DOI: 10.1039/C6CS00829A.

(2) Taylor, M. J.; Aitchison, H.; Hawker, M. J.; Mann, M. N.; Fisher, E. R.; Graham, D. J.; Gamble, L. J. Time of Flight Secondary Ion Mass Spectrometry—A Method to Evaluate Plasma-Modified Three-Dimensional Scaffold Chemistry. *Biointerphases***2018**, *13* (3), 03B415 DOI: 10.1116/1.5023005.

3:40pm **BI+AS+IPF+MN-MoA8 Imaging Plant and Plant Growth-Promoting Bacteria Interactions Using Time-of-Flight Secondary Ion Mass Spectrometry***, **Xiao-Ying Yu**, R. Komorek, Z.H. Zhu, C.J. Jansson,* Pacific Northwest National Laboratory

We present the first imaging and spectra results of plant root interactions with plant growth-promoting bacteria (PGPB) using time-of-flight secondary ion mass spectrometry (ToF-SIMS), showing the successful application of delayed image extraction to study plant biology. Compared to MALDI (Matrix Assisted Laser Desorption Ionization), an imaging mass spectrometry technique widely used in plant studies,[1] SIMS is less destructive and provides submicrometer spatial mapping of molecular species of importance in metabolic processes. *Brachypodium distachyon* (Brachypodium), a genomics model for bioenergy and native grasses, is used due to its small diploid genome, close phylogenetic links to other grass species, relative ease of genetic transformation, short life cycle, small stature, and simple growth requirements.[2] Plant growth-promoting bacteria (PGPB) such as *Pseudomonas* and *Arthrobacter* were introduced to Brachypodium roots prior to analysis, and their potential effect on root extrusion was studied using ToF-SIMS imaging. Specifically, delayed image extraction was used in data acquisition. This approach was chosen to obtain high mass and high spatial resolutions.[3] Excellent SIMS imaging gives topographical description of the root surface with and without PGPB interactions. Distinctive characteristic peaks are observed, indicating compositional changes with and without PGPB introduction to the root surface beside visible surface morphological variations. Our initial results demonstrate that ToF-SIMS is a promising imaging mass spectrometry tool to study plant biology and root-microbe interactions and provide molecular-level insight at the biointerface with high spatial resolution.

References:

[1] D Sturtevant *et al.*, Three-dimensional visualization of membrane phospholipid distributions in Arabidopsis thaliana seeds: A spatial perspective of molecular heterogeneity, Biochimica et Biophysica Acta (2017),**1862**(2)*,* 268-81.

[2] T Girin *et al.*, Brachypodium: a promising hub between model species and cereals, J. Experimental Botany (2014),**65**(19)*,* 5683-96*.*

[3] QP Vanbellingen *et al.*, Time-of-flight secondary ion mass spectrometry imaging of biological samples with delayed extraction for high mass and high spatial resolutions, Rapid Comm. Mass Spectrom. (2015), **29** (13), 1187-95.

4:00pm **BI+AS+IPF+MN-MoA9 Imaging of Cells and Tissues with Helium Ion Microscopy***, J.A. Notte, D. Wei, **Chuong Huynh**,* Carl Zeiss Microscopy, LLC

Both optical and electron microscopy are well established techniques in the life sciences with established protocols for imaging and sample preparation. However the newly developed helium ion microscope has some unique advantages, and is gaining a reputation for providing insightful, easy to interpret images over a wide range of biological samples and bio-materials. This presentation serves as both an introduction to this novel technique and a review of recent results.

Because helium ions do not suffer appreciably from diffraction effects, they can be focused to a sub-nanometer probe, providing nanometer scale image resolution with a depth of focus that is well suited to complex surfaces and structures. As helium ions interact with the sample, they provide an abundance of secondary electrons that convey surface-specific and topographical information. Distinctly different from the conventional (gallium) focused ion beams, helium ions do not significantly damage the sample from the sputtering process. And importantly, helium ion microscopy is not affected by charging artifacts when imaging insulating materials, even glass slides, so there is no need for metal over-coating which would otherwise obscure finer details.

Example images will include a pancreatic cell membrane showing the pores and cilia present on their natural surfaces. Other examples will show the complex structure of the principal cell and intercalated cells of the collecting duct of a rat kidney. Other imaging results from diverse fields include stony corals, collagen networks, bone minerals, stereocilia, otoconia, actin filaments, and cryptococcus neoformans. False colorized images of the multi-ciliated epithelial trachea of an adult mouse and T4-phages will also be presented. Finally, new results will be shown from the SIMS spectrometer which provides elemental and isotopic information, and can be the basis for true colorizaton.

In this talk, an emphasis will be placed on the physics principles that enable these imaging results. The selected examples serve to demonstrate the breadth of results that can be attained with this relatively new technique.

4:20pm **BI+AS+IPF+MN-MoA10 Quantitative Analysis of Electrolytes in Microliter-size Blood Drops Congealed via HemaDrop™ using Ion Beam Analysis and SIMNRA***, H. Thinakaran, S.R. Narayan, J.M. Day, **Nicole Herbots**, F.J. Ark, B. Wilkens, M. Mangus, R.J. Culbertson,* Arizona State University

Accurate analysis of microliter blood samples can improve medical testing and forensics. Most critically ill patients suffer from hospital-acquired anemia due to the large volume currently required for blood diagnostic tests: 7 mL per vial.

Prior attempts by Theranos to analyze microliter-sized blood droplets in liquid form exhibit systematic errors greater than 10%, higher than the acceptable medical threshold.

This research investigates the accuracy of Ion Beam Analysis (IBA) performed on microliter-sized blood droplets congealed into Homogenous Thin Solid Films (HTSFs) using HemaDrop™, a new patent-pending technique using hyper-hydrophilic coatings to condense fluids into a uniform solid state with a smooth surface.

Prior to IBA analysis, the solidification of blood droplets into HTSF's is observed with optical microscopy and compared to conventional Dried Blood Spots (DBS). DBS exhibit phase separation between platelets and serum, with non-uniform, rough surfaces. Conversely, blood droplets solidified on HemaDrop™-coated surfaces are uniform and smooth, with little phase separation.

Next, quantitative compositional analysis using IBA is performed on µL blood drops solidified on HemaDrop™ coatings and is compared to results on DBS. HTSFs congealed on HemaDrop™-coated surfaces yield well-defined 2 MeV RBS spectra where individual species and electrolytes (C, N, O, Na, K, Ca, Cl, Fe) can be identified, while none can be distinguished on DBS.

The damage curve method [1] extracts elemental composition while accounting for possible IBA damage. Several consecutive spectra are taken on the sample, and RBS yields are interpolated to their original concentrations.

IBA simulations with the software SIMNRA enable comparison between RBS data and simulations, resulting in elemental composition accurate within 1%. Blood electrolyte compositions via SIMNRA are obtained on successive IBA spectra taken on different areas of the thin solid films and on different HTSFs congealed from the same blood. Relative error analysis between different HTSF samples establishes whether reproducibility within 10% can be achieved.

HemaDrop™ reliably creates stable, uniform, thin solid films to measure blood composition from µL-volume drops based on comparative IBA results and optical observations. Measurements of elemental composition of HTSF of blood samples are accurate and reproducible. HemaDrop allows for analysis in vacuo from µL of blood, greatly expanding the range of techniques that can be applied to identify elements and molecules (e.g., antibiotics, proteins).

[1] *Int & US Patent Pending, 2016, 2017

Applied Surface Science Division
Room 204 - Session AS+BI-TuM

Applied Surface Science: From Electrochemistry to Cell Imaging, a Celebration of the Career of Nicholas Winograd

Moderators: Arnaud Delcorte, Université Catholique de Louvain, Belgium, Michaeleen Pacholski, The Dow Chemical Company

8:00am **AS+BI-TuM1 Surface Analysis and Beyond, Using Ion Beams and Lasers**, ***Nicholas Lockyer***, *J.C. Vickerman,* University of Manchester, UK **INVITED**

Applications of secondary ion mass spectrometry (SIMS) have expanded enormously from pure surface science experiments to biology and bio-medicine, driven largely by developments in instrumentation. Polyatomic primary ion beams have resulted in a step-change in the technique's capability to detect and localise molecular chemistry, in biological cells and organic devices etc. This has stimulated new mass spectrometer designs and analytical paradigms for molecular imaging in 2D and 3D. The quest for still greater lateral resolution is a quest for improved sensitivity. Here ion beam chemistry can play a role, increasing the ionized fraction of the sputtered plume. Alternative routes to improved ionization and greater quantification include laser post-ionization. In this talk I will chart the progress made in these areas by our group in Manchester, and draw parallels with the work of the Winograd group, with whom we have had fruitful collaboration over many years.

8:40am **AS+BI-TuM3 A High Resolution Tandem MS Imaging Method to Probe the Composition of Organelles in Single Cells**, ***Gregory L. Fisher***, Physical Electronics; *C.E. Chini,* University of Illinois at Urbana-Champaign; *B. Johnson, M.M. Tamkun,* Colorado State University; *M.L. Kraft,* University of Illinois at Urbana-Champaign

A goal of cellular imaging is to ascertain the composition of organelles, e.g. lipid profiling or pharmaceutical efficacy. To date most MS imaging of organelles is accomplished by stable isotope labeling because the imaging ion beam produces primarily (di)atomic ions. Such analyses are void of desired molecular specificity. We employed a TOF-TOF imaging capability [2] to achieve molecular specificity and conjectured that an ER-Tracker stain would yield characteristic molecular ions with which to image the endoplasmic reticulum (ER) and ER tubules.

We used human embryonic kidney (HEK) cells that had a high number of ER tubules near the plasma membrane (PM). Experimental cells were transfected to express GFP-Kv2.1 fluorescent ion channels. The cells were stained with ER-Tracker which selectively labels the ER. Control specimens were neither transfected nor stained.

We observed by simultaneous MS imaging and tandem MS imaging, in both the positive and negative ion polarities, the atomic and molecular moieties characteristic of an ER-Tracker stain localized to the ER and ER tubule structures. The ion species used for tandem MS imaging of the ER and ER tubules, namely F^-, $C_6H_5^-$, $C_5H_5^+$ and $C_{17}H_{15}N_2O^+$, were shown irrefutably via the product ion spectra to arise solely from the ER-Tracker stain. Two-dimensional (2D) imaging revealed intersection of some ER tubules at the PM. Three-dimensional (3D) visualization via depth profile analysis, carried out to a depth of ≈ 40 nm from the PM, revealed additional ER tubules just under the PM. Some ER-Tracker was observed in the PM indicating ER tubule contact with the PM to form ER-PM junctions. We were able to confirm the presence and position of the PM owing to the presence of characteristic lipids, lipid fragments and fatty acids which were imaged in parallel. The observed tubule features were imaged at an effective lateral resolution of 137 nm and had measured diameters in the range of approximately 500 nm to 2 µm corresponding well with previous studies [3] and present total internal reflection fluorescence (TIRF) observations. More than a dozen control cells were analyzed, and neither atomic nor molecular moieties characteristic of the ER-Tracker were observed to be present. Our next aim is to visualize the ER within entire cells and to assess the lipid composition at different locations within the ER. By extension, with organelle-specific stains, we can apply this TOF-SIMS tandem MS imaging method to aspects of pharmaceutical delivery and metabolism.

9:00am **AS+BI-TuM4 SIMS and MALDI-MS. Competitive, Complimentary or Complementary Techniques for Bio-imaging?**, ***John Stephen Fletcher***, *I. Kaya,* University of Gothenburg, Sweden

Despite imaging SIMS being a much older technique than MALDI in the bio-MS imaging area MALDI has enjoyed considerably more widespread success. The advantage of higher resolution imaging that is possible with SIMS has generally been outweighed by the low signal for intact molecular ions that are routinely delivered by soft ionisation techniques like MALDI – and MALDI is cheaper. However, advances in ion beams and mass spectrometry for SIMS analysis in parallel with new matrices, sample preparation and analysis approaches for MALDI have brought the two techniques closer together with significant overlap in the 1-10 µm "small molecule" imaging range.

In this presentation the benefits (if any) of multimodal MS imaging are discussed using examples from cancer, cardiovascular and neurological studies. Analysis was performed using high energy (40 keV) gas cluster ion beams (GCIBs) for SIMS analysis on the Ionoptika J105 and different MALDI approaches including gentle/static MALDI on the Bruker Ultraflextreme. On tissue derivatisation strategies applicable to both techniques will also be presented.

9:20am **AS+BI-TuM5 High Spatial Resolution Metabolic Imaging using the 3D OrbiSIMS - Fundamentals of Metabolite Fragmentation and Biological Applications**, *C. Newell, Y. Panina,* Francis Crick Institute, UK; *L. Matjacic, V. Cristaudo,* National Physical Laboratory, UK; *A.P. Bailey,* Francis Crick Institute, UK; *R. Havelund,* National Physical Laboratory, UK; *M. Yuneva, A.P. Gould,* Francis Crick Institute, UK; ***Ian S. Gilmore***, National Physical Laboratory, UK

Ground-breaking advances in single-cell genomics and transcriptomics are revealing the heterogeneity of cells in tissue and are transforming biological understanding. There is a great need for metabolomics with single-cell resolution. Recent advances in both SIMS and MALDI imaging have pushed the spatial resolution boundary to a few micrometres [1-3].

Here, we report on the 3D OrbiSIMS [1] which combines a gas cluster ion beam (GCIB) that is able to simultaneously achieve a spatial resolution of < 2 µm with high mass resolving power (>240 k) and mass accuracies of ~1 ppm. The GCIB significantly reduces fragmentation of metabolites compared with small cluster ion beams and we provide fragmentation data for a variety of metabolites for different energy per atom conditions.

We demonstrate the OrbiSIMS capability with two biological examples. Firstly, a study of the cuticular lipid composition and distribution of drosophila and how these change with various environmental and genetic manipulations. Drosophila secrete many different classes of lipids to form a protective surface barrier against environmental challenges and hydrocarbons which play a separate role as pheromones that influence sexual behaviour. Secondly, to identify metabolic heterogeneity in mammary gland tumours. One of the hallmarks of cancer is deregulated metabolism, often characterised by increased glucose and glutamine uptake for energetic and anabolic purposes. Metabolic changes contribute to well-established tumour heterogeneity, which is a major challenge for anti-cancer therapeutics. We demonstrate a protocol to co-register high-resolution OrbiSIMS metabolite images with immunohistochemistry microscopy images of the same sample.

References

1 Passarelli, M. K. *et al.* The 3D OrbiSIMS-label-free metabolic imaging with subcellular lateral resolution and high mass-resolving power. *Nature Methods***14**, 1175, doi:10.1038/nmeth.4504 (2017).

2 Kompauer, M., Heiles, S. & Spengler, B. Autofocusing MALDI mass spectrometry imaging of tissue sections and 3D chemical topography of nonflat surfaces. *Nature Methods***14**, 1156, doi:10.1038/nmeth.4433 (2017).

3 Dreisewerd, K. & Yew, J. Y. Mass spectrometry imaging goes three dimensional. *Nature Methods***14**, 1139, doi:10.1038/nmeth.4513 (2017).

9:40am **AS+BI-TuM6 Small Molecule Imaging in Single Frozen-Hydrated Cells using High-Resolution Gas Cluster Ion Beam Secondary Ion Mass Spectrometry (GCIB-SIMS)**, ***Hua Tian***, *N. Winograd,* Pennsylvania State Univeristy

Cell heterogeneity leads to the development of antibacterial resistance and tumor relapses in response to drug treatment. Cell-to-cell differences have been extensively investigated at the DNA level. The study of rapid and dynamic small molecule fluctuations in single cells has lagged. However, the complete spectrum of biomolecules can be a direct indicator of cell phenotype and a reflection of immediate response to environment and chemical stress. There is currently no method to directly detect small molecules in their original state because of the rapid and dynamic nature of these molecules and impossibility of amplifying the metabolites. Previously, the characterization of drug and small molecules in cells are conducted using ensembles of cells, with which the spatial distribution, a

vital piece for understanding biological processes is lost. The development of high resolution CCIB-SIMS in our lab has positioned us to directly image small molecule fluctuation in single cells under cryopreservation. The approach takes advantage of three aspects of GCIB-SIMS - low chemical damage, high yield of intact biomolecules, and the possibility of sub-micron lateral resolution. In this work, we utilize a DC beam buncher-ToF SIMS instrument to achieve high lateral resolution. Moreover, this configuration simplifies depth profiling since erosion and spectral acquisition are performed with a single beam. In addition, the flexibility of gas candidates for GCIB allows us to explore tailored beam for ionization enhancement, such as HCl, CH_4, CO_2 or H_2O (1~100%) doped Ar cluster beams. To illustrate this instrumental protocol, chemically resolved 3D images of single cells, HeLa cells and drug treated A549 (Carcinoma) and A673 (Ewing tumor) cells are imaged using a novel 70 keV $(CO_2)_{14000}$+ beam with a spot size of 1 µm. The stable intermediates from various biochemical pathways are visualized in single HeLa cells, demonstrating the sufficiency of the chemical sensitivity using GCIB. The drug propranolol is localized within the cellular structure of A673 and A549 cells, while no sign of fexofenadine is observed. This indicates that propranolol has high passive permeability in contrast to low passive permeability expressed by fexofenadine. Surprisingly, a lipid composition change is shown in A673 cells, particularly the depletion of phosphatidylinositol species after treatment. The approach provides a complete chemical picture of single cells at near original physiological and morphological state, opening the opportunities for single cell metabolomics and heterogeneity studies using SIMS.

11:00am **AS+BI-TuM10 Pushing the Limits of Measurement Science with SIMS**, ***Christopher Szakal***, *D.S. Simons, J.D. Fassett, T.P. Forbes,* National Institute of Standards and Technology (NIST) **INVITED**

The career of Dr. Nicholas Winograd was exemplified by an unwillingness to accept the scientific status quo. Both in words and actions, he set a tone that encouraged everyone he worked with to 'push the limits' of what they thought was possible within their research endeavors. In this presentation, several topics will be explored where this mindset has been directly put into practice. A mix of historical examples, recent advancements, and new science that fit within the theme will be presented. Specifically, topics related to cluster ion beams, single cell imaging, single cell quantification, precision isotopic measurements, secondary ion mass spectrometry (SIMS) standard generation, and precision atmospheric pressure ionization MS measurements will be described in terms of how the measurement science boundaries were assertively targeted. Since Dr. Winograd had a fondness for cutting-edge instrumentation throughout his career, the presented efforts will focus on pushing the limits within time-of-flight (TOF)-SIMS, large geometry (LG)-SIMS, and ultra-high-resolution (UHR)-MS quadrupole(Q)-TOF technologies.

11:40am **AS+BI-TuM12 Multiplexed Ion Beam Imaging: Cell and Tissue Imaging using Secondary Ion Mass Spectrometry for Pathology**, ***Jay Tarolli***, *R. Finck, M. Aksoy, D. Stumbo,* Ionpath, Inc.

Traditional techniques for protein imaging in tissue sections based on light microscopy are limited in the number of simultaneous targets that can be analyzed in a single sample. The need exists in pathology, however, for concurrent imaging of more than just a few of these biomolecules to determine localization of cell types in tissue biopsies. Multiplexed ion beam imaging (MIBI) uses secondary ion mass spectrometry (SIMS) to overcome these limitations and is capable of imaging over 40 biomolecules simultaneously with a spatial resolution greater than many traditional optical and fluorescence microscopy techniques.

In a typical MIBI analysis, a tissue sample is stained with target antibodies conjugated to isotopically pure lanthanide metals. The resulting mass spectra of monoatomic heavy metals exhibit a more characteristic response than the complex mass spectra of fragmented biomolecules typically acquired when analyzing tissue samples with SIMS, the benefit of which being twofold: First, as ion counts from the target analytes are preserved instead of lost due to fragmentation into uncharacteristic species, the generated images have a higher signal to noise ratio. Secondly, now that fragmentation of target analytes is not a limitation, a high current primary ion beam with a tight focus can be employed to image tissue samples with a high spatial resolution at a high throughput rate. Specifically, an oxygen duoplasmatron primary ion beam, focusable down to a spot size of 350 nm, is used in conjunction with a time-of-flight mass analyzer to enable to the simultaneous detection of more than 40 labels at a resolution where individual cells can be differentiated in tissue samples.

12:00pm **AS+BI-TuM13 Combined ToF-SIMS and AFM Protocol for Accurate 3D Chemical Analysis and Data Visualization**, ***Maiglid Andreina Moreno Villavicencio***, *N. Chevalier, J.-P. Barnes, I. Mouton,* Univ. Grenoble Alpes, CEA, LETI, France*; F. Bassani,* Univ. Grenoble Alpes, CNRS, LTM, France*; B. Gautier,* Université de Lyon, INSA Lyon, Institut des Nanotechnologies de Lyon, UMR CNRS 5270, F- 69621 Villeurbanne cedex, France

In dual-beam time-of-flight secondary ion mass spectrometry (ToF-SIMS) depth profiling, a succession of two-dimensional chemical images is acquired. The provided images can be used to generate a three-dimensional (3D) visualization of the sputtered volume. However, standard reconstruction methods do not take into account the initial sample topography or lateral variations in sputter rates.

Due to geometry and the diversity of materials the resulting 3D chemical visualization of heterogeneous and non-planar samples may be distorted. To address this issue ToF-SIMS analysis was combined with atomic force microscopy (AFM). This combination supplies the missing sample topography of the ToF-SIMS images and allows the calculation of sputter rates for the materials present in the sample.

To achieve an accurate 3D ToF-SIMS reconstruction a protocol was developed that combines AFM topographical images, crater depth measurements and sequences of ToF-SIMS images, all acquired on the same area of the sample. This combined ToF-SIMS/AFM methodology was applied to a sample consisting of GaAs selectively grown in SiO_2 patterned structures using MOCVD. The initial topography revealed that the GaAs areas were higher than SiO_2 patterns, and the large sputter rate differences (up to a factor 2) mean that a simple reconstruction (flat surface and constant sputter rate) leads to severe distortions in the 3D ToF-SIMS reconstruction.

Using the combined methodology, a 3D overlay between AFM and ToF-SIMS images at each interface can be made and the local sputter rate can be mapped. Finally, a protocol was developed for the correction of the 3D ToF-SIMS reconstruction and depth-profiles within a rendered volume defined by successive AFM imaging.

This work was carried out on the nanocharacterisation platform (PFNC) of the CEA Grenoble and this project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 688225.

References:

Moreno, M. A. et al. Combined ToF-SIMS and AFM protocol for accurate 3D chemical analysis and data visualization. J. Vac. Sci. Technol. B Nanotechnol. Microelectron. Mater. Process. Meas. Phenom. 36, 03F122 (2018).

Industrial Physics Forum

Room 101B - Session IPF+AS+BI+MN-TuM

Advanced Imaging and Structure Determination of Biomaterials

Moderators: David G. Castner, University of Washington, Michael Grunze, Max Planck Institute for Medical Research

8:00am **IPF+AS+BI+MN-TuM1 Chemical Imaging as a Tool to asses Molecular and Morphologic Content in Natural Tissues and Fabricated Models**, *R. Bhargava, T. Comi, M. Gryka,* ***Kevin Lee Yeh***, University of Illinois at Urbana-Champaign **INVITED**

Chemical imaging, in which molecular content is obtained using spectroscopy and images are formed using microscopy, is an emerging area to characterize cells and tissues. We present here a chemical imaging approach based on mid-infrared spectroscopic imaging that combines the spatial specificity of optical microscopy with the molecular selectivity of vibrational absorption spectroscopy. IR spectroscopic imaging is particularly attractive for the analysis of cells and tissue in that it permits a rapid and simultaneous fingerprinting of inherent biologic content, extraneous materials and metabolic state without the use of labeled probes. Recorded data are related to the structural and functional state of the biological material using computation. We describe the computational strategy and statistical considerations underlying decision-making for this modality. A combination of theory, novel instrumentation and signal processing forms an integrated approach to biochemical analyses. First, we describe attempts to automate histopathology without dyes or human input. Results indicate that a rapid assessment of tissue is possible. Applied

to engineered 3D tissue models for breast tumors, we show that the imaging technology is useful in rapidly assessing culture quality and that the model systems can act to inform researchers about the involvement of different cell types in cancer progression. Finally, we integrate imaging observations with those from conventional biological experiments to provide a complete view of cancer progression in these systems.

8:40am **IPF+AS+BI+MN-TuM3 Fluorescence Dynamics and Nonlinear Optical Imaging Methods for Biomedical Applications**, ***Alba Alfonso Garcia***, *L. Marcu,* University of California at Davis **INVITED**

Generation of quality bioengineered tissue constructs, a main cornerstone for regenerative medicine, require new tools to monitor their maturation processes. Optical imaging, and in particular fluorescence dynamics and nonlinear optical techniques, provides the means for non-destructive, longitudinal, and quantitative evaluation. Using fiber optics and catheterized imaging systems these strategies are implemented with flexible geometries that allow investigations be performed outside of the realm of the microscope and the microscope slide, but instead *in situ*, on bioreactors, culturing wells and chambers, or even *in vivo*. Fluorescence dynamics and nonlinear optical imaging are especially well suited as they rely on intrinsic properties of the biomaterials to generate contrast. Tissue autofluorescence allows spectroscopic evaluation of tissue components, and the analysis of its temporal dynamics leads to functional analysis of tissue status. Additionally, nonlinear light-matter interactions probe vibrational and electronic energy levels that provide enhanced biochemical specificity of tissue constituents. All these approaches are compatible with label-free strategies, avoiding the addition of labeling agents onto already complicated samples. In this presentation, I will overview applications of fluorescence dynamics and nonlinear optical imaging including fluorescence lifetime imaging, two-photon fluorescence or second harmonic generation in tissue engineering. In particular, I will discuss tracking approaches to visualize recellularization processes on bioengineered vascular constructs. I will also characterize tissue composition of carotid arteries along their length based on their autofluorescence lifetime signals, and how this correlate with the structural protein composition of the vessel wall as evaluated by gold-standard biochemical assays. Finally, we will see how these methods are also applied in different fields such as the generation of cartilage-based implants, and the real-time discrimination of healthy versus diseased tissues in the context of cancer diagnostics.

9:20am **IPF+AS+BI+MN-TuM5 Single Molecule Imaging of Receptor Signalling**, ***Katharina Gaus***, University of New South Wales, Australia **INVITED**

Antigen recognition by the T cell receptor (TCR) is a hallmark of the adaptive immune system. When the TCR engages a peptide bound to the restricting major histocompatibility complex molecule (pMHC), it transmits a signal *via* the associated CD3 complex. How the extracellular antigen recognition event leads to intracellular phosphorylation remains unclear.

We develop single-molecule localization microscopy (SMLM) apporaches and novel analysis to determine how spatial organization regulates signal initiation and propagation. For example, we used SMLM data to map the organization of TCR-CD3 complexes into nanoscale clusters and to distinguish between triggered and non-triggered receptor copies. We found that only TCR-CD3 complexes in dense clusters were phosphorylated and associated with downstream signaling proteins, demonstrating that the molecular density within clusters dictates signal initiation. This lead us to propose a model in which antigen recognition is first translated into receptor clustering and then the density of receptor nanoclusters is translated into signaling. This model may explain how T cells can respond to both the affinity and dose of pMHC molecules with a common signal transduction mechanism (Pageon et al. PNAS 2016). We also developed novel FRET sensors to monitor the rate of receptor clustering (Ma et al. Nat Commun 2017) and a sensor that reports membrane charges (Ma et al. Nat Biotech 2017) to understand how biophysical properties of the plasma membrane contribute to TCR signaling.

11:00am **IPF+AS+BI+MN-TuM10 Developing a Google-earth View of Tumour Metabolism through Multiscale Molecular Imaging**, *J. Bunch,* ***Rory T. Steven,*** National Physical Laboratory, UK **INVITED**

Mass spectrometry (MS) is one of the most powerful techniques for chemical analysis and when combined with an imaging modality allows molecular chemistry to be visualised in 2D and 3D, from the nano- to the macroscale, in ambient conditions and in real-time. There are numerous techniques each having different modes of operation including label-free and labelled analyses.

Cancer Research UK has identified that building an understanding of the inter- and intra- heterogeneity of tumours and their evolution over time and in response to therapy will require greater insight into the underlying biology, using *in vivo* and *in vitro* models and integrating biomarkers into both early- and late-phase trials. In 2017 the Grand Challenge programme was launched. Our collaborative action involves NPL, Imperial College London, The Beatson Institute, ICR, Barts Cancer Institute, The Francis Crick Institute, The University of Cambridge and AstraZeneca. Together we will develop a validated pipeline for multi-scale imaging of tumours collected from GEMMs and patients.

By pursuing a multiscale (organ to organelle) and multi-omics approach with a range of mass spectrometry imaging (MSI) techniques (MALDI, DESI, SIMS and ICP MS), we aim to deepen our understanding of the interplay of genes, proteins, metabolites and the role of the immune system in cancer development and growth.

This presentation will review early results and a discussion of the challenges associated with such a large, multi-technique, multi-site, mass spectrometry project.

11:40am **IPF+AS+BI+MN-TuM12 X-ray Diffraction and Coherent Imaging with Nano-focused Radiation: A Multi-scale Approach from Biomolecular Assembly to Cell, Tissue and Organ**, ***Jan-David Nicolas***, *T. Salditt,* University of Göttingen, Germany **INVITED**

X-rays deeply penetrate matter and thus provide information about the functional (interior) architecture of complex samples, from biological tissues and cells to novel composite materials. However, this potential of hard x-rays in view of penetration power, high spatial resolution, quantitative contrast, and compatibility with environmental conditions has to date not been fully developed, mainly due to significant challenges in x-ray optics. With the advent of highly brilliant radiation, coherent focusing, and lensless diffractive imaging this situation has changed. We show how nano-focused hard x-rays can be used for scanning as well as for full field holographic x-ray imaging of biological samples [1]. The central challenge of inverting the coherent diffraction pattern will be discussed and different reconstruction algorithms will be presented, from holographic techniques [2] to ptychography [3,4]. Next, we will present new approaches to treat the massive diffraction data recorded in scanning nano-diffraction experiments of cells and tissues [5].

By scanning the sample through the focused x-ray beam and recording full diffraction patterns in each scan point, structural parameters can be mapped throughout the cell or histological section [6], offering a 'diffraction contrast' by which one can localize also unstained biomolecular assemblies in cells and tissues, and at the same time investigate their structure. As an example, we address the sarcomeric organization in heart muscle cells (cardiomyocytes) [7,8], and show how the sarcomere organization evolves and differs between different cell types and maturation states. As a multi-scale approach, we then discuss sarcomeric structure in heart tissue sections, and then finally present phase contrast tomography reconstructions of an entire mouse heart.

[1] Bartels et al., Phys. Rev. Lett. (2015), 114, 048103

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[3] Giewekemeyer et al., PNAS (2010), 107, 529-534

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[8] Nicolas et al., J. Appl. Crystallogr. (2017), 50, 612–620

Processing and Characterization of Air-Liquid, Solid-Liquid and Air-Solid Interfaces Focus Topic
Room 202A - Session PC+AS+BI+NS+PB+SS-TuM

Solid-Liquid and Gas-Liquid Interfacial Processes and Characterization

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

8:00am **PC+AS+BI+NS+PB+SS-TuM1 Liquefied Gas Electrolytes for Electrochemical Energy Storage Devices**, *Y.S. Meng,* University of California San Diego; ***Yangyuchen Yang,*** University of California at San Diego **INVITED**

Electrochemical energy storage devices, such as Li-ion batteries and electrochemical capacitors, have seen little change in their electrolyte chemistry since their commercialization. These liquid electrolytes often limit the energy density and low-temperature operation of these devices, which hinder many potential applications. Our work uses electrolytes based on solvent systems which are typically gaseous under standard conditions and show excellent performance in electrochemical energy storage devices. It has demonstrated that these novel solvents have superior physical and chemical properties which are attributed to excellent performance over an extended temperature range and a wide potential window of stability with unique safety features. The use of fluoromethane as solvent for lithium batteries shows excellent low-temperature operation down to -60 °C with high capacity retention. The liquefied gas electrolytes also show a high coulombic efficiency for cycling dendrite-free lithium metal anodes.

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

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

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

While the interface of the aerosol gas and particle phase is the first entity encountered by incoming gas phase species, accessing it with bond-specific methods has been hindered due to a lack of tools that can operate under ambient pressure and temperature conditions. Here, we overcome this hurdle by using nonlinear optics and demonstrate the utility of vibrational sum frequency and second harmonic generation for probing the surfaces of sea spray aerosol, secondary organic aerosol, and anthropogenic influence on them. By following the heterogeneous physical and chemical processes that drive gas-to-particle conversion, aerosol formation, their transformations and phase transitions, and reactivity, we provide the molecular origin for cloud activation.

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

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

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

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

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

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

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

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

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Biomaterial Interfaces Division
Room 101B - Session BI+AS+IPF+NS-TuA

IoT Session: Biofabrication, Bioanalytics, Biosensors and Diagnostics and Flash Networking Session

Moderators: Graham Leggett, University of Sheffield, UK, Tobias Weidner, Aarhus University, Denmark

2:20pm **BI+AS+IPF+NS-TuA1 Functionalization of Silica Materials *via* Click Reaction of Surface Silanol Groups with Vinyl Sulfones*, Fang Cheng,*** *H. Wang, W. He, B. Sun, J. Qu,* Dalian University of Technology, China

Silica-based materials are widely used in the fields of catalysis, chromatography, biomaterials, biosensing and drug delivery due to their earth abundance and low cost. Success of these applications mostly relies on the functionalization of silica surfaces, among which covalent binding of organic molecules is preferred. Common strategies for the covalent functionalization of silica materials involve either silane treatments or Si-H reactions. Each has its share of limitations, with the former suffering from self-polymerization and multilayer modifications, and the latter being sensitive to moisture and oxygen. Herein, we proposed the 'click' reaction of silanol groups with vinyl sulfones, which enables a new and simple strategy for functionalization of silica materials. For the first time, the 'click' concept was extended to silanol groups that are abundant on the surface of silica materials, using compounds bearing vinyl sulfone groups. By simply immersing silica materials in vinyl sulfone solutions at 60℃, functionalization could be achieved in hours in the presence of catalysts. The chemical stability of vinyl sulfones and mild reaction conditions make this strategy advantageous than silane treatments and Si-H reactions. We demonstrated that silica materials with sizes ranging from microscale to macroscale could all be functionalized. Using compounds bearing multiple vinyl sulfone groups, silica materials can be further functionalized with varies of biomolecules due to the versatile reactivity of vinyl sulfone group towards thiol, amino and alcohols. Furthermore, the stability of resulting Si-O-C bond can be tuned by the properties of the vinyl sulfone compounds (e.g., hydrophobicity and surface density) as well as the environmental factors (e.g., solvents, pH and temperature). Increase in the hydrophobicity and functionalization density of the vinyl sulfone compounds could increase the stability of Si-O-C bonds. Contrast to the high stability in organic solvents, degradation of Si-O-C bond can be realized in aqueous solutions, which can be accelerated by addition of acid or base. This is rarely observed with bonds produced based of silane treatments and Si-H reactions. It could broaden the biomedical applications of functionalized silica, for example, to provide tailored release of drugs or proteins from silica surface.

2:40pm **BI+AS+IPF+NS-TuA2 Organosilica pH Nanosensors Applied to Realtime Metabolite Monitoring*, Kye Robinson,*** Monash University, Australia*; K. Thurecht,* University of Queensland, Australia*; S. Corrie,* Monash University, Australia

Continuous monitoring of biomarkers in biological environments is a key challenge for the development of biosensors capable of providing real-time feedback[1]. These sensors promise to aid in the treatment of diseases with a highly dynamic nature however current technologies remain scarce[1]. Nanoparticle based "optodes" have emerged as sensitive and tuneable biosensors, using chromo/ionophores to generate analyte-specific changes in fluorescence spectra in a dynamic and reversible manner. Currently this type of sensor suffers from limitations including leaching of reagents from the nanoparticles over time, combined with poor colloidal stability and resistance to fouling in biological fluids.

An organosilica core-shell pH sensitive nanoparticle containing a mixture of covalently incorporated pH-sensitive (shell) and pH-insensitive (core) fluorescent dyes has been developed. This platform demonstrates good long term stability (80 days), fast response time (<100 ms) and resistance to fouling in biological conditions[2]. This presentation will describe the modification of these pH sensing particles towards the production of a lactate responsive particle for sensing through coupling with lactate dehydrogenase. Here we will present our latest results focussed on enzyme encapsulation in addition to modulation of shell parameters including thickness and degree of crosslinking in order to tune response kinetics for application in biological tissues.

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3:00pm **BI+AS+IPF+NS-TuA3 Impact of Different Receptor Binding Modes on Surface Morphology and Electrochemical Properties of PNA-based Sensing Platforms*, Johannes Daniel Bartl,*** Walter Schottky Institut (WSI) and Physics Department, Technische Universität München, Germany*; P. Scarbolo,* Dipartimento Politecnico di Ingegneria e Architettura (DPIA), Università degli Studi di Udine, Italy*; S. Gremmo, G. Rziga, M. Stutzmann,* Walter Schottky Institut (WSI) and Physics Department, Technische Universität München, Germany*; M. Tornow,* Molecular Electronics Group and Department of Electrical and Computer Engineering, Technische Universität München, Germany*; L. Selmi,* Dipartimento di Ingegneria "Enzo Ferrari" (DIEF), Università di Modena e Reggio Emilia, Italy*; A. Cattani-Scholz,* Walter Schottky Institut (WSI) and Physics Department, Technische Universität München, Germany

Silicon-based field-effect devices have been widely studied for label-free DNA detection in recent years. These devices rely on the detection of changes in the electrical surface potential during the DNA recognition event and thus require a reliable and selective immobilization of charged biomolecules on the device surface [1]. The preparation of self-assembled monolayers of phosphonic acids (SAMPs) on metal oxide surfaces is an efficient approach to generate well-defined organic interfaces with a high density of receptor binding sites close to the sensing surface [2,3]. In this work, we report the functionalization and characterization of silicon/silicon nitride surfaces with different types of peptide nucleic acid (PNA), a synthetic analogue to DNA [4].

Differently modified PNA molecules are covalently immobilized on the underlying SAMPs either in a multidentate or monodentate fashion to investigate the effect of different binding modes on receptor density and morphology important for PNA-DNA hybridization. Multidentate immobilization of the bioreceptors *via* C_6-SH attachment groups at the *γ*-points along the PNA backbone provides a rigid, lying configuration on the device surface (PNA 1), whereas a monodentate immobilization by Cys-capped PNA molecules (PNA 2) results in more flexible and more accessible receptor binding sites. Our results indicate that the presented functionalization scheme can be successfully applied to produce morphologically and electrochemically different PNA bioreceptor binding sites on silicon/silicon nitride surfaces. Consequently, a well-chosen modification of the PNA backbone is a valid approach to influence the sensing properties of surface-immobilized PNA bioreceptors, which might provide an additional parameter to further tune and tailor the sensing capabilities of PNA-based biosensing devices.

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3:20pm **BI+AS+IPF+NS-TuA4 Biosensor for Detection of Gasotransmitter from Living Cells Employing Silver Nanorods Array*, Shashank Gahlaut,*** *C. Sharan, J.P. Singh,* Indian Institute of Technology Delhi, India

The detection of endogenous gases including H_2S is of immense interest nowadays as it opens the way to predict some diseases as well as an early stage diagnosis. These three gasotransmitter (H_2S, NO and CO) gaseous molecules transfer the information and give the signal for mainly cardiovascular diseases Therefore, its detection has crucial importance in bio-medical science. Here, we demonstrate H_2S detection from living cells using silver nanorods arrays fabricated by glancing angle deposition method. Colorimetric and wettability properties of silver nanorods are being observed for the gaseous detection. We use the model organism *E.coli* to demonstrate the feasibility of the method for the determination of live and resistant strains of the bacteria. For the human cell, we have used Hela cell line for the same. For the simplicity and feasibility of the technique, Android based mobile app has been developed for the colorimetric detection. Data obtained in this study show the potency of the system to identify live/dead bacteria with or without antibiotic treatment and compared with the time-consuming standard plating method, it a simple and cost-effective method for the estimation of living and resistant microorganism. The performance of AgNRs as H_2S gas sensor is investigated by its sensing ability of 5 ppm of gas with an exposure time of only 30 s. It has potential application in the area of antimicrobial resistance and bio-medical healthcare.

4:40pm **BI+AS+IPF+NS-TuA8 Polyzwitterion-modified Nanoparticles for Selective Antibody Separation**, *F. Cheng, C. Zhu,* ***Wei He****, B. Sun, J. Qu,* Dalian University of Technology, China

Antibody separation is a key biopharmaceutical process, which requires high specificity and efficiency in isolating the biomacromolecule from a complex biological fluid. Development of the separation adsorbent benefits diagnostics and therapeutics, such as point-of-care testing, treatment of cancer and autoimmune disease. In the process of antibody separation, Protein A chromatography is a commonly employed adsorbent, which could obtain antibody in high purity from serum or ascites. In the process-scale purification and therapeutic plasma exchange, safety issues, e.g. leakage and instability of the immobilized Protein A, and cross-contamination during regeneration, are overwhelmed in biopharmaceutics. An alternative approach to Protein A chromatography is using synthetic ligand, molecular weight of which is commonly less than 200 Da. The main advantages of synthetic ligand are well-controlled chemical structure, low cost, ease in clean-in-place, and repeatable regeneration capability in harsh conditions. However, it is a challenge to adsorb antibody in a highly selective manner from a complex biological fluid, which consists a variety of proteins with a broad range of concentrations.

Herein, we report a facile method to develop a quick separation adsorbent, which adsorbs antibody from a complex biological fluid with a high specificity. Two types of zwitterionic polymer-modified magnetic nanoparticles (NPs) are fabricated by conjugating pSBMA onto PEI-precoated NPs via either one-step method (1S NPs) or two-step method (2S NPs). For both methods, divinyl sulfone is used as linker molecule. Although 1S NPs were capable of resisting both IgG and BSA, 2S NPs exhibited specificity toward IgG adsorption in complex biological fluids, e.g. mixture of serums and IgG. The moderate interactions (Kd ~1.2 μM) between IgG and 2S NPs are three orders of magnitude lower than IgG binding with Protein A (Kd 10nM) . Through complementary characterizations and analyses, we rationalize that the surface developed herein with IgG specificity contains two key components: polyzwitterions with short chain length and sulfone groups with high density.

5:00pm **BI+AS+IPF+NS-TuA9 Orienting Proteins on Surfaces with Site-specific Bioorthgonal Ligations**, ***Riley Bednar****, R.A. Mehl,* Department of Biochemistry and Biophysics, Oregon State University

The functionalization of material surfaces with proteins is of great importance to a number of technologies, from industrial processes to biomedical diagnostics. However, while it has been proposed that orientation may be important to the function of such biomaterials, efforts to study such roles are hampered by a lack of rapid, quantitative, and orientation-specific immobilization techniques which will reduce non-specific fouling, and allow substoichiometric attachment of proteins onto surfaces in an orientation-controlled manner. Here, Carbonic Anydrase II (HCA)—a 30 kDa, monomeric metalloenzyme which catalyzes the interconversion of carbon dioxide to bicarbonate—is immobilized onto strained *trans*-cyclooctene (sTCO)-functionalized magnetic resin in an orientation-specific manner via bioorthogonal ligation with a site-specifically installed tetrazine-containing amino acid (Tet2.0).

5:20pm **BI+AS+IPF+NS-TuA10 High-throughput Study of the Role of Spatial Organization on the Activity of Surface-Bound Enzymes**, ***Nourin Alsharif****,* Boston University*; T. Lawton, J. Uzarski,* Natick Soldier Research, Development and Engineering Center*; K.A. Brown,* Boston University

Many of the exceptional properties of natural materials (e.g. fracture toughness of bones, strength to weight ratio of bamboo) can be attributed to their structural hierarchy, which originates, in part, from the nanoscale organization of the enzymes that synthesize these materials. In order to best utilize such enzymes *ex vivo* to grow engineered biomaterials, the role of this multiscale organization must be understood. Here, we report a novel strategy for studying the activity of arrangements of enzymes within a multifunctional material in a high throughput manner. In particular, we use top-down patterning techniques in conjunction with small molecule self-assembly to designate enzyme-binding regions amidst a non-binding, hydrophobic background. Key to this experimental scheme is the parallel nature of both the fabrication and the characterization processes that enable the efficient study of many geometric parameters of the enzyme-binding features. These parameters include, (1) feature size, (2) density of enzyme within each feature, and (3) distance between features. This level of control can in principle allow us to separate effects of reaction kinetics and substrate diffusion. Two strategies have been explored for the immobilization of enzymes including click chemistry to non-natural amino acids and binding to poly-histidine affinity tags. Top-down lithography and enzyme assembly were verified using a variety of surface characterization techniques including atomic force microscopy, X-ray photoelectron spectroscopy, infrared spectroscopy, spectroscopic ellipsometry, and contact angle goniometry. Initially, this high throughput paradigm is used to develop a fluorimetric assay to quantify the activity of surface-bound enzymes as a function of their spatial organization. Together with the widespread utilization of high throughput techniques in synthetic biology, the ability to study spatial organization in a rapid fashion is expected to dramatically improve *ex vivo* applications of enzymes.

5:40pm **BI+AS+IPF+NS-TuA11 Fabrication of Amino acid Contained Poly-lactic Acid Nanofibers by Electrospinning**, *C. Li,* National Yang Ming University, Taiwan, Republic of China*; J.H. Hsieh,* Ming Chi University of Technology, Taiwan, Republic of China*;* ***P.H. Lin****,* National Yang Ming University, Taiwan, Republic of China

Polylactic acid (PLA, $[C_3H_4O_2]_n$, CAS 26161-42-2) is a biodegradable and thermoplastic polymer. PLA is naturally produced and can be extracted from many plants such as sugarcane, cornstarch or cassava roots. Typical industrial production processes for PLA are direct condensation of lactic acid monomers (~100°C - 160°C) and ring-opening polymerization of lactide with metal catalysts. For applications in bulk forms, PLA can be produced by extrusion, casting, injection molding and spin coating or even 3d printing.

In cell and tissue engineering applications, amino acids are essential ingredients for cell-tissue culture, implants/replacements, drugs and treatment tests. There are twenty amino acids appearing in human genetic codes by triplet codons and usually categorized according to their polarity, acidity/basicity.

In this study, we fabricate nanofibers by electrospinning on a spin-coated PLA film. This specially designed combination of PLA films and nanofibers is meant to have enduring interfacial adhesion between the two for biomedical applications such as implants. Both PLA nanofibers and films are mixed with selected amino acids. Five amino acids were chosen: tryptophan (Trp,), methionine (Met,), serine (Ser,), glutamate (Glu,) and arginine (Arg,). The selection is based on the different electrical polarity of each amino acid. The electrical polarity has profound effects on the solubility, pH acidity of amino acids in water and many other associated biochemical functions. These amino acids are representatives of certain biochemical features for potentially different influences in our applications for cell culture.

The electrospinning process is controlled by several parameters such as the voltage of power supply, feeding velocity of polymer solution through the syringe pump, electrical field strength and distance to the collection plate of nanofibers. Different combinations of these parameters are studied to determine an optimal control for fiber formation. Properties of and microstructures of deposited films and nanofibers are investigated as following: thickness and deposition rate by surface profilometer; microstructures by Fourier transform infrared spectrometer (FTIR); surface morphology by scanning electron microscope (SEM); optical properties by UV-Visible-IR spectrometer and wettability by the contact angle.

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

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

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

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

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

Since many decades X-ray excited Photoelectron Spectroscopy (XPS) or Electron Spectroscopy for Chemical Analysis (ESCA) is a well-accepted standard method for non-destructive chemical analysis of solid surfaces. Over the last years it has been possible to develop XPS instrumentation, that can work far beyond the standard conditions of high or ultrahigh vacuum: Near Ambient Pressure (NAP)-XPS, or ESCA under environmental

conditions has become a method, that enters the field of standard surface chemical analysis and thus also the industrial sector. The main reason for this is the extremely fast solid surface analysis of any (degassing or non-degassing) material. Furthermore the environmental conditions around the sample avoid strong surface degradation due to vacuum or photon stimulated desorption. Even during the analysis the sample stays under its equilibrium conditions. Last, but not least the surrounding gas pressures of a couple of mbar acts as built-in charge neutralization on any type of material. This Environmental Charge Compensation (ECC) also decreases the negative influences of the characterization on the sample constitution. All this considered, NAP-XPS is capable of true non-destructive high throughput analysis of sample surfaces. The influence of the ambient conditions on quantification in XPS will be demonstrated and discussed.

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

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

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

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

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

Polymers used in the medical industry often undergo numerous clinical trials, laboratory testing, and development to understand the body and polymer interactions. The interactions these materials often undergo may potentially be at odds with the bulk material properties. For example, it may be desirable to modify surface properties of PTFE for polymer adhesion or modify a surface chemistry to improve bio compatibility. Methods of polymer surface modification will be presented that either enable or hinder the adhesion of a material to the surface.

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

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

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

Green production of hydrogen will be an important building block in the transition to a carbon-balanced economy and could be realized by electrolytic water splitting powered by cheap renewable energy sources. Water electrolysis is currently limited by the oxygen evolution reaction (OER) and development of the associated catalysts is proceeding slowly, mainly due to missing descriptors for activity and stability of working OER catalysts. Herein, we contribute to that emerging field with in situ XPS and NEXAFS on iridium anodes. In our in situ cell the catalyst is probed through a graphene layer, which traps an electrolyte layer around the catalyst and provides electrical contact for separated iridium nanoparticles. In this way we enhance spectroscopic signal from the active surface relative to the bulk of the catalyst and reduce mass transport problems. In taking advantage of these benefits, we found that the two well-known oxidation waves occurring before the OER onset are connected to the development of two different types of electron deficient oxygen species, which are bound to one (μ_1) or two (μ_2) iridium atoms. It appears that oxygen is not only a "non-innocent ligand", but rather a protagonist in the catalysis of the OER.

During the electrochemical reduction of oxygen, platinum catalysts are often (partially) oxidized. While these platinum oxides are thought to play a crucial role in fuel cell degradation, their nature remains unclear. We studied the electrochemical oxidation of Pt nanoparticles using in situ XPS. By sandwiching the particles between a graphene sheet and a proton exchange membrane that is wetted from the rear, a confined electrolyte layer was formed, allowing us to probe the catalyst under wet electrochemical conditions. We show that the behavior at the onset of Pt oxidation is influenced by the choice of proton exchange membrane, yet universally involves PtO_2 formation. The oxidation process is fast: even bulk oxide growth occurs on the sub-minute timescale. Thus, our observations indicate that PtO_2 may take part in the transient processes that dominate Pt electrode degradation.

5:00pm **PC+AS+BI+EM+NS+PB+SS-TuA9 The Influence of Density and Chemical Bonding on Atomic and Molecular Structures of Alcohols, Water and Oxides***, **Gabor A. Somorjai**,* University of California at Berkeley **INVITED**

Alcohol oxidation reaction over platinum nanoparticles with size ranging from 2 to 8 nm deposited on mesoporous silica MCF-17 was studied in the gas and liquid phases. Among methanol, ethanol, 2-propanol, and 2-butanol oxidations, the turnover frequency increased as the nanoparticle size became large in both reaction phases. The activation energy in the gas phase was higher than that in the liquid phase. Water co-adsorption decreased the turnover rate of all the gas and liquid phase oxidations except for the gas-phase 2-butanol case, while certain amount of water promoted 2-propanol oxidation in the liquid phase. Sum frequency generation vibrational spectroscopy (SFG) study and DFT calculation revealed that the alcohol molecules pack horizontally on the metal surface in low concentration and stand up in high concentration, which affects the dissociation of b-hydrogen of the alcohol as the critical step in alcohol oxidation.

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

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

the role of metal oxide interfaces and characteristics of fast charge transfer between metals and oxides that lead to ionization of molecules at the interface. The molecular ions produce so-called acid-base reactions. The electronic configuration of metal-oxide nanocatalysts during catalytic reactions will be introduced and its influence on heterogeneous catalysis will be outlined.

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

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

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

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

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

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

Molecular self-assembly is an attractive bottom-up approach to nanostructure fabrication. Using molecules as building blocks and carefully tuning the non-covalent intermolecular interactions, unique nanostructured architectures can be designed. Given the structure/function relationship on the nano- and meso-scale, this bottom-up approach to designing new architectures is critical in the careful design of novel materials with desired chemical properties. In this study, the role of hydrogen bond donor/acceptor position in metastable cluster formation is explored using scanning tunneling microscopy (STM) with complementary density functional theory (DFT) calculations. We observe a metastable cyclic pentamer for isatin (1H-indole-2,3-dione) with DFT providing support for a cyclic structure stabilized by both NH...O and CH...O hydrogen bonds between neighboring molecules. The CH...O hydrogen bond is made between the 7-position proton acting as the hydrogen bond donor and the 3-position carbonyl as the hydrogen bond acceptor, and calculations indicate that the isatin pentamer structure is 12 kJ/mol more stable than the dimer on the per molecule basis. To probe the importance of the CH...O hydrogen bond in stabilizing the isatin pentamer, we compare to isatin derivatives: we replace the 3-position carbonyl with a methyl group (3-methyl 2-oxindole), the 7-position proton with a fluorine (7-fluoroisatin), systematically move the location of the hydrogen bond donor/acceptor by one position, (phthalimide), and remove of the primary hydrogen bond donor (1,2-indandione and 1,3-indandione). We show that cyclic pentamer formation is either altered or precluded as a result of these substitutions. Additionally, the importance of CH...O bonding in forming isatin pentamers is supported by electrospray ionization mass spectrometry (ESI-MS) measurements, which include a magic-number isatin pentamer peak, whereas the derivative molecules show little clustering under the same conditions. This work is significant in understanding the role that the position of the hydrogen bond donor/acceptor groups has on the resulting 2D supramolecular assemblies.

Biomaterial Interfaces Division
Room Hall B - Session BI-TuP

Biomaterial Interfaces Division Poster Session

Moderator: Joe Baio, Oregon State University

BI-TuP3 Stimuli-responsive Thin Films made from Highly Methoxylated Citrus Pectin, ***Zeinab Veisi,*** *N. Alcantar, R. Toomey,* University of South Florida

We have used high-methoxyl citrus pectin polysaccharides to fabricate ultra-thin responsive coatings to be potentially implemented as elements of stimuli-responsive systems with diverse applications in drug delivery, tissue engineering, biomedicine, and etc.

Pectin is composed of a backbone chain structure of D-galacturonic acid units linked by α-1,4-glycosidic bonds. The carboxyl groups present in a polygalacturonic acid chain may exist as charged carboxyl acid groups or esterified with methyl groups. The ratio of methyl esters per total number of carboxyl groups is defined as the degree of esterification (DE). Low-methoxyl pectin (DE<50%) can be cross-linked in the presence of divalent ions such as Ca^{2+} ions. High-methoxyl pectin exhibits weak affinity for Ca^{2+} cations due to the lower charged carboxyl group content challenging their Ca^{2+}-induced cross-linking.

Herein, thin coatings of high-methoxyl citrus pectin were fabricated as surface-attached hydrogel networks by spin-casting solutions of pectin onto a solid surface followed by Ca^{2+} induced crosslinking. The cross-linking was performed by introducing the cross-linker (Ca^{2+}) in a poor solvent for pectin to eliminate water in the cross-linking process. Cross-linking the coatings in a non-solvent ensures that the coatings remain intact by preventing dilution of the pectin chains. However, the Ca^{2+} ions freely diffused into and cross-linked the pectin to form robust coatings. Using this strategy, pectins with up to 70% esterification were cross-linked. Generally, high-methoxyl pectins do not cross-link in the presence of calcium unless at high pectin concentrations.

The coatings prepared in this manner demonstrated a volume-phase transition induced by temperature. The responses of coatings were assessed by characterizing their swelling behaviors using ellipsometry and ATR-FTIR to provide insights into the nature of the transition. Our findings show that at temperatures below approximately 35 ˚C, the coatings were hydrophilic. At higher temperatures, the coatings expelled water and collapsed giving rise to distinctive de-swelling profiles. The hydrophilic/hydrophobic transition was driven by dehydration of methoxyl groups whereas water remained bound to the carboxylate groups. It was also observed that the response of the coatings can be tuned by adjusting temperature, degree of cross-linking, and pH of the surroundings to induce a desired response. Our finds show that thin films of the high-methoxyl pectin polysaccharides can be employed for establishing responsive surfaces with tunable responses suitable for the pharmaceutical and biotechnology industries.

BI-TuP4 Fluorescent DNA Nanosphere Barcdoe System by Rolling Circle Amplification for Tumor Cells Detection, *SW. Han,* ***JongBum Lee,*** University of Seoul, Republic of Korea

Nucleic acid-based nanotechnologies have been developed with the base pairing property and applied to numerous bioengineering fields of study. As a novel engineering material, DNA has been used to fabricate nanostructures from simple 2D structures to complex 3D structures. With this development of DNA nanoarchitecture, enzymatic replication technique has been also attracted as a new strategy for building nucleic acid-based nanostructures. Here, DNA nanosphere (DNANS) is fabricated by rolling circle amplification (RCA) and coated with antibodies for target cells detection. DNANS can be applied as a barcode system which can distinguish the tumor cells by recognizing tumor-specific protein. As a proof of concept, the capability for target detection of DNANS barcode system was demonstrated. This target-specific antibody-coated DNANS suggests a new route for the simple and selective recognition of cancer cells.

BI-TuP7 Vapor-Deposited Porous Polymers for the Fabrication of Giant Lipid Vesicles, ***Nareh Movsesian,*** *M.T. Matthew Tittensor, G. Dianat, N.M. Malmstadt, M. Gupta,* University of Southern California

Giant unilamellar vesicles (GUVs) are cell-sized biomimetic model membranes useful for examining membrane properties and building artificial cells. Hydrogel-assisted rehydration is an emerging technique to form GUVs under physiological conditions at high yields circumventing the shortcomings of traditional techniques such as electroformation and gentle hydration. Herein we present porous negatively charged poly (methacrylic acid-co-ethylene glycol diacrylate) *(xPMAA)*membranes fabricated using an unconventional solvent-free initiated chemical vapor deposition (iCVD) technique and utilized as hydrogel substrates for vesicle formation. Physicochemical properties of the hydrogel substrates such as morphology and crosslinking density are controlled by iCVD process parameters. Zwitterionic and charged lipid mixtures are applied on hydrogel membranes as thin lipid films and subsequently swollen in an aqueous hydration buffer. Here we show that vesicle yield and size are controlled by the morphology, the density, and the charge of the polymer. Our findings show that high hydrogel porosity and reduced electrostatic interactions between the polymer and the lipid are preferred for vesicle formation.

BI-TuP8 Developing a pH Responsive Hydrogel for the Encapsulation of Poly(ethylene glycol) 3350, ***Phuong Anh Nguyen***[1], *B. Matheson, D. Cuylear, H.E. Canavan,* University of New Mexico

Colorectal cancer (CRC) is the second leading cause of cancer-related deaths in the United States. The most reliable screening method of CRC is a colonoscopy which requires a 4-Liter poly(ethylene glycol) electrolyte lavage solution (PEG-ELS) for preparation. Two in five patients are non-compliant to their colonoscopy schedules, with many patients who abstain reporting refusal due to significant discomfort associated with this preparation. Furthermore, there are distinct gender differences in the tolerance of PEG-ELS in male and female populations. We hypothesize the differences in clinic are a result of cytotoxicity effects of PEG. PEG is approved by the FDA for use in medical devices, and has been recognized for many years as a biocompatible/bioinert polymer but few studies have truly studied the short-term and long-term effects of high concentrations of PEG on multiple cell lines. We have developed a pH responsive hydrogel to control the release of PEG – reducing adverse effects associated with colonoscopy preparations. The hydrogels have been characterized using NMR, FTIR, and XPS to ensure chemical identity, rheometry to assess the stiffness/robustness of the hydrogels in varying environments, and SEM and other techniques to confirm uniformity of size. Biocompatibility testing of exposure to increasing PEG concentrations over a period of 3 hours, 6 hours, 12 hours, 24 hours, and 48 hours shows PEG is biocompatible to mammalian cell lines in low concentrations, and in fact, increases their growth and viability. At higher concentrations, however, PEG is cytotoxic to cells. Although it would be difficult to get to toxic levels of PEG in the body in a single dose, current uses of PEG should be re-evaluated due to possible adverse cumulative effects due to the cytotoxicity effects seen *in vitro.* Further directions of this work will evaluate the pH responsiveness of our hydrogel formulation to deliver PEG *in vitro* and *in vivo,* and assessment of the cellular response to the hydrogels using mammalian cells specific to the gastrointestinal system of humans, as well as imaging analysis to envision their penetration.

BI-TuP9 Hemocompatibility of the Endexo™ Fluoro-oligomeric Surface, ***Bill Theilacker,*** Medtronic*; J. Ho, J. Swenor,* Interface Biologics*; M.F. Wolf, J.L. Kalscheue, S. Thinamany,* Medtronic*; S. Ubl,* medtronic

Blood represents one of the most complex biochemical systems in living organisms. As a result, the design of medical device materials is often tailored to reduce platelet adhesion and activation, protein adsorption, and thrombus formation. With roughly 50% or more of Medtronic products contacting vascular tissue, medical device materials that show evidence of biocompatibility with blood (aka 'hemocompatibility') are of high interest. The Endexo™ surface treatment from Interface Biologics is asserted to show improved hemocompatibility through the action of low molecular weight fluoro-oligomeric additives that bloom to the surface and reduce or inhibit blood platelet activation and procoagulant protein formation. Incorporating Endexo technology into materials is straightforward and does not change the mechanical or functional properties of the underlying medical device.

Through a collaborative effort, we examined the IBI fluoro-oligomeric additive added to a common copolyester base polymer used in blood-contact applications and evaluated the platelet and coagulation protein activating capacity. Tritan™ polyester (Eastman) was formulated with several different concentrations of Endexo™ fluoro-oligomeric additive. The surface chemistry of the samples was characterized by Scanning Electron Microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS). An in vitro vacuum test tube model developed at Medtronic was employed to asses

[1] **National Student Award Finalist**

hemocompatibility. Complete blood count analysis, platelet activation (via ELISA immunoassay for platelet plasma protein βTG), and coagulation protein formation (via ELISA immunoassay for the thrombin coagulation protein indicator TAT) was evaluated in the exposed blood.

The Endexo™ surface modifying agent appeared to show improved interaction with blood platelets. Similar favorable performance as assessed by TAT and βTG indicators of hemocompatibility may suggest a viable avenue for incremental improvement in the hemocompatibility of blood contacting devices and device materials. Surface analysis results show the Endexo formulated materials are modified with F-rich chemistry with no change in surface morphology. Medical devices that show improved performance in *in vitro* studies of hemocompatibility have potential to show improved performance in the *in vivo* clinical setting.

BI-TuP10 High Performance Dopamine Sensor Based on Field-Effect Transistor (FET) with H uman Dopamine Receptor Integrated-Multidimensional Conducting Polymer Nanofiber, ***Jinyeong Kim***, *S.J. Park,* Korea Research Institute of Bioscience and Biotechnology (KRIBB), Republic of Korea

Dopamine (DA) has been studied in the field of nervous and cardiovascular systems. Abnormal levels of dopamine is an indicator of neurological disorders, resulting in Alzheimer's and Parkinson's diseases. Therefore, dopamine is a clinically useful diagnostic sign and requires a novel approach with high sensitivity, selectivity and a rapid response. Various sensors have been developed, such as high-performance liquid chromatography (HPLC), mass spectroscopy, and spectrophotometry. However, they are limited by their high cost, low sensitivity, and variable label response.

The field-effect transistor (FET) has been used in the development of diagnosis for several decades. It is gated by changes of charge carrier density in the channel induced by the binding of target molecules, leading to high-performance biosensors. In addition, the FET platform has attracted due to their low cost, easy operation, fast response, label-free operation, parallel sensing as well as high sensitivity.

In this article, we introduced a high performance dopamine sensor based on FET assay. Multidimensional carboxylated poly(3,4-ethylenedioxythiophene) (MCPEDOT) NFs membrane was utilized as the conductive channel of sensor in the FET system. Interestingly, it provided high performance sensing due to enhanced interaction from high surface area and gate-potential modulators. Moreover, hDRD1, G protein-coupled receptors (GPCRs) as the recognition elements, was first expressed in Escherichia coli and modified with the surface of MCPEDOT NFs, leading to high selectivity. As a results, the hDRD1−MCPEDOT NF-based FET exhibits a rapid real-time response (<2 s) with high dopamine selectivity and sensitivity performance (approximately 100 fM).

BI-TuP11 Detection of B-type Natriuretic Peptide in Human Serum Based on Flexible Biosensors and Data Analysis Methodology, ***Xinruo Yi***, *A. Khalaf, R. Gunasekeran, M.H. Yun, M. Akcakaya,* University of Pittsburgh*; Y.Z. Zhang, S. Marc, N. Petroni,* UPMC

The demand on using biosensor during clinical diagnosis to detect the heart failure (HF) becomes increasing at market. B-type natriuretic peptide (BNP), as we know, is a hormone in response to stretching resulting from increased ventricular blood volume. The detection of BNP plays an important role in HF and various diagnosing cardiovascular diseases. Hence, it is important to alarm abnormal BNP levels and to monitor BNP changes appropriate to the diagnostic ranges for an HF event. In particular, BNP levels in human blood range from < 100 ng/l for normal humans to 101 ~ 1000 ng/l for HF patients. Finding BNP level will help the physician make decisions on whether the patient should be admitted to hospital or discharged.

We present a simple, high yield, low-cost and label-free method based on a two-dimensional (2-D) flexible polyaniline (PANI) biosensor along with ultra-sensitivity and specificity for biomarker detection. The 2-D PANI film which was chemically synthesized in a facile and controllable way had high surface-to-volume (S/V) ratios and showed good semiconducting properties. In order to prepare our biosensor, first, we performed surface modification using 1-ethyl-3-(3-dimethyaminopropyl) carbodiimide (EDC), and N-hydroxysuccinimde (NHS) to fix the monoclonal antibodies onto the 2-D PANI film. Second, the 2-D PANI film was treated by using non-target protein like bovine serum albumin (BSA) to block the free sites on the surface and further avoid getting noise signals. After that, our label-free biosensor for the detection of BNP is ready for the test. The detection of BNP in real human blood becomes complicated by the precipitation of red blood cells which will bind with the BNP antibody and block them to get the position of BNP antibody near biosensor surface. Instead, serum samples from patients with heart failure, obtained directly from the University of Pittsburgh Medical Center (UPMC) after separating the red blood cells from the whole blood by centrifugation, were tested.

In this work, we did the mixed blind test with two healthy samples (healthy sample) and two patient samples (with high BNP concentration). In addition, we used various approaches including electrical analysis, standard deviation method, principle component analysis (PCA), quadratic discriminant analysis (QDA) and linear discriminant analysis (LDA) to successfully identify these blind samples, which could be used to determine whether the patient has HF or not.

BI-TuP12 Characterizing Hetero-oligomer of Amyloid-beta and Alpha-synuclein with Bio-AFM, ***Eun Ji Shin***, *J.W. Park,* Pohang University of Science and Technology, Republic of Korea

Alzheimer's Disease (AD) and Parkinson's Disease (PD) are neurodegenerative diseases resulting in progressive degeneration or death of neuron cells. These are associated with the aggregation of peptides, 'amyloid-beta (Aβ)' and 'alpha-synuclein (α-syn)'. It is believed that Aβ and α-syn oligomers are intermediates in the fibril formation, and both oligomers and fibrils are primarily responsible for the pathogenesis. Further study showed that rate of the oligomerization (or aggregation) increases when Aβ and α-syn co-exist, and the co-existence causes the diseases even worse. It is very likely that hetero-oligomers could be formed, but presence and structure of the hetero-oligomers have not been elucidated.

Herein, we employed atomic force spectroscopy with a liquid cell to characterize the hetero-oligomers generated in vitro. For comparison, homo-oligomers were prepared separately. In particular, antibodies recognizing N-terminal of Aβ and N-terminal of α-syn were conjugated at AFM probes, and the specific interaction between the antibodies and surface of the oligomers was followed. After adsorbing the oligomers on mica surface, a tip tethering Aβ antibody was used to get high resolution force maps of a target oligomer, and subsequently another tip tethering α-syn antibody was brought to the same target for the examination. The overlaid map revealed that specific unbinding events with respect to two different antibodies were observed within an oligomer, and it holds for all sizes under investigation. Because homo-oligomers were not observed at all, it can be said that formation of hetero-oligomers is strongly favored. It is intriguing to note that the percentage of recognizing pixels for α-syn increases in comparison with the α-syn homo-oligomer, suggesting a different mode of aggregation for the hetero-oligomerization. We believe that such structural information helps to understand the relationship between the misfolded proteins and the pathogenesis in brain.

BI-TuP13 Creation of de novo Nucleic Acid Binding Disordered Proteins using the Thermally Responsive Behavior of Elastin-like Polypeptides, ***Telmo Diez***, *G.P. Lopez, N.J. Carroll,* University of New Mexico

Intrinsically disordered proteins (IDPs) are dynamic polypeptides used by eukaryotic cells in cell signaling, transcription, and chromatin remodeling functions are frequently employed in packaging and un-packaging of nucleic acids (NAs). Elastin-like polypeptides (ELPs) are biosynthetic biopolymers that have similar structural features to natural IDPs. Importantly, ELPs condense to form coacervates above a lower critical solution temperature (LCST). In this research, we focus on the combination of thermally responsive ELPs with natural nucleic acid binding domains to create promising responsive engineered protein constructs. In this study, we show how an ELP comprising nine positive charges from eight lysine interspersed within the chain is capable of interacting with NAs above its LCST. We characterize the amount of DNA captured by ELP and we use microfluidics to form aqueous microdroplets containing the ELP and fluorescent DNA to visualize DNA capture within ELP coacervate spheres via fluorescence microscopy. We characterize the thermodynamic binodal phase boundary (i.e. in the temperature-concentration dependent phase diagram) of the ELP[Office3] [#_msocom_3] /NA mixture to resolve the ELP volume fraction within the coacervate to predict the optimal temperature to maximize DNA capture. Finally, we combined this ELP with smaller RRM and RGG domains that bind nucleic acids found in natural FUS protein, a common NA binding protein that plays a role in genomic integrity.[Office4] [#_msocom_4] RRM is a 70 amino acid domain found to bind promiscuously to nucleic acids, and RGG is a 100 amino acid long domain rich on arginine and glycine found to be essential in the RRM interactions with nucleic acids. These studies have implications for, and yield insights into, the tailoring of engineered protein constructs that bind nucleic acids with predictable behavior and controlled release that could have many applications in gene therapy and other areas of bionanotechnology.

Processing and Characterization of Air-Liquid, Solid-Liquid and Air-Solid Interfaces Focus Topic
Room Hall B - Session PC+AS+BI+EM+NS+PB+SS-TuP

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

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

The quest for suitable semiconductor photoelectrodes to build efficient and stable photoelectrochemical (PEC) cells for solar water splitting is continually growing in the material sciences and solar energy community. Along with good stability in aqueous media, such photoelectrodes should have suitable band-edges and band-gap energies properly matching both the water oxidation-reduction potential and the solar spectrum, respectively. Copper-based oxide semiconductors are promising candidates fulfilling these criteria, but little is known about the interfacial properties of these compounds with H_2O under operational conditions. Therefore, knowledge of their surface dynamics and interfacial reactions under realistic conditions is essential to improve our understanding of water-splitting mechanism, as well as to increase the stability and efficacy of PEC devices. Ambient pressure X-ray photoelectron spectroscopy was used to characterize the semiconductor surface and study the chemical reactions occurring at the interface under the reaction conditions. In this study, thin films of $CuFeO_2$ and $CuFe_{1-x}Ga_xO_2$ composites were exposed to various H_2O pressures and temperatures. Water interactions with the Cu-based oxide surface and the electronic structures of the surface atoms were evaluated from the Cu 2p, Fe 2p, C 1s and O 1s photoemission spectra to identify surface species newly formed.

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

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

We have recently performed near ambient pressure photoemission studies of Pt/Si micromotor surfaces activated by oxygen plasma in water atmosphere at the NAPP endstation of the CIRCE beamline at the ALBA synchrotron near Barcelona. We have used p-type silicon substrates with one half covered with a Pt film with a thickness of about 50 nm grown by both e-beam and sputtering deposition. The results reveal a chemical gradient at the Si/Pt edge with a reduction of the Pt species. The analysis has to carefully consider the photochemical reactions induced by the combined action of the impinging beam and the water condensed at the surfaces. The beam induced damage evolves in two regimes: an initial preferential reduction of Pt4+ species and then the reduction of Pt2+ species, which increases the metallic character of the surface.

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

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

In this project, we have used attenuated total reflection infrared absorption spectroscopy (ATR-IR) to investigate the details of the adsorption of such cinchona-alkaloid chiral modifiers on the Pt surfaces of supported catalysts in situ at the liquid-solid interface. It was determined that adsorption can be only observed after H_2 pretreatment of the catalyst. A comparison study in terms of adsorption strength was carried out using not only cinchona alkaloids such as cinchonidine and cinchonine but also simpler alternatives such as (R)- or (S)-(−)-1-(1-naphthyl) ethylamine (NEA), naphthylmethyl amine, and dimethyl naphthyl ethylamine.The adsorption strength of the different modifier molecules was found to be quite different among those compounds. This is illustrated by the fact that quinoline can displace s-NEA from Pt but not vice versa, for instance, and by the observation that when Pt is exposed to a solution containing both quinoline and s-NEA only the quinoline's signature peaks can be detected by ATR-IR spectroscopy. The ordering of the modifiers studied in terms of adsorption strength was found to correlate with their ability to chirally modify the Pt catalyst during the hydrogenation of unsaturated aldehydes.

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

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

Superhydrophobic and superhydrophilic surfaces have been widely investigated due to their diverse range of applications such as self-cleaning, microfluidic application in biotechnology, corrosion, Anti-reflecting coatings and microelectronic mechanical system etc. Here, a facile chemical vapour deposition method is reported for the synthesis of carbon nanospheres (CNSs). Henceforth, the morphology of as-synthesized sample is characterized using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). X-ray diffraction (XRD), Raman spectroscopy and FTIR spectroscopy are used to determine the phase purity, chemical composition and presence of chemical bonds on the surface of synthesized CNSs. TEM and SEM results reveal the presence of CNSs with a diameter ranging from 50 nm to 400 nm. Raman spectroscopy confirms the presence of disordered carbon and low graphitization, which are also confirmed by TEM and XRD results. Optical properties of as-synthesized CNSs is investigated by UV-Vis spectroscopy and photoluminescence. Wettability behaviour of as-synthesized carbon nanospheres is investigated by contact angle measurements. CNSs shows a water contact angle of 152^0, which confirms the fabrication of superhydrophobic carbon nanosphere surface. After the proper explanation of wettability behaviour, it also discusses the application of as-synthesized CNSs as a photocatalyst. As it is well known, catalyst enhances the chemical reaction rate without changing its properties. Therefore, various kind of catalysts has been developed for the purpose to enhance the catalysis for environmental applications. Among different materials, carbon-based materials are widely used as a catalyst support due to their excellent properties. Considering these facts, the degradation of an organic pollutant under UV light is discussed here using CNSs.

PC+AS+BI+EM+NS+PB+SS-TuP5 Thermally Driven Solid-solid Li^+ Transfer into Nanostructured TiO_2, ***Tiffany Kaspar,*** *T. Varga,* Pacific Northwest National Laboratory*; D.A. Shapiro,* Advanced Light Source, Lawrence Berkeley National Laboratory*; A. Martinez, Y. Shin, K.S. Han, M.-S. Lee, S. Thevuthasan, V. Murugesan,* Pacific Northwest National Laboratory

Due to their good chemical stability, strong oxidation capability, and desirable lithium electrochemical activity, nanostructured titanium dioxide (TiO_2) anode materials have received considerable attention recently. Decreasing the particle size to 10-20 nm can increase the electrochemical capacity to 200-300 $mAhg^{-1}$. Furthermore, nanostructured TiO_2 anodes are non-toxic and would be suitable for cost effective mass production. Among the rutile, anatase, and brookite polymorphs of TiO_2, anatase nanoparticles have shown the best Li ion insertion properties and maximum reduction, indicating increased Li ion intercalation into the material. Here, we have synthesized 10-20 nm anatase TiO_2 nanoparticles and contacted them with solid Li- bis(trifluoromethanesulfonyl)imide (LiTFSI) as a function of temperature to understand the chemical and structural effects associated with thermally driven solid-solid Li^+ transfer to, and intercalation in, TiO_2 nanoparticles. We have used a combination of x-ray photoelectron spectroscopy (XPS), Ti L-edge scanning transmission x-ray microscopy (STXM), Raman spectroscopy, and nuclear magnetic resonance (NMR) spectroscopy to gain a fundamental understanding of the structural evolution of TiO_2 nanoparticles during Li^+ intercalation. Our results indicate that thermally driven solid-solid Li^+ transfer to TiO_2 has occurred, and altered the TiO_2 structure at the edges of the agglomerated nanoparticles.

Industrial Physics Forum
Room 101B - Session IPF+AS+BI+NS-WeM

IoT Session: Bioanalytics, Biosensors and Diagnostics

Moderators: Anna Belu, Medtronic, Sally McArthur, Swinburne University of Technology and CSIRO

8:40am **IPF+AS+BI+NS-WeM3 Harnessing Bacteria for Fabrication of Photoelectrodes and Pressure Sensors**, *Y. Feng, K.E. Marusak, Y. Cao, E. Ngaboyamahina, J. Glass, L. You,* ***Stefan Zauscher,*** Duke University **INVITED**

Conventional methods for material fabrication often require harsh reaction conditions, have low energy efficiency, and can cause a negative impact on the environment and human health. In contrast, structured materials with well-defined physical and chemical properties emerge spontaneously in diverse biological systems. However, these natural processes are not readily programmable. By taking a synthetic-biology approach, we demonstrate a method for the fabrication of semiconducting, transition metal nanoparticles (NPs) with tunable bandgap and useful photoelectric properties, through bacterial precipitation. Surface analytic measurements revealed that our bacterially precipitated CdS NPs are agglomerates of quantum dots (QDs) 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. We determined the photoelectrochemical properties and energy band structure of thin films prepared from these NPs by electrochemical measurements. By taking advantage of the organic matrix, which is residual from the biosynthesis process, we fabricated a prototype photo-charged capacitor electrode by incorporating the bacterially precipitated CdS with a reduced graphene oxide sheet. Furthermore, we show the programmable, three-dimensional (3D) material fabrication using pattern-forming bacteria growing on top of permeable membranes as the structural scaffold. When the bacteria are equipped with an engineered protein that enables the assembly of gold (Au) nanoparticles into a hybrid organic-inorganic dome structure, the resulting hybrid structure functions as a pressure sensor that responds to touch. We furthermore show that the response dynamics are determined by the geometry of the structure, which is programmable by the membrane properties and the extent of circuit activation. By taking advantage of this property, we demonstrate signal sensing and processing using one or multiple bacterially assembled structures. Our work provides the first demonstration of using engineered cells to generate functional hybrid materials with programmable electronic properties and architectures for energy conversion, energy storage, and for signal sensing and transduction.

9:20am **IPF+AS+BI+NS-WeM5 Surface Chemistry and Surface Analysis: Their Importance and Application in Industrial Genomics**, ***Fiona Black,*** Illumina Inc. **INVITED**

Understanding the genome has the power to revolutionize health. However, building robust and scalable tools to interrogate single base variants with high robustness requires a system level approach to integrate surface patterning and activation, biosensing, and imaging. This talk will review how micro-patterning, bioanalytical controls, surface analytical techniques and measurement tools are applied in an industrial setting to develop and manufacture cutting edge systems for sequencing and genotyping applications

11:00am **IPF+AS+BI+NS-WeM10 Design and Evaluation of Organosilica Nanosensors for Continuous Molecular Monitoring in Complex Biological Environments**, ***Simon Corrie,*** Monash Univ., Melbourne AU **INVITED**

Continuous monitoring of biomarkers in biological environments is a key challenge for the development of biosensors capable of providing real-time feedback. Sensors capable of continuous pH monitoring have already found applications in detection of bacterial infections and have potential for aiding in treatment of dynamic diseases. Nanoparticle based “optodes” have emerged as sensitive and tuneable biosensors, using chromo/ionophores to generate analyte-specific changes in fluorescence spectra in a dynamic and reversible manner. Current key limitations of these materials include leaching of reagents from the nanoparticles over time, combined with poor colloidal stability in biological fluids.

Organosilica is a promising material for developing stable biosensors, allowing simple control over size, interfacial chemistry and porosity. This presentation will describe the development of a core-shell nanoparticle containing a mixture of covalently incorporated pH-sensitive (shell) and pH-insensitive (core) fluorescent dyes. Attachment of anti-fouling polymers is used reduce aggregation and biofouling in biological media. Fluorescence analysis of the nanoparticles reveals that the shell/core fluorescence ratio is highly sensitive to pH over a physiological range with the response time <1s. The sensitivity and dynamic range can be tuned by varying material properties of the shell (primarily thickness and porosity). We will present our latest results on the application of these nanosensors for continuous, real-time monitoring, including in bacterial cultures, subcutaneous mouse “tattoos," and in 3D hydrogel scaffolds.

11:40am **IPF+AS+BI+NS-WeM12 Optoregulated Biointerfaces**, ***Aránzazu del Campo,*** INM-Leibniz Institute for New Materials, Germany **INVITED**

Cells interact with their microenvironment by engaging membrane receptors with complementary partners at the surrounding matrix or at other neighbouring cells. These receptor complexes, often associated to cytoskeletal structures, allow exchange of biochemical and mechanical information. The ability to quantify this exchange is crucial for our understanding of cellular behavioru and responses to external factors. Using model bionterfaces with optoregulated interaction possibilities, selective membrane receptors in living cells can be addressed in situ, i.e. on a sensor surface, while quantifying specific cellular responses. Light-regulated tools to apply and sense cell biochemical and mechanical interactions will be presented.

Processing and Characterization of Air-Liquid, Solid-Liquid and Air-Solid Interfaces Focus Topic
Room 202A - Session PC+AS+BI+EM+PB+SS-WeM

Novel Approaches and Challenges of Interfaces

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

8:00am **PC+AS+BI+EM+PB+SS-WeM1 Probing Chemical Species and Potential Profiles of Electrified Interfaces**, ***Ethan J. Crumlin,*** Advanced Light Source, Lawrence Berkeley National Laboratory **INVITED**

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

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

Riboflavin is of vital significance in living processes as a precursor of the two important coenzymes flavin mononucleotide (FMN) and flavin adenine dinucleotide (FAD).[1] The isoalloxazine ring in riboflavin plays an important role in energy supplementation and cellular respiration, since it has the capability to accept electrons in some redox reactions.[2] Understanding riboflavin reduction could potentially bring insight into the electron transfer process between cell surfaces and conductive materials. Thus, the electrochemical reduction process of riboflavin has drawn increasing attention. In this study, the riboflavin reduction mechanism in an aqueous solution has been investigated using time-of-flight secondary ion mass spectrometry (ToF-SIMS) with the electrochemical cell.[3, 4] Positive and negative ion mode mass spectra were used to depict the molecular information of species dissolved in the electrolyte. The distribution of key reduction intermediates were mapped at the electrode-electrolyte interface using dynamic depth profiling. To examine product formation as a function of applied potentials, measurements were made by holding the potential at 0, -0.3, 0.3, and 0.6 V respectively, once interesting electrochemistry was determined using the cyclic voltammogram.

Furthermore, gold and graphite electrodes were both used in our experiment to investigate if the electrode surface plays a role in in the electrochemical reaction mechanism. Preliminary spectral principal component analysis (PCA) results have shown key chemical distinctions in the electrolyte at 0, -0.3, 0.3, and 0.6 V. Selected peak spectral PCA is required to gain a better understanding of this observation, which will allow for a more comprehensive chemical profile of the electron transfer process in riboflavin redox reactions.

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

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

Electrowetting behavior of liquid drops has been followed in-situ and in-vacuum using XPS in a chemically resolved fashion, under both dc and ac excitations. Various Liquid drops, compatible with the UHV conditions, consisted of an Ionic Liquid (DEME-TFSI), Poly-ethylene-glycol (M.W. ~600 amu) and their mixtures. For the dielectric substrate, a ~300 nm thick silicon oxide (SiO_2/Si) without and with a thin hydrophobic coating (CYTOP) has been employed. XPS data have been recorded both in the conventional scan- and also in the fast (<1s) snap-shot modes. Intensity and position of the peaks, representing the liquid drops (F1s in the case of the IL, or C1s/O1s of the PEG) as well as those of the substrates (Si2p for the oxide only and F1s for the hydrophobic coated one) have been recorded under various electrical excitations. Under ac excitation at a fixed frequency, intensity modulations in the XPS peaks reveal geometrical changes of the drops, while the peak position modulations reveal electrical potentials developed. Monitoring position modulations as a function of the changes in the ac frequency (10^{-2} – 10^{5} Hz) allows us to tap into ionic, dipolar and electrical contributions of the dielectric susceptibility of both the liquid drops and the substrates. Experimental details and various application will be presented and discussed.

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

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

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

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

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

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

Biomaterial Interfaces Division
Room 104B - Session BI+AC+AS+HC+NS+SS+TF-WeA

Current and Future Stars of the AVS Symposium II

Moderator: David Boris, U.S. Naval Research Laboratory

2:20pm **BI+AC+AS+HC+NS+SS+TF-WeA1 Medard W. Welch Award Lecture: A Surface Scientist's Journey from Small Molecules to Biomolecules and Biomaterials*, David G. Castner*[1],** University of Washington **INVITED**

Surface science plays an important role in a wide range of research and development areas such catalysis, biomaterials, microelectronics, clean energy and corrosion. The toolbox of surface scientist allows us to easily move across research topics and make significant impacts in both industrial and academic settings. The typical surface scientist is an expert in multiple techniques, surface modification, sample preparation/handling and instrumentation. We have all benefited from the significant and numerous advances that have occurred in the past 40 years in terms of improved instrumentation, introduction of new techniques and development of sophisticated data analysis methods, which has allowed us to perform detailed analysis of increasing complex samples. For example, comprehensive analysis of surfaces and surface immobilized molecules with modern surface science instrumentation provides an unprecedented level of detail about the immobilization process and the structure of the immobilized molecules. Results from x-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS), near edge x-ray absorption fine structure (NEXAFS), surface plasmon resonance (SPR) and quartz-crystal microbalance with dissipation (QCM-D) biosensing, atomic force microscopy, and sum frequency generation (SFG) vibrational spectroscopy combined with computation methods such as molecular dynamic (MD) and Monte Carlo (MC) simulations provide important information about surface chemistry and structure. However, even with the advances that have been achieved with these powerful surface science techniques, there still remain many significant challenges for surface scientist. These include characterizing the surface chemistry and structure of nanoparticles, determining the atomic level structure of complex molecules bound to surfaces, 3D imaging of samples, and improved sample preparation methods that maintain materials in a relevant state when using ultra-high vacuum based analysis techniques.

This talk will discuss my adventures as a surface scientist starting from chemisorption and reactivity studies of small molecules on single crystal surfaces followed by industrial catalysis research and eventually moving to biomedical surface analysis with side ventures into areas such as clean energy. It has been an exciting journey and I will use it to provide some examples of the multidisciplinary nature of surface science as well as discuss opportunities for addressing future challenges.

3:00pm **BI+AC+AS+HC+NS+SS+TF-WeA3 Invited Talk-Future Stars of AVS Session: Making, Studying, and Designing Hierarchically Structured Soft Materials*, Keith A. Brown*[2],** Boston University

Nature realizes extraordinary materials by structuring them precisely from the molecular scale to the macroscopic scale. While nature may have perfected this process over evolutionary time scales, synthetically recapitulating this level of control is tremendously difficult due to the large number of length scales involved and our limited knowledge of interactions between these scales. Faced with the daunting challenge of synthetically realizing soft hierarchical materials, we have adopted a three pronged strategy to: (1) make structures with control from the molecular scale to the macroscopic scale by directing bottom-up growth processes with top-down control, (2) learn how the properties of such materials emerge from their hierarchical structure, and (3) design the best performing structures using novel approaches borrowed from machine learning and autonomous research. In this talk, we will on report recent progress in this complementary areas of making, studying, and designing hierarchical materials. In particular, we will focus on two major classes of materials, nanoparticle-based structures where the assembly and organization of particles leads to emergent mechanical properties at the bulk scale and polymer-based materials where we are connecting the synthesis, patterning, and properties of polymer structures across scales. In addition to lessons about the fundamental properties of hierarchically organized soft matter, we will highlight the synergies possible when combining, synthesis, detailed characterization, and advances in materials design.

3:20pm **BI+AC+AS+HC+NS+SS+TF-WeA4 Invited Talk-Future Stars of AVS Session: Vapor Phase Infiltration for Transforming Polymers into Hybrid Materials: Processing Kinetics and Applications*, Mark Losego*[3],** Georgia Institute of Technology

Vapor phase infiltration (VPI) is an emerging processing technology for infusing polymers with inorganic constituents to create new organic-inorganic hybrid materials with novel chemical, electrical, optical, and/or physical properties. These new hybrid materials have demonstrated applications including chemical separations, photovoltaics, and microelectronics patterning. This talk will focus on our development of a fundamental VPI processing kinetics phenomenology to create a pathway for rational design of material composition and structure. By measuring VPI compositional profiles as a function of space or time and temperature, we can extract fundamental energy barriers for the sorption, diffusion, and reaction processes and delineate amongst different rate limiting steps. In our materials development, we often find that partial infiltration of a polymer film, fiber, or foam is sufficient to impart desired properties; so rational design of the infiltration kinetics can enable desired performance without waste in processing time or materials. Here, we will demonstrate several examples including our work to create chemically insoluble polymers and membranes. We find, for example, that infiltration depths of about 0.75 microns are sufficient to yield PMMA chemically insoluble in organic solvents regardless of whether it is in a thin film geometry or a macroscopic plexiglass object of centimeters in dimension. In PIM-1 membranes used for chemical separations, we find that we can achieve > 30 wt% inorganic loading with a single infiltration exposure. After infiltration, these membranes become stable in new separations solvents that previously swelled and/or dissolved the polymer.

(Submitted for the Future Stars of the AVS Symposium.)

4:20pm **BI+AC+AS+HC+NS+SS+TF-WeA7 Invited Talk-Future Stars of AVS Session: Surface Preparation Methods for the Selective Oxidation of Ethanol to Acetaldehyde over TiO_2/Au(111)*, Ashleigh Baber*[4]*, D.T. Boyle, J. Wilke, V. Lam, D. Schlosser,*** James Madison University

Obtaining a molecular-level understanding of the reaction of alcohols with heterogeneous model catalysts is critical for improving industrial catalytic processes, such as the production of hydrogen from alcohols. The use of reducible oxides provides a source of oxygen on Au(111) for the reaction of ethanol, which is easily regenerated in the presence of an oxygen background. The redox chemistry of small alcohols, including methanol and propanol, has been studied on Au(111) supported TiO_2 nanoparticles, yet the active site for the chemistry has not yet been elucidated. Depending on the surface preparation conditions, Au(111) supported TiO_2 nanoparticles react with small alcohols to form either reduced and oxidized products. The desire to selectivity form oxidized or reduced products merits an investigation of alcohol reactivity over differently prepared TiO_2/Au(111) surfaces. In this work, a systematic study of ethanol reactivity over several TiO_2/Au(111) surfaces elucidates the effect of surface conditions on the selectivity of the reaction between ethanol and TiO_2/Au(111). The reactivity of the surface for ethanol oxidation was altered by controlling the oxidation state of TiO_x (x<2). Atomic force microscopy (AFM) provides information regarding the structure of the Au(111) supported TiO_2 nanoparticles and ultrahigh vacuum temperature programmed desorption (TPD) monitors the selectivity of the reaction between ethanol and TiO_2/Au(111). The presence of TiO_2 nanoparticles on Au(111), ~25 nm in diameter, led to the catalytic conversion of ethanol to acetaldehyde at temperatures greater than 400 K. Low coverages of fully oxidized TiO_2 nanoparticles on Au(111) are active for the selective oxidation of ethanol to form acetaldehyde.

4:40pm **BI+AC+AS+HC+NS+SS+TF-WeA8 Invited Talk-Future Stars of AVS Session: Single Atom Catalysis: An Atomic-Scale View*, Gareth Parkinson*[5],** TU Wien, Austria

Single-atom catalysis is a rapidly emerging area of research that aims to maximize the efficient usage of precious metals through "single atom" active sites. Although catalytic activity has been demonstrated for several single-atom catalyst systems, an inability to accurately characterize the catalyst based on single atom active sites ensures that that the field remains controversial, and little is really known about how a single atom

[1] **Medard W. Welch Award Winner**
[2] **Future Stars of the AVS**
[3] **Future Stars of the AVS**
[4] **Future Stars of the AVS**
[5] **Future Stars of the AVS**

adsorbed on a metal oxide support catalyzes a chemical reaction. In this lecture, I will describe how we are addressing the crucial issues of stability and reaction mechanism using a surface science approach. The work is based on the magnetite (001) surface, which exhibits an unusual reconstruction based on subsurface cation vacancies.

The surface stabilizes ordered arrays of metal adatoms (of almost any variety) with a nearest neighbor distance of 0.84 nm to unprecedented temperatures as high as 700 K. Crucially, because the geometry of the adatoms is uniform and precisely known, reactivity experiments are performed on a well-defined model system, and theoretical calculations can be performed to shed light on the mechanisms at work. Several examples of our recent work will be used to illustrate the trends discovered to date, including how strong CO adsorption destabilizes Pd and Pt adatoms leading to rapid sintering, and how extraction of lattice oxygen from the metal-oxide is central to catalytic activity in the CO oxidation reaction.

5:00pm **BI+AC+AS+HC+NS+SS+TF-WeA9 Invited Talk-Future Stars of AVS Session: Multimodal Chemical and Functional Imaging of Nanoscale Transformations Away from Equilibrium**, ***Olga Ovchinnikova***[1], Oak Ridge National Laboratory

The key to advancing energy materials is to understand and control the structure and chemistry at interfaces. While much of the dynamic chemistry can be studied on macro-scale systems, there is a lack of means to localize chemical measurements and correlate them to nanoscale structure of the material. Through a unique merger of advanced scanning probe microscopy and mass spectrometry techniques rooted in innovative data processing and control algorithms, we are now able to understand the interplay between chemical and physical functionality at the fundamental length using multimodal chemical imaging. This multimodal imaging transcends existing techniques by providing nanoscale structural imaging with simultaneous quantitative nanomechanical properties and quantitative chemical analysis. In this talk I will discuss how we have developed and used this capability to visualize dynamic material transformations at interfaces, to correlate these changes with chemical composition, and to distil key performance-centric material parameters. One exciting capability is that the AFM can be used to drive materials away from equilibrium at the nanoscale with highly localized electric fields. This allows field confinement effects on localized chemistry in materials to be locally probed, especially at interfaces. This in turn yields direct information on key energy related questions such as electron and ion motion distribution and transport at and between interfaces. We have applied this approach to the study of systems and processes that underlie energy capture, conversion and storage, including photovoltaics and oxide ferroelectrics, which have historically eluded comprehensive understanding of the mechanisms behind the spatially heterogeneous interfacial chemistry and its link to material performance. Overall, I will focus on ways to unlock the mystery of active interface formation through intertwining data analytics, nanoscale elemental and molecular characterization, with imaging; to better grasp the physical properties of materials and the mechanistic physics-chemistry interplay behind their properties.

5:20pm **BI+AC+AS+HC+NS+SS+TF-WeA10 Invited Talk-Future Stars of AVS Session: Expanding the Structural Toolkit to Characterize Heavy Actinide Complexes**, ***Rebecca Abergel***[2], Lawrence Berkeley Lab, University of California, Berkeley; *G. Deblonde, A. Mueller, P. Ercius,* Lawrence Berkeley National Laboratory; *A.M. Minor,* Lawrence Berkeley Lab, University of California, Berkeley; *C.H. Booth, W.A. de Jong,* Lawrence Berkeley National Laboratory; *R. Strong,* Fred Hutchinson Cancer Research Center

Structural characterization of actinide elements from actinium to einsteinium can be a challenging task due to the high radioactivity and limited availability of some of the isotopes of interest. However, significant work is needed to address a certain lack of understanding of the fundamental bonding interactions between those metal centers and selective ligands. Such understanding presents a rich set of scientific challenges and is critical to a number of applied problems including the development of new separation strategies for the nuclear fuel cycle, the need for decontamination after a nuclear accident or the use of radio-isotopes for new cancer treatments. Our studies utilize luminescence sensitization, UV-Visible, X-ray absorption, and X-ray diffraction spectroscopic techniques as well as transmission electron microscopy and electron energy loss spectroscopy to investigate specific heavy actinide coordination features. Using simple inorganic complexes but also strong hard oxygen-donor ligands as well as more elaborate higher molecular weight protein assemblies allows the differentiation of heavy actinide species even when limited to minute amounts of materials. Innovative structural characterization approaches based on X-ray absorption, X-ray diffraction and electron microscopy that were applied to series of isostructural systems and used to derive coordination trends in the later 5*f*-element sequence will be discussed.

5:40pm **BI+AC+AS+HC+NS+SS+TF-WeA11 Invited Talk-Future Stars of AVS Session: Trends in Adsorbate Interactions with Bimetal Surfaces**, ***Liney Arnadottir***[3], *L.H. Sprowl,* Oregon State University

Surface chemistry plays an important role in a large range of applications and technologies, such as catalysis and electrocatalysis, device fabrication through film growth, and degradations through oxide formation, carbonization, and corrosion. Bimetal surfaces are of increasing interest for single atom catalysis and corrosion resistance of alloys. Previous studies have shown correlations between adsorbate interactions and d-band shifts for different metals as well as for alloying effects of metal sandwich structures, but for mixed metal surfaces the nature of the adsorption site can change (ensemble effect) as well as the number of electrons in the surface layer which effects the d-band center. Here we explore correlations of adsorbate interactions with mixed metal surfaces through density functional theory calculations of adsorbate interactions with different facets, (100) and (111), of pure Ni and eleven Ni-based surface alloys as well as Ni in different host metal. We find that the addition of surface alloying atom has little effect on the binding of CO and C but C binding varies for different facets. On the other hand, O binding is highly dependent on the alloying element due to ensemble effect. This has an interesting effect on the predicted reaction energies of CO dissociation which is endothermic on the (111) facet and exothermic on the (100) facet governed by C interactions but the changes in the reaction energy within each facet are mostly governed by the ensemble effect on O adsorption. The relationship between the formation energy of the mixed metal surface and adsorbate interactions will also be discussed.

Biomaterial Interfaces Division
Room 101B - Session BI-WeA

Microbes and Fouling at Surfaces

Moderator: Caitlin Howell, University of Maine

3:00pm **BI-WeA3 Gaede-Langmuir Award Lecture: From Description to Prediction of Biointerphase Reactions**, ***Michael Grunze***[4], Max Planck Institute for Medical Research, Germany; *H.J. Kreuzer,* Dalhousie University, Canada **INVITED**

Many experiments in Biointerphase Research aim to determine the number of cells or organisms adsorbing on a surface. In order to discriminate between physisorbed and settled cells, a rinsing step is applied when the sample is removed from solution. However, no information is obtained which shear flow is required to overcome the activation barrier of detachment to remove the cell. In this lecture I want to address the question to what extend we can use the formalism derived in gas phase adsorption and desorption experiments to describe the analog reactions in solution quantitatively and predictably? Predictive models would help to advance microfluidic based diagnostics and contribute to the design of environmental benign anti-fouling surfaces.

Recent experiments and theoretical work to understand adsorption and detachment of small (cell size) objects from a surface under shear flow will be discussed with reference to the formalism used in basic gas phase adsorption/desorption experiments. In the most basic experiments, the probability that a molecule will adsorb or desorb is measured as a function of pressure, temperature, and coverage. Monolayer adsorption of a gas is described by the Langmuir isotherm (or its derivatives if interactions between the molecules need to be considered) and desorption by an Arrhenius type equation to determine the activation energies.

The kinetic equation used in gas phase experiments can be modified to describe adsorption and detachment of particles from a surface under shear flow, where temperature is replaced by shear force to determine activation energies. The shear force is ramped up in a programmable way, and by fitting the experimental data with a rate equation gives highly

[1] **Future Stars of the AVS**
[2] **Future Stars of the AVS**
[3] **Future Stars of the AVS**
[4] **Gaede Langmuir Award Winner**

reproduceable results from which the activation energy of detachment of these particles can be derived. The activation energy values determined from these experiments will be discussed in the context of separately measured adhesion energies of these particles in an aqueous environment to derive a mechanistic understanding for attachment and detachment of small objects in laminar shear flow.

4:20pm **BI-WeA7 Unraveling Complexities at the Adhesive Interface of Acorn Barnacles**, ***Kenan Fears,*** *C.R. So, D.H. Leary, H. Ryou, J. Schultzhaus, C. Wang,* US Naval Research Laboratory*; B. Orihuela, D. Rittschof,* Duke University Marine Laboratory*; C.M. Spillmann, K.J. Wahl,* US Naval Research Laboratory **INVITED**

Marine macro-foulers (e.g, barnacles, tubeworms, mussels) create robust underwater adhesives capable of attaching themselves to almost any material. While proteomic analysis has provided insight into the chemical composition of these natural adhesives, developing synthetic analogs that mimic their performance remains a challenge due to an incomplete understanding of adhesion processes. Through the use of in vivo confocal microscopy with multiple fluorescent probes, we have identified that acorn barnacles (*Amphibalanus (= Balanus) amphitrite*) secrete a phase-separating surfactant mixture to clean and protect the surface ahead of growth and cement deposition. This mixture consists of a phenolic laden gelatinous phase that holds a phase rich in lipids and reactive oxygen species at the seawater interface. This secretion oxidizes and lifts off adhered biofilms surrounding the barnacle base as it expands. These findings show barnacles repurpose phenolic chemistries ubiquitious to adhesives and cuticles as part of their own antifouling strategy. The discovery of this critical step in underwater adhesion represents a missing link between natural and synthetic adhesives, and provides new directions for the development of environmentally-friendly biofouling solutions.

5:00pm **BI-WeA9 Ultra Low Fouling Zwitterionic Coatings – Influence of Molecular Architecture on Fouling Inhibition**, ***Axel Rosenhahn,*** *J. Koc,* Ruhr-University Bochum, Germany*; S. Bauer,* Ruhr-Universität Bochum, Germany*; J. Finlay, A.S. Clare,* Newcastle University*; E. Schoenemann,* University of Potsdam*; A. Laschewsky,* Unversity of Potsdam

Zwitterionic polymers are promising ultra-low fouling coating materials. While their outstanding properties are undisputed, a precise understanding of how the molecular architecture leads to optimized polymer function is still missing. Here we compare the influence of different anionic groups using a range of self-assembled monolayers and compare it against a series of photocrosslinkeable zwitterionic polymers. In all cases, the intramolecular arrangement was varied in order to determine if the spacing between the oppositely charged moieties, the nature of the charged group, and the backbone affect their non-fouling properties. A comparison of self-assembled monolayers consisting of mixed, oppositely charged thiols and custom designed zwitterioinic thiol compounds showed that in particular sulfate groups showed promising properties and an horizontally adjacent arrangement was preferred. As approach towards polymeric coatings, zwitterionic methacrylates were co-polymerized with benzophenonemethacrylates to obtain a photocrosslinkable polymer. We applied the polymers by spin-coating and subsequent photocrosslinking. All coatings were characterized by AFM, IR, and XPS prior to biological testing and protein resistance was characterized by SPR. The antifouling activity against marine biofilm formers, algae, and invertebrate larvae was determined in laboratory assays. On the basis of the obtained data, design criteria for optimized zwitterionic components for fouling-release technologies will be discussed.

5:20pm **BI-WeA10 Biomimetic Surfaces on Chitosan Membranes with Enhanced Antibacterial Properties Produced by Directed Plasma Nanosynthesis**, ***Camilo Jaramillo,*** *A.F. Civantos, J.P. Allain,* University of Illinois at Urbana-Champaign

First reported in the late 1950s, antibiotic-resistant bacteria have become an issue of major concern [1]. This has motivated the study of other mechanisms to provide interfaces with antibacterial activity, including surface chemistry, surface topography and other physicochemical properties [2]. Among these mechanisms, the physico-mechanical effects have also attracted attention. An example of this concept can be found in natural nanostructured surfaces. The nanopatterned surface of the cicada wings has been observed to possess very effective bactericidal activity, via a chemistry-independent mechanism [3]. Chitosan, a biodegradable and non-toxic biopolymer with antibacterial properties, has been used for wound treatment, drug delivery and biosensing applications [4]. These properties make it an attractive material to be used in biointerfaces. Following the same concept of the cicada wings, nanopatterned silicon surfaces coated with CS showed enhanced antibacterial activity, when compared to un-coated Si surfaces [5].

In previous works from our group, we had shown that Directed Plasma Nanosynthesis (DPNS) can induce the formation of nanofeatures on the surface of chitosan. In this work, we further study the effects of DPNS on the formation of nanopatterns on the surface of different chitosan membranes are further studied, using angle of irradiation as a control parameter. Additionally, the biocidal action of the modified surfaces is studied by running in vitro tests with *E. coli*. SEM images were used to evaluate the nanofeatures induced on the surfaces, as well as their effects on the incubated bacteria. Studying the antibacterial activity of these nanopatterned surfaces constitutes a step towards elucidating the mechanisms of antibacterial activity based on physico-mechanical effects.

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5:40pm **BI-WeA11 How Do Geobacter Aggregates Communicate: New Understanding from In Situ Liquid SIMS**, ***Wenchao Wei,*** *R. Komorek,* Pacific Northwest National Laboratory*; C. Yang, F. Liu,* Yantai Institute of Coastal Zone Research*; Z.H. Zhu, X-Y. 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 [1, 2]. In this talk, a more complex microbial communities consisting of syntrophic *Geobacter metallireducens* and *Geobacter sulfurreducens* was investigated using ToF-SIMS [3]. As a surface technique, in situ liquid SIMS provides direct measurement of initial attachment of the co-cultured aggregates. Our 3D imaging results give spatial distribution of amino acid fragments and lipids, indicative of the role of proteins and lipids played in the co-cultured aggregate formation. The planktonic cells seem to show strong evidence of hydrogen transfer in liquid by the direct observations of lipid fragments with the addition of water and hydrogen. This pheromone indicates that higher direct electron interspecies transfer may exist in co-culture aggregates whereas hydrogen transfer is dominant in planktonic cells. More interestingly, distinct water distribution is observed between co-cultured aggregates and planktonic cells, indicating the change of hydrogen bonding as a result of the complex microbial syntrophic community communication. 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.

Key words: microfluidics, biofilm, co-cultured aggregate, electron transfer, EPS, ToF-SIMS

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

Plasma Agriculture & Environmental Applications

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

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

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

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

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

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

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

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

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

For many years, cold atmospheric plasma techniques have been used for a large variety of applications such as surface modification, film deposition, nanoparticles synthesis or pollutants degradation. One of their main advantage is the possibility to work with a gaseous, liquid or solid phase. In this study, the plasma water treatment is investigated for a potential application in agriculture. When water solutions are treated by plasma, in air environment, several reactive oxygen and nitrogen species (RONS) are generated [1,2]. The main RONS are hydrogen peroxide (H_2O_2), nitrites (NO_2^-) and nitrates (NO_3^-). Nitrates are one of the most essential molecules for plants because, together with ammonium, they represent an important source of nitrogen which is mandatory for DNA, RNA, enzymes, chlorophyll, ATP and many other molecules. For some applications such as hydroponics or urban agriculture, the local production of pure nitrates fertilizers directly available in the flowing water feeding system would be of great interest.

In this study, a DC atmospheric microplasma system is used for the investigation of the formation mechanism of NO_3^- in water. The liquid phase is analyzed by Ionic Chromatography (IC), UV-visible spectrometry (UV-vis) and pH-metry, whereas the gas phase is probed by Optical Emission Spectroscopy (OES) and atmospheric Mass Spectrometry (MS).

Firstly, the influence of the inner diameter of the microplasma stainless steel needle is investigated (internal diameter of 0,76 mm, 0,50 mm and 0,20 mm). The amount of NO_x^- (NO_2^- and NO_3^-) synthesized varies with the diameter and the shape of the plasma is different for a larger internal diameter. Furthermore, the total amount of NO_x^- formed in a solution shows a linear trend with the total charge injected into the plasma with, however different slopes for nitrites and nitrates.

The oxidation mechanism of NO_2^- to NO_3^- is then explored and the influence of other reactive species on this mechanism is then studied. Indeed, it is known from the literature that H_2O_2 may play a role in the process for different atmospheric plasma systems [2]. The formation of oxygenated water and its role as an oxidant is highlighted in the microplasma system. Therefore, the amount of H_2O_2 synthesized by microplasma is compared to other plasma systems. The nature of the atmosphere above the solution is modified in order to determine the species formed in the gaseous phase and their respective influence.

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

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

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

5:40pm **PB+BI+PC+PS-WeA11 Radicals and Ozone Generated in Ar/He and Ar/He/H_2O Plasma by using Atmospheric Pressure Plasma Jet Systems and their use in Methylene Blue Degradation**, *J.H. Hsieh,* ***YiJinWei Wei,*** Ming Chi University of Technology, Taiwan, Republic of China*; C. Li,* National Yang Ming University, Taiwan, Republic of China

Optical emission spectroscopy (OES) and UV absorption spectrometry were first used to gather information about the excited species present near/in the plasma plume generated using Ar/He and Ar/He/H_2O gases with an atmospheric pressure plasma jet (APPJ). Afterward, the APPJ system was used to study its efficiency in degrading methylene blue as a function of radical and ozone density. According to the results, it was found that the degradation of methylene blue was directly related to the ozone concentration and, perhaps, OH radical density. Additional moisture may be used to control the ratio of ozone and OH radical density, resulting in the variation of degradation rate. Complete degradation of MB can be achieved in 80 seconds.

Biomaterial Interfaces Division
Room 101B - Session BI-ThM

Biomolecules and Biophysics at Interfaces

Moderator: Joe Baio, Oregon State University

8:00am **BI-ThM1 Bioinspired Adaptive Reconfigurable Material Systems based on Smart Hydrogels**, ***Ximin He***, University of California, Los Angeles **INVITED**

From the cellular level up to the body system level, living organisms cooperatively sense to adapt to or self-regulate the local environment, and can also harvest energy from the environment to keep alive and perform various functionalities. These graceful capabilities arise from the chemo-mechanical actions that transform the molecular configuration changes to micro/macroscopic mechanical motions, in response to environmental cues. Inspired by these unique adaptive abilities, we have developed a series of adaptive material systems, which are based on stimuli-responsive hydrogels capable of adaptively reconfiguration. This presentation will introduce three novel functionalities that this broad-based platform has demonstrated, including ultrafast optical sensing of chemical and biological species and autonomous regulating of local conditions. Living organisms ubiquitously display colors that adapt to environmental changes, relying on the soft layer of cells or proteins. Inspired by this strategy, we created a simple and universal adaptive color platform based on a hydrogel interferometer (*Adv. Mater.* 2018). Such interference colors provide a visual and quantifiable means of revealing rich environmental metrics. The single material-based platform has advantages of remarkable color uniformity, fast response, high robustness, and facile fabrication. Its versatility has been demonstrated by diverse applications: a volatile-vapor sensor with highly accurate quantitative detection, a colorimetric sensor array for multi-analyte recognition, breath-controlled information encryption, and a colorimetric humidity indicator. Portable and easy-to-use sensing systems are demonstrated with smartphone-based colorimetric analysis. Second, based on this platform, we further realized a novel function - fully autonomous separation of target molecules from a mixture fluid such as wastewater or biofluid.

8:40am **BI-ThM3 Importance of a In Depth Characterisation for the Design of Functional Gold Nanoparticles for Bioapplications**, *R. Capomaccio, I. Ojea-Jimenez, D. Mehn, P. Colpo, D. Gilliland,* European Commission - Joint Research Centre, Italy*; R. Hussain, G. Siligardi,* Diamond Light Source Diamond House, Harwell Science and Innovation Campus, UK*; L. Calzolai,* ***Giacomo Ceccone***, European Commission - Joint Research Centre, Italy

The design and fabrication of functionalized nanoparticles (NPs) are of great interest in biotechnology and biomedicine, especially for diagnostic and therapeutic applications.[1] However, at the moment the challenges related to the characterization of complex, multi-functional nanoparticles are still hampering the development of advanced bio-nano-materials.[2,3] In particular the interaction of NPs with protein has been the subject of many investigations in the last years and although important advances were made, several important issues (e.g. thermodynamic constants, protein structure changes) are still not completely understood.[4-6]

In this work, the interaction of gold nanoparticles (AuNPs) with human serum albumin (HSA) has been investigated as model system. First a simple method to determine the structure and morphology of the AuNPs-HSA complexes will be described.[7] Then the interaction of HSA with a model system consisting of AuNPs functionalized with two differentially-terminated poly(ethylene oxide) ligands, providing both "stealth" properties and protein-binding capabilities to the nanoparticles have been investigated. In particular, the purpose of this study was to: i) monitor and quantify the ratios of ligand molecules per nanoparticle; ii) determine the effect of coating density on non-specific protein adsorption; iii) to assess the number and structure of the covalently-bound proteins. For this a combination of techniques, including Centrifugal Liquid Sedimentation, Dynamic Light Scattering, Flow Field Flow Fractionation, Transmission Electron Microscopy, Circular Dichroism, XPS and ToF-SIMS have been employed to compare complementary outcomes from typical and orthogonal techniques used on nanoparticle characterisation.[8]

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[8] I. Ojea-Jimenez, et a., Nanoscale 2018 (in print)

9:00am **BI-ThM4 A Model Membrane Microsystem for Measurement of the Kinetics of Transmembrane Proton Transport**, *J.P. Madsen, A. Johnson, M.L. Cartron, N.C. Hunter, S.P. Armes,* ***Graham Leggett***, University of Sheffield, UK

Binary brush structures consisting of poly(cysteine methacrylate) (PCysMA) "corrals" enclosed within poly(oligoethylene glycol methyl ether methacrylate) (POEGMA) "walls" are fabricated simply and efficiently using a two-step photochemical process. First, the C-Cl bonds of 4-(chloromethyl)phenylsilane monolayers are selectively converted into carboxylic acid groups by patterned exposure to UV light through a mask and POEGMA is grown from unmodified chlorinated regions by surface-initiated atom-transfer radical polymerization (ATRP). Incorporation of a ratiometric fluorescent pH indicator, Nile Blue 2-(methacryloyloxy)ethyl carbamate (NBC), into the polymer brushes facilitates assessment of local changes in pH using a confocal laser scanning microscope with spectral resolution capability. Moreover, the dye label acts as a radical spin trap, enabling removal of halogen end-groups from the brushes via *in situ* dye addition during the polymerisation process. Second, an initiator is attached to the carboxylic acid-functionalised regions formed by UV photolysis in the patterning step, enabling growth of PCysMA brushes by ATRP. Transfer of the system to THF, a poor solvent for PCysMA, causes collapse of the PCysMA brushes. At the interface between the collapsed brush and solvent, selective derivatisation of amine groups is achieved by reaction with excess glutaraldehyde, facilitating attachment of aminobutyl(nitrile triacetic acid) (NTA). The PCysMA brush collapse is reversed on transfer to water, leaving it fully expanded but only functionalized at the brush-water interface. Following complexation of NTA with Ni^{2+}, attachment of histidine-tagged proteorhodopsin and lipid deposition, light-activated transport of protons into the brush structure is demonstrated by measuring the ratiometric response of NBC in the POEGMA walls.

9:20am **BI-ThM5 Theranostics Gold Nanoparticles for Brain Cancer Applications**, *I. Naletova, L.M. Cucci, F. D'Angeli, C.D. Anfuso, G. Lupo,* University of Catania, Italy*; A. Magrì,* National Council of Research (CNR), Italy*; C. Satriano,* University of Catania, Italy*;* ***Diego La Mendola***, University of Pisa, Italy

In this work, hybrid assemblies of plasmonic gold nanoparticles (AuNPs) and peptides mimicking the putative cell binding domain of angiogenin protein (60-68 sequence)[1] were investigated in their interaction with artificial membranes of supported lipid bilayers (SLBs) and cellular membranes of cancer cell lines. In particular, the response of glioblastoma cell line (A172), as model of the most aggressive cancer that begins within the brain[2], and neurons obtained by differentiated neuroblastoma cell line

(SHSY5Y), as 'normal cells', was scrutinized. The influence of copper, which is a pivotal co-player of cellular homeostasis in both physiological and pathological angiogenesis, was investigated in parallel with the gold nanoparticles functionalized with a fluorescent derivative of Ang(60-68) peptide. Control experiments using the non-fluorescent peptide analogous immobilized onto the AuNPs either by physisorption (Ang(60-68)) or chemisorption (Ang(60-68)Cys) were also included. The hybrid peptide/AuNP/copper systems were characterized by means of UV-visible, AFM and CD, to address the plasmonic changes, the nanoparticle coverage and conformational features at the hybrid biointerface. Lateral diffusion measurements on SLBs after their interaction with the peptide-functionalised AuNPs pointed to a stronger membrane interaction in comparison with the uncoated nanoparticles. Cell viability and proliferation assays indicated significant differences, in the presence or absence of copper, for the two cell lines. Cell imaging by confocal microscopy evidenced dynamic processes modulated in a synergic way by the different components (peptide, gold nanoparticle, copper) of the hybrid nanoplatforms at the level of the cell membrane (cytoskeleton features observed by actin staining) as well as at the sub-cellular compartments (copper-binding proteins).

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11:00am **BI-ThM10 Non-equilibrium Thermodynamic Model for DNA at Nanochannel Junctions***, **Saroj Dangi,*** North Carolina State University

DNA, often studied as a polymer molecule, extends along the axis of confining channel if the size of channel is less than the radius of gyration of the molecule. Extended molecule can be manipulated for wide range of applications such as DNA sorting, gene mapping, single molecule experiment, and fundamental polymer physics experiment. The optimization and advancement of these nanofluidic applications necessitates the understanding of physics behind the confinement of DNA in nanochannel. So far, most of the studies have considered linear and uniform channels. However, many nanofluidic applications such as sorting, single molecule experiment require complex manipulation of DNA in branched channels with junctions. Dynamics response of DNA in such nanofluidic networks with junctions and asymmetric channels is relatively unknown. We studied the transport of DNA in a nanofluidic device made up of series of nanochannel junctions with asymmetric channel size. Here we present a non-equilibrium thermodynamic model for a nanochannel junction with asymmetry in channel size. We show that the transport direction of DNA in the device can be tuned locally by altering the confinement free energy of DNA or the flow potential in nanochannels. Using our model, we show that the motion of DNA in branched nanofluidic networks can be predicted stochastically.

11:20am **BI-ThM11 Dipeptide Nanocontainers Immobilised on Graphene Nanoplatforms for Drug-delivery Applications***, V.C.L. Caruso,* University of Catania, Italy*; G. Trapani,* University of Catania and Scuola Superiore di Catania, Italy*; L.M. Cucci, I. Naletova,* University of Catania, Italy*; D. La Mendola,* University of Pisa, Italy*; **Cristina Satriano,*** University of Catania, Italy

Graphene oxide (GO) nanosheets, owing to their high surface-to-volume ratio and the richness of oxygen-containing moieties (including carboxyl, hydroxyls and epoxide groups) represent ideal 2D nanoplatforms for drug delivery applications [1]. The integration of GO with homo-aromatic dipeptides, which are able to self-assemble into ordered structures such as nanotubes and nanowires [2], may offer unique potentialities at the biointerface because of the increased biocompatibility of the hybrid system and, remarkably, for the capability to load/protect a cargo into the peptide nanocontainers. Moreover, metal ions can influence/drive the peptide self-assembling process as well as to induce additional properties of the hybrid system (e.g., antibacterial and angiogenic properties in the case of Cu^{2+}ions [3]).

In this work, the hydrophobic dipeptides Phe-Phe (FF) and Tyr-Tyr (YY) were grown in the presence of graphene oxide (GO) and copper ions, to fabricate hybrid peptide-GO-metal nanoassemblies with multifaceted features.

The nanoassemblies were scrutinised spectroscopically (UV-visible, fluorescence and circular dichroism) and microscopically (atomic force microscopy and confocal microscopy). Quartz crystal microbalance with dissipation monitoring (QCM-D) was used for real-time acoustic sensing of the interaction of the hybrid nanoplatforms with supported lipid bilayers, used as model cell membranes. Promising results of cellular uptake in neuroblastoma cells were measured by confocal microscopy for the assemblies loaded with the anticancer drug doxorubicine.

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11:40am **BI-ThM12 Seriatim Operando STM and FTIR Study of Phospholipid Membrane Phase Transition Driven by Electrochemical Potential Control***, **Taro Yamada,*** RIKEN, Japan*; S. Matsunaga, H. Shimizu,* The University of Tokyo*; T. Kobayashi,* RIKEN, Japan*; M. Kawai,* The University of Tokyo

Phospholipid (1,2-dialkanoyl-sn-glycero-3-phosphocholine, DHPC for alkyl=C_6H_{13}, DDPC for $C_{10}H_{21}$) monolayers were prepared on 1-octanethiol-terminated gold surface, as a model of biological cell membrane, and nano-scopically observed by electrochemical scanning tunneling microscopy (EC-STM) and internal multiple reflection Fourier-transformed infrared absorption spectroscopy (FTIR) within aqueous electrolytic solutions. This dual-technique in situ operando observation revealed structural changeover of the phospholipid membrane according to the applied electrode potential. In 0.05 M NH_4ClO_4 solution (pH 7.0) at 0 V vs RHE, DHPC monolayer was a fluidic monolayer along the underlying thiol monolayer, with mobile chasms through which underlying vacancy islands of the substrate were frequently seen.by application of -0.2 V, the monolayer was slowly converted into solid striped structure. This is designated as "hemimicellar aggregation" [1] with a periodicity of 4.3 nm, and observed also for DDPC. By returning the substrate potential, the lipid monolayers restored fluidic phase. This transition was reversible and repeatable. By application of +0.2 V the fluidic feature was maintained despite a slight increase of monolayer height. When the potential was swept from +0.2 V to -0.2 V, elliptic agglomerates with an average diameter of 13 nm was observed. After this, the hemimicellar aggregation was never observed by any kind of potential cycling. This irreversible change of phase coincided with the seriatim FTIR observation, using deuterium-labelled DHPC molecules. The initial change of fluidic to hemimicellar did not exhibit drastic change in IR spectra, except a reversible splitting of the P-O stretching in the region of 1200-1300 cm-1. After application of +0.2V DHPC with the head-group choline part ($-C_2D_4N^+(CD_3)_3$) was lost as a surface IR signal. This is an evidence for irreversible dissociation of DHPC into choline and phosphatidyl acid. The elliptic grains correspond to the phosphaticyl acid, differently agglomerated from that of intact DHPC hemimicelles. The potential shift of this amplitude is similar to the membrane potential of real cells. It is seen that phospholipid molecules, the robust solid component of cell membrane, can be easily involved chemical reactions under such membrane potential by the aid of membrane proteins for example. This series of experiment also demonstrates the applicability of seriatim surface observation techniques such as IR spectroscopy in addition to STM, which does not always distinguish the molecular species and detect chemical reactions.

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12:00pm **BI-ThM13 Mitochondria Localized Polymerization for New Cancer Therapy***, **Ja-Hyoung Ryu,*** Ulsan Natioanl Institute of Science and Technology, Republic of Korea

Recently, targeting mitochondria, the vital organelle for cell survival, as it plays a central role in energy production and apoptotic pathways, has been recognized as an efficient strategy in different therapeutic techniques by disturbing the normal function. Specifically, the conjugation of drug to triphenylphosphonium (TPP), a lipophilic cation, enables its accumulation into the mitochondria of cancer cells more than ~10 times greater than into normal cells as the mitochondrial membrane potentials (~ -220 mV) of cancer cells exhibits more negative charge than that of normal cells (~ -160 mV). The conjugation of TPP with bioactive molecules (e.g. small molecules and peptides) thus would provide a promise approach to target and disrupt the mitochondria of cancer cells, enhancing the efficacy of cancer chemotherapy. Recently, we reported that the supramolecular polymerization of dipeptide inside the mitochondria induced the dysfunction of mitochondria by disrupting the membrane, resulting in the

selective apoptosis of cancer cells. Due to the more negative mitochondria membrane potentials in cancer cells compared to normal cells, the TPP-conjugated molecules highly accumulated in the cancer cells and induced the self-assembled structures.

In addition, we describe a mitochondria-targeting biomineralization system that favorably can induce silicification and consequent apoptosis of various cancer cells. The biomineralization system features triphenylphosphonium (TPP) and triethoxysilane (mineralization monomer). The TPP enabled its accumulation into the mitochondria of cancer cells more than 7 times, compared with normal cell. Very intriguingly, the silicification of the triethoxysilane moiety to form biomierals in cancerous mitochondria results in apoptosis thorough mitochondria dysfunction, while there is no toxic effect into normal cell at the same concentration. Furthermore, this system efficiently inhibits the tumor growth of the mouse xenograft cancer model, which is very interesting and efficient anti-cancer therapy with simple molecular design. These results provide a new insight into the use of the mitochondrial targeting molecules for the regulation of cellular functions and a therapeutic approach

Biomaterial Interfaces Division
Room 101B - Session BI-ThA

Biolubrication and Wear / Women in Bio-surface Science

Moderators: Anna Belu, Medtronic, Sally McArthur, Swinburne University of Technology and CSIRO

2:20pm **BI-ThA1 Super Lubrication and Extremewear Protection using Bioinspired Polymers**, ***Xavier Banquy***, *J. Faivre,* Universite de Montreal, Canada*; G. Xie, M. Olszewski,* Carnegie Mellon University*; L. David, T. Delair, G. Sudre, A. Montembault,* Univ. Claude Bernard Lyon I*; K. Matyjaszewski,* Carnegie Mellon University*; R. Shrestha,* Universite de Montreal, Canada **INVITED**

The coming end of earth's fossil energy is pressing humanity to develop more efficient and environmentally friendly technologies. Control of wear and fatigue of machine parts has become one of the most important field of research to meet the outstanding energy crisis the world is currently facing. The design of lubricating fluids able to protect surfaces against wear and high friction has been one the several tools used by engineers to improve machines' life time and decrease energy consumption. Inspired by many different biological systems that can resist fatigue wear for decades such as our synovial joints, different coating/lubricating technologies involving polymer brushes either in their molecular form or grafted on the surface have emerged. All these strategies require the lubricating or wear protecting molecules to be strongly anchored to the surfaces in order to avoid close contact between the surfaces. Strong anchoring of molecules on surfaces requires a good knowledge of the chemistry and the structure of the surface which complicates dramatically the translation of these technologies towards industrial settings.

We will describe our efforts in the design of lubricating and wear protecting fluids based on synergistic mixtures of bottle brushes (BB) and linear polymer solutions that mimic human synovial fluid. Individually, these two polymers exhibit poor wear protecting capabilities compared to saline solutions. Mixture of the two polymers in pure water or in saline allows to drastically increase wear protection of surfaces under a wide range of shearing conditions. We demonstrate that this synergy between the BB and linear polymer emerges from a strong, yet transient, cohesion between the two components forming the boundary film due to entanglements between both polymers. We show that this concept can be applied to other types of linear polymers and surfaces and is independent of the chemical and mechanical properties of the surfaces. We further extended this approach by engineering different types of molecular interactions between the BB polymer and the linear partner and showed that wear protection can be finely tuned independently of the lubricating properties of the mixture. Different applications of these materials will be described in the biomedical field.

3:00pm **BI-ThA3 A Billion Force Runs: The AFM/Single-molecule Version of the Pitch Drop Experiment**, ***Laila Moreno Ostertag,*** Vienna University of Technology, Austria*; T. Utzig,* Max Planck Institute for Iron Research, Germany*; C. Klinger,* TU Bergakademie Freiberg, Germany*; M. Valtiner,* Vienna University of Technology, Austria

The "fly-fishing" and breaking of single molecular bonds to study their properties has been extensively studied via Atomic Force Microscopy (AFM) and optical tweezers. A good example for this are various ligand-receptor bonds or surface to molecule bonds such as the gold-amine bond, for which a free energy of ~ 37 k_BT has been determined. The experimental setup and design has evolved over the years, and so have the technology and analysis strategies involved. In the last 15 years, using Jarzynski's equality emerged as a powerful theoretical tool for estimating interaction free energies via the analysis of non-equilibrium work distributions from single-molecule pulling experiments with optical tweezers and AFM. [1] However, some of the questions remain the same and others appear as the field becomes broader. For example, what happens when the chemical model used to connect the probe with the interacting surface and head groups is varied? We recently tested the variation of linker lengths and changing pulling speeds [2] and found strong correlations that confirm the predictions of bias in such experiments by Gore *et al*. [3] in 2003. In particular, the longer the length of the polymeric chain, the more work dissipates during the retraction of the tip, and so does in turn the estimated ΔG_0, which leads to an increasing bias between the average values and those calculated using Jarzynski's equality. This is also reflected in the broadening of work distributions when using the same sample size. Longer polymeric chains show no convergence, unless millions or even billions of events were used. With this order of magnitude in mind, we started our very own "pitch drop experiment": an ambitious project which aims to collect an ever-increasing number of single-molecular force runs for a single system, which will allow us to directly and step-by-step further evaluate equations, work-distributions, convergence behavior, and expected biases in single-molecule experiments. This work will continue along the PhD times of many students - first non-converged results will be discussed in detail and compared to systems that are well converged. Part of this mammoth task is the development of an automated single-molecule recognition algorithm that is capable of distinguishing with high reliability very low work single-molecule events from thermal noise. Some of our advances in this direction will be discussed in detail as well.

References:

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3:20pm **BI-ThA4 Ionic Liquid Behaviour in Biologic Environments: Structuring and Lubrication at Aqueous Solid/liquid Interfaces**, *H.-W. Cheng,* TU Wien, Germany*; H. Weiss, M. Mezger,* Max Planck Institute for Polymer Research, Germany*;* ***Markus Valtiner,*** Vienna University of Technology, Austria

Bio and aqueous applications of ionic liquids (IL) such as catalysis in micelles formed in aqueous IL solutions, lubrication or extraction of chemicals from biologic materials rely on surface-active and self-assembly properties of ILs. Here, we discuss qualitative relations of the interfacial and bulk structuring of water-soluble and highly surface-active ILs on chemically controlled surfaces over a wide range of water concentrations using both force probe and X-ray scattering experiments. Our data indicate that IL structuring evolves from surfactant-like surface adsorption at low IL concentrations, to micellar bulk structure adsorption above the critical micelle concentration, to planar bilayer formation in ILs with <1 wt % of water and at high charging of the surface. Interfacial structuring is controlled by mesoscopic bulk structuring at high water concentrations. Surface chemistry and surface charges decisively steer interfacial ordering of ions if the water concentration is low and/or the surface charge is high. We also demonstrate that controlling the interfacial forces by using self-assembled monolayer chemistry allows tuning of interfacial structures. Both the ratio of the head group size to the hydrophobic tail volume as well as the surface charging trigger the bulk structure and offer a tool for predicting interfacial structures. Based on the applied techniques and analyses, a qualitative prediction of molecular layering of ILs in aqueous systems is possible. Potential applications in biomedical applications will be discussed.

4:00pm **BI-ThA6 Synergistic Mechanisms of Selenium and Tellurium based Nano-Alloys Towards Biofilm Inhibition**, ***Kelly Nash***, *S. Tek, B. Vincent, C. Smith, R. Robledo,* University of Texas at San Antonio **INVITED**

Selenium (Se) and Tellurium (Te) are two elements under-utilized in medicinal treatments that naturally occur in the human body. Selenium is a bioessential element that exists as a micronutrient throughout most biological systems. In mammalian species, selenium is found in the form of selenocycteine, an amino acid found in selenoproteins. Selenoproteins play an important role in cell metabolism and is an active participant in anti-oxidant glutathione peroxidase mechanism which aids in DNA synthesis. Given selenium's crucial role within biological functions, recent efforts have investigated the antimicrobial properties of selenium as a means to reverse, suppress or prevent the development biofilms. Tellurium, belonging to the same family as oxygen, sulphur and selenium, has been far less studied for its bioactivity. In part, this is due to its classification of being a non-essential biological element. However, recent evidence points to the possible existence and role in biological activity, abet to a lesser extent than selenium. Given that Selenium (Se), a bioessential element, and tellurium (Te), its related analog, are under-utilized elements in the medicinal libraries of antimicrobial treatments, recent research on these elements reveals that they may have numerous therapeutic applications beyond antimicrobial effects including for anti-inflammatory, anti-fouling and anti-cancer treatments. The focus of the work has been to develop novel nano-alloys composed of Se and Te by bio-friendly and chemical free synthesis methods and to evaluate their antimicrobial effects in conjunction with complementary studies on their toxicity against normal cells. Using nano-alloy formulations of these elements will form the basis of a new type of nature-inspired microbial prevention. We demonstrate that

the Seand Te nano-alloys provide a reduced toxicity to normal cells while providing enhanced therapeutic efficiency of these compounds towards biofilm inhibition including on surfaces. The short-term impact of this work will provide novel approaches to inhibiting biofilm formation. The long-term impact of this work will provide the basis for treatment of some difficult to treat nosocomial infections caused by *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *E. coli* and *Candida albicans*.

4:40pm **BI-ThA8 From Bedside Back to Bench: Combining Human Centered Design with Biointerfacial Research**, *P.A. Nguyen, T. Martin, D. Cuylear, L. Mckenney, B. Matheson, A. Yingling, L. Ista,* ***Heather Canavan,*** University of New Mexico

In 1978, the Worth Health Organization's Alma Ata Declaration asserted individuals' "right and duty to participate individually and collectively in the planning and implementation of their health care". The expansion of these policies began in the 1980s and by the 1990s, social movements across the world demanded greater public accountability and the inclusion of regular citizens in the decision-making process. Today, patient-centered healthcare has continued to progress, and in 2009 a new definition was made by the president of the Institute for Healthcare Improvement Donald Berwick "The experience (to the extent the informed, individual patient desires it) of transparency, individualization, recognition, respect, dignity, and choice in all matters, without exception, related to one's person, circumstances, and relationships in health care". These ideas have transformed over time to become “patient-centered design.” In patient-centered design, the focus is to redefine how people experience healthcare by focusing on their needs. The focus of the design is on the wants, needs, and skills of the products’ end-users, including patients, doctors, nurses, caretakers, and others.

In our laboratory, we apply our expertise in bioactive and stimulus-responsive polymers, cell/surface interactions, and cytotoxicity to create therapies that improve patient outcomes by improving the patient’s experience. For example, we have developed a pH-responsive hydrogel to control the release of the medications used to prepare patients for colonoscopy screening. Using standard surface science techniques such as NMR, FTIR, and XPS, the chemical identity, robustness of the hydrogels in varying environments, and uniformity of size of the hydrogels have been assessed. Using standard cytotoxicity assays such as Live/Dead, XTT, and MTS, the biocompatibility of the hydrogels have been established at increasing concentrations from 1-25% out to four days in vitro with appropriate mammalian cell lines. Our model also shows promise in targeted delivery of biotherapeutics and encapsulated bacterial strains within the GI tract of immunocompromised individuals.

5:00pm **BI-ThA9 Liquid-Infused Surfaces Coated on Paper Improve Bacteria Handling Efficiency and Detection**, *D. Regan, C. Lilly, A. Weigang, H. Patanwala,* ***Caitlin Howell,*** University of Maine

Issues such as the rise of antibiotic resistance highlight the need for constant innovation in the field of point of care (POC) microbial diagnostics. Current approaches that do not require the use of energy for storage or detection are hindered by low sample concentration and adhesion challenges which arise when handling these often “sticky” organisms. To overcome these limitations, we combine two approaches in complex analyte handling: infused polymers, which provide a universal anti-adhesion surface against microorganisms, and paper-based microfluidics, which present a lightweight, rugged, and low-cost platform for POC diagnostics, to create paper-supported liquid-infused polymer surfaces. The results showed that the liquid-infused system could be created on multiple different types of paper, including commercially-available silicone release paper which is already manufactured at an industrial scale. Folding the paper liquid-infused surfaces produced chambers which could be used to concentrate the organisms into single point via evaporation with >60% efficiency, compared to <20% efficiency for controls without an infused polymer layer. Sample containing bacteria could be moved from point to point without the loss of cells due to surface adhesion. Finally, integrated proof-of-principle tests showed that the use of liquid-infused surfaces to handle bacteria in this way resulted in positive colorimetric indication of *Staphylococcus aureus* significantly faster than control surfaces. These results demonstrate the use of paper-supported liquid-infused surfaces for improved microorganism handling in POC diagnostics.

5:20pm **BI-ThA10 Tailoring Interactions at the Nanoparticle-nucleic Acid Interface using Molecular Modelling**, *M. Manning, J.A. Nash,* ***Yaroslava Yingling,*** North Carolina State University

The design of nanoparticles (NPs) that can induce specific structural transitions in nucleic acids (NA) is important for nanotechnology applications including gene delivery and nanoelectronics. NP biocompatibility and efficacy is determined by geometry, charge, and surface chemistry. Advancing NPs to the clinic requires optimization, which is prohibitively expensive, and a mechanistic understanding of NP-NA interactions, which remains unknown. This project will advance tailored NP gene delivery by a multiscale optimization employing all-atom molecular dynamics (MD) simulations and leveraging machine learning algorithms. It is known that in biological systems, the binding of cationic proteins induces structural changes in DNA or RNA, which can affect gene expression or cause the compaction of DNA into chromatin. The anionic backbone of the nucleic acids DNA and RNA allow for non-specific electrostatic interactions with cationic proteins, nanoparticles, or dendrimers. The interaction of nucleic acids and nanoparticles may be tuned through changes in nanoparticle size, charge, polarity, or shape. However, the factors that affect structural transitions are not fully understood. We performed atomistic molecular dynamics simulations of the binding of nucleic acids to monolayer-protected gold nanoparticles to elucidate structural changes that take place for nanoparticles and DNA upon binding. Results from these simulations were analyzed to determine modes of DNA and RNA bending with nanoparticles. Our simulations show that highly charged nanoparticles cause DNA to bend with little damage to the helix structure, similar to DNA in the nucleosome. Nanoparticle shape as well as charge is shown to affect the wrapping of nucleic acids with the nanoparticle. Low salt concentrations and high nanoparticle charge cause greater disruptions to DNA structure. We find that the roll parameter is the most important base-pair parameter for DNA bending. Requirements for bending differed significantly between DNA and dsRNA. The degree of DNA bending is controlled by the charge of the NPs, but ligand flexibility played a more significant role in dsRNA bending. These results allowed us to determine the training data for machine learning algorithms and design a novel ligands capable of controlled wrapping of NA around NP. We have shown that the designer gold NPs are capable of wrapping NAs with fine control of binding strength through NP charge and ligand stiffness. These findings are useful for designing gene delivery systems with enhanced biocompatibility and selectivity.

5:40pm **BI-ThA11 Biomolecule Interaction with Polymer Thin Films Based on Zwitterions and Polymer Nanoparticles**, ***Eva Bittrich,*** *C. Naas,* Leibniz-Institut für Polymerforschung Dresden e.V., Germany*; F. Mele,* Leibniz-Institut für Polymerforschung Dresden e.V. and Polytechnic University of Turin, Italy*; A. Münch,* Leibniz-Institut für Polymerforschung Dresden e.V., Germany*; P. Uhlmann,* Leibniz-Institut für Polymerforschung Dresden e.V.,Germany*; D. Appelhans, K.-J. Eichhorn, B. Voit,* Leibniz-Institut für Polymerforschung Dresden e.V., Germany

Controlling and understanding the interaction behavior of biomolecules with polymer surfaces is one key aspect for the design of new biomaterials. Thin hydrogel coatings offer a huge variety of possibilities to tune physical and chemical surface properties and to create functional biocompatible interfaces supported on a substrate material. Among polymer architectures studied for biocompatible systems are dendritically structured polycations decorated with oligosaccharide shell [1, 2], and zwitterionic copolymers based on phosphorylcholine groups [3]. We prepared two types of thin hydrogel films: 1) based on dendritic polymer core-shell nanoparticles of hyperbranched poly (ethylene imine) (PEI) with maltose shell and 2) based on the statistical copolymer poly[(2-methacryloyloxyethyl phosphorylcholine)-co-(glycidyl methacrylate)] (MPC-*co*-GMA). For both surface types swelling and the interaction with selected biomolecules from small drug molecules to proteins and phospholipids was analyzed quantitatively by in-situ spectroscopic ellipsometry and quartz crystal microbalance with dissipation monitoring. The adsorbed amount of biomolecules was correlated to changes in hydration, thickness and viscoelastic properties of the films to obtain new insights into the specific interaction processes.

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Magnetic Interfaces and Nanostructures Division
Room 203A - Session MI+BI-ThA

Interdisciplinary Magnetism

Moderator: Markus Donath, Westfälische Wilhelms-Universität Münster, Germany

2:40pm **MI+BI-ThA2 Chiral Induced Spin Selectivity in Molecular Bond Dissociation***, Richard Rosenberg,* Argonne National Laboratory

Since nearly all biological compounds are homochiral, any model of the origin of life must be able to incorporate a mechanism that could lead to preferential chirality. Since chiral molecules have a certain handedness, many researchers have investigated the possible influence of circularly polarized UV photons and longitudinal spin-polarized electrons in creating an enantiomeric excess.[1-3] However, in general the demonstrated effects have been small and/or on the order of the experimental error. Previously we demonstrated [4] that chiral-selective chemistry occurs when X-rays irradiate a chiral molecule bound to a magnetic substrate and suggested that a previously unappreciated source may play a role in chiral-selective chemistry: low-energy (0-20 eV) spin-polarized secondary electrons, produced by photon, electron, or ion irradiation. In the present work, we explore a possible alternative mechanism based on the chiral induced spin selectivity (CISS) effect [5] which suggests that the lifetime of an excited electron in a chiral molecule bound to a magnetic substrate should depend on the magnetization direction of the substrate. To investigate this possibility, we examined the photon-stimulated desorption yield of hydrogen ions from D- and L-Hystidine bound to a magnetized cobalt film. The data indicates differences in the N K edge spectra of the H^+ ion yield depending on the substrate magnetization direction. These results suggest a possible CISS effect on the excited state lifetime of the dissociative state. Such a mechanism would be applicable to any process that leads to an excited electron in a dissociative state of a chiral molecule bound to a magnetic substrate. Iron is one of the most common elements and many iron compounds are magnetic, so such a mechanism could be applicable in a wide range of prebiotic environments.

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3:00pm **MI+BI-ThA3 The Chiral Induced Spin Selectivity Effect- From Spintronics to Controlling Chemistry***, Ron Naaman,* Weizmann Institute of Science, Israel **INVITED**

Spin based properties, applications, and devices are commonly related to magnetic effects and to magnetic materials. However, we found that chiral organic molecules can act as spin filters for photoelectrons transmission, [i] in electron transfer, [ii] and in electron transport. [iii]

The new effect, termed Chiral Induced Spin Selectivity (CISS), [iv] enables new type of spintronics, [v] has interesting implications in Biology, [vi] varying from allowing long-range electron transfer, controlling multiple electrons reactions, and in enantio-recognition.

The effect and its various applications and implications will be discussed.

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4:00pm **MI+BI-ThA6 Multifunctional Ferromagnetic Disks for Life Sciences Applications***, Elena Rozhkova, V. Novosad,* Argonne National Laboratory **INVITED**

The impact of modern nanomaterials and engineered architectures on biological modulation, bioanalytical techniques, and healthcare technologies can hardly be overestimated. Magnetic nanomaterials are attractive for life sciences applications because they can be detected and operated remotely, biological barriers-free, using external magnetic field. Using top-down micro-/nano-fabrication techniques allows for production of monodisperse magnetic particles of virtually any composition and shape, with tunable magnetic properties. Such particles have been exploited as multi-spectral MRI contrast enhancement labels, for *in vitro* detection of molecular markers and cell sorting. This talk will summarize successful applications of lithographically defined disk-shaped particles composed of ferromagnetic $Fe_{20}Ni_{80}$ permalloy core for biomedical applications in both low- and high frequency magnetic field regimes as mediators of biological mechanotrasduction, as delivery vehicles, contrast agents and ultrasensitive detection labels. Advanced synchrotron imaging was used to visualize interaction of engineered nanomagnetic hybrids with living systems and study their chemical stability at subcellular, cellular and 3D multicellular levels.

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4:40pm **MI+BI-ThA8 Magnetic Nanoparticles in Biomedicine: Recent Developments in Imaging, Diagnostics and Therapy***, Kannan Krishnan,* University of Washington **INVITED**

The Néel relaxation of magnetic nanoparticles (MNP), subject to alternating magnetic fields in solution, depends exponentially on their core diameter while the complementary Brownian relaxation mechanism depends critically on their hydrodynamic volume [1]. Recent developments [2] in the synthesis of highly monodisperse and phase-pure magnetite nanoparticles allows for reproducible control of the former in biological environments, enabling novel imaging [3,4] and spectroscopic modalities, under ac excitations such as magnetic particle imaging/spectroscopy (MPI/MPS) with superior resolution and sensitivity [5]. [8] .

Magnetic Particle Imaging (MPI) is an emerging, tracer-based, whole-body medical imaging technology with high image contrast (no tissue background) and sensitivity (~250 nm Fe) to an optimized tracer consisting of an iron-oxide nanoparticle core and a biofunctionalized shell. MPI is linearly quantitative with tracer concentration and has zero tissue depth attenuation. MPI is also safe, uses no ionizing radiation and clinically approved tracers. MPI is also the first biomedical imaging technique that truly depends on nanoscale materials properties; in particular, their response to alternating magnetic fields in a true biological environment needs to be optimized.

In this talk, I will introduce the underlying physics of MPI, the alternative approaches to image reconstruction, and describe recent results in the development of our highly optimized and functionalized nanoparticle tracers for MPI. I will then present state-of-the-art imaging results of preclinical *in vivo* MPI experiments of cardiovascular (blood-pool) imaging [6], stroke [7], GI bleeding [8], and cancer [9] using rodent models. I will also discuss a related diagnostic method using magnetic relaxation and illustrate its use for detecting specific protease cancer markers in solution [10]. If time permits, I will introduce therapeutic applications of magnetic nanoparticles [11].

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Surface Science Division
Room 203C - Session SS+AS+BI+MI+NS-ThA
Organic/Inorganic Surfaces, Interfaces and Nanostructures

Moderator: Denis Potapenko, Princeton University

2:20pm **SS+AS+BI+MI+NS-ThA1 Investigation of the Stability of Ag Monolayers on Au(111) as a Function of Metal Adatom Diffusion**, *J.A. Phillips, L.K. Harville, H.R. Morgan, L.E. Jackson, G. LeBlanc,* ***Erin Iski***, University of Tulsa

The formation of an atomically thin, Ag layer on a Au(111) surface has been shown to significantly alter the thermal properties of the underlying substrate (1). A further exploration into the chemical mechanisms by which these thin films are deposited reveals two different sources of Ag during the formation of the monolayer. Electrochemical Scanning Tunneling Microscopy (EC-STM) and Cyclic Voltammetry (CV) are used to probe the *in-situ* interfaces of these metal systems as well as the adsorption of molecules on metals. EC-STM is a unique technique that, in addition to providing a local probe of the atomic surface structure, also functions as a 3-electrode cell in which redox chemistry can be performed to understand the chemical reactivity of the surface. Also, cyclic voltammograms (CVs) can be generated to provide specific information regarding the nature of the redox events occurring at the surface. The two sources of silver used for the Underpotential Deposition (UPD) process on Au(111) result in significantly different thermal stabilities of the surface. An important question is whether this stability can extend beyond thermal properties, which will be probed using the assembly of amino acids on Ag/Au(111). Using both EC-STM and UHV-STM (ultra-high vacuum STM), it has been shown that amino acids assist in the immobilization of diffusing adatoms on the surface and in the subsequent formation of metal islands (2). Since the molecular deposition in both cases takes place at room temperature, the current understanding is that the atoms on the surface are a function of the temperature of the surface and are not pulled out of the surface itself. Importantly, these systems provide a unique glimpse into metal surface diffusion and offer the ability to study the mass transport of metal atoms. This study focuses on how an application of the thin Ag film on the Au(111) will disrupt or assist in the metal adatom transport and whether the known thermal stability can extend to other surface properties, thus making the afforded stability more general. The interaction of the amino acids with the Ag films deposited at the two different potentials and the associated mass transport as measured by the size of metal islands on the surface will shed light on the stabilities of the two types of Ag layers. The ability to experimentally choose different surface properties based on electrochemical parameters and solution composition during metal deposition could lead to exciting new directions for thin film technologies.

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2:40pm **SS+AS+BI+MI+NS-ThA2 Chain-Length Dependent Reactivity of Thiolate Self-Assembled Monolayers with Atomic Gas Species**, ***Jeffrey Sayler***, *S. Brown, S.J. Sibener,* University of Chicago

Thiolate self-assembled monolayers (SAMs) provide platforms for easily customizable organic interfaces, making them an excellent model system for studying the chemical properties of organic thin films. In particular, their reactions with atomic gas species such as hydrogen and oxygen yield important information about gas-surface interactions in organic films, how static and dynamic disorder influence passivation, as well as various hydrogenation and oxidation reactions. We are currently investigating the reactions of these SAMs with atomic hydrogen (H), using an angle-directed atomic gas source and *in situ* ultra-high vacuum scanning tunneling microscopy (UHV-STM). First, a series of alkanethiolate SAM samples of varying chain length (8 to 11 carbon atoms long) were reacted with H, resulting in the monolayers' conversion from close-packed standing-up phase to lower density lying-down phase. Regardless of chain length or even-/oddness, which were expected to impact the effectiveness of H penetration into the monolayer due to differences in the chains' lateral mobility and terminal structure, all samples exhibited common kinetic mechanistic details. The relative reaction rates of different chain lengths were obtained using simultaneous dosing of multiple samples. Second, a close-packed 1H,1H,2H,2H-perfluorodecanethiol SAM (a fluorinated analog of the 1-decanethiol SAM) was reacted with H. Dosing this sample under the same conditions as the 1-decanethiol sample revealed little to no reactivity. Ongoing studies continue to explore the reactivity of this family of saturated SAM systems including investigation of the kinetics and mechanism of the lying-down phase's reactivity with H. Further investigations involving atomic oxygen and different SAM chemical compositions and structures will follow.

3:00pm **SS+AS+BI+MI+NS-ThA3 Scan Probe Studies of Lithium Transfer through Solid State Electrochemical Interfaces**, ***Janice Reutt-Robey***, University of Maryland College Park **INVITED**

All solid-state electrical energy storage devices are of immense interest as safer alternatives to those based upon flammable liquid electrolytes. Understanding the rates and elementary processes for lithium ion transport through anode-solid electrolyte-cathode interfaces is essential, but obscured by heterogeneous samples and unknown local potentials. I will present new nanoscale studies of lithiation/delithiation across well-defined interfaces created with actuated nanobattery junctions. Conventional STM metallic tips, clad with a thin film of electrode material ($LiCoO_2$ or Li) and a capping film of solid electrolyte ($Li_xAl_2O_3$ or Li_20), function as ½ cells. Probes are positioned and electrochemically cycled at singular surfaces of model electrodes – Si(111), Si(100), C(0001). At the nanoscale, hysteresis in charging/discharging is monitored as a function of interface structure and materials properties. UHV measurements preserve the chemical integrity of the material interfaces and allow traditional (cyclic voltammetry, stepped potential) and nontraditional (stepped stress) electrochemical measurements to separate electron/ion contributions to charge transfer. The data reveal how induced variations in local lithium concentration impact rates for charging/discharging and contribute to hysteretic behavior. Further, stress-induced current transients show non-Cotrellian time behavior, attributed to a lithium ion concentration gradient in the solid electrolyte. Modeling of nanobattery data allows for testable predictions of material properties. Finally we show how "inverted" Scanning Tunneling Spectroscopy provides a useful tool to characterize the electrical band gap of the tip 1/2 cell materials, while imaging reveals the distribution pattern of lithium ions at the cycled electrode surfaces.

This work was supported as part of the Nanostructures for Electrical Energy Storage (NEES), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award number DESC0001160.

4:00pm **SS+AS+BI+MI+NS-ThA6 Adsorption and Self-assembly of Halogenated Organic Molecules on the Si(111) √3×√3-Ag Surface**, ***Renjie Liu***, Lakehead University, Canada; *C. Fu, A.G. Moisseev, M.R. Rao, Y. Chen, D.F. Perepichka,* McGill University, Canada; *M.C. Gallagher,* Lakehead University, Canada

Given potential applications in molecular electronics, organic thin films continue to attract a great deal of scientific attention. Furthermore, organic-inorganic semiconductor hybrids have been identified as a possible platform for future devices. Generally such a device would require thin films of functionalized organic molecules grown on silicon surfaces. To promote the growth of high quality films, the Si surface needs to be passivated. For example, the Si(111) √3×√3-Ag surface has been shown to be weakly interacting, allowing molecules to remain mobile and form well ordered layers [1].

In this work we compare the adsorption and self-assembly of two halogenated molecules of threefold symmetry; 2,4,6-tris(4-iodophenyl)-1,3,5-triazine (TIPT), and tribromotrioxaazatriangulene (TBTANG) on the Si(111)-√3×√3-Ag surface. The self assembly of TIPT on HOPG and Au(111) has been reported previously [2], and heteroatom forms of triangulene are of particular interest in molecular electronics [3].

We find that both molecules display high mobility on the √3-Ag surface. With increasing molecular dose, TIPT forms supramolecular domains defined by a 2.0 nm by 1.8 nm rectangular cell. The size and symmetry of the unit cell provides strong evidence that a large fraction of the monomers do not undergo de-halogenation, and that the dominant interaction within the domains is intermolecular I···H hydrogen-bonding. As the coverage approaches one monolayer, the film consists of supramolecular domains of limited extent separated by regions of disorder.

STM images at lower coverage reveal that molecular adsorption increases the defect density of the underlying √3-Ag layer. We believe that a small fraction of the TIPT molecules de-iodinate on adsorption and that the iodine subsequently reacts with the Ag overlayer. The increased defect density limits the extent of the supramolecular domains on this surface.

In contrast, TBTANG exhibits long-range self-assembly of intact molecules. The ordered structure is characterized by several closely packed rows of molecules. Within the rows the repeating motif is two-molecules linked together by Br···Br interactions. With increasing coverage, the √3 surface remains unaffected and the self assembled layer extends over the entire surface.

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4:20pm **SS+AS+BI+MI+NS-ThA7 Electron Interactions with Alkanethiol Self-assembled Monolayers on Au(111)***, **Jodi Grzeskowiak,*** University at Albany-SUNY*; C.A. Ventrice, Jr.,* SUNY Polytechnic Institute

Self-assembled monolayers (SAMs) are often used for applications such as molecular electronics, selective deposition, and various forms of surface modification. Advanced lithography within the semiconductor industry is adopting ever shorter wavelengths of light such that the interaction of secondary electrons with the organic resist is becoming the primary mechanism for photo-initiated electro-chemical solubility changing reactions. In order to study the interaction of low energy electrons with thin organic films, measurements have been performed on electron decomposition of alkanethiol molecules grown on Au(111) substrates. SAMs have been grown via both solution and vapor phase methods. These monolayers arrange into two distinct phases commonly referred to as lying down and standing up. The lying down phase is a physisorbed layer that is only weakly interacting with the substrate via Van der Waals forces. Conversely, the standing up phase is a chemisorbed species that is more strongly bound to the substrate. Various surface analysis techniques were used to characterize the monolayers before and after electron exposure. Low energy electron diffraction (LEED) was used to determine the structure of the SAM and the rate of decomposition. Temperature programmed desorption (TPD) in combination with mass spectrometry was used to evaluate the thermal stability and bonding strength of the attached SAMs and the decomposition products from electron exposure.

4:40pm **SS+AS+BI+MI+NS-ThA8 Measuring the Electronic Properties of Organic Single Crystals***, **Sujitra Pookpanratana**, E.G. Bittle, C.A. Hacker, S.W. Robey,* National Institute of Standards and Technology (NIST)*; R. Ovsyannikov, E. Giangrisostomi,* Helmholtz-Zentrum Berlin, Germany

Organic and molecular-based compounds have found commercial application in consumer-based electronics. Organic semiconductors can be integrated onto device structures in different physical forms such as single crystals, polycrystalline thin-films, or amorphous thin-films. The structural order of the molecular solid profoundly influences the electronic properties, that in turn controls important properties, such as the transport gap and binding energy of the highest occupied molecular orbital (HOMO) [1, 2], that govern how an electronic device operates. Photoemission can play a vital role in illuminating these important electronic properties. While there are numerous photoemission spectroscopic measurements of organic semiconductors in thin-film structures, far fewer attempts have been made to determine the "fundamental" electronic properties for pristine organic single crystals.

Here, we present results of photoemission measurements for single crystalline (SC) dinaphthothienothiophene (DNTT). DNTT is a small molecule-based thienoacene and has demonstrated carrier mobilities approaching 10 $cm^2/(V\ s)$ [3], is air-stable [4] and durable against accelerated temperatures and humidity conditions.[5] While there are many device studies that establish DNTT and other related thienoacenes for a variety of applications, detailed electronic and chemical structure studies are lacking. Electronic "band" structure measurements using a novel angle-resolved time-of-flight electron spectrometer is performed on SC-DNTT, and multiple highest occupied molecular orbitals are resolved of varying widths. Modest dispersion of the frontier HOMO is observed, and this result will be discussed in context of the charge carrier behavior of DNTT reported in the literature.

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5:00pm **SS+AS+BI+MI+NS-ThA9 Surface Functionalization of Porous Substrates via Initiated Chemical Vapor Deposition***, **Christine Cheng**, M. Gupta,* University of Southern California

Porous materials are used in various applications including separation membranes, paper-based microfluidics, and flexible electronics. Tuning surface properties of porous materials enhances the versatility of existing materials, giving them new functions and applications. However, traditional surface modification methods are typically solvent-based, which limits the range of substrates that can be coated. In this work, initiated chemical vapor deposition was used to continuously modify the surface of large areas of porous substrates in an all-dry vacuum process. A superhydrophobic polymer was deposited onto a porous substrate and the coating was characterized using contact angle goniometry, X-ray photoelectron spectroscopy, and scanning electron microscopy to study the uniformity of the coating along the entirety of the substrate. The superhyodrophobicty of the coated porous substrate is attributed to the deposited polymer and the roughness of the substrate. Addition of a perfluorinated liquid to the superhydrophobic porous substrate formed a slippery liquid-infused porous surface. A hydrophilic polymer was deposited on top of the superhydrophobic polymer to demonstrate the facile stacking of polymer layers with different chemistries using this process.

5:20pm **SS+AS+BI+MI+NS-ThA10 Atomic-Scale Understanding of Anatase Nanocatalyst Activation***, **William DeBenedetti**[1], E.S. Skibinski, M.A. Hines,* Cornell University

Our ability to predict the chemical reactivity of nanocatalysts has been stymied by our lack of atomic-scale understanding of nanocatalyst surface structure. Specifically, do nanocatalyst surfaces adopt a bulk-terminated structure or do they reconstruct to minimize their surface free energy, thereby lowering their chemical reactivity as observed in ultra-high vacuum? Furthermore, do nanocatalysts processed at higher temperature maintain their low-chemical-reactivity, reconstructed surfaces when used at low temperatures and under typical operating conditions?

Using a new technique for the growth of highly aligned anatase (001) nanocatalysts, we will show that solution-synthesized anatase is terminated by a monolayer of fluorine, which acts as an atomic-scale protective coating against adventitious contamination. We will also show that carboxylic acid solutions, the most common TiO_2 functionalization chemistry, causes a spontaneous reorganization of a reconstructed nanocatalyst, leading to a five-fold increase in the number of reactive sites. This surface reorganization is not observed when carboxylic acids are dosed from the gas phase, indicating that experiments in ultra-high vacuum environments lead to trapped states that may not be relevant to nanocatalysts in ambient conditions. *Ab initio* calculations show that although the carboxylic acid termination is slightly less effective at removing surface stress than the reconstructed surface, it is more effective in lowering the surface free energy. These findings suggest that bulk-terminated metal oxide nanocatalysts may be common under ambient operating environments, even after high-temperature processing or if reactants are rinsed off.

5:40pm **SS+AS+BI+MI+NS-ThA11 Mechanistic view of Solid-Electrolyte Interphase Layer Evolution at Li-metal Anode***, **Venkateshkumar Prabhakaran**,* Physical Sciences Division, Pacific Northwest National Laboratory*; M.H. Engelhard, A. Martinez,* Environmental Molecular Science Laboratory, Pacific Northwest National Laboratory*; G.E. Johnson,* Physical Sciences Division, Pacific Northwest National Laboratory*; S. Thevuthasan,* Environmental Molecular Science Laboratory, Pacific Northwest National Laboratory*; V. Murugesan,* Physical Sciences Division, Pacific Northwest National Laboratory

A molecular-level understanding of structural and chemical transformations of electrolyte at solid-electrolyte interfaces (SEI) is critical for rational design of electrochemical materials. Despite numerous studies, evolution of the transient and metastable species which dictates the cascade of interfacial reactions are still not clear. The challenge is to establish the chemical homogeneity within interface to clearly delineate the origin of various decomposition reaction products and their energetic

[1] **National Student Award Finalist**

pathways. Soft landing of mass-selected ions is ideally suited for building the interface with selected constituent which can alleviate the complexity associated with diverse and correlated processes within SEI layer.[1-4] Herein, we report the development and first demonstration of new capabilities that combine ion soft landing with *operando* infrared reflection-absorption spectroscopy (IRRAS) to study the decomposition of counter anions and solvent molecules on bare lithium metal surfaces. Specifically, we discreetly deposited sulfonyl imide based electrolyte anion ($TFSI^-$) and solvated Lithium cations without corresponding counter ions onto bare lithium metal using soft landing approach and monitored their decomposition using *in-situ* IRRAS and *ex-situ* x-ray photoelectron spectroscopy (XPS). *Operando* IRRAS and XPS measurements captured the signatures of transient species arising from decomposition of electrolyte anions and solvent molecules in real time. We will discuss, our unique approach of building interface with precise control over the constituents and subsequently detect the spectroscopic signatures of transient species during decomposition processes.

References:

1. Johnson, G. E.; Hu, Q.; Laskin, J., Soft landing of complex molecules on surfaces. *Annual Review of Analytical Chemistry* **2011,***4*, 83-104.

2. Prabhakaran, V.; Mehdi, B. L.; Ditto, J. J.; Engelhard, M. H.; Wang, B.; Gunaratne, K. D. D.; Johnson, D. C.; Browning, N. D.; Johnson, G. E.; Laskin, J., Rational design of efficient electrode–electrolyte interfaces for solid-state energy storage using ion soft landing. *Nature Communications***2016,***7*, 11399.

3. Prabhakaran, V.; Johnson, G. E.; Wang, B.; Laskin, J., *In situ* solid-state electrochemistry of mass-selected ions at well-defined electrode–electrolyte interfaces. *Proceedings of the National Academy of Sciences* **2016,***113*, 13324-13329.

4. Gunaratne, K. D. D.; Johnson, G. E.; Andersen, A.; Du, D.; Zhang, W.; Prabhakaran, V.; Lin, Y.; Laskin, J., Controlling the Charge State and Redox Properties of Supported Polyoxometalates via Soft Landing of Mass-Selected Ions. *Journal of Physical Chemistry C* **2014,***118*, 27611-27622.

Biomaterial Interfaces Division
Room 101B - Session BI+AS+NS-FrM

Characterization of Biological and Biomaterial Surfaces
Moderator: Bill Theilacker, Medtronic

8:20am **BI+AS+NS-FrM1 Novel Insights into Skin Biology and Permeation of Actives using ToF-SIMS and 3D OrbiSIMS.**, ***David Scurr,*** The University of Nottingham, UK **INVITED**

This work presents the use of mass spectrometry imaging (specifically ToF-SIMS and 3D OrbiSIMS) as an emerging tool for skin analysis, offering the ability to perform chemical histology and monitor the distribution of xenobiotic compounds, namely antibacterial, cosmetic and pharmaceutical agents. Both 2D and 3D spatial distribution profiles of analytes within skin are achievable for both topically applied compounds following permeation and inherent compounds present in native tissue. Data acquired using the 3D OrbiSIMS can identify a significant number of biological molecules, unavailable using ToF-SIMS, including subtle chemical variations within single skin strata and / or individual cells.

Individual tape stripped layers of human *stratum corneum*, both native and following application of a topical compound can be imaged using ToF-SIMS and 3D OrbiSIMS. The sensitivity of these techniques has also enabled the detection of analytes from native tape stripped samples highlighted differences in the lipid composition of the *stratum corneum* relating to both intrinsic and extrinsic aging effects[1]. In particular, a significant increase in the presence and a localised spatial distribution was observed for cholesterol sulfate, which has been shown to play a key role in desquamation.

In conducting an analysis of native *ex vivo* porcine tissue we were successfully able to detect and spatially map chemical biomarkers of both the *stratum corneum* and underlying epidermis. In addition, using a gas cluster ion beam (GCIB), the 3D distribution of analytes throughout the epidermis could be visualised for both pharmaceutical and cosmetic topical products following Franz cell experiments. These methods can be used to illustrate enhanced topical delivery, for example in the use of supramolecular gels encapsulating ascorbic acid and microneedles applied prior to the application of imiquimod used for cosmetic and pharmaceutical purposes respectively.

[1] Starr, Johnson, Wibawa, Marlow, Bell, Barrett & Scurr, *Anal. Chem*. **2016**, 88 (8), pp 4400–4408

9:00am **BI+AS+NS-FrM3 Multivariate Analysis of ToF-SIMS Data using Mass Segmented Data Matrices: Polymers and Biointerfaces**, *R.M.T. Madiona,* La Trobe University, Australia*; N.G. Welch,* CSIRO Manufacturing, Australia*; D.A. Winkler,* La Trobe University, Australia*; J.A. Scoble,* CSIRO, Australia*; B.W. Muir,* CSIRO, Australia*;* ***Paul Pigram,*** La Trobe University, Australia

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is continuously advancing. The data sets now being generated are growing dramatically in complexity and size. More sophisticated data analytical tools are required urgently for the efficient and effective analysis of these large, rich data sets. Standard approaches to multivariate analysis are being customised to decrease the human and computational resources required and provide a user-friendly identification of trends and features in large ToF-SIMS datasets.

We demonstrate the generation of very large ToF-SIMS data matrices using mass segmentation of spectral data in the range 0 – 500 m/z in intervals ranging from 0.01 m/z to 1 m/z. No peaks are selected and no peak overlaps are resolved. Sets of spectra are calibrated and normalized then segmented and assembled into data matrices. Manual processing is greatly reduced and the segmentation process is universal, avoiding the need to tailor or refine peak lists for difficult sample types or variants.

ToF-SIMS data for standard polymers (PET, PTFE, PMMA and LDPE) and for a group of polyamides are used to demonstrate the efficacy of this approach. The polymer types of differing composition are discriminated to a moderate extent using PCA. PCA fails for polymers of similar composition and for data sets incorporating significant random variance.

In contrast, artificial neural networks, in the form of self organising maps (SOMs) deliver an excellent outcome in classifying and clustering different and similar polymer types and for spectra from a single polymer type generated using different primary ions. This method offers great promise for the investigation of more complex bio-oriented systems.

9:20am **BI+AS+NS-FrM4 Can you dig it? ToF-SIMS Tissue Depth Profiling**, ***Daniel Graham,*** *T.B. Angerer, L.J. Gamble,* University of Washington

ToF-SIMS has been shown to provide detailed chemical information about cells and tissues with excellent lateral resolution. This has enabled looking at the 2D chemical distribution of lipids and other biological molecules within tissues and cells. Since cells and tissues are three dimensional constructs, it is of interest to be able to characterize their chemical composition in 3D. With the use of gas cluster ion beams (GCIBs) ToF-SIMS can attain very fine z-resolution (<10 nm) in depth profiles, however the use of ToF-SIMS for 3D imaging of biological samples is limited. This is likely due to the complexity of the materials and artifacts often encountered because of the presence of salts. In this work we use ToF-SIMS 3D depth profiling to optimize accurate reconstruction of depth profiles of planarian worm cross-sections. For this, dual beam depth profiles with a 25 keV $Bi3^+$ liquid metal ion gun (LMIG) for imaging and 10 keV Argon 1000 clusters for sputtering were acquired using an Iontof 5 system. Data reconstruction was carried out using the NBToolbox (https://www.nb.uw.edu/mvsa/nbtoolbox) ZCorrectorGui. It is well known that due to the fixed angle to of the analysis beam, the sequential images taken at each layer of the profile shift as a function of depth. Adjusting the beam steering during data acquisition and image shifting post data acquisition are used to account for this image shifting and more accurately reconstruct a 3D representation of the data. Areas with distinct structural features were chosen for depth profiles in order to aid in ascertaining the accuracy of the 3D data reconstruction. These studies will help establish the viability of 3D data reconstruction of complex biological samples and could be instrumental in being able to localize chemical distributions throughout tissues and cells.

10:00am **BI+AS+NS-FrM6 Novel Insights into Drug Release by a Functionalized Biomaterial and Dispersion into Bone using Surface Analytical Techniques**, ***Marcus Rohnke,*** *C. Kern, B. Mogwitz, S. Ray,* Justus-Liebig University Giessen, Germany*; J. Thomas,* IFW Dresden, Germany

Bone is a complex composite material with similarities to hierarchically structured functional materials. In the case of a fracture or the need for a replacement (e.g. hip prosthesis) filler or replacement materials are necessary. Next generation bone implants are functionalised with drugs to stimulate bone healing locally or to provoke antibiotic effects. Here we focus on the release and dispersion of the anti-osteoporotic agent Sr^{2+} from strontium enriched bone cement. The knowledge of the release and dispersion kinetics of the drug plays an eminent role for the performance optimisation of the biomaterial.

Due to practical and technical reasons it is almost impossible to track the drug release kinetics, drug dispersion and the degradation of the implant material in vivo. Here we apply time of flight secondary ion mass spectrometry (ToF-SIMS) depth profiling to obtain the diffusion coefficient of Sr^{2+} in the mineralised areas of healthy and osteoporotic rat bone in post mortem examinations. For data evaluation of the depth profiles in mineralised bone we applied a simple diffusion model. The obtained diffusion coefficient for trabecular osteoporotic bone is with 1.76×10^{-10} cm^2/s more than two decades higher than that for healthy bone (2.91×10^{-12} cm^2/s). In cortical bone no significant difference in the diffusion coefficient (healthy 1.33×10^{-12} cm^2/s, osteoporotic 4.17×10^{-12} cm^2/s) could be found. The varying diffusion coefficients can be explained by the different bone nanostructure, which was investigated by focused ion beam scanning electron microscopy (FIB-SEM) and high-resolution transmission electron microscopy (HR-TEM).

The data of cement dissolution experiments into water in combination with inductively coupled plasma mass spectrometry (ICP-MS) analysis account for dissolution kinetics following Noyes-Whitney rule. For dissolution in A-MEM cell culture media the process is kinetically hindered and can be described by Korsmeyer-Peppas kinetics. An adsorbed protein layer on top of the cement surface, which was detected by ToF-SIMS, is responsible for the kinetic inhibition. Based on the results of various analytical experiments we developed a two-phase model and performed a finite element calculation for the release and dispersion of Sr^{2+} in bone. The validity of the applied model is proven by animal experiments. We compared the calculated images to mass spectrometric images of bone cross sections and achieved good conformity. It appears that drug removal via the vascular system is negligible. This is a good basis for predictions of drug mobility in bone.

10:20am **BI+AS+NS-FrM7 Spatial Distributions of Epithelial Growth Factors in Hydrogels Studied by ToF-SIMS and TIRF Microscopy for the Development of Biocompatible Multiple-protein Delivery Systems for Wound Healing**, ***Shohini Sen-Britain,*** State University of New York, Buffalo*; W. Hicks,* Roswell Park Comprehensive Cancer Center*; J.A. Gardella Jr.,* State University of New York, Buffalo

This work reports the use of ToF-SIMS imaging, TIRF microscopy, and depth profiling to visualize and map the interactions of (hydroxyethyl)methacrylate (HEMA)-based hydrogels with mixtures of growth factors that are often secreted by the epithelium during wound healing. During re-epithelialization, hydrogels can act as both tissue scaffolds at the interface between healing epithelium and surrounding connective tissue, and as delivery vehicles of therapeutic proteins that expedite the wound healing process.

The spatial distribution of multiple growth factors at hydrogel surfaces can influence biocompatibility and release kinetics, orientation and conformation of the individual growth factors. Hydrogels interact with mixtures of growth factors in vivo and also when they are developed into multiple-protein delivery systems. To address these concerns, this work presents 2D and 3D spatial distributions of fluorophore-labeled growth factors varying in size, secondary structure, and hydrophobicity at the hydrogel surfaces to model the interface between porous, phase segregated drug delivery systems and complex macromolecular mixtures.

HEMA hydrogel blends incorporating methyl methacrylate (HEMA/MMA) and methacrylic acid (HEMA/MAA) cause increased hydrophobicity or hydrophilicity at the hydrogel surface, respectively. They also present phase segregation and porous topography at the surface. Depth profiling shows that smaller proteins, such as epidermal growth factor (EGF) permeate deeper into porous regions than larger proteins such as keratinocyte growth factor (KGF) and platelet-derived growth factor (PDGF). SIMS and TIRF imaging shows that proteins with more hydrophobic character such as PDGF and EGF localize at phase segregated regions containing MMA, while those with more hydrophilic character such as KGF localize at phase segregated regions containing MAA or HEMA. Biological ramifications of these results regarding biocompatibility and multiple-protein delivery systems are the focus of future work.

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