Biomaterial Interfaces
Room: 211D - Session BI+AS-MoM

Characterization of Biological and Biomaterials Surfaces (1)

Moderator: Dan Graham, University of Washington, Joe Baio, Oregon State University

8:20am **BI+AS-MoM1 Characterizing the Dissociative Properties of Surface-Bound Biomolecules by *In Vacuo* XPS**, ***Kenan Fears***, Naval Research Laboratory

In vacuo X-ray photoelectron spectroscopy (XPS) was used to determine the dissociation constant for pH-tunable, peptide nanostructures on a gold substrate. To validate these protocols, dissociation constants of GG–X–GG and X_5 peptides (X = G, D, H, or K), and bovine albumin (BSA) and fibronectin (FN) were measured for comparison with published values. Drops of biomolecules in 100 mM sodium phosphate buffers (pH 1-12) were deposited on gold substrates and allowed to dry at room temperature. Due to the ca. +1.3 eV shift in binding energy (BE) of protonated amines, pK values of basic amino acids were calculated by plotting the fraction of protonated amines as a function of solution pH. Similarly, the BE of carboxyl groups shifted ca. -1.3 eV upon deprotonation. While C 1s spectra were convoluted by the multiple chemical states of carbon present in the samples, the ratio of the C 1s components centered at BE=289.0 ± 0.4 and BE=287.9 ± 0.3 proved to reliably assess deprotonation of carboxyl groups. The pK values for the Asp (3.1 & 2.4), His (6.7), and Lys (11.3 & 10.6) peptides, and the pI of BSA (4.8) and FN (5.7), were consistent with published values; thus, validating the pK value obtained for our surface-bound nanostructures using these methods.

9:00am **BI+AS-MoM3 Quantifying the Surface Chemistry and Overlayer Thickness of Functionalized Nanoparticles**, ***David Castner***, University of Washington **INVITED**

Nanoparticles exhibit unique surface properties and require well-controlled surface properties to achieve optimum performance in complex biological or physiological fluids. Despite the widespread appreciation of the unique properties of high surface area nanoparticles there is a surprising lack of detailed surface characterization of these materials, especially for nanoparticles used in biomedical applications. This is in part because nanoparticles present significant challenges for surface characterization. Thus, there is a need to develop rigorous and detailed surface analysis methods for characterizing the surface of nanoparticles. Model systems with well-defined, systematic variations of surface properties are an excellent starting point for developing comprehensive, multi-technique surface characterization methodologies. We have developed methods for quantifying the thickness and structure of carboxylic acid (COOH) SAM functionalized Au nanoparticles (AuNPs) using XPS, SESSA and LEIS. The size, shape, and size distribution of the AuNPs was determined by TEM. Additional surface properties were characterized using ToF-SIMS and FTIR spectroscopy.

These methods were then extended to the covalent attachment of proteins to AuNPs functionalized with OEG SAMs. For the OEG functionalized AuNPs the type of end group (OH vs. OCH_3) doesn't have a significant effect on the SAM thickness and structure, but the size of the AuNP does. The C11 alkyl portion of the thiol molecules was well ordered on all surfaces (flat, 14nm and 40nm). In contrast, the OEG portion of the thiol molecules was better ordered and more densely packed on the 40nm AuNPs compared to the 14nm AuNPs. LEIS measurements showed OEG SAMs had a thickness of 2.0 nm on the 14nm AuNPs compared to 2.6 nm on the 40nm AuNPs. Protein G was immobilized onto the HO-terminated OEG SAMs via carbonyl diimidazole chemistry. On flat Au surfaces XPS showed a monolayer of Protein G was covalently immobilized with little non-specific adsorption. On AuNPs a monolayer of Protein G could also be immobilized, but significant non-specific adsorption was detected.

Recent studies on NPs with Au cores and Ag shells have shown that it is important to account for non-spherical particle shapes of the Ag shell and off-center locations of the Au cores to obtain good agreement between the SESSA and XPS results. Both deviations from ideal core-shell spherical particles result in higher than expected XPS Au concentrations, with the off-center Au cores having the largest contribution to this effect for the particular core-shell NPs examined in this study.

9:40am **BI+AS-MoM5 Structure-Function Relation in Gizzard Plates of Cephalaspidean Gastropod**, *M. Shepelenko, V. Brumfeld, E. Klein,* Weizmann Institute of Science, Israel, *H. Lubinevsky,* Israel Oceanographic & Limnological Research (IOLR) and National Institute of Oceanography, *L. Addadi, S. Weiner,* ***Sidney Cohen***, Weizmann Institute of Science, Israel

Processing food is an essential function of all organisms. Although grinding of food is typically done by teeth, there are a number of species that perform this action in the muscular stomach or gizzard. This places unique demands on the food processing mechanism, a study of which provides fascinating insights into compositional, structural, and mechanical design of the organism at the nanoscale. The Cephalaspidean gastropods are common marine mollusks with a specialized digestive apparatus containing 3 hardened plates of millimeter size inside the gizzard. The gizzard plates are reported to either grind or crush shelled prey. In this study we apply a variety of techniques including micro-CT, scanning electron microscopy with energy dispersive x-ray spectroscopic analysis, infrared and Raman spectroscopies, powder x-ray diffraction and nanoindentation to understanding the manner in which the gizzard plates of the cephalaspid *Philine quadripartita* function in the overall digestion process. We determined that the gizzard plates, used to crush the shelled prey, have distinct structure and composition which promote optimal performance of their function. Specifically, the plate composition, a mixture of amorphous calcium carbonate and amorphous calcium phosphate embedded in a chitinous matrix, varies systematically with depth into the plate. The corresponding elastic moduli and hardness of the plates vary accordingly. In contrast to typical teeth, for which the surface comprises the stiffest and hardest material, the hardest and stiffest layer of the gizzard plates is below the working surface. Analysis of the elasticity index (H/E) of the gizzard plates, and comparison with sea urchin teeth, which we have extensively studied in the past, provided interesting insights into the connection between the biological function and mechanical properties of the gizzard plates. Sea urchin teeth, which serve a grinding function, exhibit higher wear resistance and stiffness than gizzard plates which are used for crushing. Nonetheless, the difference in toughness between the two, as determined by comparison of respective in elasticity indices, is relatively small.

10:00am **BI+AS-MoM6 Photothermal AFM-IR of Bacteria on Polymer Films: Impact of Cantilever Damping on Quantitative IR Measurements**, ***Daniel Barlow***, *J.C. Biffinger,* Naval Research Laboratory, *A.L. Cockrell,* Nova Research, *M. Lo, K. Kjoller, D. Cook,* Anasys Instruments, *W. Kyung Lee, P.E. Pehrsson,* Naval Research Laboratory, *W.J. Goodson,* Air Force Research Laboratory, *J.N. Russell, Jr.*, Naval Research Laboratory

Synthetic polymers can be prone to degradation in microbial and other biological environments, often through enzymatic activity. Quantitative assays are important to characterize these degradation mechanisms and accurately correlate relationships with environmentally dependent microbial physiology. For microbial degradation of polyurethane films, conventional FTIR microscopy has been previously applied in quantitative assays with micron – scale spatial resolution. Photothermal AFM-IR offers the potential to extend this analysis to the nanoscale, allowing early degradation processes and mechanisms relative to single microbes to be quantified. As a first step towards this, we have used AFM-IR to characterize a known polyurethane degrading microbe (*Pseudomonas fluorescens*, Pf01) grown on films of a polyether – polyurethane (PU) formulation known to resist enzymatic degradation. This allowed us to conduct preliminary AFM-IR assessments with a relevant microbe and polymer, but without additional complications from biodegradation. Height images of air-dry samples showed the growth procedure in liquid media resulted in monolayer Pf01 biofilm clusters on top of the ~250 nm PU layer, providing a conducive model system for AFM-IR in an ATR configuration. Both bacteria and PU spectral signatures were detectable by AFM-IR spectroscopy and showed generally good agreement with FTIR. However, PU AFM-IR absorption intensities were observed up to 2x higher in regions covered by dried bacteria, versus uncovered regions, even though the PU thickness was uniform over the substratum. This was due to damping variations which were reflected in the cantilever ring-down and attributed to differences in loss modulus and tip – sample adhesion for the two materials. This shows that local cantilever damping can be an important property to assess in AFM-IR analysis of combined biological / polymer samples, a factor that has received little attention thus far. Analysis of the cantilever ring-down will be discussed regarding extraction of damping parameters for normalization of the IR signal.

10:40am **BI+AS-MoM8 Where's Waldo? 3D Localization of Polymer Nanoparticles in Cells using ToF-SIMS**, ***Daniel Graham***, University of Washington, *J.T. Wilson*, Vanderbilt University, *J. Lai, L.J. Gamble, P.S. Stayton, D.G. Castner*, University of Washington

Polymeric nanoparticles have shown promise for delivery of therapeutics intracellularly. The diversity of polymer chemical and physical properties enables a wide range of cellular targeting and applications. We have initiated a project investigating the use of 3D ToF-SIMS imaging to localize and characterize polymer nanoparticles within cells. Though other imaging modalities can localize polymer nanoparticles in cells, ToF-SIMS presents the advantage of localization combined with chemical characterization of the particles and the surrounding cell. However, the ability to locate polymer nanoparticles in cells is complicated by the fact that most polymers are made of organic elements such as C, N, and O and produce secondary ion fragments that are the same as those generated from the surrounding cell. Herein we will demonstrate a method we have developed to isolate polymer nanoparticle signal from cell signal and generate 3D images of nanoparticle clusters within cells. Initial results with polymer nanoparticles targeted for endosomal uptake showed punctate localization of nanoparticle clusters within areas consistent with endosomal localization. Areas enriched in nanoparticles could be localized in spite of peak overlap of polymer and cellular signals.

11:00am **BI+AS-MoM9 XPS and ToF-SIMS Analysis of Functiionalized Nanoparticles: Effects of Sample Cleaning and Preparations**, *R. La Spina, V. Spampinato, I. Ojea, F.J. Rossi, D. Gilliland,* ***Giacomo Ceccone***, European Commission, Joint Research Centre, IHCP, Italy

It is recognized that detailed physico-chemical characterization of nanomaterials is becoming increasingly important both from the technological and from health and safety point of view. Moreover, an incomplete characterisation may inhibit or delay the scientific and technological impact of nanoscience and nanotechnology. However, nanomaterials characterization based on individual instrumental methods is a very challenging issue because their stability, coating and environmental effects may lead to outputs that are not very easy to interpret unequivocally. For this reason multiple analysis methods are needed to understand the nature of nanomaterials, especially if we consider that surface and interfaces are critical to the behaviours of nano-sized materials [1].

Surface chemical analysis methods, such as X-ray Photoelectron Spectroscopy (XPS) and Time of Flight Secondary Ion Mass Spectrometry, can provide an important contribution to more fully characterizing nanomaterials, so these methods should be more generally applied as part of a characterisation set of tools for nanomaterials and nanoparticles synthetized for different applications [2].

In this work, we have investigated the surface chemistry of nanoparticles, gold (AuNPS) and silica (SiO2NPs), functionalized with different thiols. In particular, the effects of sample cleaning by centrifugation and dialysis have been studied. Moreover, the challenges and problems related to sample preparation for the surface analysis will be also addressed and discussed The different steps of sample cleaning have been characterised by DLS, CPS and SEM, whilst the surface chemistry has been mainly assessed by XPS. Our results indicate that the cleaning process may influence the functionalization process. For instance, the AuNPs functionalized with CF3 terminated SAMs shows differences in the efficiency depending upon sample cleaning.

Finally, preliminary results about the behaviour of AuNPs-CF3 in protein solution (HSA) will be also presented.

[1] Baer D, et al., Anal. Bioanal. Chem., **2010**, 396(3), 983–1002

[2] Grainger D and Castner D, Adv. Mater., **2008**, 20, 867–877

11:20am **BI+AS-MoM10 Engineered Surfaces for Bio-Relevant Applications**, ***Marlon Walker***, NIST, *A. Vaish*, University of Delaware, *D. Vanderah*, NIST/Institute for Bioscience and Biotechnology Research

Polydopamine (PDA) is a useful bio-inspired coating for surface modification. Substrates from noble metals such as gold to semiconductors such as silicon can be modified to exhibit useful biomimetic properties that may not be available on the underlying surface. However, conditions of preparation can lead to wide variability in the attributes (such as roughness) of the generated surface, and can affect subsequent functionalization and applicability. Wider adoption of the routine use of PDA is hindered by this uncertainty of the nature of the prepared surface. We present strategies for greater control of the properties of a PDA coating, which could lead to enhanced predictability of surface attributes and greater utility in surface engineering strategies.

11:40am **BI+AS-MoM11 Breast Cancer Tumor Metabolism Investigated with ToF-SIMS**, ***Lara Gamble***, *B.M. Bluestein, D.J. Graham*, University of Washington

Imaging time-of-flight secondary ion mass spectrometry (ToF-SIMS) was utilized to analyze 21 breast tissue biopsy samples. Eighteen of the biopsy samples were obtained at diagnosis and three after neoadjuvant therapy. Principal component analysis (PCA) was used to reduce the spectral data and determine major variants in the data. PCA analysis of the mass spectral data was used to test for correlation to phenotypes (ER+/PR+, HER2+, and ER-/PR-/HER2-) as well as determine the chemical changes pre and post neoadjuvant therapy.

PCA imaging analysis of the ToF-SIMS tumor tissue images showed that the combination of PCA and ToF-SIMS imaging was able to distinguish different tissue regions that correspond with similar regions in H&E stained serial tissue slices from the same block. Most notably the stromal and cellular regions could be distinguished by imaging PCA. Utilizing regions of interest (ROIs), chemical makeup of stromal regions from different tumor biopsy samples was compared.

While the cellular region showed the clearest separation for pre and post treatment chemistry, spectral PCA analysis of the stromal region shows better separation in scores plots when comparing different tumor types. Chemical analysis of the stromal regions also separated out chemical differences in triple negative tumor samples (with five different triple negative rated tumors investigated to date). In an initial sample set, the pCR (patient complete recovery) and ‘near’ pCR samples both score negatively in the PC2 scores plot. The key fatty acids associated with pCR samples are myristic acid (14:0), palmitic acid (16:0), stearic acid (18:0) and a 20:3 fatty acid as well as fragments of sphingomyelin and various triglycerides. The main peaks associated with the non-pCR samples were fatty acid 18:1 (consistent with oleic acid) along with cholesterol and vitamin E related peaks. Coincidentally these peaks correlate well with the loadings from the pre neoadjuvant therapy treatment samples, while the highest loadings from the pCR samples correlate with the post treatment tissue loadings.

Accelerating Materials Discovery for Global Competitiveness Focus Topic
Room: 114 - Session MG+BI+MS+NS+TF-MoM

Development of Novel Materials
Moderator: Talat Rahman, University of Central Florida

9:00am **MG+BI+MS+NS+TF-MoM3 Molecular Engineering of Dyes for Dye-Sensitized Solar Cells via Rational Design**, ***Jacqueline Cole***, University of Cambridge, UK **INVITED**

Dye-sensitized solar cells (DSCs) have unique attributes that afford them prospective applications as smart windows - windows in buildings that generate electricity from sunlight. This electricity will be fed into a local grid that will create sustainable buildings for future cities.

Materials discovery of new DSC dyes is one of the remaining bottlenecks to technological progress of smart windows. This talk shows we are attempting to overcome this materials bottleneck via two complementary routes to molecular design: (i) a 'top down' approach that uses large-scale data mining to identify brand new classes of DSC dyes [1]; (ii) a 'bottom up' approach that computationally transforms well-known non-DSC dyes into suitable DSC dyes [2,3].

The ‘top down’ approach involves large-scale data-mining to search for appropriate dye candidates [1]. Here, structure-property relationships for DSC dyes have been codified in the form of molecular dye design rules, which have been judiciously sequenced in an algorithm to enable large-scale data mining of dye structures with optimal DSC performance. This affords, for the first time, a DSC-specific dye-discovery strategy that predicts new classes of dyes from surveying a representative set of chemical space. A lead material from these predictions is experimentally validated, showing DSC efficiency that is comparable to many well-known organic dyes.

The ‘bottom up’ approach concerns case studies on families of well-known laser dyes that are transformed into functional DSC dyes using molecular engineering [2,3]. The underlying conceptual idea is to implement certain electronic structure changes in laser dyes, using molecular engineering, to make DSC-active dyes; while maintaining key property attributes of the laser dyes that are equally attractive to DSC applications. This requires a concerted experimental and computational approach; results predict new dye co-sensitizers for DSC applications.

References

[1] J. M. Cole, K. S. Low, H. Ozoe, P. Stathi, C. Kitamura, H. Kurata, P. Rudolf, T. Kawase, "Data Mining with Molecular Design Rules Identifies New Class of Dyes for Dye-Sensitised Solar Cells" *Phys. Chem. Chem. Phys*. 48 (2014) 26684-90

[2] S. L. Bayliss, J. M. Cole, P. G. Waddell, S. McKechnie, X. Liu, "Predicting solar-cell dyes for co-sensitization", *J. Phys. Chem. C* 118 (2014) 14082–14090

[3] F. A. Y. N. Schroeder, J. M. Cole, P. G. Waddell, S. McKechnie, "Transforming benzophenoxazine laser dyes into chromophores for dye-sensitized solar cells: a molecular engineering approach", *Advanced Energy Materials* (2015) DOI: 10.1002/aenm.201401728

10:40am **MG+BI+MS+NS+TF-MoM8 Controlled Spontaneous Nanoscale Patterning of Nonstoichiometric Reconstructions for Catalysis and Light Harvesting**, *J.M. Martirez, D. Saldana-Greco,* University of Pennsylvania*, W.A. Saidi,* University of Pittsburgh*, J.S. Lim, **Andrew Rappe***, University of Pennsylvania **INVITED**

The ability to manipulate the atomic and electronic structure and stoichiometry of surfaces is of utmost importance in optimizing heterogeneous catalysts. A critical requirement in this endeavor is a deep thermodynamic and kinetic understanding of surface reconstruction behavior, under various thermal and chemical constraints. We explore the reconstruction behaviors of Ti- and Mn-based perovskite type oxides: $BaTiO_3$, $PbTiO_3$, and $CaMnO_3$: the former two exhibit ferroelectricity, while the latter undergoes surface-induced magnetic ordering. Due to the characteristic properties of these oxides, we investigate the effect of their switchable polarization (for ferroelectric oxides) and near surface magnetic ordering ($CaMnO_3$) in their surface phase evolution, in addition to the effects of temperature and the chemical potentials of their constituent elements. We find that these oxides undergo surface reconstruction transformations that generally result in enrichment of their catalytically active components (Ti and Mn). These reconstructions show rich bonding and structural motifs that affect the active sites' reactivity and accessibility. Furthermore, these surface transformations, as in $BaTiO_3$ and $PbTiO_3$, can be tuned with the help of an electric field. An applied electric field changes the material's polarization, which then alters the surface electronic properties, and thereby also affects their sensitivity towards stoichiometric changes. In addition to the thermodynamic understanding of the surface reconstructions, we introduce the kinetic tunability of the surface reconstruction. We demonstrate this from a particular surface phase coexistence observed in $BaTiO_3$, namely the $c(2x2)$ and $c(4x4)$, where the diffusion behavior of the TiO units that compose both surfaces strongly dictate their degree of agglomeration. Finally, based on our interest in $CaMnO_3$ (001) surfaces, we have started to explore the more complex $CaMn_7O_{12}$. The electronic properties of this oxide yield interesting physical phenomena including charge ordering, non-collinear magnetism and improper ferroelectricity. We are currently investigating the ground state non-collinear magnetic configuration in this compound and its role on the stability of the charge-ordered state.

11:20am **MG+BI+MS+NS+TF-MoM10 Developing Evolutionary Algorithms for *a priori* Crystal Structure Prediction and Applications towards Novel Pressure-Stabilized Materials**, ***Eva Zurek***, University at Buffalo-SUNY **INVITED**

One way to accelerate the development of new materials is via *a priori* crystal structure prediction (CSP) of hitherto unknown systems, followed by the computation of their properties and determination of promising synthesis conditions. A number of algorithms designed to solve global optimization problems have recently been applied to CSP with much success, and evolutionary algorithms (EAs) have emerged as one of the most promising methods for systems where little or no experimental data is available. Therefore, we have developed the open-source XtalOpt EA for CSP as an extension to the widely used chemical builder and visualizer, Avogadro. In this talk we present new developments within XtalOpt that allow it to successfully predict the structures of crystals with larger and more complex unit cells. Furthermore, we summarize the application of XtalOpt towards the prediction of hydrogen-rich solids with unique stoichiometries that are computed to be stable at pressures that are attainable within diamond anvil cells. The influence of the structure of the hydrogenic lattice on the electronic structure and the propensity for high temperature superconductivity is discussed.

Biomaterial Interfaces
Room: 211D - Session BI+AS-MoA

Characterization of Biological and Biomaterials Surfaces (2)
Moderator: Joe Baio, Oregon State University, Dan Graham, University of Washington

2:20pm **BI+AS-MoA1 Characterization of Protein G B1 Immobilized Gold Nanoparticles using Time of Flight Secondary Ion Mass Spectrometry and X-ray Photoelectron Spectroscopy**, ***Yung-Chen Wang****, *D.G. Castner*, University of Washington

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

In this work, Protein G B1, a protein that will selectively bind to the Fc tail of IgG, was immobilized onto gold NPs (AuNPs) functionalized with maleimide and oligo-(ethylene glycol)(OEG) self-assembled monolayers (SAMs). Protein G B1 was immobilized on AuNPs using either carbonyldiimidazole (CDI) chemistry or maleimide-cysteine interaction. We use the surface sensitive analysis techniques of x-ray photoelectron spectroscopy (XPS) and time of flight-secondary ion mass spectrometry (ToF-SIMS) to characterize the immobilization of protein G B1. Unlike conventional NP characterization techniques such as dynamic light scattering (DLS) and UV/Vis, XPS and ToF-SIMS can provide additional information on the surface elemental composition, protein coverage and orientation.

XPS analysis confirmed the CDI activation of the OEG-SAMs AuNPs by detecting the nitrogen containing active intermediate and the attenuation of gold signal. After incubation with protein, the immobilization of the protein was demonstrated by the increased nitrogen signal on the surface. ToF-SIMS analysis also confirmed the successful functionalization, CDI activation, and protein immobilization by identifying signature secondary ions from each step of the protein immobilization process.

By comparing the ratio of secondary ion intensity originating from opposite ends of the protein, it was possible to determine the orientation of immobilized protein G B1. As expected, the non-site specific CDI chemistry did not lead to a specific protein orientation on the AuNPs. In contrast to CDI chemistry, we expect to control the orientation of the immobilized protein using maleimide functionalized AuNPs and cysteine mutants of Protein G B1 through site-specific carbon-sulfur interaction.

Overall, the systematic characterizations in this study will provide detail information of protein-NP interactions and serve as a platform for controlling the orientation of IgG on AuNPs.

2:40pm **BI+AS-MoA2 Controlled Molecular Mechanisms of Engineered Solid Binding Proteins on Surfaces**, ***Christopher So***, National Research Council postdoc cited at Naval Research Laboratory, *S. Walper*, US Naval Research Laboratory, *R. Stine*, Nova Research, *D.E. Barlow*, *K. Wahl*, US Naval Research Laboratory

Persistent and uncontrolled aggregation of proteins at surfaces remains a major challenge for biocompatibility, fouling, and biosensing. To fully realize the rich properties of proteins at interfaces, a critical link between displayed protein sequence and surface assembly mechanisms is required. Here we use rational protein mutations combined with *in situ* microscopy and spectroscopy methods to demonstrate that manipulation of solid binding and intermolecular interactions by proteins can dictate their surface behavior and induce nanostructure formation. We use streptavidin (SA) as a robust scaffold to control the density and localization of aromatic residues, expected to interact with surfaces such as graphite and graphene through pi-bonding. The surface adapted SAs are generated by placing aromatic side chains of varying polarity (Phenylalanine, Tyrosine, Tryptophan) along three putative permissive sites in a coplanar arrangement. The effects of these mutations on bulk solution structure, surface-associated structure, as well as surface affinity, orientation and spatial organization are studied *in situ* using attenuated total reflectance (ATR) infrared spectroscopy (IR) with linear polarization (LP), fluid-mode atomic force microscopy (AFM), and circular dichroism (CD). We have found that our simple modifications to mSA have little effect on the solution state of the protein, while having a pronounced effect on affinity and secondary structure in the adsorbed state. Through fabricating graphene-coated ATR-IR prisms, we find that unmodified mSA exhibits an ordered beta sheet structure at surfaces, while tryptophan modifications to mSA (Trp-mSA) induces a more disordered structure. We quantify by temporal ATR-IR spectra a *ca.* 4.5x enhancement in sticking probability for Trp-mSA over mSA to graphene. Fluid-mode AFM studies on graphite support a surface-mediated coarsening mechanism: while mSA forms no obvious surface structures, Trp-mSA aggregates and forms islands 10-50 nm in size over the course of an hour. Such disordered SA aggregates provide high affinity sites for slow lateral island growth processes, giving rise to a bi-modal exponential adsorption curve for Trp-mSA but absent in mSA. Ultimately, defining the molecular basis of protein self-assembly and the impact of displayed chemistries at liquid-solid interfaces will enable rationally designed biological surface coatings and engineered biointerfaces with tailorable functionalities.

3:00pm **BI+AS-MoA3 Molecular-Level Surface Analysis Demonstrates the Impact of Detergent Selection on Decellularized Tissues**, ***Adam Taylor***, University of Washington, *L.J. White*, University of Nottingham, UK, *D.M. Faulk*, *L.T. Saldin*, University of Pittsburgh, *D.G. Castner*, University of Washington, *S.F. Badylak*, University of Pittsburgh, *B.D. Ratner*, University of Washington

Decellularized matrix scaffolds may be prepared through a range of techniques. Detergents are frequently used in decellularization protocols due to their ability to solubilize cell membranes and dissociate DNA from proteins. Whilst removal of cellular material is regularly assessed, the impact of detergent selection on extracellular matrix (ECM) structure and composition is less commonly investigated. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is a powerful surface analysis technique to probe biological structures with high mass resolution and surface specificity, and has previously been used to distinguish decellularized ECM by anatomical location or culture conditions. The objective of this study was to utilize ToF-SIMS to investigate the influence of detergent selection upon a representative decellularized tissue, specifically the basement membrane complex (BMC) of porcine urinary bladder matrix (UBM) prepared by treatment with 1% SDS, 4% deoxycholate, 8 mM CHAPS or 3% Triton X-100 for 24 hours.

Principal components analysis (PCA) revealed spectral differences between treatment groups. High mass peaks associated with specific detergent fragments were observed on the scaffolds exposed to SDS and deoxycholate. Peaks indicative of phospholipid membranes were observed in all samples, but to a greater extent with scaffolds not exposed to detergent. We further probed these data sets to investigate how detergent selection impacts proteinaceous ECM components. Using a reduced peak list of known characteristic amino acid fragments, PCA distinguished native bladder tissue from decellularized UBM and highlighted spectral differences between UBM treated with ionic vs. charge-neutral detergents. Notably, the basement membrane surface of UBM prepared with ionic detergents SDS and deoxycholate yielded less intense characteristic peaks from hydrophobic amino acids than UBM treated with charge neutral detergents CHAPS and Triton X-100. Harsher detergents may denature protein structure and break protein-protein interactions through binding of their hydrophobic tail to hydrophobic amino acid residues. Such damage is hypothesized to cause sub-optimal in vitro and in vivo responses. We further examined cell-matrix interactions of human urothelial cells seeded on the BMC of UBM, investigating how detergent exposure affected cell proliferation and permeability of the cell monolayer. An understanding of the effects of detergent exposure on the structure, composition and surface molecular functionality of decellularized scaffolds will facilitate a rational strategy for successful recellularization and subsequent positive clinical outcomes.

3:20pm **BI+AS-MoA4 Liquid Repelling Surfaces Based on Candle Soot are Non-Fouling**, ***Lars Schmüser***, *M. Paven*, *N. Encinas*, Max Planck Institute for Polymer Research, Mainz, Germany, *D.J. Graham*, *D.G. Castner*, University of Washington, *D. Vollmer*, *H.J. Butt*, *T. Weidner*, Max Planck Institute for Polymer Research, Mainz, Germany

Super non-fouling surfaces resist protein adhesion and have a broad field of possible application like implant technology, drug delivery, blood compatible materials, biosensors and marine coatings. Non fouling properties can be fabricated by using liquid repelling surfaces, which

*** ASSD Student Award Finalist**

minimize the contact area of water soluble particles with the non fouling surface. For a surface to be "amphiphobic" – to repel a range of liquids including oil and water – requires a micro to nanometer scale surface roughness in combination with a hydrophobic coating. Paven et al. (*1*) described the production of an amphiphobic surface with remarkably low production requirements. This surface is made of a glass slide, candle soot and 2 commercially available chemicals which are deposited via chemical vapor deposition. Soot deposition and chemical vapor deposition can be applied to a broad variety of substrate shapes, such as the inner wall of tubes. This makes the soot coating a promising tool for blood compatible material design for stents and tubing including applications such as dialysis. Here we present a protein adsorption study onto these amphiphobic surfaces made of candle soot. Since even nanograms per cm^2 levels of protein on biomaterial surfaces can cause detrimental effects for patients, we employed surface sensitive spectroscopic methods, X-ray photoelectron spectroscopy (XPS) and time of flight secondary ion mass spectrometry (ToF-SIMS) to quantify protein adsorption. We did not detect any adsorbed proteins within a detection limit of better than 1 ng/cm² of adsorbed proteins, which demonstrates the super non-fouling property of soot-coated surfaces. Interestingly, the naturally amphiphobic cuticle ("skin") of springtails – small ancient arthropods who live in soil – use an approach very similar to the artificial soot surfaces to achieve protein repellency: Nanometer roughness with hydrophobic coatings. We will discuss XPS, ToF-SIMS and fluorescence microscopy studies quantifying the amount of protein adsorbed onto these surfaces.

1. M. Paven *et al.*, Super liquid-repellent gas membranes for carbon dioxide capture and heart–lung machines. *Nat Commun***4**, (2013).

3:40pm **BI+AS-MoA5 Time-of-Flight Secondary Ion Mass Spectrometry Investigations of the Pancreatic Islet Tumor Microenvironment**, ***Blake Bluestein***, Department of Bioengineering, University of Washington, *F.M. Morrish, D. Hockenbery*, Fred Hutchinson Cancer Research Center, *L.J. Gamble*, Department of Bioengineering, University of Washington

Imaging time-of-flight secondary ion mass spectrometry (ToF-SIMS) provides chemical information with subcellular spatial resolution. In this work, imaging ToF-SIMS is used to analyze tumor microenvironments from mouse model (Myc/p53-/-) biopsies with Myc-dependent inducible and regressible pancreatic β-cell neoplasia. The Myc oncogene is overexpressed in many human cancers and has major effects on cellular metabolism, including lipid metabolism. While imaging ToF-SIMS analysis of tumor tissue will provide a new perspective by visualizing tumor progression/regression, the system itself can also act as a model system for investigating stroma-tumor interactions in cancerous tissues.

Pancreatic tissues were harvested and frozen in optimal cutting temperature (OCT) at 6 days post Myc induction. 4 µm cryosections were serially cut, with one used for H&E staining, one for ToF-SIMS analysis, and another for immunohistochemistry. High mass and high spatial resolution data was acquired with the pulsed 25 keV Bi_3^+ ion beam rastered over a 1 mm x 1 mm area (1280 x 1280 pixels). ROIs of the tumor and stromal tissue were then investigated further with imaging principal components analysis (PCA) to identify peaks that correspond to species of interest. Regions identified by analysis and PCA were cross-referenced against immunohistochemical and H&E images to differentiate tumor areas from the surrounding tissue.

ToF-SIMS data suggests a preferential uptake of fatty acids 18:3 and 18:2 within the tumor. The 6 day Myc-induced islet tumor exhibits a signal of 14:0, possibly a product of de novo fatty acid synthesis within the tumor. The tumor also exhibits an increased localization of sphingomyelin fragments and vitamin E compared to the surrounding tissue. Interestingly, the data shows an absence of Mg^+ within the islet tumor and small, higher signal regions on the periphery of the tumor. These peripheral tumor regions also show an increased, localized signal of CN^-, CNO^-, $C_7H_{10}O^+$, and Fe^+, but further histologic correlations are needed to discern if these structures are inflammatory zones, mitochondrial dense regions, or related to vasculature. Once these localized areas have been defined, a comparison to the chemistry identified by ToF-SIMS may aid in interpreting the Myc oncogene and its effect on pancreatic β-cell neoplasia. PCA was applied to image data and revealed different chemistries within the tumor and surrounding tissue. PCA was also applied to selected tumor region images to spatially and chemically analyze within the tumor to compare chemistries between different tumor sizes, where tumor size is potentially indicative of different tumor stage development.

4:00pm **BI+AS-MoA6 Paper-based Device for Home Phenylalanine Monitoring from a Sample of Whole Blood**, *R. Robinson*, ***Elain Fu***, Oregon State University

Paper microfluidics is a rapidly growing subfield of microfluidics that makes use of paper-like porous materials to create devices for use in low-resource settings. Advantages of the use of porous materials include capillary flow, removing the need for equipment for pumping fluids, and lower material costs compared to traditional microfluidics-based devices composed of silicon or glass. In the current presentation, we describe the development of a paper-based device for home therapy monitoring. For persons with phenylketonuria (PKU), maintaining a restricted level of phenylalanine (Phe) in the body is a continuing challenge. Given the large inter-person variation in Phe metabolism, maintaining nutritional therapy can be a lengthy and difficult process that would be aided by the ability to perform real-time monitoring of Phe levels. Adherence to diet therapy is an even greater challenge for young children, adolescents, and women during pregnancy, and for these groups in particular, rapid feedback could be critical in tailoring a diet to be optimal for each individual. Current tests for Phe require a high-resource laboratory environment and are not suitable for the rapid detection of Phe levels and feedback to the patient that is needed for effective monitoring of PKU therapy. Our solution is a semi-quantitative, paper-based device that is rapid, easy to use, and low cost for patient home use. Device operation is based on simple user steps. The user applies whole blood (40 mL) to a plasma separation membrane, which filters out the cellular components of the blood and releases plasma to two downstream glass fiber pads. There, Phe in the sample and NAD+, catalyzed by the enzyme phenylalanine dehydrogenase, react to form Phe-pyruvate, NADH, and NH_3. At 6 min, the user folds the card closed and fluid is transferred to a final glass fiber detection pad, in which NADH, nitroblue tetrazolium, and methoxy phenazine methosulfate react to form NAD+ and a purple-colored product. The device is read at ~7.5 min. Visibly distinct signal intensities are generated from whole blood samples containing 0 (normal), 3.75 (slightly elevated), and >7.5 mg/dL (substantially elevated) spiked-in Phe. Thus, this test may allow users to distinguish between normal versus elevated levels of blood Phe on a rapid timescale that could inform their diet therapy. The assay exhibited reasonable reproducibility with coefficients of variation between 11 and 24%. A focus of the presentation will be on the controled patterning and drying of biochemical reagents in porous materials for later rehydration on the device, which is key to the robust operation of the device.

4:20pm **BI+AS-MoA7 Multivalent Probes for Tuneable 'Superselective' Targeting**, *G.V. Dubacheva*, CIC biomaGUNE, Spain, *T. Curk*, University of Cambridge, UK, *R. Auzély-Velty*, Cermav, Cnrs, France, *D. Frenkel*, University of Cambridge, UK, ***Ralf Richter***, CIC biomaGUNE & University Grenoble Alpes, Spain **INVITED**

A basic requirement in biomedical research is the ability to specifically target cells and tissues. Targeting typically relies on the specific binding of a 'ligand' on a tailor-made probe to a 'receptor' on the desired cell or tissue. Conventional probes efficiently distinguish a cell surface displaying the receptor from others that do not. They exhibit limited selectivity, however, when the surfaces to be distinguished display a given receptor at different densities.

Based on theoretical arguments, it has been proposed that multivalent probes that bind several receptors simultaneously can sharply discriminate between different receptor densities. Here, we present an experimental model system that demonstrates such 'superselective' targeting. To this end, recent achievements of synthetic chemistry and surface characterization were combined to create well-defined multivalent polymers and surfaces that interact with each other through highly specific host/guest interactions. With this model system, we show that superselective binding can be tuned through the design of the multivalent probe to target a desired density of binding sites. We develop an analytical model that provides simple yet quantitative predictions to tune the polymer's superselective binding properties by its molecular characteristics such as size, valency, and affinity.

This work opens up a route toward the rational design of multivalent probes with defined superselective targeting properties for practical applications in life sciences (analytics, diagnostics and therapy). It also provides mechanistic insight into the regulation of multivalent interactions in biology, notably the superselective targeting of the extracellular matrix polysaccharide hyaluronan to its main cell surface receptor CD44.

5:00pm **BI+AS-MoA9 Targeted Ultrathin Silica Nanoshells as HIFU Sensitizing Agents for *In Vivo* LnCAP Prostate Tumor Removal**, ***James Wang***, *A. Liberman, C. Barback, S. Blair, R. Mattrey, W. Trogler, A.C. Kummel*, UC San Diego

Diagnostic ultrasound (US) is a prevalent medical imaging modality due to its low-cost, high resolution, and therapeutic capability when coupled with high intensity focused ultrasound (HIFU) systems. 500 nm rigid silica ultrathin nanoshells were synthesized as a chemically stable US tumor marking contrast agent with continuous *in vivo* US imaging lifetime. Iron (III) was included into the silica shell network to promote biodegradability from serum transferrin proteins. It was shown previously that the removal of iron from the silica shell network via transferrin fragments the nanoshells for effective biodegradation. Folate was conjugated to the surface of the

silica nanoshells via the 3-aminopropyltriethoxysilane (APTES) linker. Folate has been shown in the literature to bind to prostate specific membrane antigen (PSMA) with a high binding affinity due to folate hydrolase activity. Conjugating the silica nanoshell surface with folate targets the ultrathin silica nanoshells towards the LnCAP tumor where PSMA is significantly up-regulated. The surface modified ultrathin silica nanoshells were filled with liquid perfluorocarbon (PFC) which underwent acoustic droplet vaporization (ADV) during US insonation. The phase transition of PFC from liquid to vapor generated a large amount of PFC microbubbles that created contrast during US imaging. *In vitro* experiments with US have demonstrated that the ultrathin silica nanoshells can be imaged for at least 3 hours under color Doppler imaging, exhibiting a continuous US imaging lifetime. *In vivo* experiments have shown that folate conjugated silica nanoshells were able to accumulate and persist within the tumor region for up to 12 days post-injection, observable with US imaging. Surface conjugation with polyethylene glycol (PEG) increased the ultrasound signal at the tumor by increasing the particles accumulating at the tumor site. When exposed to high intensity focused ultrasound (HIFU), the particles were able to enhance the HIFU power and liquefy tumor tissue. With particles present, the HIFU duty cycle can be lowered to 2 %, minimizing tissue thermal deposition. By synthesizing ultrathin silica nanoshells with a folate-conjugated surface, it is has been demonstrated that folate-conjugated ultrathin rigid silica nanoshells can accumulate in the LnCAP tumor persistently for 12 days. PEGylation of the particles further increase the particle accumulation concentration in the tumor, acting as a HIFU sensitizing agent for ultrasound histotripsy. Through intelligent surface modification, liquid PFC filled silica particles can act as a multi-functional theranostic agent for ultrasound diagnosis.

5:20pm **BI+AS-MoA10 Transparent Field Effect Sensor with Nanostructured Amorphous In-Ga-Zn-O Wires**, ***Xiaosong Du***, *Y. Li*, *J. Motley*, *G. Herman*, Oregon State University

Amorphous In-Ga-Zn-O (a-IGZO) materials have a wide range of applications in high performance electronic devices, from the active material in thin film transistors for flat-panel displays and as the transducer for field effect sensors. A key benefit of a-IGZO over amorphous silicon is that it enables low processing temperatures, while retaining relatively large electron mobilities, low operating voltages, and very low off currents. In this study, we have fabricated a-IGZO films with well-defined nanostructures using colloidal lithography. These nanostructured a-IGZO films were then patterned into wires using electrohydrodynamic printing of an etch resist followed by wet chemical etching. We have characterized these nanostructured a-IGZO wires using field effect test structures to evaluate their electronic properties. To improve selectivity and stability of the nanostructured a-IGZO wires for sensing applications we have functionalized the back-channel surface with molecular receptors, where glucose oxidase was successfully attached as a sensing enzyme. Depletion/accumulation of carriers in the a-IGZO back-channel was observed upon reaction of the glucose oxidase with the analyte, which leads to significant changes in the sensors electronic signals. Continuous monitoring of glucose concentration can be achieved by measuring a direct change in channel conductance, turn on voltage shift, and/or electrical hysteresis. The results obtained for nanostructured a-IGZO wires will be compared to blanket a-IGZO films, where we have found that the nanostructured a-IGZO wires provide a significant enhancement in sensitivity to subtle changes in glucose concentrations in physiological buffers. These results provide insight into a route to develop low-cost transparent biochemical sensors based on the emerging a-IGZO technology.

Plasma Science and Technology
Room: 210A - Session PS+BI+SM-TuM

Plasmas for Medicine and Biological Applications
Moderator: Satoshi Hamaguchi, Osaka University, Japan

8:00am **PS+BI+SM-TuM1 Glow-Discharge Plasma Applications in the Biomedical Sciences: Frontiers and Horizons**, ***Buddy D. Ratner***, University of Washington **INVITED**

Plasma treatments for biomedical applications have been explored since the early 1960's, possibly earlier than that. Plasma treatments for medical devices and for materials used in biotechnology are now widely used and have improved he performance and safety of many devices. A few advanced technologies for biomedicine exploiting plasma deposition of organic thin films will be described. These include non-fouling surfaces, thermally responsive surfaces, biodegradable surfaces, rate-limiting barriers for controlled release and surfaces that permit the growth of precision polymeric brushes by atom transfer radical polymerization (ATRP). Frontiers for plasma deposition include better control of deposition chemistry, strategies to deposit unusual chemistries and depositions that integrate biological molecules and plasma-deposited chemistries.

8:40am **PS+BI+SM-TuM3 Non-Equilibrium Plasmas in Contact with Solutions: Biological Interactions and Material Synthesis**, ***Peter Bruggeman***, University of Minnesota **INVITED**

Non-equilibrium atmospheric pressure plasmas interacting with liquids offer a unique source of highly reactive chemistry beneficial for many applications in biology, medicine and advanced materials manufacturing. It has been shown that these plasma-liquid interactions can lead to inactivation of bacteria and virus and the synthesis of nanoparticles. Nonetheless the underpinning mechanisms are at least poorly understood. My group has been strongly involved in the study of the reactive chemistry of a well-characterized RF driven atmospheric pressure plasma jet and its interaction with liquids.

The presentation will highlight some examples of reaction pathways responsible for the inactivation of bacteria and virus in solution and the synthesis of silver nanoparticles from $AgNO_3$ solutions. I will illustrate the importance of reactive plasma chemistry induced by neutral gas phase reactive species such as OH, H_2O_2 NO, O, H, O_3 and singlet oxygen. In addition, we will show that UV emission, which is often neglected as a possible mechanism, can be important in some cases.

9:20am **PS+BI+SM-TuM5 Plasma Biomedicine and Reactive Species**, ***David Graves***, University of California at Berkeley **INVITED**

Low temperature plasma research directed towards biomedical applications such as sterilization, surgery, wound healing and anti-cancer therapy has seen remarkable growth in the last 3-5 years, but the mechanisms responsible for the biomedical effects have remained mysterious. It is known that CAP readily create reactive oxygen species (ROS) and reactive nitrogen species (RNS). Other potentially important plasma-generated species effects include charges, fields and photons. ROS and RNS (or RONS), in addition to a suite of other radical and non-radical reactive species, are essential actors in an important sub-field of aerobic biology termed 'redox' (or oxidation-reduction) biology. I will review the evidence suggesting that RONS generated by plasmas are responsible for their observed therapeutic effects. In addition, I will present several ideas about the most likely biological response mechanisms that are likely involved in therapeutic plasma biomedicine.

11:00am **PS+BI+SM-TuM10 Cold Atmospheric Plasma for the Treatment of Chronic Infected Wounds**, ***Jennifer Granick***, *V.S.S.K. Kondeti, A. Truong, R.C. Hunter, P.J. Bruggeman*, University of Minnesota

Two percent of the US population suffers from chronic non-healing wounds, often complicated by antibiotic-resistant bacterial infections, and the staggering cost of wound care exceeds $50 billion per year. Of increasing concern are multi-drug resistant bacteria, including methicillin-resistant *Staphylococcus aureus* and multi-drug resistant *Pseudomonas aeruginosa* infections. Within wounds, these bacteria adopt a biofilm-like state, and become notoriously recalcitrant to conventional antibiotic therapies. Currently approved products for the treatment of chronic wounds have not proven to be a panacea due to the complex nature of wound healing.

The ideal therapy for chronic, infected wounds would be non-painful, bactericidal without risk of resistance, able to break-up biofilms and enhance wound healing. Recently, there has been interest in the use of cold atmospheric plasma (CAP) technology for the treatment of infections and non-healing wounds. The technology could potentially fulfill the requirements of an ideal wound healing therapy. CAP devices producing ionized gas have been developed that can operate in ambient air and that are safe to touch without any pain sensation. CAP generates a complex mixture of reactive oxygen and nitrogen species (RONS) that are able to kill bacteria, while stimulating host cell growth. CAP has the potential to combine antiseptic and wound healing capabilities in a single treatment procedure and could eliminate the risk of cytotoxicity present in many current treatment methodologies for infected wounds.

The effects of CAP on bacteria and mammalian keratinocytes and fibroblast cells have been evaluated *in vitro*. Our prototype argon CAP device produces antibacterial effects on planktonic bacterial cultures of *S. aureus* and *P. aeruginosa* at a maximal treatment duration of 20 ml/min at conditions that do not impact cell viability of fibroblasts and keratinocytes *in vitro*. We have also recently demonstrated that CAP is effective in reducing the viability of *P. aeruginosa* biofilms grown *in vitro*. When grown on the surfaces of PVC microtitre plates for 48 h, argon-air derived CAP treatment of established biofilms showed a 95% reduction in cell viability, as determined by resazurin fluorescence, relative to untreated controls, when treated at a dose of 30min/ml, which is similar to the treatment time equivalent of mammalian cell treatment.

As part of the early investigations of the use of CAP treatment as a viable therapy for chronic-infected wounds, the presentation will focus on bacterial biofilm reduction by CAP treatment *in vitro* as well as in a mouse skin wound model. The effects on mouse host cells will be examined.

11:20am **PS+BI+SM-TuM11 Humidity Effect on the Surface Modification and Bio-Deactivation of Lipopolysaccharide (LPS) by Surface Micro-Discharge (SMD)**, ***Pingshan Luan***, *E.A.J. Bartis, A.J. Knoll*, University of Maryland, College Park, *C. Anderson, D.B. Graves*, University of California at Berkeley, *J. Seog, G.S. Oehrlein*, University of Maryland, College Park

The surface micro-discharge (SMD), due to its scalable large area and flexibility of working gases, has great potential for many applications such as material processing and plasma medicine. The SMD normally works under ambient air conditions that contain not only N_2 and O_2 but also water vapor which can have a large impact on both the discharge behavior and plasma gas chemistry. In this study, we evaluate the effect of ambient humidity on SMD in various N_2/O_2 mixtures and the subsequent effect on the surface modification and bio-deactivation of lipopolysaccharide (LPS). Electrical behavior and optical emission spectrum (OES) of the SMD source were studied. We found that while the additional moisture did not help create strong OH (A-X) emission from SMD, it resulted in lower plasma density and extra power dissipation. We used X-ray photoelectron spectroscopy (XPS) to characterize the surface modification of LPS after treatment. We found that all SMD-treated LPS surfaces show oxygen uptake and formation of surface-bound NO_3, while the amount of these modifications was strongly dependent on the ambient gas composition. By comparing the XPS of wet-treated (50% relative humidity at 20 °C) surfaces with their dry counterparts, we find that the water vapor reduces both the oxygen uptake and surface NO_3 formation, and that the difference between wet- and dry-treated surfaces decreases with the increasing fraction of ambient N_2. When the N_2 fraction is up to 80% (synthetic air), the LPS surface shows comparable amount of modification with or without humidity. Among all the dry- and wet-N_2/O_2 mixtures, the dry 5% of N_2 ambient shows the greatest modification rate. We also evaluated the bio-deactivation efficiency of the SMD on LPS using enzyme-linked immunosorbent assay. Similar to surface modification, we found that the bio-deactivation rate of SMD in dry ambient is much higher than that of SMD in their wet counterparts, except the synthetic air condition which shows similar amount. The authors gratefully acknowledge financial support by the US Department of Energy (DE-SC0001939) and National Science Foundation (PHY-1004256 and PHY-1415353).

11:40am **PS+BI+SM-TuM12 Plasma Diagnostics of Dielectric Barrier Discharge within a Sealed Meat Package**, ***Vladimir Milosavljevic***, Dublin Institute of Technology, Ireland, *J. Lalor, P. Bourke, P.J. Cullen*, Dublin Institute of Technology

Atmospheric pressure, non-thermal plasma DBD is increasingly used in many processing applications. Despite their widespread usage, it remains largely unknown whether cold atmospheric plasma DBD maintains similar characteristics, such as gas temperatures and particle flux, when they breakdown while arcing or whether they possess different operating modes. It is essential for laboratory/industrial adoption of such plasmas that plasma diagnostics of the process are provided. Optical emission and absorption

spectroscopy have been used as diagnostics techniques with an added avantage of their non-intrusive nature.

The type of operating gas influences the stability of atmospheric plasma discharges. In this study is used a sealed meat package filled with one of two gas mixtures: O_2-CO_2 and N_2-CO_2 . Different concentrations of nitrogen or oxygen and carbon-dioxide could cause the transition from a stable homogeneous discharge into a filamentary discharge. Atmospheric plasma discharges are affected by the surrounding ambient air, and for sealed packages from transfer between the package gas and the surrounding ambient atmosphere. In the vast majority of atmospheric plasma discharges, reactive nitrogen species dominates the ionic composition of atmospheric discharge and has an impact on the breakdown voltage. When N_2 is added/mixed with CO_2 plasma discharges, the CO_2 emission lines are significantly quenched. In the case of O_2-CO_2 chemistry, nitrogen is not a carrier gas but it still present in the package due to contaminant transfer with the surrounding ambient air, modifying the plasma chemistry in the package. The plasma's optical spectrum in O_2-CO_2 chemistry shows molecular oxygen, nitrogen and OH peaks. Oxygen could come from the ambient air, the O_2-CO_2 gas mixture or from humidity in the package. Electron impact excitation of molecular oxygen, at low collision energies, is of particular importance because of its role in atmospheric physics and has been objective of this study. In our study we have also recorded the O_3 band-head that belongs to the Hartley Band. Ozone plays very important role for the biological aspect of this study and shows the highest change in a concentration with the processing time. Combining the results from spectral radiation in the package provides an electron energy distribution function. The study includes a detailed experimental investigation of the spatial and temporal spectroscopic data and links them with plasma kinetics.

The research leading to these results has received funding from the European Union´s Seventh Framework Programme managed by REA Research Executive Agency (FP7/2007-2013) under Grant Agreement number 605125.

12:00pm **PS+BI+SM-TuM13 Low-Temperature Plasma Surface Modification of Porous Polymeric Materials for Environmental and Medical Applications**, ***Michelle Mann***, *A. Pegalajar-Jurado, E.R. Fisher*, Colorado State University

Three-dimensional (3D) porous polymeric materials are widely used in biomedical and environmental applications, such as wound healing and water filtration. Polymers used for these applications are chosen for their mechanical properties and porosity, yet the surface properties, such as hydrophobicity, limit their use in aqueous environments. For example, polymeric ultrafiltration membranes typically require pretreatment before use and tend to foul due to adsorption of biomolecules in the watercourse. Bioresorbable polymeric scaffolds used for wound healing are prone to attachment of bacteria, leading to prolonged infection at the wound site. These issues can be addressed with two simultaneous approaches. To prevent bacterial attachment and proliferation, antibacterial properties can be introduced into the materials via incorporation of biocidal agents or antibacterial coatings. Moreover, surface modification can be used to create more compatible polymeric materials by increasing wettability. Through plasma processing, tailored surface modification can be achieved while retaining the morphology and bulk properties of the material. Here, we will describe the modification of ultrafiltration polysulfone (UPS) membranes and poly(ε-caprolactone) (PCL) scaffolds to create low-fouling materials with enhanced wettability. $H_2O_{(g)}$ plasma treatment of UPS membranes and PCL scaffolds results in materials with significantly enhanced wettability while scanning electron microscopy (SEM) images demonstrate porous morphology is maintained. X-ray photoelectron spectroscopy (XPS) data show an increase in surface oxygen content throughout the membrane cross-section after plasma treatment, and modified UPS membranes demonstrate a significant increase in initial water flux. In addition, the performance of modified UPS membranes in the filtration of biological solutions will also be discussed. Furthermore, the biological performance of PCL scaffolds incorporated with various biocidal agents will be presented along with biocidal agent leaching studies.

Applied Surface Science
Room: 212D - Session AS+BI-TuA

Challenges in the Characterization of Polymer/Organic/ Biological Systems

Moderator: Bonnie Tyler, National Physical Laboratory (NPL), Jeffrey Fenton, Medtronic plc

2:20pm **AS+BI-TuA1 ASSD 30th Anniversary Lecture: 30 Years (ToF-)SIMS of Organic Materials: from Monolayer to 3D Microarea Analysis**, ***Birgit Hagenhoff***, Tascon GmbH, Germany **INVITED**

The presentation will follow the development track and the learning curve of (ToF)-SIMS for the characterization of organic materials.

Starting in the early 70s of the last century, when Alfred Benninghoven, based on research results for Ag catalyst samples, started into what would later become the wide-spread field of Static SIMS, the talk will cover the following areas

· Static SIMS: early beginnings

· Static SIMS: the importance of noble metal substrates

· Static SIMS: from quadrupoles to Time-of-Flight Analyzers

· Charge compensation: the gateway to bulk analysis

· Organic Imaging: limits of lateral resolution

· Cluster ion guns: getting sub-µm using Au and Bi LMIGs

· The road to organic depth profiling: SF_5^+ and C_{60}^+ sputtering

· Organic depth profiling: the use of Ar cluster ion sputtering

· 3D Microarea Analysis: Status-quo and challenges for the future

3:00pm **AS+BI-TuA3 Characterization of the Buried Interface between a Bacterial-Biofilm Resistant Coating and a Silicon Catheter by using Gas Cluster ToF-SIMS and Raman Microscopy**, ***Bonnie Tyler***, National Physical Laboratory (NPL), UK, *A.L. Hook, M.R. Alexander,* University of Nottingham, UK, *A. Giovannozzi,* INRIM, *A. Pelster, H.F. Arlinghaus*, University of Muenster, Germany

Thin film coatings are widely used in medical devices in order to improve the biological response to the device without compromising its mechanical performance. These coatings are frequently organic in nature and are applied to a wide range of substrate materials. The challenge of ensuring a stable linkage between the coating and the underlying substrate is common to all of these systems. Defects at the interface between the coating and the substrate can result in failure of the medical device with potentially serious consequences. The study of buried interfaces in organic systems, like those common in medical devices, has in the past been a nearly intractable problem because sputter depth profiling with monatomic ions destroys the relevant chemical information. Recent advances in Gas Cluster Ion Beam technology have opened up exciting possibilities to better understand these buried interfaces. In this work, we have studied adhesion between an bacterial-biofilm resistant polymer coating and an oxygen plasma-treated polymer surface using Argon Cluster 3D-imaging Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and Raman Microscopy. Analysis has been performed in both dry and hydrated state. The analysis provided several analytical challenges. Because the overlayer was not of uniform thickness, a depth scale correction was needed to reduce misleading artefacts at the interface. Analysis of the hydrated catheters required cryogenic analysis conditions. From the ToF-SIMS data we have been able to observe the presence of particles, cracks and water, and to monitor hydrophobic recovery at the interface between the coating and the catheter. Raman analysis has provided complementary information on the Van-Der-Waal interactions at the interface. The results have been compared to mechanical adhesion tests and help to provide a better understanding of the processes that influence adhesion between the coating and the catheter.

3:20pm **AS+BI-TuA4 How to Measure Reaction Rates on Surfaces?: Ambient Mass Spectrometry and XPS to Study the Rate of Organic Reactions on Functionalized Surfaces.**, *R. Sen, J. Escorihuela,* ***Han Zuilhof***, Wageningen University, Netherlands

Ultrathin coatings like self-assembled monolayers and polymer brushes have been used for a wide variety of studies and applications. Reactions within such monolayers or brushes are often difficult to follow, and their rates are typically not measurable: apart from a handful of cases in which electrochemical methods have been used, no rigorously measured kinetics on reactions within e.g. self-assembled monolayers are available. The current presentation will outline a generic approach, combining ambient mass spectrometry and XPS, to fill this gap, and provide a truly generic method to measure the rate of intramonolayer or intrapolymer organic reactions. Examples will include a variety of so-called click reactions, as these display a very high potential in materials science.

4:20pm **AS+BI-TuA7 Surface versus Bulk Chemistry of Reverse Osmosis Membranes**, ***Tamlin Matthews***, *R. Cieslinski, M. Paul, A. Roy*, The Dow Chemical Company

The polyamide layer of reverse osmosis (RO) thin-film composite membranes is ~100 nm thick. Separation of this thin layer from the supporting layers is a complex process and can only be done chemically, which results in a fragile polyamide layer and makes characterization challenging. X-ray photoelectron spectroscopy (XPS, near-surface) and Rutherford backscattering spectrometry (RBS, bulk) have been applied to characterize the polyamide layer, without the need to separate polyamide from the supporting layers. The combination of these methods allows the comparison of bulk vs. near-surface carboxylic acid content, which is a driver in RO performance. Additionally, elemental composition, thickness, and roughness of the RO membranes can be compared in systems with systematically changed monomers. This talk will focus on how the application of XPS and RBS can be used together for surface vs bulk chemical composition.

4:40pm **AS+BI-TuA8 Effect of Deep UV Irradiation on Polyester Family Polymers**, ***Lopamudra Das***, *M.J. Kelley*, College of William and Mary

In films and fibers, desired attributes of these polymers are often surface-mediated. Radical chemistry launched by deep UV offers attractive opportunities for surface modification, free of the environmental burdens of wet chemistry. We report the effect of 172 nm irradiation in the absence of oxygen on PET, PTT, PBT and PEN films, observed by FTIR, XPS and ToF-SIMS. Initial findings include carboxylic acid production and a loss of carbonyl carbon. To better understand surface reactivity, samples of each polymer were treated with silver trifluoroacetate or with heavy water.

5:00pm **AS+BI-TuA9 Going beyond State of the Art in SIMS Imaging in the Life-Sciences and for Organic Devices**, ***Ian Gilmore***, National Physical Laboratory, UK **INVITED**

In this celebratory 30th year of the Applied Surface Science Division, we can be sure that secondary ion mass spectrometry will feature strongly in the "Top-30" hit-parade. For example, SIMS, with its ability for high-sensitivity analysis has played an important role in the semiconductor industry measuring dopant profile concentrations. The rapid growth of the semiconductor industry is popularly summarised by Moore's law[1]; which shows that over the last five decades the number of transistors in a chip doubles every two years. Recently, Scannell et al[2] show that the reverse is the case for the pharmaceutical industry and the number of drugs per billion dollars of investment has dropped from around 50 to less than 1 over a similar timescale. They call this "Eroom's" law, Moore's law in reverse.

Analogously to the semiconductor industry, SIMS could now provide important benefits to the pharmaceutical industry. The challenge here is to measure where drugs go at the cellular level, even within specific organelles, to answer long-standing questions about whether drug concentrations are sufficiently high in the right places to have a therapeutic effect, or if the medicine is lodging within cellular components and causing toxicity. If anomalies were spotted earlier it might help to explain toxicities or lack of efficacy of a medicine and reduce costly late-stage failures. [3,4]

To meet this challenge, NPL in collaboration with GlaxoSmithKline, ION-TOF GmbH, Thermo Fisher Scientific and the University of Nottingham is building a revolutionary new instrument, the 3D nanoSIMS,[4] which incorporates the powerful Thermo Scientific™ Orbitrap™ mass analyzer for high-performance identification of drugs and metabolites. The stunning capability of SIMS to study drugs in tissue and cells will be highlighted and the characteristics of the new instrument will be outlined. The benefits of combining SIMS with the new generation of ambient mass spectrometry techniques and the rapidly rising challenge of Big Data will also be discussed.

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[3] C T Dollery, Clinical Pharmacology & Therapeutics, (2013); 93, 263–266.

[4] The 3D nanoSIMS project, http://www.npl.co.uk/news/3d-nanosims-label-free-molecular-imaging [2013 [http://www.npl.co.uk/news/3d-nanosims-label-free-molecular-imaging%20%5b2013]]

5:40pm **AS+BI-TuA11 Can *In Situ* Liquid SIMS Provide Enough Signals for Biology and Environmental Research?**, ***Zihua Zhu***, *Y. Zhou, X. Hua, J. Yu, J.E. Evans, D. Lao, X.-Y. Yu*, Pacific Northwest National Laboratory

In situ liquid SIMS is an R&D 100 award winner that was developed in PNNL since 2010. System for analysis at the liquid vacuum interface (SALVI) coupled with liquid SIMS has proven to be a promising new tool to provide molecular information at solid/liquid interfaces.[1,2] However, our initial data showed that signals of secondary positive ions were too low to be usable in some cases.[2,3] In addition, it was difficult to obtain strong negative molecular ion signals with m/z > 100.[2] These two drawbacks make SIMS community wonder the potential applications of this new analytical approach. In this presentation, we report that strong positive and negative molecular signals are achievable after we optimize the SIMS experimental conditions. Our results show that both beam current and primary ion species (e.g., Bi^+, Bi_3^+, Bi_3^{2+}) play important roles in achieving optimal molecular signals at the liquid interface. Data sets from three model systems, including an ionic liquid, water, and several liposome solutions, will be presented. In addition, beam damage at the liquid surface will also be discussed.

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6:00pm **AS+BI-TuA12 Fundamental Metrology for Tissue Imaging by SIMS - A Study of Cholesterol and Determination of the Argon Cluster Sputtering Yield**, *P.D. Rakowska, M.P. Seah,* ***Rasmus Havelund***, *I.S. Gilmore*, National Physical Laboratory, UK

Secondary Ion Mass Spectrometry (SIMS) has become an invaluable tool to study organic and biological samples. An important biological application is in the analysis of mammalian cellular membranes. Considerable contribution to the field comes with the use of large cluster ion beams, and in recent years the application of argon gas cluster ion beam has emerged as the prevailing method.

Cholesterol, as a key component of nearly all mammalian cell membranes, is of particular interest. It alters the physical properties of the membranes, interacts with neighbouring lipids and proteins and is involved in numerous biomolecular processes. Being able to detect, identify and characterise the distribution of cholesterol in biological samples has vast implications in medical sciences. To do this, we need to underpin the basic metrology involved. It is important to evaluate cholesterol sputtering yields for argon cluster sputtering over a range of energy and cluster sizes so that a general description of the molecule behaviour may be established.

In this study, we compared the use of $C_{60}^{+(+)}$ and Ar_n^+ as sputtering ions for depth profiling of cholesterol thin films. Films of different thicknesses were prepared by thermal evaporation and the sputtering yields of cholesterol were measured from depth profiles made using 2.5 to 20 keV Ar_{1000}^+ and Ar_{5000}^+ and 10 and 20 keV $C_{60}^{+(+)}$ sputtering beams. We show that, at room temperature, the $C_{60}^{+(+)}$ ions caused significant damage but gave a well-behaved depth profile whereas Ar_n^+ gas clusters left the material undamaged but the very clean layer readily restructured making the profiles much more complex. This restructuring does not occur at room temperature normally but results from the actions of the beams in the sputtering process for profiling in SIMS. The sputtering yields from these restructured films are up to twice that for material not so restructured. Good profiles may be made by reducing the sample temperature. This is likely to be necessary for many lower molecular weight materials (below 1000 Da) to avoid the movement of molecules. The yields for both $C_{60}^{+(+)}$ and Ar_n^+ fit the universal yield equation [1]. Our results show that considerable differences can occur between the measurements performed with the two ion clusters, affected, in addition, by factors such as sample temperature or exposure to light. These will be discussed.

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Biomaterial Interfaces
Room: 211D - Session BI-TuA

Cells and Microorganisms at Surfaces
Moderator: Axel Rosenhahn, Ruhr-University Bochum, Markus Valtiner, Max-Planck Institut für Eisenforschung GmbH

2:20pm **BI-TuA1 Control of Surface Physical Properties for Effectively Promoting and Maintaining Cell Clusters such as Stem Cell Colonies at Interfaces**, ***YingChih Chang***, *P.Y. Yeh*, Academia Sinica, Taiwan, Republic of China

A series of biomimetic polypeptide layer-by-layer conjugated supported lipid bilayers as lubricated thin films were constructed and characterized for their physical properties under cell-surface contact. The construct was used to promote the selection and maintenance of stem/progenitor cell colonies from the primary culture in one example, and to isolate circulating epithelial cells from human peripheral blood in another example. The adsorption of serum proteins, and nonspecifically bound cells are clearly reduced when a lipid coating was employed as the underneath layer, as studied by quartz-crystal microbalance with dissipation, and immunohistochemistry.

2:40pm **BI-TuA2 Immobilized Liquid Layers for Controlled Bacterial, Fungal, and Mammalian Cell Attachment**, ***Caitlin Howell***, *N. Juthani, N. MacCallum, Y. Kovalenko, S. Kelso, J. Lin, C. Nemr, P. Kim, J. Aizenberg*, Harvard University

Immobilized liquid layers, inspired by the *Nepenthes* pitcher plant, are emerging as a powerful new approach to the control of cellular attachment to surfaces. These layers present a "moving target" for the adhesion of fouling organisms and have shown promise as biofilm-resistant coatings. Tests on clinically-relevant bacteria and fungi such as *E. coli*, *S. aureus*, *S. epidermidis*, *P. aeruginosa*, and *C. albicans*, have shown significantly decreased adhesion without toxic effects. Immobilized liquid layers also show promise as tunable platforms for the attachment and detachment of mammalian cells, opening new directions in the area of tissue engineering. Finally, these surfaces can be made to be continuously self-replenishing through the incorporation of a bio-inspired vascular system, extending their longevity. We anticipate that these layers will prove a unique and adaptable platform for controlling the attachment of cells on surfaces.

3:00pm **BI-TuA3 Quantitative Characterization of Bacterial Cells Mixed with Nanoparticles**, *P.M. Martins, A.R. Silva,* University of Minho, Portugal, *I.M. Pinto, C. Sousa,* International Iberian Nanotechnology Laboratory, Portugal, *S. Lanceros-Méndez,* University of Minho, Portugal, ***Dmitri Petrovykh***, International Iberian Nanotechnology Laboratory, Portugal

The unique physicochemical properties of nanoparticles (NPs) are the basis for their potential applications in nanomedicine and biomedical research, whereby NPs interacting with cells provide a means for detecting, monitoring, or controlling cell functions via non-biological (magnetic, electronic, optical, mechanical) properties of NPs. When considering interactions of NPs with bacterial cells, the single-digit micrometer or even submicron sizes of typical bacteria have to be taken into account, in addition to their biological properties. For mixed suspensions of bacteria and NPs, therefore, both biological and physicochemical properties are involved in creating the corresponding micrometer- and nanometer-scale biointerfaces. While some methods are available for characterizing the biological properties of bacteria in suspension, reliable characterization of their physicochemical properties remains challenging, even for basic parameters, such as size distribution and concentration. *Staphyloccus aureus* bacteria are a convenient model system for developing and validating such physicochemical analysis of bacterial cells, due to their robust viability and nearly-spherical shapes with diameters of approximately 1 micrometer. We will describe the use of multiple complementary techniques, including flow cytometry, high-resolution microscopy, and optical spectroscopy, scattering, and absorption, for quantitative characterization of *S. aureus* suspensions and for extending these methods to investigations of NP-bacteria interactions.

3:20pm **BI-TuA4 Tethered Antimicrobial Peptide WLBU2 for Capture of Circulating Bacteria and Endotoxin in Sepsis**, ***Ramya Raman***, *K.F. Schilke*, Oregon State University

Severe sepsis is a blood infection that affects over 750,000 people each year in the US alone, killing 28-50% (more than prostate cancer, breast cancer and AIDS combined). Symptoms result from a highly dysregulated immune response, which, if untreated, can lead to multiple organ failure and death. Currently, treatment uses wide-spectrum antibiotics, but this is hindered by

the rise of antibiotic-resistant 'superbugs'. One potential novel treatment is a high-throughput microfluidic hemoperfusion device, which specifically removes circulating bacteria and cell wall fragments ("endotoxin") from blood. A device with a biocompatible and bioactive surface coating could selectively bind circulating bacteria and endotoxins from blood, enabling rapid, safe treatment of bacterial sepsis. WLBU2 is an α-helical, cationic amphiphilic peptide (CAP) with 13 positively-charged arginine and 11 hydrophobic tryptophan/valine residues oriented on opposite faces of the helix. WLBU2 has high anti-microbial potency against a variety of pathogens, and integrates into bacterial cell membranes (Deslouches, et al. J. Antimicrob. Chemother. 2007; 60: 669-672). Biocompatible, non-fouling surfaces can be made by covalently tethering a dense brush of polyethylene oxide (PEO) polymer chains at the surface. Longer PEO tethers terminated with WLBU2 should enable increased mobility and solvent accessibility to tethered WLBU2, allowing it to bind bacterial cells, without compromising the biocompatibility of the coated surface. Poly-L-arginine and poly-L-Lysine served as controls for charge effects, and Cys-WLBU2 served as a tether-free control. The surface chemistry is consistent with peptide immobilization at the surface using X-ray Photoelectron Spectroscopy (XPS). Atomic Force Microscopy (AFM) images demonstrated the uniform coverage of gold surfaces with PEO and peptides. Scanning Electron Microscopy (SEM) and Quartz Crystal Microbalance with Dissipation (QCMD) were used to demonstrate capture of bacteria at the coated surfaces. Tethered WLBU2 may more effectively bind P. aeruginosa than surface-bound WLBU2. Future work will focus on optimization of the coating to enable high loading of tethered bioactive molecules, without compromising surface biocompatibility. We are also developing a novel surface coating platform, using self-assembly and immobilization of PEO-based surfactants. This method shows promise in providing biocompatibility and biological function to a variety of polymers used in medical devices, without requiring expensive and toxic crosslinking reagents.

4:20pm **BI-TuA7 Concentration Dependent Acceleration of hMSC Differentiation on Orthogonal Concentration Gradients of RGD and BMP-2 Peptides**, ***Matthew Becker***, The University of Akron **INVITED**

Self-assembled monolayer substrates containing tethered orthogonal concentration profiles of GRGDS and BMP-2 peptides are shown to synergistically accelerate the proliferation and osteoblastic differentiation of human mesenchymal stem cell (hMSC) populations *in vitro* without the use of osteogenic additives. Concurrently, the single peptide gradient controls (RGD or BMP-2 only) were found to induce significantly different proliferation and differentiation behavior from the orthogonal substrates. hMSC cells were individually isolated for qPCR at specified points along the gradients using laser capture microdissection. Bone sialoprotein (BSP) and Runt-related transcription factor 2 (Runx2) qPCR data corresponded spatially and temporally to protein marker data obtained from immunofluorescent imaging tracking the differentiation process. Genomic and protein data at high concentrations of both BMP-2 (25 pmol/cm^2) and GRGDS (71~83 pmol/cm^2) were shown to have a cooperative acceleration on the hMSC differentiation timeline relative to the individual peptide concentrations. These data highlight the utility of the orthogonal gradient approach to help identify the synergistic concentrations of peptides and growth factors that can be advanced in translationally relevant systems.

5:00pm **BI-TuA9 How Does Plasma Surface Modification Affect Biological Responses?**, ***Adoracion Pegalajar-Jurado***, *M.J. Hawker, M.N. Mann, E.R. Fisher*, Colorado State University

Biofouling causes severe and costly problems in industries including, but not limited to water filtration, food packaging and preservation, marine operations and biomedical devices. Depending on the industrial context, the term biofouling assumes different meanings including bacterial attachment and biofilm formation, undesired protein adsorption, or prevention of cell growth and tissue regeneration. Nevertheless, the process commences with undesired interactions of biological agents with the material surface.Consequently, the ability to tune surface properties to tailor biological response highlights an exceptional route towards preventing issues associated with biofouling. Although surface micro- and nanotopography, surface free energy, and surface chemistry are known to affect biological agent-surface interactions, this presentation will focus specifically on the effects of surface chemical modifications of 3D constructs (i.e. drug delivery systems and polymeric membranes and scaffolds) on biological responses. Among others, plasma surface modification offers a tunable and versatile parameter space for tailored and reproducible surface modification while retaining the morphology of the material, to produce *bio-nonreactive materials* (limit bacterial and cell attachment and low cytotoxicity). On 2D substrates, plasma polymerized cineole films have demonstrated limited *Escherichia coli* (*E. coli*) attachment over 18 hours and non-cytotoxic to mammalian fibroblast .[1] Herein, such films were used to conformally encapsulate 3D constructs. Results from both *E. coli* attachment studies as well as cytotoxicity studies will be presented. Alternatively, allylamine/allyl alcohol plasma copolymerized films applied to 3D materials and water plasma treated nitric-oxide releasing materials will be included as *bio-reactive* materials. In this case, human dermal fibroblast attachment and growth was enhanced in comparison to unmodified materials. Through these model systems, we will explore the use of plasma surface modification to minimise fouling and/or enhance biocompatibility of a 3D material resulting in the extension of device lifetime, and enhancement of performance.

Keywords: plasma surface modification, bio-reactive, bio-nonreactive

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5:20pm **BI-TuA10 Stereoscopic Tracking Reveals Responses of Barnacle Larvae to Surface Cues**, *S. Maleschlijski, G.H. Sendra, S. Bauer*, Karlsruhe Institute of Technology (KIT), Germany, *A. Di Fino*, Newcastle University, UK, *L. Leal-Taixe*, Leibnitz University Hannover, Germany, *T. Ederth*, Linköping University, Sweden, *N. Aldred*, Newcastle University, UK, *B. Liedberg*, NTU Singapore, *A.S. Clare*, Newcastle University, UK, *B. Rosenhahn*, Leibnitz University Hannover, Germany, ***Axel Rosenhahn***, Ruhr-University Bochum, Germany

The critical step in surface colonization by marine biofouling organisms is surface exploration and settlement of the sessile stages (larvae, spores). Barnacles are one of the most important biofouling organism and surface selection of their larvae is a highly selective process [1]. 3D stereoscopic tracking enables quantitative analysis of the pre-settlement behavior and thus to understand how larvae respond to chemical and physical surface cues. We developed a transportable, submersible stereoscopic system which can be applied to record three dimensional video data and to extract swimming trajectories of multiple, label-free objects. The pre-settlement ritual can be classified in different motion patterns which vary in characteristic parameters, such as distance to the surface, velocity, or the curvature of the motion [2]. In general the larvae favor both, liquid-solid and liquid-air interfaces. The distribution within the water column and the fraction of larvae exploring the solid surface is determined by its chemistry. Using different self assembled monolayers we found a positive correlation of the settlement probability with both, the fraction of larvae exploring the interface and their mean swimming velocity [3]. Thus, 3D tracking provides a predictor for settlement probability. A combination of stereoscopic tracking with imaging surface plasmon resonance reveals that a temporary adhesive is an important ingredient in the mechanosensing process. Surfaces with high settlement probability and low swimming speeds tend to bind the adhesive stronger than the sensory setae while inert surfaces with low settlement probability and high swimming speeds interact only very weakly.

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5:40pm **BI-TuA11 New Materials Toolboxes for Tissue Engineering and Regenerative Medicine Applications**, ***Adam Celiz****, Harvard University, *J. Smith*, University of Nottingham, UK, *A. Patel, R. Langer, D. Anderson*, Massachusetts Institute of Technology, *D. Mooney*, Harvard University, *L. Young, M. Davies, C. Denning, M.R. Alexander*, University of Nottingham, UK

A key hurdle in translating stem cell therapies from research to industrial scale and clinical application is to produce the necessary numbers of cells in xeno-free, defined culture systems. For example, a heart attack can cause a loss of 1 billion cardiomyocytes and similar cell numbers are lost during progression of other conditions such as multiple sclerosis and diabetes. To meet the demand for such high cell numbers, materials scientists have been challenged to discover new synthetic biomaterials as xeno-free growth substrates.[1] We apply a high throughput materials discovery approach to identify a novel polymer for hPSC culture using microarray screening of an unprecedented chemical space (141 monomers, polymerized alone and mixed to form 909 unique polymers, tested in 4356 individual assays). This identified the first synthetic polymeric substrate that achieves both pluripotent hPSC expansion (in the commercially available defined culture media, StemPro and mTeSR1) and subsequent multi-lineage differentiation into representatives of the three germ layers, namely cardiomyocytes, hepatocyte-like cells and neural progenitors.[2] Surface analysis techniques such as ToF-SIMS and XPS were used to identify chemical moieties at the biomaterial interface that contributed to maintaining hPSC pluripotency. The identification of these controlling surface moieties was essential in the

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development of a facile scale up procedure from arrayed spots to coated cultureware that can be used *off-the-shelf*.

An alternative strategy for cell and tissue regeneration is to harness the natural regenerative capacity of the human body through activation of quiescent cell populations. Biomaterials such as hydrogels that mimic native extracellular matrix can be synthesized and implanted *in vivo* to present biophysical and biochemical cues to their surroundings and activate/traffic these cell populations towards a desired therapeutic effect.[3] Novel bioactive hydrogels, synthesized through bioorthogonal click chemistry methods, will be presented that can activate and regulate quiescent cell populations to aid regeneration of lost tissue after trauma or injury. The utility of these new materials will be demonstrated through muscle regeneration in a hind limb ischemia mouse model.

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MEMS and NEMS
Room: 211A - Session MN+BI-TuA

BioMEMS/NEMS, Wearable and Implantable Devices

Moderator: Wayne Hiebert, University of Alberta and The National Institute for Nanotechnology, Beth L. Pruitt, Stanford University

2:20pm **MN+BI-TuA1 Entrepreneurial Environment for Implantable and Wearable BioMEMS**, ***Kurt Petersen***, Silicon Valley Band of Angels **INVITED**

Several converging trends are transforming the entrepreneurial process for starting MEMS companies and for transitioning MEMS devices into production and into the market. First, it is well-known that recent market set-backs have caused traditional VC funds to view any hardware start-ups with renewed scrutiny and skepticism. Hardware, and particularly bioMEMS, start-ups typically require large amounts of capital ($50-$100M) and many years (7-10), before getting close to a reasonable exit. This large investment in money and time is on top of the already inherently risky prospects for such a start-up being commercially successful. Secondly, MEMS is recognized, by investors, by foundries, and by large consumer electronics companies, as a very successful new product area because of the huge up-take of MEMS components in mobile devices during recent years. Third, key strategic issues in huge upcoming new consumer markets, such as wearables and IoT, are sensors and contextual awareness; areas which are uniquely solved by MEMS devices. And fourth, the sheer number of successful, high volume MEMS devices currently on the market, has created a huge pool of skilled MEMS developers and manufacturers which can be drawn upon for new devices and new start-up companies. All these factors dramatically influence how such companies get funding and how they operate. We will discuss all these issues as they relate specifically to new implantable and wearable MEMS start-up companies. As examples, we will also discuss a number of current technical developments/devices/companies involving implantable and wearable bioMEMS.

3:00pm **MN+BI-TuA3 MEMS Sensors Make Up the Frontline of Wireless Health Solutions: Tremendous Growth Prospects**, ***Mehran Mehregany***, Case Western Reserve University **INVITED**

Use of sensor-enabled wearable wireless health solutions to monitor the health condition of chronic disease patients is key to the quality of life of the patient and to reduction of cost of health care—by keeping the patient out of the hospital and emergency rooms. Monitoring for early intervention is key to avoiding long-term adverse outcomes for those at risk of developing chronic diseases. This presentation will elaborate on the important role that MEMS sensors play in enabling wearable, health monitoring solutions. Capturing data is the key to such solutions, which requires sensors of various modalities. MEMS sensors have the advantage s of miniaturization, integration and batch fabrication—driving size, performance and cost advantages.

Annual heath care expenditure in the United States was ~$2.7 trillion in 2011 (i.e., $8,680 per person), well above other developed countries. Health spending grew 3.9% in 2011, the same as in 2009 and 2010; spending as a share of GDP has remained stable from 2009 through 2011, at 17.9%. The US health care system is built on fee-for-service, wherein the service is reactive to illness. An aging population, longer lives and increasing cases of chronic diseases are some of the key drivers escalating health care expenditures.

Chronic diseases account for 75%+ of the US health care expenditures, i.e., $2 trillion. 141 million (45% of the population) have at least one chronic disease, 72 million of which have two or more. Top 10 significant chronic diseases are: hypertension, obesity, arthritis, asthma, chronic kidney disease, depression, chronic obstructive pulmonary disease (COPD), diabetes, sleep disorder and heart failure.

4:20pm **MN+BI-TuA7 GC-MS to GC-NOMS: A Step Towards Portable Analysis**, ***Anandram Venkatasubramanian***, *S.K. Roy, V.T.K. Sauer, W.K. Hiebert*, National Institute for Nanotechnology and University of Alberta, Canada

The Gas Chromatography (GC) – Mass Spectrometer (MS) system is the industry benchmark in research and chemical analysis. However given that MS systems are large and complicated instrumentation, chemical analyses have a long turnaround time. In this regard, portable GCs have carved a market niche but they have poor sensitivities. Recent demonstrations with Nanooptomechanical (NOMS) resonators at atmospheric pressure have proven that these kind of sensors have the breakthrough potential to improve the sensitivity of portable GCs. In this regard we have built an experimental rig to integrate the GC system with our NOMS device. The goal of this study is two-fold. One will be to replace the GC sensor with NOMS devices, integrate with the portable GCs for better sensitivity, and ultimately match the analytical power of conventional GC-MS. The other will be to demonstrate the NOMS sensing capabilities for next generation genomic applications like personalized medicine. In this regard, we have designed and developed a free space interferometry system. The probe laser is coupled in and out of the photonic waveguide using grating couplers. Using the evanescent field of the waveguide, the shift in resonant frequency of the nanoscale resonators is recorded using lock in amplifier. Here we have tracked the response of both the ring resonators using the photodetector output and the nanomechanical resonator using the phase locked loop (PLL). GC peak sensing can be done with either or both of the mechanical and the photonic sensors. During the initial testing with analyte standards we observed the ring resonator to respond faster than the nanomechanical resonator on par with the GCs flame ionization (FID) detector. We were also able to capture the analyte peaks effectively with the sensitivity of the resonators to be about 77 zg/Hz.

4:40pm **MN+BI-TuA8 Label-Free Biosensing Platform Integrating a Nanofluidic Preconcentrator with Surface Plasmon Resonance Sensors**, ***Wei-Hang Lee***, *P.S. Chung*, National Taiwan University, Taiwan, Republic of China, *P.K. Wei*, Academia Sinica, Taiwan, Republic of China, *W.C. Tian*, National Taiwan University, Taiwan, Republic of China

For bioMEMS applications, the integration of preconcentration and sensing has been studying to detect low-abundance analytes without labelling. In the past few years, an electrokinetic trapping (EKT)-based nanofluidic preconcentrator had been reported for providing a million-fold concentration factors that enable the validation of concentration process and the detection of trace and fluorescence-labelled analytes. However, the use of fluorescence-labelled analytes has suffered several disadvantages, e.g., additional sample preparation, high cost of labeling reagents, and difficulty in analyzing trace analytes. To monitor the concentration process without labelling, previously we have presented a real-time dual-loop electric current measurement system for label-free EKT-based nanofluidic preconcentrators. In this work, we further demonstrate a label-free biosensing platform by integrating a label-free nanofluidic preconcentrator with label-free SPR sensors.

The label-free biosensing platform was realized by a nanofluidic preconcentrator and two nanograting-structured SPR sensors. The preconcentrator is consisted of two parallel microchannels, i.e., one concentration channel and one buffer channel, cast in PDMS and connected by nanochannels. The two SPR sensors, i.e., one for control group and the other for experimental group, are fabricated on glass slide by e-beam lithography, e-gun evaporation and lift-off process. Then, we patterned a Nafion thin film on glass and at the position adjacent to the SPR sensors by using a microflow patterning method. Finally, the PDMS-based microchannels were sealed onto the by oxygen plasma bonding process.

We have demonstrated the ultra-sensitive label-free biosensing platform by detecting the amplified redshift magnitude of a specific range of a SPR spectrum. First, before preconcentration process, several reference spectra were measured. Second, after ten-minute preconcentration process for the 20 ng/ml BSA in PBS, a 5 nm-redshift spectrum was measured. Comparing the experimental spectrum with the reference spectra, the redshift magnitude of 20 ng/ml BSA in PBS after preconcentration process is equivalent to that of the 200 μg/ml BSA in PBS. Hence, we demonstrate a preconcentration factor of ten-thousand folds and a sensing limit of at least 20 ng/ml BSA in PBS in this label-free biosensing platform.

In summary, by utilizing the electric current measurement system and the commercial optical system, low abundance analytes can be preconcentrated and sensed by the developed biosensing platform, which enables a label-free approach on preconcentrating and detecting trace molecules with high sensitivity.

5:00pm **MN+BI-TuA9 Microparticle Patterning Using Multimode Silicon Carbide Micromechanical Resonators**, ***Hao Jia***, *H. Tang*, *P.X.-L. Feng*, Case Western Reserve University

In recent years, there have been increasing interests in manipulating and patterning microparticles and biological cells on microscale planar surfaces[1],[2],[3], among which "Chladni figures"[4], enabled by resonant microelectromechanical systems (MEMS)[5], offer a noninvasive, fast, and highly-controllable approach by simply programming frequency.

In this work, we report experimental demonstration of manipulating microparticles in fluidic environment using multimode silicon carbide (SiC) MEMS resonators, forming diverse microscale Chladni patterns. Silica microspheres with various diameters (0.96, 1.70, 3.62, 7.75μm) sprinkled onto suspended surfaces of SiC doubly-clamped beams (60×10μm, 100×10μm and 100×20μm) and square trampolines (50×50μm and 90×90μm) are quickly manipulated into one dimensional (1D) and two dimensional (2D) geometrical patterns, such as "dots (.)", "line (/)", "cross (×)" and "circle (○)" by piezoelectrically exciting those resonators at their flexural resonance modes.

SiC MEMS resonators, with its unique biocompatibility[6](indicating biological applications), are fabricated based on a SiC-on-Si platform, with device structures patterned by the focused ion beam (FIB) and suspended by an isotropic Si etching (HNA, 10% HF: 70% HNO_3=1:1). Multimode resonances in liquid (up to 5MHz) are characterized using laser interferometry[6], based on which the piezoelectric driving frequencies are switched in real-time to strongly excite the microspheres and manipulate them into a series of Chladni patterns. Such SiC resonating platform, by taking advantage of its straightforward device fabrication and engineerable multimodes, offer new means for microparticle manipulation and patterning, and may further facilitate cell manipulation, and other biophysical and biomedical studies.

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Biomaterial Interfaces
Room: Hall 3 - Session BI-TuP

Biomaterial Interfaces Poster Session

BI-TuP1 Flash Networking Poster: Simple Method Toward Lignin Based Surface Coatings, ***Patrick Burch***, *P.B. Messersmith*, University of California at Berkeley

Lignin is the second most abundant biopolymer on earth. Millions of tons are produced annually as a byproduct of the paper industry but yet its use is limited to mostly low-value applications, such as concrete additives or fuel for paper mills. Significant research efforts are devoted towards the disruption of lignin into its monomers with the aim to create high-value applications. This task remains challenging due to the heterogeneity of lignin and the harsh conditions needed to degrade the covalent bonds linking the monomers together. Our approach instead takes advantage of this intrinsic stability of lignin by further polymerizing lignin building blocks on surfaces to form organic coatings. These coatings consequently alter the surface properties of these substrates in a simple, scalable, versatile and renewable fashion.

BI-TuP2 Flash Networking Poster: Characterising Hydrogel Chemistry Through Low Temperature ToF-SIMS, ***Michael Taylor***, *D. Scurr*, The University of Nottingham, UK, *M. Lutolf*, Ecole Polytechnique Fédérale de Lausanne (EPFL), Swtizerland, *L. Buttery*, *M. Zelzer*, *M.R. Alexander*, The University of Nottingham, UK

Over the last decade the beneficial properties of hydrogels as artificial cell culture supports have been extensively investigated[1]. Certain synthetic hydrogels have been proposed to be similar in composition and structure to the native extracellular matrix of the stem cell niche, their *in vivo* cell habitat, which is a powerful component in controlling stem cell fate[2]. The stem cell differentiation pathway taken is influenced by a number of factors. When culturing cells within or upon hydrogels this choice can be strongly dependent on the underlying 3D hydrogel chemistry which strongly influences hydrogel-cell interactions[3]. The interrelationship between hydrogel chemistry and that of biomolecules in controlling cellular response ideally requires analysis methods to characterise the chemistry without labels and often in 3D. Time-of-flight secondary ion mass spectrometry (ToF SIMS) has the potential to be utilised for through thickness characterisation of hydrogels. The frozen-hydrated sample format is well suited to minimise changes associated with dehydration or the chemical complexity of 'fixation', a challenging aspect in vacuum analysis conditions[4]. Frost formation can occur in the ambient atmosphere preventing ready depth profiling of the frozen hydrogels. We develop a simple method to remove this frost by blowing with gas prior to entry into the instrument which is shown to produce remarkably good profiles on a poly(2-hydroxyethyl methacrylate) (pHEMA) hydrogel film where a model protein, lysozyme, is incorporated to demonstrated how biomolecule distribution within hydrogels can be determined. A comparison of lysozyme incorporation is made between the situation where the protein is present in the polymer dip coating solution and lysozyme is a component of the incubation medium. It is shown that protonated water clusters $H(H_2O)_n^+$ where n=5-11 that are indicative of ice are detected through the entire thickness of the pHEMA and the lysozyme distribution through the pHEMA hydrogel films can be determined using the intensity of characteristic fragment secondary ions. Early stage data from more complex gel systems will be presented to determine the limitation of this approach.

BI-TuP3 Flash Networking Poster: Molecular-Level Insights into the Wet Adhesion Mechanisms of the Lady Beetle (*Cocinella septempunctata*), ***James Fowler***, Oregon State University, *J. Franz*, Max Planck Institute for Polymer Research, Germany, *S. Gorb*, University of Kiel, Germany, *T. Weidner*, Max Planck Institute for Polymer Research, Germany, *J.E. Baio*, Oregon State University

Humans have always marveled at the ability of insects to cling and climb along virtually any surface – whether it's vertically up a wall or upside-down supporting masses orders of magnitude greater than their own. Many insects have adapted to a range of environmental surfaces by evolving a wet adhesion process that combines an expansive array of hairy contacts on their feet, known as setae, and an adhesive fluid that forms contact between the setae and a substrate. Previous studies of this adhesion mechanism have focused almost exclusively on the mechanical and kinematic aspects of adhesion, and not on the molecular interactions at the fluid – substrate interface. In the work presented here, we probe the molecular interactions between the adhesive fluid taken from lady beetles (*Cocinella septempunctata*) on two model substrates (deuterated-PMMA and deuterated-polystyrene) with vibrational sum frequency generation (SFG) spectroscopy and scanning electron microscopy (SEM). High-resolution SEM images of individual seta-fluid footprints on both sets of surfaces indicate localized water-oil emulsion de-wetting with no sign of distinct patterning within the footprint. SFG spectra collected at the C-H stretching region (2800-3100 cm^{-1}) contain peaks at 2848 cm^{-1} and 2867cm^{-1}, characteristic of symmetric CH_2 and CH_3 stretches, respectively. For the fluid on both the PMMA and polystyrene, we observe a large ratio of the 2867/2848 cm^{-1} peaks suggesting a well-ordered hydrocarbon monolayer with methyl groups oriented normal to the substrate. Spectra at the amide I stretching region (1500-1800 cm^{-1}) collected from the PMMA-fluid sample contain a single peak at 1700 cm^{-1} indicating the presence of ordered free fatty acids; however, this signal is absent from the polystyrene-fluid spectra. Combined, this set of SFG spectra demonstrate that during adhesion to a polar surface, fatty acids within the fluid form a highly ordered layer at the substrate surface. While on a non-polar surface, the mechanism changes and some other hydrocarbon species present within the fluid orders at the interface.

BI-TuP5 Flash Networking Poster: Structured Noble Metal Nanosurfaces for Biosensing and Bioanalysis (1): Controlling Galvanic Displacement Reaction for Creation of Silver Nanostructures, ***Shingo Yoneda***, Toyo University, Japan, *T. Okamoto*, RIKEN, Japan, *H. Vieker*, *A. Beyer*, *A. Gölzhäuser*, Bielefeld University, Germany, *H. Takei*, Toyo University, Japan

There has been an increasing interest in creating silver nanostructures for optical analytical techniques such as surface-enhanced Raman spectroscopy. Galvanic displacement reaction, exploiting the difference in ionization tendency of different metals, can be used for such purposes, but previously there was not much room for controlling the final morphology of nanostructures when bulk metal was simply treated with silver nitrate solution. However, recently it was reported that use of copper colloids rather than bulk copper allows finer structural controls. We have also found that surface-adsorbed copper structures can be transformed to silver nanostructures with various morphologies. The size and amount of copper were crucial for the morphology of the final structures. Recently we have also begun experimenting with addition of polyvinylpyrrolidone (PVP) to the silver nitrate solution because PVP was known to affect the morphology of the silver nanostructures with the conventional galvanic displacement reaction using bulk metal. Here we describe its results.

Our base metal nanoparticles are formed by evaporation of a base metal on surface-adsorbed monodisperse SiO_2 nanospheres. Variable parameters are the metal deposition thickness and the nanosphere diameter. We treated these base metal nanoparticles with an aqueous silver nitrate solution containing PVP. In this experiment, we investigated effects of changing the concentration of PVP, the molecular weight of PVP (K15, K30, K90), and the deposition thickness of copper (10, 30, 60 nm). For evaluation of the structures, we observed their morphologies with SEM and obtained Raman spectra of 1 mM rhodamine 6G, R6G.

Use of PVP leads to silver nanostructures with different morphologies. When PVP is used, massive silver nanostructures are formed. When not, however, silver nano-filaments are formed instead. It was also confirmed that the form of silver nanostructres is dependent on the molecular weight of PVP used and the deposition thickness of the original base metal. When these nanostructures are used as a substrate for SERS, the enhancing effect becomes greater when prepared with PVP.

BI-TuP7 Preparation of Bioglass-ZrO_2 Functionalized Coatings by EPD, ***Ana Arizmendi-Morquecho***, *M.A. Aguilera-Bustos*, Centro de Investigación en Materiales Avanzados, Mexico, *A.C. Chávez-Valdez*, Consultant, *M.S.D. Sánchez-Domínguez*, *M.S.V. Sánchez-Vázquez*, Centro de Investigación en Materiales Avanzados, Mexico

Surface functionalization is an important tool for many technical and biomedical applications. The modification of a nanoparticle surface can alter its adhesion characteristics, improve the dispersion in matrices or enhance catalytic properties. In this work, strategies for surface functionalization of inorganic materials with a special focus on zirconia (ZrO_2) synthetized nanoparticles as reinforcement for bioglass ceramic matrix are discussed. The density of functionalization in nanoparticles using different organosilanes molecules was measured by Si–O and hydroxyl (–OH) bonds. The reactivity between organosilanes and the surface of nanoparticles was measured by electrostatic potential using molecular simulations with Gaussian software. This simulation showed the regions from silane molecules with the lowest electrostatic potential representing the sites were the metallic oxides are attached. The morphology of nanoparticles and functionalization layer was characterized using TEM-EDS, FTIR and TGA. Due to the low stability of bioglass in organic

suspensions, the modification of its surface was necessary using functionalized nanoparticles which allowed the preparation of Bioglass-ZrO_2 reinforced composites. Suspensions were prepared using ethanol as dispersing media. Bioglass suspensions showed poor stability, while suspensions with Bioglass and functionalized nanoparticles showed improved stability. The formation of bonds between bioglass particles and functionalized ZrO_2 nanoparticles allowed the dispersion of the material which is necessary for the preparation of coatings by Electrophoretic Deposition (EPD). The Bioglass and Bioglass-ZrO_2 coatings were characterized by SEM-EDS and XRD. A uniform coating was obtained with well dispersed ZrO_2 nanoparticles. These coatings using functionalized ZrO_2 as reinforcement can improve the mechanical properties as well as the biocompatibility of the composite.

BI-TuP9 Flash Networking Poster: Gold Nanoparticle-Delivered RNA Genetic Control Devices, ***Michael Newton***, *J.M. Carothers, D.G. Castner*, University of Washington

Gold nanoparticles (AuNPs) promise to offer a minimally toxic, easily modifiable, and high payload carrying drug or biologic delivery agent. Despite this promise and the emphasis placed on their intrinsically high surface area to volume ratio, surface functionalized AuNP conjugates in biomedical applications often lack detailed surface characterization. Consequently, there is little experimental validation of a surface attached ligand's orientation or conformation. Nucleic acids are one such ligand and biologic diagnostic or therapeutic agent currently being investigated. RNA-based logic circuits responsive to small molecules, endogenous proteins, and miRNAs have been demonstrated to diagnose the state of a cell and implement a programmed therapeutic outcome. A truncated RNA circuit such as this could benefit from local targeting and concentrated delivery on a nanoparticle platform and prove more effective. Proper tools and techniques to characterize biomedical AuNP conjugates would inform their design and result in better understanding the observed cellular uptake, efficacy, toxicity, and clearance.

Short single-stranded DNA oligo's on AuNPs have been used to sense a complementary nucleic acid, or as a capture strand to facilitate assembly of larger constructs. Additionally it is often recognized that the method of attachment and incorporation of spacers will play a factor in the assembled conjugate's performance. A thiol attachment to Au is often used with a polynucleotide spacer for simple assembly and increased performance. These investigations typically neglect to consider other types of spacers like ethylene glycol chains of various lengths. We will compare the polynucleotide and ethylene glycol spacers used individually and jointly in a single-stranded DNA capture oligo conjugated AuNP in terms of particle surface characterization and nucleic acid functionality. This will be realized through X-ray Photoelectron Spectroscopy and Localized Surface Plasmon Resonance in conjunction with standard bulk characterizations like Dynamic Light Scattering, Electrophoresis, and Transmission Electron Microscopy, and through incorporation of strand-displacement and RNA aptamer nucleic acid devices with distinct programmed fluorescent outputs from a specific small molecule or oligo input.

BI-TuP11 Flash Networking Poster: Exhaled Breath Analysis of Ammonia Gas using Colorimetric Attenuated Total Reflectance Spectroscopy, ***MariaAntoaneta Bratescu***, *K. Isawa*, Nagoya University, Japan, *T. Kiguchi*, Shibaura Institute of Technology, Japan, *O.L. Li, N. Saito*, Nagoya University, Japan

The identification of exhaled breath volatile organic compounds represents a metabolic biosignature with the potential to recognize some diseases. There are various techniques to analyze exhaled breath gases, as spectrometry, gas chromatography, and spectroscopy. The recent trend towards breath analysis instruments has led to the development of fully integrated prototypes of point-of-care devices.

In this research we develop a miniature sensor using attenuated total reflectance spectroscopy to detect breath gases in the range of hundreds ppb. A 0.2 mm thick, 20 mm wide, 65 mm long, fused silica plate with 60° beveled edges (Shin-Etsu Quartz Products, Inc.) was used as the internal reflection element (IRE).[1] The IRE surface was coated with the chemical sensor specific to one of the gases from the breath, embedded in a polymer, using a layer-by-layer electrostatic assembly method. The evanescent light produced by multiple total internal reflections penetrates a few tens of nanometers in the film leading to a high detection sensitivity.

For ammonia gas detection Poly(diallyldimethylammonium chloride) (PDDA, Mw: 200000-350000, 20 wt% in H_2O) and tetrakis(4-sulfophenyl)porphyrin (TSPP, Mw: 934.99) were used as polymer and chemical sensor, respectively.[2,3] The detection consists in measuring the decrease of light intensity of the Soret band of the porphyrin molecule around 483 nm under the chemical reaction with ammonia. First we recorded absorption spectra through the IRE using a broadband visible light source and a spectrograph for different film conditions and ammonia concentrations. Then the broadband light source and the spectrograph were replaced with a 450 nm light emitting diode (LED) and a photodiode (PD). The ammonia sensing capability of the porphyrin film was tested in both liquid and gas phases and a 500 ppb detection limit was found. We studied the ammonia gas detection limit in dependence with the number of layers of the chemical sensor and the polymer deposited on the IRE surface. AFM measurements show the surface modifications after the ammonia gas adsorption on the chemical sensor film. Stability, reversibility, and the humidity influence will be discussed.

[1]M. A. Bratescu, et al., Attenuated total reflectance spectroscopy of coumarin organosilane molecules adsorbed on a fused silica surface, Applied Surface Science, 257, 1792, 2010.

[2]K. S. Suslick, et al., An optoelectronic nose for the detection of toxic gases, Nature Chemistry, 1, 562, 2009.

[3]S. Korposh, et al., Sensor and Materials, 21, 179, 2009.

BI-TuP12 Flash Networking Poster: Structured Noble Metal Nanosurfaces for Biosensing and Bioanalysis (3): Surface-Enhanced Fluorescence Detection with Cap-shaped Silver Nanoparticles, ***Miki Ebisawa***, *T. Kawakami, H. Takei*, Toyo University, Japan

OBJECTIVE

Surface-enhanced fluorescence, SEF, is a highly sensitive method for detecting fluorescent molecules using a noble metal structure. We used cap-shaped silver nanoparticles that were fabricated by vacuum deposition of silver onto a dense layer of silica nanoparticles immobilized on a glass slide. While there is much in common with surface-enhanced Raman spectroscopy, SEF requires that molecules be placed at a certain distance away from the metal surface in order to avoid quenching. To satisfy this requirement, we have evaluated the effect of introducing a dielectric layer on the substrate surface. Furthermore we have investigated a number of techniques for patterning different antibodies or DNA fragments as we are targeting immunoassay and DNA diagnosis for the application of SEF, up to several dozens of different target molecules at the same time.

METHODS

Cap-shaped silver nanoparticles prepared with the above method were soaked in a silane coupling agent (tetraethylorthosilicate, TEOS) to form a dielectric layer. With DNA measurements, we used a probe DNA (19 mer) and FITC-labeled target DNA (13 mer). After immobilization of the probe DNA, the target DNA was made to hybridize. We examined two methods for patterning. One way was to prepare polymer fibers at whose end silver nanoparticles were formed. Fibers modified with different capture molecules were bundled together to be used for measurements. As a second method, after a substrate surface was uniformly modified by a single type of capture molecule, the molecule was locally destroyed: a "subtractive" method. For destruction, ozone treatment or additional deposition of silver was used.

RESULTS

From results by a microarray scanner, we confirmed that the signal intensity of the fluorescent modified DNA from a silver nanoparticle substrate with a dielectric layer was more than doubled compared with the control substrate, demonstrating the effect of a dielectric layer. As for the ozone cleaning, the treatment of the substrate enhanced the signal intensity if applied prior to adsorption of the target molecules; if afterward, the same treatment was found to diminish the signal, as we expected. However, the effect of additional silver deposition was unexpected. We assumed that the signal would be diminished by additional deposition several nm in thickness, but on the contrary the signal was enhanced by additional deposition, the signal intensity being maximized when the thickness was 150 nm. In the future, we will examine this phenomenon in greater detail, with a hope of obtaining a fundamental insight into the mechanism of SEF.

BI-TuP13 Flash Networking Poster: Structured Noble Metal Nanosurfaces for Biosensing and Bioanalysis (2): Localized Surface Plasmon Resonance Sensor Operating in the Near-IR Regime, ***Takumi Miyashita***, *N. Bessho*, Toyo University, Japan, *T. Okamoto*, Riken, Japan, *H. Vieker, A. Beyer, A. Gölzhäuser*, Bielefeld University, Germany, *H. Takei*, Toyo University, Japan

Noble metal nanoparticles possess an optical extinction peak due to localized surface plasmon resonance, LSPR. The peak shifts when the refractive index in the immediate vicinity changes, a useful property for making biosensors. While there are numerous ways to prepare noble metal nanostructures, we find that evaporating a noble metal on a surface coated with a monolayer of monodisperse silica nanospheres is a convenient method. With the above method, it is easy to form highly dense nanostructures, with the extinction peak in excess of O.D. 2. The spectrum can be readily modified by varying the sphere diameter and metal deposition thickness. While this method has been used by a number of groups, we found that resulting structures possess not only a peak in the

visible but also an additional peak in the near-IR. The latter peak has four times the sensitivity of the peak in the visible.

There are many ways to use LSPR sensors other than the traditional antigen-antibody monitoring. One has to do with improving a colorimetric diagnostic method. Often it is implemented in the form of immunochromatographic assays, ICA. It is, however, used mostly only for qualitative assays, such as detection of flu. We believe that bestowing it with a quantitative detection capability as well as an increased dynamic range would further boast the use of ICAs. In some colorimetric assays, an enzyme is used to generate a colored product. By using the alkaline phosphatase-NBT/BCIP system, here we describe various techniques for maximizing the interaction between the enzymatic reaction product and the sensor surface. Another application is detection of nanoscopic gas bubbles. If bubbles form on the sensor surface, even with the size of 5 nm or less, it should lead to a detectable shift of the peak. We have decided to test this concept on detection of useful microorganisms from soil samples obtained below the ocean bed where very few are expected. Our strategy is to look for catalase which is secreted by practically every life form. When catalase, captured on the sensor, reacts with H_2O_2, oxygen bubbles form so that the presence of microorganisms can be potentially detected by monitoring bubble formation. Another set of experiment involves monitoring of vascular endothelial cells in the presence of elevated amounts of glucose. We have cultivated VE cells on our LSPR sensor. It is our intention to use the sensor signal for monitoring changes in the morphology of cells induced by glucose, leading to a better understanding of diabetes.

BI-TuP14 Flash Networking Poster: Exploration of Conformational Changes of Nucleic Acids as a Function of Interactions with Histone-mimic Nanoparticles using All-atom Simulations, ***Yaroslava Yingling***, *J.A. Nash*, North Carolina State University

Nucleic acid based nanotechnology and gene therapy approaches depend on the compaction, or packaging, of the nucleic acids DNA and RNA. Though there has been much experimental work on the interactions of DNA with proteins, the atomic details of DNA-nanoparticle binding remain to be comprehensively elucidated. Even less is known about the binding of double stranded RNA with cationic molecules. Here, we report the results of a comprehensive large scale all-atom molecular dynamics simulation investigation of the binding ligand-functionalized gold nanoparticles (NPs) binding to the nucleic acids double stranded DNA and RNA as a function of NP charge and solution salt concentration. Our simulations show that low charge NPs bind to DNA and cause little distortion of the DNA helix, however, nanoparticles with charges of +30 or higher cause DNA to bend and wrap in a way similar to nucleosome. Moreover, shape of the NP ligand corona plays an essential role in quality of DNA wrapping. The nanoparticles cause different behavior with short segments of RNA in that they are not able to induce bending for even the most highly charged nanoparticles in 0.1M NaCl. To compact RNA, a combination of highly charged nanoparticles with low salt concentration is required. Results from this paper can be used for future design of efficient NP vectors for gene delivery and other biomimetic materials.

BI-TuP17 Flash Networking Poster: Nanoscale Structures in Live Cells Visualized through High Resolution Imaging and Mechanical Property Mapping, ***Bede Pittenger***, Bruker, *H. Schillers*, Univ. Muenster, *A. Slade, J. Shaw, S. Hu, I. Medalsy, T. Mueller*, Bruker

Nanoscale structures on or just beneath the cell surface often strongly influence cell function. Atomic Force Microscopy allows measurement of both topography and mechanical properties of these structures on live cells at resolutions far below the diffraction limit. When integrated and synchronized with optical microscopy (including fluorescence, confocal microscopy, and super-resolution imaging) AFM provides new methods of studying the relationship between cell structure and function in near-physiological conditions.

One class of these nanoscale structures is the microvillus -- a structure commonly found on epithelial cells. Epithelial cell function is coupled to the density of microvilli and degradation can cause malabsorption and diarrhea [1]. Observing the both tiny and very flexible structures such as microvilli on the apical surface of a live cell has been very challenging because the native microvilli structures are displaced and deformed by the interaction with the AFM probe.

Another class of nanoscale structure within cells is the actin fibril. These structures make up the actin cytoskeleton and are thought to play an important role in many types of cancer [2]. AFM allows observation of the actin fibrils, their position and their stiffness. PeakForce Tapping (with PeakForce QNM) provides fast, high resolution, quantifiable maps of the distribution of the actin fibrils in the cytoskeleton.

In this talk we will present the first images of microvilli on the membrane surface of living kidney cells obtained by AFM. Because the data was collected with PeakForce Tapping, it is possible to compare the response of the microvilli to different applied forces, and observe the effect of force on microvilli structure. Finally, we will also present mechanical maps of live MDCK cells showing the distribution and stiffness of individual actin fibrils.

[1] E. Cutz, J.M. Rhoads, et al., N. Engl. J. of Med. 320, 646 (2009).

[2] M. F. Olson and E. Sahai, Clin. Exp. Metastasis 26, 273 (2009).

Biomaterial Interfaces
Room: 211D - Session BI-WeM

Biomolecules at Interfaces
Moderator: Axel Rosenhahn, Ruhr-University Bochum

8:00am **BI-WeM1 Understanding Hydration of Proteins by SALVI and Liquid ToF-SIMS**, ***Jiachao Yu***, *Y. Zhou, X. Hua, Z. Zhu,* Pacific Northwest National Laboratory, *S. Liu,* Southeast University, China, *X.-Y. Yu*, Pacific Northwest National Laboratory

Hydration is crucial to the structure, conformation, and biological activity of proteins. Proteins without water molecules surrounding them would not have viable biological activity. Specifically, water molecules will interact with the surface and internal structure of proteins, and different hydration states of proteins make such interactions distinct. Thus, it is important to understand the hydration of proteins on surfaces, which can provide a fundamental understanding of the mechanism of their structure, conformation, and biological activity. Our group developed an important technique to study liquid surfaces and interfaces, namely System for Analysis at the Liquid Vacuum Interface (SALVI). It has been recently applied to study hydrated protein biofilms. SALVI is a vacuum compatible microfluidic device that consists of a SiN window as the detection area and a microchannel made of polydimethylsiloxane (PDMS). The protein solution was introduced into the microchannel. After incubating for a period of time, a hydrated protein biofilm formed on the back side of the SiN membrane. The information of hydrated proteins was collected using the time-of-flight secondary ion mass spectrometry (ToF-SIMS) in the SALVI device in the liquid state. Compared with previous results from dry protein samples, we not only confirmed the amino acid compositions of proteins, but also firstly discovered that the distribution of water molecules surrounding and inside proteins were varied among different types of proteins. Our liquid ToF-SIMS results show that 1). The water clusters number and relative counts vary among the same hydrated proteins, which imply that the distribution of water molecules surrounding and inside a protein is inhomogeneous; 2). The same water clusters have varied content in different types of proteins, which indicate that the distribution of water molecules have a strong relationship with the structure and conformation of the proteins at the biointerface. These first observations of hydrated protein biofilms on a surface will pave the investigation of the structure, conformation, and biological activity of proteins in the future.

8:20am **BI-WeM2 Direct Measurement of the Interaction Free Energies of Single Hydrophobic Peptides with Extended Hydrophobic Surfaces**, ***Philipp Stock***, *T. Utzig, M. Valtiner*, Max-Planck Institut für Eisenforschung GmbH, Germany

Placing hydrophobes into an aqueous medium gives rise to what is well known as so-called hydrobobic interaction (HI) or hydrophobic force. This thermodynamic driven force gives rise to interaction and/or self-organisation of solvated hydrophobes in water. Famous examples are protein folding, lipid-bilayer membrane stability and enzymatic catalysis.

Here we will describe a SM-AFM setup to measure the interaction free energies (ΔG_0) of eight different hydrophobic peptides interacting with extended hydrophobic surfaces. First, we estimate the free energy of a single hydrophobic unit interacting with an extended hydrophobic surface. Secondly, we measured the change in free energy upon increasing the number of hydrophobic units in different sequences (synergies vs antagonistic effects).

In particular, we studied the change in free energy by placing a spacer groups (glycine) between the hydrophobic units. Interestingly our data shows that the interaction free energy scales with the number of hydrophobic units. Each hydrophobic unit seems to contribute about 4.8 kT. As such we observe a good agreement with values measured for two interacting benzene molecules in water.

Hence, hydrophobic interaction energies of hydrophobic surfaces with hydrophobic peptide fragments on a flexible peptide chain seem to linearly add up, irrespective of the incorporation sequences.

8:40am **BI-WeM3 Cells and Extracellular Matrices as Smart Materials: Dissecting and Rebuilding Mechaniobiological Units**, ***Sanjay Kumar***, University of California, Berkeley **INVITED**

Living cells are capable of processing a variety of mechanical signals encoded within their microenvironment, which can in turn act through the cellular structural machinery to regulate many fundamental behaviors. In this sense, cells may be regarded as "smart materials" that dynamically and locally modulate their physical properties in response to environmental stimuli. I will discuss our recent efforts to understand and control these living materials, and to create new, bio-inspired materials that mimic sequence/structure/function relationships of cytoskeletal networks. Key areas of emphasis will include: (1) Understanding and targeting biomechanical regulation of tumor infiltration in the brain; (2) Engineering stimulus-sensitive intrinsically disordered protein brushes based on neuronal cytoskeletal networks. These efforts exemplify the important notion that biomaterials can be extremely valuable platforms with which to understand and control cell behavior, and that understanding cellular structural networks can yield unexpected insights that inform the creation of novel biomaterials.

9:20am **BI-WeM5 Molecular Modeling of Biofunctionalized Hydrogels to Guide Hydrogel Design**, *X. Li,* Clemson University, *M.L. Becker,* University of Akron, *N.S. Murthy,* Rutgers University, ***Robert Latour***, Clemson University

Peptide-functionalized PEG-based hydrogels represent the workhorse material for tissue engineering and regenerative medicine applications because of their potential to mimic the extracellular matrix and serve as a substrate to direct cellular response. In order for a bioconjugated hydrogel to exhibit its intended bioactivity, the peptides that are tethered within the hydrogel must be accessible at the hydrogel surface for cell-receptor binding. Surface availability for a given peptide and hydrogel system will be a function of design parameters such as tether length, tether structure, and hydrogel crosslinking density. While the surface-accessibility of the peptide can be readily assessed experimentally, reasons for low accessibility (if encountered) are not easily determined. To address this type of problem, we are developing molecular modeling and simulation methods that will provide the ability to understand and visualize hydrogel behavior at an atomistic level to serve as a potentially powerful tool for hydrogel design. We are developing the molecular models using a multiscale approach. Coarse-grained (CG) parameters are first obtained from all-atom models of the various structural elements of the hydrogel system in aqueous solution using the polymer consistent force field (PCFF). A coarse-grained structure of the hydrogel is then first created at the experimental crosslink density using an efficient on-lattice method. The CG model is then removed from the lattice and equilibrated using the TIGER2 advanced sampling algorithm. The resulting equilibrated CG system is then reverse-mapped to an all-atom model. The all-atom model is then hydrated in water and equilibrated once more to yield the final predicted structure of the system. The resulting models are validated by comparing with structure-factor plots obtained by neutron scattering and/or X-ray diffraction. The resulting molecular models provide an atomistic-level view of peptide accessibility at the hydrogel surface. If low accessibility is encountered for a given design, the molecular models can provide clear direction regarding the cause of the problem and indicate the design changes that should be made to improve the bioactivity of the system.

9:40am **BI-WeM6 Physisorption of Stimuli-Responsive Polypeptides with Genetically Programmable Aqueous Phase Behavior**, ***Linying Li***, *C. Mo, Q. Tu, N.J. Carroll, A. Chilkoti, S. Zauscher,* Duke University, *M. Rubinstein,* University of North Carolina at Chapel Hill, *G.P. López*, Duke University

The ability to control the physical adsorption (physisorption) of proteins to solid surfaces is of fundamental importance in the design of engineered bio-interfaces for many biomaterial, industrial and bioanalytical applications. We present a study of the kinetics of adsorption and consequent single- and multi-layered architectures of recombinant, intrinsically disordered proteins whose aqueous phase behavior is programmable at the sequence level. Elastin-like polypeptides (ELPs) are a class of engineered repetitive polypeptides that undergo a reversible, lower critical solution temperature (LCST) phase transition in water. Their phase behavior is programmable by tuning the amino acid sequence, concentration, and molecular weight of the ELPs. We used light scattering assays to investigate the phase diagrams of the peptides and quartz crystal microbalance with energy dissipation (QCM-D) to investigate the diffusion-limited adsorption kinetics of ELPs onto surfaces. Below the critical temperature, ELPs are soluble and only form single monolayers of peptides on surfaces upon adsorption, while above the critical temperature, ELPs phase separate, leading to multilayer adsorption. We used ellipsometry and atomic force microscopy (AFM) to characterize the thickness and roughness of the protein assemblies on surfaces. The elemental composition of the protein-modified surfaces was analyzed by X-ray photoelectron spectroscopy (XPS). Contact angle measurements were performed to examine the temperature-responsive nature of the surfaces. This study demonstrates that, based on their genetically encoded phase behaviors, the adsorption behavior of ELPs can be controlled to attain

desired architecture, thermal-responsive behavior and functionality. It also provides insight into protein adsorption at the molecular level that can be useful in a number of contexts including immunoassays, drug delivery and cell culture.

11:00am **BI-WeM10 Evidence of a Molecular Boundary Lubricant at Snakeskin Surfaces**, ***Joe Baio***, Oregon State University, *M. Spinner*, University of Kiel, Germany, *C. Jaye, D.A. Fischer,* National Institute of Standards and Technology (NIST), *S. Gorb*, University of Kiel, Germany, *T. Weidner*, Max Planck Institute for Polymer Research, Germany

Snake scales have direct mechanical interaction with the environment. During slithering the ventral scales at a snake's belly are permanently in contact with the substrate, while the dorsal scales have an optical function for camouflage and thermoregulation. Recently it has been shown that ventral scales have adapted to this biological function and provide improved lubrication and wear protection compared with dorsal scales. While biomechanic adaption of snake motion to specific habitats is of growing interest in material science and robotics, the molecular level mechanism for the frictional influence of ventral scales is unknown. In this study, we characterize the outermost surface of snake scales using sum frequency generation (SFG) spectra and near edge x-ray absorption fine structure (NEXAFS) images collected from freshly molted California kingsnake (*Lampropeltis californiae*) scales. NEXAFS microscopy enables the mapping of specific molecular bonds at the C and N K-edges. The resulting NEXAFS images highlight the intensities of C=C π^*, σ^* (C−H), C=O π^*, and amide π^* bonds, demonstrating that the chemistry across the scale surfaces is uniform. SFG spectra at the amide I vibrational band (1550-1850 cm^{-1}) were collected from ventral and dorsal scales across three different individuals. Within the spectra taken from both types of scales, we observe a single peak at 1746 cm^{-1} that originates from ordered ester groups. In the CH stretching region, we observe two distinct vibrational modes in the spectra collected from the dorsal scale - 2850 and 2865 cm^{-1}. Both of these modes stem from symmetric CH_2 vibrations. Three bands are present in the CH spectra from the ventral scale - 2850, 2875, and a broad peak at 2975 cm^{-1}. Again, the peak at 2850 cm^{-1} is related to CH_2 symmetric vibrations, while the peaks at 2875 and 2975 cm^{-1} are related to symmetric and in plane anti-symmetric CH_3 stretches, respectively. Combined this analysis reveals the existence of a previously unknown lipid coating on the surfaces of both the ventral and dorsal scales with molecular structure closely related to their biological function: lipids on ventral scales form a highly ordered layer which provides both lubrication and wear protection at the snake's ventral surface.

11:20am **BI-WeM11 Selective Self-Assembly of Acidic Nanofibrils by a Calcite-Binding Barnacle Cement Protein**, *C. So,* National Research Council postdoc cited at Naval Research Laboratory, *J. Liu, K. Fears, D. Leary, J. Golden,* ***Kathryn Wahl***, US Naval Research Laboratory

Barnacles adhere by secreting a micron-thick proteinaceous layer between themselves and the marine environment that persists throughout their lifespan. These proteins play a dual role in adhering to both the native organism and a foreign substratum, which are often crystalline calcium carbonates from other marine invertebrates, cuticular exoskeleton or sedimentary minerals. Though the sequence and composition of several barnacle cement proteins have been reported, little is known about how these proteins become stably bound to surfaces. Here we use *in situ* atomic force microscopy (AFM) to examine a recombinantly expressed, acidic, calcite-binding 20kDa cement protein, MRCP20. We find that the protein immobilizes on the surface through recognition of distinct atomic steps on the [1014[face of calcite, further assembling on these features into stable nanofibrils. The protein fibrils are continuous and organized at the nanoscale, exhibiting striations with a period of *ca.* 45 nm. The acidic fibrils are also found to manipulate calcite surfaces through the dissolution of underlying calcite features that display the same atomic arrangement. To quantify selectivity, we compare the velocity of atomic steps from calcite etch pits when exposed to water, bulk protein solution, and surface-associated nanofibrils. MRCP20 is found to favor interaction with distinct fast moving steps, where velocity is increased by four- and eight-fold upon exposure to bulk proteins and fibrils, respectively, over steps exposed to solution without protein present. Calcite mineralized in the presence of MRCP20 results in asymmetric crystals, suggesting a similar step-selective behavior by MRCP20 during crystal growth. Cooperative molecular processes with step edge atoms reveal a new regime of biotic interactions with calcite, where specific surface interactions are enhanced through templated long-range nanostructures.

11:40am **BI-WeM12 Thiolene Reaction Applied to Passive Metal Oxide Surfaces for Addressing Protein Adsorption and Cell Adhesion**, ***Anouk Galtayries***, *V. Semetey, A. Dellinger*, Chimie ParisTech, France

The aim of this work is to design surfaces allowing controlling biomolecule adhesion by the study of protein adsorption and cell adhesion. In order to answer this challenge,: the optimization of grafting conditions using the thiol-ene reaction of thiol-terminated ethylene glycol (EG) chains (Oligo-EG or Poly-EG) on a undecenyltrichlorosilane self-assembled monolayer was investigated [1], with the help of surface characterization (angle contact measurement, ellipsometry, fluorescence microscopy, attenuated total reflection infrared *IR-ATR*, X-ray Photoelectron Spectroscopy *XPS*, Time-of-Flight Secondary Ion Mass Spectrometry *ToF-SIMS*) after each reaction step.

Varying different reaction parameters in the methodological investigation of thiol-ene grafting conditions exhibits the development of a bilayer structured system after a 1 minute reaction time as regards OEG grafting, and 1 hour time for PEG grafting. By using different passivated substrates (model silicon single crystal, polycrystalline titanium), different OEG-thiol or PEG-thiol molecules (from 7 to 220 ethylene unit long, methyl-, carboxyl- or amine-terminated), we highlight the range of available versions of this strategy. The terminal chemical functions lead on demand either to protein adsorption inhibition or to biomolecule adsorption, bovine serum albumin (BSA) or fibronectin (Fn) giving access to specific adhesion.

By controlling the light-exposed areas (100 mm-large bands or half-moon surfaces), the photochemistry occurring during the thiol-ene grafting allows to design surface patterning for addressing both protein adsorption and cell adhesion on such sample biointerface on metal oxides.

[1] ``A Facile and Versatile Approach to Design Self-Assembled Monolayers on Glass using Thiol-ene Chemistry", B. Oberleitner, A. Dellinger, M. Déforet, A. Galtayries, A.-S. Castanet,V. Semetey, Chemical Communication, 49, 1615-1617 (2013).

12:00pm **BI-WeM13 Scaling from Single Molecule to Macroscopic Adhesion at Polymer/Metal Interfaces**, ***Thomas Utzig***, *S. Raman, M. Valtiner*, Max-Planck Institut für Eisenforschung GmbH, Germany

Understanding the evolution of macroscopic adhesion based on the fundamental molecular interactions is crucial to design strong and smart polymer/metal interfaces, which play an important role in many industrial and bio-medical applications. Here we show how macroscopic adhesion can be predicted based on single molecular interactions. In particular, we carry out dynamic single molecule force spectroscopy (SM-AFM) in the framework of Bell-Evans' theory to gain information about the energy barrier between the bound and unbound state of an amine/gold junction. Further we use Jarzynski's equality to obtain the equilibrium ground state energy difference of the amine/gold bond from these non-equilibrium force measurements. In addition, we perform Surface Forces Apparatus (SFA) experiments to measure macroscopic adhesion forces at contacts where approximately 10^7 amine/gold bonds are formed simultaneously. The SFA approach provides an amine/gold interaction energy (normalized by the number of interacting molecules) of 36 ± 1 k_BT, which is in excellent agreement with the interaction free energy of 35 ± 3 k_BT calculated using Jarzynski's equality and single molecule AFM experiments. Our results validate Jarzynski's equality for the field of polymer/metal interactions by measuring both sides of the equation. Furthermore, the comparison of SFA and AFM shows how macroscopic interaction energies can be predicted based on single molecular interactions, providing a new strategy to potentially predict adhesive properties of novel glues or coatings as well as bio- and wet adhesion.

Biomaterial Interfaces
Room: 211D - Session BI-WeA

Biophysics, Membranes and Nanoscale Biological Interfaces
Moderator: Stephanie Allen, The University of Nottingham, UK

2:20pm **BI-WeA1 Direct Measurement of Single Molecule Interaction Free Energies at Solid/Liquid Interfaces for the Prediction of Macroscopic Properties**, ***Markus Valtiner***, *S. Raman, T. Utzig, P. Stock*, Max Planck Institut fur Eisenforschung GmbH, Germany

Unraveling the complexity of the macroscopic world based on molecular level details relies on understanding the scaling of single molecule interactions towards integral interactions at the meso- and macroscopic scale. Here, we discuss how one can decipher the scaling of individual single binding interactions at solid/liquid interactions towards the macroscopic level [1], where a large number of these bonds interacts simultaneously. We developed a synergistic experimental approach combining Surface Forces Apparatus (SFA) experiments and single molecule force spectroscopy (SMFS). We show that equilibrium SFA measurements scale linearly with the number density of a model acid-base bond at an interface, providing acid-amine interaction energies of 10.9 ± 0.2 kT. Using Bell-Evans theory together with Jarzynski's equality, we can demonstrate how a set of single molecule interaction forces measured by SMFS similarly converges to an interaction energy of 11 ± 1 kT, with unbinding energy barriers of 25 kT ± 5 kT. This indicates excellent predictive power of our newly developed scaling approach.

In addition, we tested a number of other bonds including hydrophobic, ligand-receptor and metal-polymer bonds with our model and find that our model is widely applicable. Hence, we will discuss in detail how single molecule unbinding energy landscapes can be utilized to predict scenarios where a large number of molecules simultaneously interact, giving rise to both macroscopic equilibrated and non-equilibrated interaction energies during adhesive failure. As such, our experimental strategy provides a unique framework for molecular design of novel functional materials through predicting of large-scale properties such as adhesion, self-assembly or cell-substrate interactions based on single molecule energy landscapes.

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

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

2:40pm **BI-WeA2 Multipurpose Biomembranes of Sandwiches Layers: Deposition and Characterization with Surface and Biological Methods**, *H. Heidari Zare,* Munich University of Applied Sciences, Germany, *D. Jocham,* University Hospital of Schleswig-Holstein, Germany, ***Gerhard Franz***, Munich University of Applied Sciences, Germany

For coating of medical implants, two different strategies have been evolved, either films which can be decomposed after a certain time of impact, or "eternal" layers. Both types can be composed as a homogeneous film or a heterogeneous sandwich layer, which have the charm that the same coating layer can be used not only to protect different pharmaceutical depot layers on top of different substrates but also to allow a retarded emission of drugs, which can be adjusted by its porosity. Our coatings are made of FDA-passed poly-(p-xylylene), or parylene, PPX. It is employed it two systems: for coronary stents, or in antibacterial urinary catheters. In the first case, it protects a restenotic drug which is applied on top of a plasma-roughened metallic surface, in the second application, the porous cap layer protects a silver film, which is deposited on the interior walls of a catheter in a random zebra-stripe design without application of a mask technology. Its morphology can be adjusted by the conditions of preparation.

For capillaries, one challenge is the homogeneous thickness on the interior sidewall from the mouth to the dead end of the capillary, which has been solved by application of a temperature seesaw: Since condensation is an exothermic process, application of the principle of Le Chatelier moves the equilibrium of diffusion with deposition loss to the side with higher internal energy, i. e. to the vaporous phase, thereby equalizing the deposition rate, downward at the mouth and upward at the dead end.

The porosity of the cap layer can be adjusted by its thickness between zero and approx. 1000 nm [1]. Especially for the Gorham method, which is widely applied for the deposition of PPX, thicknesses below 1 µm are difficult to obtain. Applying a method which resembles Papin's principle, this challenge could also be met [2].

The porosity is judged by atomic force microscopy (AFM) and electrochemical impedance spectroscopy (EIS), the loss rate by ICP-OES and polarography, the medical impact by measuring the optical density and applying a growth inhibition test [3]. One of the medical challenges is the confirmation of the minimum inhibition concentration of these compound layers.

[1] F. Schamberger, A. Ziegler, and G. Franz, J. Vac. Sci. Technol. B 30, 051801 (2012)

[2] G. Franz and F. Schamberger,. J. Vac. Sci. Technol. A 31, 061602 (2013)

[3] H. Heidari Zare, St. Sudhop, F. Schamberger, and G. Franz, Biointerphases 9, 031002 (2014)

3:00pm **BI-WeA3 Vascularized Micro-Tissue Engineered Constructs for Drug Screening**, ***Noo Li Jeon***, Seoul National University, Korea **INVITED**

Vasculature is a fundamental building block of tissues. In order to design and fabricate in-vitro organ-on-chip systems, vasculature needs to be integrated with the micro-tissue constructs.

This presentation will describe the development of a novel microfluidic device with perfusable network of blood vessels that: 1) reproduce angiogenesis and vasculogenesis, 2) allow formation of network of perfusable endothelial vessels in 3D tissue, 3) allow observation of cancer and immune cell intravasation and extravasation, and 3) allow measurement of microvessel permeability. Cancer cells can be introduced and their intravasation and extravasation can be observed with live-cell imaging for extended periods and thus control the tumor microenvironment for investing different steps of metastatic cascade. Characterization of the vessels with immuno-histochemical techniques show that tight-junctions form between the endothelial cells and laminin and collagen IV are deposited along the length of the vessel.

The development of vascularized micro-tissue represents a step forward in building organ-on-chip systems. Drug screening and other assays can be performed using live-cell imaging and immunohistochemistry techniques enabling high throughput testing of multiple conditions simultaneously.

4:20pm **BI-WeA7 Controlling Cell Adhesion on Device Surfaces by Nanotopography**, ***Elena Liang***, *E. Mah, S. Wu, A. Yee*, University of California, Irvine

The ability to control cell adhesion on material surfaces is critical to the performance and biointegration of implanted medical devices. Of particular interest to our research is developing an understanding of what role surface topography plays in cell adhesion, which could lead to simple and durable ways to engineer surfaces without having to chemically modify the surface of biomaterials. Our group found that human embryonic stem cells grown on nanopillar structures have a significantly reduced number of focal adhesions per cell and concordantly exhibit increased cell motility on the nanopillars (Kong *et al*. 2013). We hypothesized that pillar nanostructures would prevent cells from adhering. To test this hypothesis, we counted the number of fibroblasts adhering to a variety of surface topographies, which consisted of a flat surface, nanolines, and nanopillars, and examined cell morphology on these surfaces. We created a library of nanopillared polymethylmethacrylate (PMMA) surfaces, including a biomimetic cicada wing replicate (the surface of the wing has a high density of nanopillars with dimensions that are ideal for our studies) made by compressing a negative hPDMS stamp of the cicada wing into PMMA, and pillar arrays of approximately 200 nm diameter nanopillars with center-to-center spacing ranging from 320 nm to 692 nm fabricated with nanoimprint lithography. We also observed the focal adhesions using fibroblasts transfected with paxillin-GFP and tracked migration. After 24 hours, we found that the fibroblasts showed a spread-like morphology on the flat film while those on pillars were smaller and more equiaxed. Preliminary results show that there are noticeably fewer cells on PMMA pillars than on flat PMMA. The focal adhesions on cells on nanopillars appear smaller than focal adhesions of cells on a flat surface. Lastly, cells on nanopillars on average traveled a greater distance than cells on a flat surface. Our study shows that protruding structures in the 100-500 nm size range affect cell adhesion dynamics and structure dimensions modulate the adhesion of cells. This may provide researchers a useful means of controlling cell adhesion on surfaces of implants.

4:40pm **BI-WeA8 Condensation-Mediated "Living" Chain Growth Polymerization: Towards New DNA Nanostructures**, *L. Tang, R. Gu,* Duke University, *J. Lamas,* Texas State University, *N. Li,* North Carolina State University, *S. Rastogi,* Texas State University, *A. Chilkoti,* Duke University, *W. Brittain,* Texas State University, *Y.G. Yingling,* North Carolina State University, ***Stefan Zauscher***, Duke University

Polynucleotide co-polymers promise a rich micellization behavior in solution and hold promise for novel functional materials in nano- and biotechnological applications. We report on the synthesis of biologically-inspired polynucleotides with well-defined sequence, dispersity, and assembly function that have large potential for applications ranging from delivery vehicles of medical therapeutics, sensing applications, to scaffolds for nanowires. Specifically, we exploit the ability of the DNA polymerase, terminal deoxynucleotidyl transferase (TdT), to polymerize long chains of single strand DNA (ssDNA) and to incorporate unnatural nucleotides with useful functional groups into the growing polynucleotide chain. Furthermore, we demonstrate the reversible micellar aggregation of a DNA-azobenzene conjugate, in which the photoisomerization of the initially apolar *trans*-azobenzene moiety to the polar *cis* isomer causes disassembly of the aggregates. Finally, we show how coarse-grained simulations can be used to describe the conformational characteristics of the engineered ssDNA blocks and their self-assembly into a rich spectrum of biomolecular nanostructures in solution and on surfaces.

5:00pm **BI-WeA9 Simple Routes to All-Polymeric Corrals, Flow-Channels and Traps for Studies of Lipid and Protein Diffusion in Supported Lipid Bilayers**, *A. Johnson, P.M. Chapman, A.M. Alswieleh,* University of Sheffield, UK, *P. Bao,* University of Leeds, UK, *A. Tsargorodska, S.P. Armes,* University of Sheffield, UK, *S.D. Evans,* University of Leeds, UK, ***Graham Leggett***, University of Sheffield, UK

We describe simple routes to the fabrication of corrals, channels, traps and other structures for the fabrication of spatially organized lipid bilayers and membrane proteins. These utilize photochemistry and polymer brushes. In the first approach, UV exposure of films of (chloromethylphenyl)trichlorosilane (CMPTS) causes dehalogenation of the surface creating carboxylic acid groups to create hydrophilic, anionic regions, in which lipid mobilities are observed that are similar to those observed on glass surfaces. In masked regions, the halogen remains intact, and is used to grow poly(oligoethyleneglycol methacrylate) (POEGMA) brushes by atom-transfer radical polymerization (ATRP), defining lipid-free walls within which SLBs may be formed by vesicle fusion. Two-component structures are fabricated by using an aminosilane film in which the amine group is protected by a photoremovable nitrophenyl group. Selective exposure, through a mask or using a Lloyd's mirror interferometer, causes patterned deprotection of the film leading to patterned brush growth by ATRP. Poly(Cysteine methacrylate) (PCysMA) is a new, highly biocompatible, stimulus-responsive zwitterionic polymer that forms thick brushes when grown from surfaces by atom transfer radical polymerization (ATRP). Lipid mobility similar to that observed on glass is observed on PCysMA brushes. Measurements of membrane protein diffusion have been made using ac trap structures. After lithographic definition of corrals, channels and other structures, PCysMA is end-capped and the remainder of the surface deprotected; POEGMA brushes are grown by ATRP, enclosing the PCysMA structures. Using interferometric lithography, arrays of close-packed gold nanostructures may be defined on the substrate. These are strongly coupled to photosynthetic membrane proteins, yielding intense extinction spectra. These gold nanostructures are incorporated into brush corrals and other structures, with polymer brushes grown to the same height as the gold nanostructures, enabling the formation of a continuous SLB with integral plasmonic reporters for membrane protein activity.

5:20pm **BI-WeA10 Measuring Cardiomyocyte Contractions on Silicon Carbide Micromechanical Resonators**, ***Hao Tang***, *H. Jia, P.X.-L. Feng*, Case Western Reserve University

Heart functions are mainly determined by its contractility. Monitoring the contraction curve at single cell level may help attain a deeper understanding of cardiomyocyte contraction process[1], heart failure mechanism[2] and potential methods for drug screening. The contraction frequency, contraction amplitude as well as contraction and relaxation rates of cardiomyocytes all together compose the contraction curve and reflect the health condition of heart tissues.

At the single-cell level, most contractility measurement methods are based on measuring the length change[2] or force change[3] of single cardiomyocyte. Methods based on length change often require massive and fast image processing, therefore, its time resolution is restricted by the capturing and processing speed, and spatial resolution is limited by the diffraction of optical system (typically 0.2um). Methods based on force change require complex readout elements that are compatible with biological environments, which on the other hand results in complex fabrication process.

In this work, we take an initial step to measure the cardiomyocyte contraction in a dynamic mode using SiC micromechanical resonators. As a superior material for bioMEMS platforms, SiC has excellent mechanical, optical, chemical, thermal properties as well as unique biocompatibility[4],[5]. Frequency-shift-based sensing using micromechanical resonators[6],[7] offers possibilities of monitoring mass distribution changes during cardiomyocyte contraction process with high sensitivity. Our dynamic sensing method provides an alternative for cardiomyocyte contraction measurement, with promising applications in heart failure research and drug screening.

[1] D.M. Bers, *Nature*, vol. 415, no. 6868, pp. 198-205, 2002.

[2] R.V. Yelamarty, et al., *Am. J. Physiol.*, vol. 262, no. 4, pp. C980-C990, 1992.

[3] G. Lin, et al., *IEEE Trans. Biomed. Eng.*, vol. 48, no. 9, pp. 996-1006, 2001.

[4] H. Jia, et al., *MEMS 2015*, pp. 698-701, Estoril, Portugal, Jan. 18-22, 2015.

[5] C. Coletti, et al., *Silicon Carbide Biotechnology*, 1st Edition, pp. 119-152, 2012.

[6] K. Park, et al., *Proc. Natl. Acad. Sci. U.S.A.*, vol. 107, no. 48, pp. 20691-20696, 2010.

[7] M.S. Hanay, et al., *Nature Nanotech.*, vol. 10, no. 4, pp. 339-344, 2015.

5:40pm **BI-WeA11 Programming the Robust Self-organization of Human Tissues using Interfacial Interactions**, ***Zev Gartner***, University of California, San Francisco **INVITED**

Developing tissues contain motile populations of cells that can self-organize into spatially ordered tissues based on differences in their interfacial surface energies. However, it is unclear how self-organization by this mechanism remains robust when interfacial energies become heterogeneous in either time or space. The ducts and acini of the human mammary gland are prototypical heterogeneous and dynamic tissues comprising two concentrically arranged cell types. To investigate the consequences of cellular heterogeneity and plasticity on cell positioning in the mammary gland, we reconstituted its self- organization from aggregates of primary cells in vitro. We find that self-organization is dominated by the interfacial energy of the tissue–ECM boundary, rather than by differential homo- and heterotypic energies of cell–cell interaction. Surprisingly, interactions with the tissue–ECM boundary are binary, in that only one cell-type interacts appreciably with the boundary. Using mathematical modeling and cell-type-specific knockdown of key regulators of cell–cell cohesion, we show that this strategy of self-organization is robust to severe perturbations affecting cell–cell contact formation. We also find that this mechanism of self-organization is conserved in the human prostate. Therefore, a binary interfacial interaction with the tissue boundary provides a flexible and generalizable strategy for forming and maintaining the structure of tissues that exhibit abundant heterogeneity and plasticity. Our model also predicts that mutations affecting binary cell–ECM interactions are catastrophic and could contribute to loss of tissue architecture in diseases such as breast cancer.

In-Situ Spectroscopy and Microscopy Focus Topic
Room: 211B - Session IS+SS+NS+BI+VT+MN+AS-WeA

In situ Imaging of Liquids using Microfluidics

Moderator: Xiao-Ying Yu, Pacific Northwest National Laboratory, Stephen Nonnenmann, University of Massachusetts - Amherst

2:20pm **IS+SS+NS+BI+VT+MN+AS-WeA1 *In Situ* Multimodal Biological Imaging using Micro- and Nanofluidic Chambers**, ***James Evans***, *C. Smallwood*, Pacific Northwest National Laboratory **INVITED**

Biological organisms have evolved a number of spatially localized and highly orchestrated mechanisms for interacting with their environment. Since no single instrument is capable of probing the entire multidimensional landscape, it is not surprising that one of the grand challenges in biology remains the determination of how dynamics across these scales lead to observed phenotypes.

Therefore, there is a need for in-situ correlative multimodal and multiscale imaging to fully understand biological phenomena and how chemical or structural changes at the molecular level impact the whole organism. We have been advancing new methods for both cryogenic and in-situ correlative analysis of biological samples using electron, ion, optical and x-ray modalities. Central to this work is the development of new micro- and

nanofluidic chambers that enable in-situ observations within precisely controlled liquid-flow environments. In this talk I will review the design of these new chambers, highlight current science applications and outline our future goals for adding additional functionality and expanding the versatility of the devices to other disciplines.

3:00pm **IS+SS+NS+BI+VT+MN+AS-WeA3 Glyoxal Aqueous Surface Chemistry by SALVI and Liquid ToF-SIMS**, ***Xiao Sui***, *Y. Zhou, Z. Zhu,* Pacific Northwest National Laboratory, *J. Chen,* Shandong University, China, *X.-Y. Yu*, Pacific Northwest National Laboratory

Glyoxal, a ubiquitous water-soluble gas-phase oxidation product in the atmosphere, is an important source of oxalic acid, a precursor to aqueous secondary organic aerosol (SOA) formation. Many recent laboratory experiments and field observations suggest that more complex chemical reactions can occur in the aqueous aerosol surface; however, direct probing of aqueous surface changes is a challenging task using surface sensitive techniques. The ability to map the molecular distribution of reactants, reaction intermediates, and products at the aqueous surface are highly important to investigate surface chemistry driven by photochemical aging. In this study, photochemical reactions of glyoxal and hydrogen peroxide (H_2O_2) were studied by a microfluidic reactor, System for Analysis at the Liquid Vacuum Interface (SALVI), coupled with Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS). Aqueous surfaces containing glyoxal and hydrogen peroxide were exposed to UV light at variable lengths of time and were immediately analyzed in the SALVI microchannel by in situ liquid ToF-SIMS. In addition, various control samples were conducted to ensure that our findings were reliable. Compared with previous results of bulk solutions using ESI-MS, our unique liquid surface molecular imaging approach provided observations of glyoxal hydrolysis (i.e., first and secondary products, dimers, trimers, and other oligomers) and oxidation products (i.e., glyoxylic acid, oxalic acid and formic acid) with sub-micrometer spatial resolution. We potentially provide a new perspective and solution to study aqueous surface chemistry as an important source of aqueous SOA formation of relevance to atmospheric chemistry known to the community.

3:20pm **IS+SS+NS+BI+VT+MN+AS-WeA4 Investigating *Shewanella* Oneidensis Biofilm Matrix in a Microchannel by *In Situ* Liquid ToF-SIMS**, ***Yuanzhao Ding***, Nanyang Technological University, Singapore, *X. Hua, Y. Zhou, J. Yu, X. Sui, J. Zhang, Z. Zhu,* Pacific Northwest National Laboratory, *B. Cao,* Nanyang Technological University, Singapore, *X.-Y. Yu*, Pacific Northwest National Laboratory

Biofilms consist of a group of micro-organisms attached onto surfaces or interfaces and embedded with a self-produced extracellular polymeric substance (EPS) in natural environments. The EPS matrix, like the "house of the cells", provides bacteria cells with a more stable environment and makes them physiologically different from planktonic cells. *Shewanella oneidensis* MR-1 is a metal-reducing bacterium, forming biofilms that can reduce toxic heavy metals. This capability makes *S. oneidensis* biofilms very attractive in environmental applications. To better understand the biofilm EPS matrix composition at the interface, in situ chemical imaging with higher spatial resolution and more molecular level chemical information is strongly needed. Traditionally, electron microscopy and fluorescence microscopy are common imaging tools in biofilm research. However, the bottlenecks in these imaging technologies face the limitations that it is difficult for them to provide chemical information of small molecules (e.g., molecule weight <200). In this study, we use an emerging technology liquid Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) to observe *S. oneidensis* biofilm cultured in a vacuum compatible microchannel of the System for Analysis at the Liquid Vacuum Interface (SALVI) device. Chemical spatial distributions of small organic molecules that are considered to be the main building components of EPS in live biofilms are obtained. Principal component analysis is used to determine differences among biofilms sampled along the microchannel. This new approach overcomes previous limitations in live biofilm analysis and provides more chemical information of the EPS relevant to biofilm formation. Better understanding of the biofilm matrix will potentially fill in the knowledge gap in biofilm surface attachment and detachment processes and improve the engineering and design of *S. oneidensis* biofilms with high efficiencies in heavy metal reduction.

4:20pm **IS+SS+NS+BI+VT+MN+AS-WeA7 Ultrafast Proton and Electron Dynamics in Core-Level Ionized Aqueous Solution**, ***Bernd Winter***, Helmholtz-Zentrum Berlin für Materialien und Energie/Elektronenspeicherring BESSY II, Germany **INVITED**

Photo- and Auger electron spectroscopy from liquid water reveals a novel electronic de-excitation process of core-level ionized water in which a pair of two cations forms, either $H_2O^+ \cdot H_2O^+$ or $OH^+ \cdot H_3O^+$. These reactive species are the delocalized analogue to H_2O^{2+}, formed in a localized on-site Auger decay, and are expected to play a considerable role in water radiation chemistry. Both cationic pairs form upon autoionization of the initial ionized water molecule, and we are particularly interested in the situation where autoionization occurs from a structure that evolves from proton transfer, from the ionized water molecule to a neighbor molecule, within a few femtoseconds. The actual autoionization is either through intermolecular Coulombic decay (ICD) or Auger decay. Experimental identification of the proton dynamics is through isotope effects. A question that arises is whether such so-called proton-transfer mediated charge separation (PTM-CS) processes occur in other and similarly hydrogen-bonded solute molecules as well. This is indeed the case, and is illustrated here for ammonia and glycine in water, as well as for hydrogen peroxide in water, where characteristic differences are detected in the Auger-electron spectra from the light *versus* heavy species, *i.e.*, NH_3 in H_2O *versus* ND_3 in D_2O, glycine(H) in H_2O versus glycine(D) in D_2O, and H_2O_2 in H_2O versus D_2O_2 in D_2O. The important spectral feature here is the high-kinetic energy tail of the Auger spectrum, which has no gas-phase analogue, and hence reflects the participation of solvent water in the relaxation process. The probability of the proton dynamics, judged from the intensities of the electron signal and inferred from methods of quantum chemistry and molecular dynamics, is found to depend on hydrogen-bond strength and hence on the specific hydration configuration. Favorable configurations for hydrogen peroxide(aq) occur due to the molecule's flexible structure. In ammonia(aq) the PTM processes are found to be less probable than for water(aq), which is attributed to the planarization of the ammonia molecule upon core-level ionization. The effect is smaller for the neutral $-NH_2$(aq) group of glycine at basic pH, where intramolecular dynamics is less likely. Nature and chemical reactivity of the initial transient species and their role for radiation chemistry and for local reactions relevant for biological molecules in an aqueous environment are discussed for the different molecular hydrogen-bonded systems.

5:00pm **IS+SS+NS+BI+VT+MN+AS-WeA9 Water Dissociation in Metal Organic Frameworks with Coordinatively Unsaturated Metal Ions: MOF-74**, ***Kui Tan***, The University of Texas at Dallas, *S. Zuluaga,* Wake Forest University, *E. Fuentesf,* The University of Texas at Dallas, *H. Wang,* Rutgers University, *P. Canepa,* Wake Forest University, *J. Li,* Rutgers University, *T. Thonhauser,* Wake Forest University, *Y.J. Chabal*, The University of Texas at Dallas

Water dissociation represents one of the most important reactions in catalysis, essential to the surface and nano sciences. However, the dissociation mechanism on most oxide surfaces is not well understood due to the experimental challenges of preparing surface structures and characterizing reaction pathways. To remedy this problem, we propose the metal organic framework MOF-74 as an ideal model system to study water reactions. Its crystalline structure is well characterized; the metal oxide node mimics surfaces with exposed cations; and it degrades in water. Combining *in situ* IR spectroscopy and first-principles calculations, we explored the MOF-74/water interaction as a function of vapor pressure and temperature. Here, we show that, while adsorption is reversible below the water condensation pressure (~19.7 Torr) at room temperature, a reaction takes place at ~150 ˚C even at low water vapor pressures. This important finding is unambiguously demonstrated by a clear spectroscopic signature for the direct reaction using D_2O, which is not present using H_2O due to strong phonon coupling. Specifically, a sharp absorption band appears at 970 cm^{-1} when D_2O is introduced at above 150 ˚C, which we attribute to an O-D bending vibration on the phenolate linker. Although H_2O undergoes a similar dissociation reaction, the corresponding O-H mode is too strongly coupled to MOF vibrations to detect. In contrast, the O-D mode falls in the phonon gap of the MOF and remains localized. First-principles calculations not only positively identify the O-D mode at 970 cm^{-1} but derive a pathway and kinetic barrier for the reaction and the final configuration: the D (H) atom is transferred to the oxygen of the linker phenolate group, producing the notable O-D absorption band at 970 cm^{-1},while the OD (or OH) binds to the open metal sites. Experimental data and theoretical modeling further shows that the reaction is facilitated by a cooperative effect of several H_2O molecules. This finding explains water dissociation in this case and provides insight into the long-lasting question of MOF-74 degradation. Overall, it adds to the understanding of molecular water interaction with cation-exposed surfaces to enable development of more efficient catalysts for water dissociation.

Ref: K. Tan, S. Zuluaga, Q. Gong, P. Canepa, H. Wang, J. Li, Y. J. Chabal and T. Thonhauser, *Chem. Mater.*, 2014, **26**, 6886-6895.

5:20pm **IS+SS+NS+BI+VT+MN+AS-WeA10 Competitive Co-Adsorption of CO_2 with H_2O, NH_3, SO_2, NO, NO_2, N_2, O_2, and CH_4 in M-MOF-74 (M= Mg, Co, Ni): The Role of Hydrogen Bonding**, *K. Tan,* The University of Texas at Dallas, ***Sebastian Zuluaga***, Wake Forest University, *H. Wang,* Rutgers University, *Y. Gao,* The University of Texas at Dallas, *J. Li,* Rutgers University, *T. Thonhauser,* Wake Forest University, *Y.J. Chabal,* The University of Texas at Dallas

The importance of co-adsorption for applications of porous materials in gas separation has motivated fundamental studies, which have initially focused on the comparison of the binding energies of different gas molecules in the pores (i.e. energetics) and their overall transport. By examining the competitive co-adsorption of several small molecules in M-MOF-74 (M= Mg, Co, Ni) with *in-situ* infrared spectroscopy and *ab initio* simulations, we find that the binding energy at the most favorable (metal) site is not a sufficient indicator for prediction of molecular adsorption and stability in MOFs. Instead, the occupation of the open metal sites is governed by kinetics, whereby the interaction of the guest molecules with the MOF organic linkers controls the reaction barrier for molecular exchange. Specifically, the displacement of CO_2 adsorbed at the metal center by other molecules such as H_2O, NH_3, SO_2, NO, NO_2, N_2, O_2, and CH_4 is mainly observed for H_2O and NH_3, even though SO_2, NO, and NO_2, have higher binding energies (~70-90 kJ/mol) to metal sites than that of CO_2 (38 to 48 kJ/mol) andslightly higher than water (~60-80 kJ/mol). DFT simulations evaluate the barriers for H_2OàCO_2 and SO_2àCO_2 exchange to be ~ 13 and 20 kJ/mol, respectively, explaining the slow exchange of CO_2 by SO_2, compared to water. Furthermore, the calculations reveal that the kinetic barrier for this exchange is determined by the specifics of the interaction of the second guest molecule (e.g., H_2O or SO_2) with the MOF ligands. Hydrogen bonding of H_2O molecules with the nearby oxygen of the organic linker is found to facilitate the positioning of the H_2O oxygen atom towards the metal center, thus reducing the exchange barrier. In contrast, SO_2 molecules interact with the distant benzene site, away from the metal center, hindering the exchange process. Similar considerations apply to the other molecules, accounting for much easier CO_2 exchange for NH_3 than for NO, NO_2, CH_4, O_2, and N_2 molecules. In this work, critical parameters such as kinetic barrier and exchange pathway are first unveiled and provide insight into the mechanism of competitive co-adsorption, underscoring the need of combined studies, using spectroscopic methods and *ab initio* simulations to uncover the atomistic interactions of small molecules in MOFs that directly influence co-adsorption.

Ref: K. Tan, S. Zuluaga, Q. Gong, Y. Gao, N. Nijem, J. Li, T. Thonhauser and Y. J. Chabal, *Chem. Mater.*, 2015, **27**, 2203-2217.

6:00pm **IS+SS+NS+BI+VT+MN+AS-WeA12 *In Situ* STM Observation of Pd(110) Under the Hydrogen Pressure Between 10^{-6} Pa and 10^{-3} Pa**, ***Jun Yoshinobu***, *H. Kikuchi, T. Koitaya, K. Mukai, S. Yoshiomoto*, University of Tokyo, Japan

Hydrogen adsorption and absorption on/in Pd and Pd alloys are vital processes for the hydrogen storage and hydrogen permeation materials. We investigated the Pd(110) surface under the hydrogen pressures between 10^{-6} Pa and 10^{-3} Pa at room temperature using in-situ atom-resolved scanning tunneling microscopy (STM). We observed missing-atom, missing-row and added-row structures and the number of atoms in these structures were quantitatively analyzed as a function of exposure time. Note that adatoms were not detected probably because they were mobile in the present experimental conditions. At 10^{-6} Pa, the numbers of missing-row and added-row atoms increased up to ~20 L (langmuir) and after that they were gradually reaching the saturation (steady-state). On the other hand, the number of missing-atoms decreased gradually from the initial stage. With increasing the hydrogen pressures the number of missing-row atoms and added-row atoms increased, and the whole surface was covered with these reconstructed structures after large exposures (>1000 L). It has been known that not only hydrogen adsorption but also hydrogen absorption occur in such conditions. Thus, the missing-row and added-row reconstructed structures are inevitable for hydrogen absorption on Pd(110).

Thin Film
Room: 114 - Session TF+AS+BI-WeA

Thin Films for Biological and Biomedical Applications
Moderator: Christophe Vallee, LTM, Univ. Grenoble Alpes, CEA-LETI, Angel Yanguas-Gil, Argonne National Lab

2:20pm **TF+AS+BI-WeA1 On-chip Characterization of Engineered Nanomaterial Surface Properties by Real-time Affinity Monitoring**, *C. Desmet, A. Valsesia, P. Colpo,* European Commission, Joint Research Centre (JRC), ***Francois Rossi***, European Commission, Joint Research Centre (JRC), Italy **INVITED**

The exhaustive characterization of the physico-chemical properties of engineered nanomaterials (ENMs) is essential to understand their mode of action and potential impact on health and environment. The development of characterization methods has been the object of important work in the past years, and has led to a better understanding on the ENM interaction with cellular systems and living organisms. One of the important surface properties of ENMs is the surface energy, for which there is no standard characterization technique established. Here, we demonstrate the feasibility of a characterization method based on a disposable microfluidic chip connected to an optical reader. The detection platform is based on the use of a micropatterned surface with tuned surface properties to bind ENMs selectively by hydrophobic forces and electrostatic interactions. The real-time absorption of ENMs on the differently functionalized micro domains is monitored by a microscope-coupled camera and gives information on the kinetics of adsorption, related to the affinity of the ENMs for the different surfaces as a function of their sizes and shapes. Interpretation of the results within the extended DLVO theory allows retrieving the surface energy characteristics of the ENMs surfaces. The key advantage of the device is the increase of the characterization throughput thanks to the all-in-one characterization process and the multiplexing that is able to replace the use of different methods and expensive equipment. In this way, the full characterization of ENMs could be expanded in all the areas covering nanomaterial-related applications.

4:20pm **TF+AS+BI-WeA7 Titanium-Niobium Thin Films Deposited by Magnetron Sputtering on AISI 316L Stainless Steel Substrate**, *D. Gonzalez, T.C. Niemeyer, C.R.M. Afonso,* ***Pedro Nascente***, Federal University of Sao Carlos, Brazil

Metallic biomaterials such as AISI 316L stainless steel (SS), chromium-cobalt alloys, titanium and its alloys are commonly used in medical implants due to their interesting mechanical properties and thermal stability. However, 316L SS and Cr-Co alloys have much higher elastic modulus than bone, causing the loss after some years of implantation [1]. The elastic modulus of Ti-based alloys ranges from 55 to 110 GPa, being significantly lower than those for 316L SS (210 GPa) and Cr-Co alloys (240 GPa), making them more suitable for use in dental and orthopedic applications. Also Ti alloys present high strength, low density, high corrosion resistance, and good biocompatibility [1]. Pure Ti has two allotropic forms: hexagonal closest-packed (hcp), known as α phase, and body centered cubic (bcc), known as β phase, structures. Studies have shown that the addition of alloying β-stabilizing elements such as V, Mo, Nb, Zr, Mo, and Ta causes the decreasing of the modulus of elasticity of the β-Ti alloys without compromising the strength [1]. In this study, thin films of Ti-Nb alloys were deposited on AISI 316L stainless steel substrate by magnetron sputtering, and the structure, morphology, and composition of the films were analyzed by means of X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM). Thin films of three compositions were produced: $Ti_{85}Nb_{15}$ (Ti-26wt% Nb), $Ti_{80}Nb_{20}$ (Ti-33wt% Nb), and $Ti_{70}Nb_{30}$ (Ti-45wt% Nb). Structural characterization by XRD indicated that only the β phase was present in the thin films. XPS analysis showed a predominance of oxidized Ti and Nb on the film surfaces. TEM analyses were carried out in the following image modes: bright field (BF) images, selected area diffraction (SAD), scanning mode (STEM) BF and in annular dark field (ADF), and X-ray mapping using energy dispersive spectroscopy (EDS). For the $Ti_{80}Nb_{20}$ alloy film, TEM analysis showed columnar grains (~100 nm width) of -Ti phase, with a Nb-rich transition layer ranging from finer grains (in contact with SS substrate) to a coarser columnar grains. For the $Ti_{75}Nb_{25}$ alloy film, TEM analysis showed columnar grains (~50 nm width) of β-Ti phase, with a transition layer away from the SS substrate.

Acknowledgements: A.L. Gobbi, C.A. Silva, S.R. Araujo, and J. Bettini from the Brazilian Nanotechnology National Laboratory, for their assistance in the growth and characterization of the thin films; and CNPq and CNPEM (Brazil), for support.

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4:40pm **TF+AS+BI-WeA8 SAM-based Models of Cell Surfaces to Study the Interactions with Lectins and Bacterial Fimbriae**, ***Andreas Terfort***, University of Frankfurt, Germany, *K. Lindhorst*, University of Kiel, Germany

Biologically important events such as cell-cell adhesion or infection typically start by directed and selective interactions with the highly glycosylated layer surrounding most eukaryotic cells. This layer, called the glycocalyx, consists of intricate glycopolymers, which – although in apparent disorder – clearly identify the cells. It is therefore of paramount interest to understand, which structural elements are important for the cell identification.

Self-assembled monolayers (SAM) can be used to simulate the chemical and sterical environment within such a glycocalyx. For this, glycosides are attached to oligoethyleneglycol (OEG) chains, which simulate the hydrogel matrix for the respective receptor. In this talk, we will focus on mannose-derivatives, which can be selectively recognized either by a lectin, concanvalin A, or by the adhesive fimbriae (tiny protein extrusions) of E. coli cells.

We would like to present different strategies for the construction of such SAMs [1,2] and discuss the advantages and disadvantages of these approaches. In extension of the mostly static systems, we will also present an approach to dynamically reorient the glycoside at the interface to determine the influence of steric factors on surface recognition [3].

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5:00pm **TF+AS+BI-WeA9 Improving the Long-Term Stability of Thin-Film Contact and Electrode Metallizations for Implantable Silicon Neural Interfaces**, ***Brian Baker***, *R. Caldwell*, University of Utah, *H. Mandal*, Blackrock Microsystems, *R. Sharma, P. Tathireddy, L.W. Rieth*, University of Utah

The Utah Electrode Array (UEA) is a penetrating multi-electrode interface designed to be implanted and communicate directly with the brain and peripheral nerves through recording and stimulation. These devices are used for treating neural disorders and controlling prosthetics.

The UEA is micromachined out of single crystal silicon and uses a Pt/Ir/IrOx thin film metallization stack as an electrical interface on the electrode tip and a Pt/Ir/Pt stack on the backside contacts. Delamination of these thin metal layers has been observed during fabrication processes, soak testing, and in vivo operation, and is the critical failure mode examined in this study.

Db-FIB and Cross-sectional STEM analysis were used to identify Kirkendall voids as the root cause of the adhesion failures. This investigation showed that these voids form during the platinum silicide annealing process at the interface between the PtSi and the Ir layers.

Typical thicknesses of the UEA metallization are 200 nm/500 nm/520 nm Pt/Ir/IrOx, and 200 nm/200 nm/325 nm Pt/Ir/Pt. We report the results of replacing the 200 nm base layer with 1) a 25 nm Pt base layer or 2) a 50 nm co-sputtered PtSi base layer. These layers were subjected to typical UEA annealing conditions of 375 °C in forming gas for 45 minutes, followed by a 475 °C, 30 minute oxygen anneal.

Cross-sectional STEM elemental mapping of each film stack showed complete transformation of the platinum layer to PtSi, with a 40 nm layer of iridium silicide formed at the PtSi/Ir interface. In addition, a a reduction in the nanogaps caused by Kirkendall voiding was demonstrated by STEM analysis in the two new film stacks.

Both the 25 nm Pt base layer stack and the 50 nm co-sputtered PtSi base layer stack demonstrate low-resistance Ohmic contacts and wire bondability after annealing. Further electrical characterization of these thinner base layer stacks used on tip metal demonstrated impedances of 5-10 kOhms and charge injection capacities of 1-2 mC/cm^2 for typical electrode tip surface areas. Cross-sectional STEM analysis of the reactively sputtered iridium oxide film reveals a three dimensional morphology whose nanostructures provide a large augmentation of electrode surface area and a corresponding increase in charge injection capacity. In vitro stimulation and accelerated lifetime tests are ongoing and electrical measurements and thin film adhesion stability will be reported.

5:20pm **TF+AS+BI-WeA10 On-Surface Synthesis of Organic Nanostructures on Copper Surfaces**, *Q.T. Fan*, University of Science and Technology of China, *J.M. Gottfried*, Philipps-Universität Marburg, Germany, ***Junfa Zhu***, University of Science and Technology of China

The on-surface synthesis of organic nanostructures known as bottom-up approach paves a new way for surface structuring, which plays a vital role in catalysis, sensor systems, or organic electronics. In this presentation, we will report our recent studies on the on-surface synthesis of 2D organic nanostructures on Cu(111) and Cu(110) surfaces using a specially designed bromo-terphenyl precursor, namely 4,4''-dibromo-*meta*-terphenyl (DMTP). The study was performed under ultra-high vacuum conditions using a combination of scanning tunneling microcopy (STM) and X-ray photoelectron spectroscopy (XPS). The results indicate that the two different surface structures of Cu drive the precursor molecule to form different nanostructures on the surface. We will show temperature-dependent organic nanostructures formed after DMTP adsorbed on Cu(111) and Cu(110). These organic nanostructures include large-area, defect-free 2D ordered nonostructures of intact DMTP on Cu(111), 1- or 2D polymeric zigzag organometallic intermediates formed on Cu(111) and Cu(110), and the macromolecular nonostructures including hexagonal close-packed arrays of cyclo-octadecaphenylene (hyperbenzene), oligophenylene nanowires formed through Ullmann reaction mechanism. *This work is supported by the National Natural Science Foundation of China (21173200,* 21473178*) and National Basic Research Program of China (*2013CB834605*)*

5:40pm **TF+AS+BI-WeA11 Carbon Nanotube-Templated, Porous Films for Thermal Isolation**, *J.M. Lund, D.B. Syme, R. Vanfleet, R.C. Davis, B.D. Jensen*, ***Brian Iverson***, Brigham Young University

Sensor usage has increased dramatically in detection applications due to miniaturization of components through micro and nanofabrication. These fabrication methods have also greatly increased production rates, as several sensors can be constructed in parallel. Reduction in feature size of sensors has resulted in an increase in sensor component proximity, making thermal diffusion or cross talk detrimental to proper function. This work investigates the use of carbon nanotube-templated manufacturing (CNT-M) to create thin-film, isolation layers for use in thermal sensors. CNT-M is a process wherein carbon nanotubes are used as a scaffold and coated with insulating materials (e.g. SiO_2) to create porous insulating films. Carbon nanotubes are removed in a post-deposition, burn out process rendering a porous matrix of insulating material. Thin-films are characterized using scanning electron microscopy, nanoindentation and the 3-omega method to determine mechanical and thermal properties. Thermal conductivity on the order of air has been observed while still maintaining a rigid structure that is compatible with subsequent MEMS processing.

Surface Modification of Materials by Plasmas for Medical Purposes Focus Topic
Room: 211D - Session SM+AS+BI+PS-ThM

Plasma Processing of Biomaterials
Moderator: Deborah O'Connell, University of York, UK, Satoshi Hamaguchi, Osaka University, Japan

8:00am **SM+AS+BI+PS-ThM1 Potential of Low Temperature Plasma Sources in Cancer Treatment**, ***Jean-Michel Pouvesle***, GREMI CNRS/Université d'Orléans, France, *G. Collet*, CNRS, *E. Robert*, GREMI CNRS/Université d'Orléans, France, *L. Ridou*, CNRS-CBM, France, *S. Dozias*, *T. Darny*, GREMI CNRS/Université d'Orléans, France, *B. El Hafni-Rahbi*, *C. Kieda*, CNRS-CBM, France **INVITED**

The last decade has seen an impressive increase of the research dedicated to the biomedical applications of low temperature Non Thermal Plasmas (ltNTP), especially with plasma sources working at atmospheric pressure. Medical applications of ltNTP now concern a very wide range of domains including cancer treatment. The antitumor effect of ltNTP has been clearly shown *in vivo* on murine modelswith various cancer types (bladder, colon, glioblastoma, melanoma, ovary, pancreas). Although the involved mechanisms are far from being fully understood, the therapeutic effect is now totally admitted and the first clinical study (head and neck) has been reported [1]. In case of plasma jet experiments, the observed effect are most of the time attributed to the very rich chemistry generated by the interaction of the rare gas plasma plume with the surrounding environment constituted either from the ambient air, or this latter in complex interaction with liquids at the interface with the targeted organ. Our recent experiments performed on tissue oxygenation[2] or breast cancer treatments on immunocompetent mice [3] lead to the conclusion that probably the involved chemistry couldn't, alone, completely allow describing the observed phenomena. This, especially under very soft treatment conditions, is suggesting possible triggering of some immune system chain processes and also possible modifications in the microenvironment of tissue and tumors. In this context, there is still an unknown role of the electric field associated with the ionization front or generated in the environment of the plasma plume tip. Taking into consideration the recent vessel normalization based-cancer treatment, the ltNTP effect should be further investigated in view of blood vessels structure and function (blood flow) as well as tumor hypoxia compensation to confirm a possible ltNTP-based adjuvant approach for cancer treatments. These results suggest new ways, especially combined therapy, to consider the plasma and its therapeutic delivery in ltNTP-based tumor therapy. In this talk, after a presentation of the context and the plasma devices, we will go through the specific case of cancer treatment with what have been already demonstrated *in vitro* and *in vivo*, what can be directly linked with the produced discharges, including recent results on electric field measurements in plasma biological application conditions.

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8:40am **SM+AS+BI+PS-ThM3 Plasma Polymerized Polypyrrole Thin Films and Their Use in Drug Release Control**, *C. Li*, National Yang Ming University, Taiwan, Republic of China, ***Yung Te Lee***, National Central University, Taiwan, Republic of China, *J.H. Hsieh*, Ming Chi University of Technology, Taiwan, Republic of China

Polypyrrole thin films were deposited using a plasma polymerization process. During deposition, power input (between 30W to 70W), monomer (pyrrole) flow rate (30 sccm to 50 sccm), and Ar flow rate were varied. Optical emission spectroscopy (OES) was used to study the plasma characteristics under each deposition condition. After deposition, these films were characterized using FTIR, AFM, ellipsometry, ultraviolet–visible (UV–vis) spectroscopy, and surface profilometer. Eventually, these films were applied to control drug release rate under different thickness and structure. The results were correlated with the process parameters and plasma conditions.

9:00am **SM+AS+BI+PS-ThM4 Thin Film Metallic Glass: A Novel Coating for Various Biomedical Applications**, ***Chia-Chi Yu***, *Y. Tanatsugu*, *S. Chyntara*, *C.M. Lee*, *W. Diyatmika*, *J.P. Chu*, National Taiwan University of Science and Technology, Taiwan, Republic of China, *M.J. Chen*, *S.H. Chang*, *W.C. Huang*, Mackay Memorial Hospital Tamsui Campus, Taiwan, Republic of China

Thin film metallic glasses (TFMGs) exhibit unique properties such as high strength, smooth surface as well as good wear- and corrosion-resistances due to their amorphous atomic structure. The biocompatibility and antibacterial property of TFMGs can also be obtained, which show great potential for biomedical applications. In addition, the low surface free energy of TFMGs in certain compositions can be achieved and leads to the relatively high hydrophobicity and the low friction coefficient.

In this presentation, various applications of TFMG are discussed, including the property enhancements of dermatome blade and syringe needle, thrombosis reduction for intravenous catheter, and the suppression of cancer cell attachments. A Zr-based TFMG is coated on substrates by using magnetron sputtering. The TFMG-coated dermatome blade show a great enhancement of durability and sharpness, compared with those of the bare one. For the syringe needle, significant reductions in insertion and retraction forces for TFMG-coated needle are achieved due to the non-sticky property and relatively low coefficient of friction. For thrombosis reduction, less platelet aggregations are observed on the TFMG than that on the bare glass in platelets adhesion test, suggesting TFMG-coated catheters is potentially useful to be placed into vessels for long periods of time with reduced numbers of the aggregation of blood platelets. For cancer cell attachment suppressions, TFMG exhibits the least cancer cell attachment among other control groups. Thus, anti-proliferation and anti-metastasis of medical tools can be achieved with TFMG coating.

9:20am **SM+AS+BI+PS-ThM5 Plasma Surface Functionalization of Nano-structured Materials for Biomedical Applications**, ***Masaaki Nagatsu***, *H. Chou*, *A. Viswan*, *T. Abuzairi*, *M. Okada*, *M.A. Ciolan*, Shizuoka University, Japan, *N.R. Poespawati*, *R.W. Purnamaningsih*, University of Indonesia, *A. Sakudo*, University of the Ryukyus, Japan, *S. Bhattacharjee*, Indian Institute of Technology, Kanpur, India **INVITED**

In this study, we will present the recent experimental results on plasma surface functionalization of nano-structured materials for bio-medical applications.

First, with the graphite-encapsulated magnetic nanoparticles(MNPs), we studied the surface functionalization by using the Ar plasma pre-treatment followed by NH_3 plasma post-treatment, to introduce the amino groups onto the surface of the nanoparticles.[1)] The amino group population of each nanoparticle with a typical diameter of 20 nm was evaluated by using the conventional chemical technique using SPDP and DTT solutions and we obtained about 8×10^4 amino groups per nanoparticle.[2)] Immobilization of the antibody of influenza virus onto the surface of amino-modulated magnetic nanoparticles was then performed for aiming at studying the feasibility of collection and condensation of virus. After magnetic separation, we succeeded in a significant concentration of the influenza virus number compared with that of the initial sample.[3)] Using the same method, we also demonstrated a higher concentration of Salmonella about 70 times higher than that of initial sample by the magnetic separation.[4)] The present results suggest the feasibility of the proposed plasma surface functionalized MNPs for rapid concentration of influenza virus or various bacteria.

As the second topic, the selective ultrafine surface modification of functional groups onto the polymeric substrate or vertically aligned CNT dot-array with a dot size of several μm was investigated using the atmospheric pressure plasma jet with a nano/micro-sized capillary. The micro-sized surface modification of amino or carboxyl groups introduced onto the CNT dot-array were confirmed by the fluorescence labelling technique.[5)] With fluorescence-labeled avidin molecules, we also confirmed efficient capturing of avidin molecules by the biotin-immobilized CNT dot array through strong biotin-avidin binding process. The present result supports the feasibility of future biochip sensor to detect specific protein, virus or bacteria. In addition to these results, the other experimental results will be presented and discussed at the conference.

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11:00am **SM+AS+BI+PS-ThM10 Tailoring Biomaterials-cell Interaction through Reactive Surface Modification**, ***Salvador Borros***, Institut Químic de Sarrià, Ramon Llull University, Barcelona, Spain **INVITED**

The immobilization of biologically active species is crucial for the fabrication of smart bioactive surfaces. For this purpose, plasma polymerization is frequently used to modify the surface nature without affecting the bulk properties of the material. Thus, it is possible to create materials with surface functional groups that can promote the anchoring of all kinds of biomolecules. Different methodologies in protein immobilization have been developed in recent years, although some drawbacks are still not solved, such as the difficulties that some procedures involve and/or the denaturalization of the protein due to the immobilization process. However, along with the chemical signals, the mechanical forces are critical for many tissues, since they are constantly suffering tension, shear, loading, etc. Essentially, the cell signaling exerted by forces is transduced through receptors that are in intimate contact with the matrix. Therefore, the main consequence of this receptor-matrix interaction is that cells and matrix are mechanically coupled, so that matrix deformation is considered the main cause of the mechanical signaling. By mimicking these mechanical forces in the surface of a material, it would be possible to obtain more physiological environments and thus a more physiological cell response. Again, the use of plasma polymerization techniques can help to design surfaces that can be tailored in terms of mechanical properties and chemical compositions and thus have a high potential for cells signaling.

This paper reports the work that we have developed in the last 10 years in the design, synthesis and characterization of thin films that can be a platform for studying the interaction between cells and separate influences of physical and chemical cues of a matrix on the adhesion, growth and final phenotype of cells.

11:40am **SM+AS+BI+PS-ThM12 Analysis of Amino Group Formation on Polystyrene Surfaces by Nitrogen-Hydrogen-Based Plasma Irradiation**, ***Kensaku Goto***, *D. Itsuki, M. Isobe, S. Sugimoto, S. Miyamoto, A. Myoui, H. Yoshikwa, S. Hamaguchi*, Osaka University, Japan

Polystyrene is a widely used cell-culture plate material. Currently cell culture plates on the market include those whose inner surfaces are covered with amino and/or carbonyl groups for a better control of cell adhesion to the plate surfaces. Such functional groups on a cell culture plate surface may immobilize glycoproteins or other biopolymers that function as extracellular matrices (ECM) and thus affect the environments where the cells are cultured. The goal of this research is to understand how such functional groups, especially amino groups, are formed on a polystyrene surface, depending on the deposition methods. Of particular interest are plasma-based methods of surface functionalization. In this study, we have observed experimentally how exposure of N_2/H_2 or N_2/CH_3OH plasmas to polystyrene surfaces form amino-group-like structures and also examined using molecular dynamics (MD) simulation how a polystyrene surface interacts with incident energetic ions such as NH_3^+ as well as abundant low-energy radicals such as NH_2 under conditions similar to our experiments. In the experiments, we used parallel-plate discharges with an inverter power supply whose peak-to-peak voltage was about 3kV and frequency was 20kHz at a relatively high gas pressure of 250 - 2,500 Pa. In MD simulation, we used a simulation code with interatomic potential functions that had been developed in-house based on quantum mechanical calculations of atomic interactions involved in this system. Results of MD simulations under the conditions similar to plasma enhanced chemical vapor deposition (PE-CVD) by ammonia plasmas or cyclopropylamine (CPA) [1] suggest that, with energetic ion bombardment, amino groups tend to be broken to form new covalent bonds by ion bombardment. Preliminary results of cell culture experiments with plasma-treated polystyrene cell plates will be also reported.

[1] A. Manakhov, L. Zajickova, *et al*. Plasma Process. Polym.11, (2014) 532.

12:00pm **SM+AS+BI+PS-ThM13 Tailoring the Surface Properties of Three-Dimensional, Porous Polymeric Constructs for Biomedical Applications Using Plasma Processing**, ***Morgan Hawker***, *A. Pegalajar-Jurado, E.R. Fisher*, Colorado State University

Utilizing bioresorbable polymers to fabricate constructs with three-dimensional (3D), porous architectures is desirable as these constructs mimic the extracellular matrix– a critical characteristic for many biomedical applications including tissue engineering, controlled-release drug delivery, and wound healing. Although the bioresorbability and architecture of these materials are suitable for such applications, the surface properties (i.e., chemical functionality and wettability) must often be customized depending on the desired function. Plasma processing is an attractive tool for surface modification of these delicate polymeric materials as it provides a low-temperature, sterile environment with a variety of precursor choices. The presented work will highlight the plasma modification of a variety of 3D, porous polymeric constructs. Specifically, we fabricated scaffolds via electrospinning and porogen leaching techniques using both poly(ε-caprolactone) (PCL) and polylactic acid (PLA) to develop a repertoire of native polymer constructs with differing bulk properties. We evaluated the efficacy of plasma-modifying 3D constructs using contact angle goniometry, X-ray photoelectron spectroscopy, and scanning electron microscopy to assess changes in wettability, chemical functionality, and scaffold architecture. The interactions of plasma-modified scaffolds with different biological species, including human dermal fibroblasts and *Escherichia coli* were explored, specifically to assess scaffold bioreactivity. Notably, we demonstrate that scaffold properties, and thus bioreactivity, can be customized depending on the choice of plasma precursor. We show that plasma treatment using fluorocarbon and hydrocarbon precursors (i.e., octofluoropropane, hexafluoropropylene oxide, and 1,7-octadiene) results in hydrophobic and bio-non reactive scaffolds. Additionally, precursors with nitrogen and oxygen functionality (i.e., allylamine, allyl alcohol, water, and ammonia) can be used to fabricate scaffolds that are hydrophilic and bio-reactive. Altogether, this work illustrates the comprehensive tunability of biologically-relevant polymeric constructs in terms of their bulk properties, surface properties, and cell-surface interactions.

Spectroscopic Ellipsometry Focus Topic
Room: 112 - Session EL+AS+BI+EM-ThA

Optical Characterization of Nanostructures and Metamaterials

Moderator: Bernard Drevillon, LPICM-CNRS, Ecole Polytechnique, France, Mathias Schubert, University of Nebraska - Lincoln

2:20pm **EL+AS+BI+EM-ThA1 Electrostatic Coating with Ligandless Copper Nanoparticles**, ***Lance Hubbard***, *A.J. Muscat*, University of Arizona

Electroless deposition (ELD) produces conformal coatings at low temperatures. ELD occurs by chemical reduction of metal ions without an externally applied potential or catalyst layer. In this paper, we report on a nonaqueous ELD process that uses a charge compensator, but not a ligand or complexing agent. The weak electrostatic attachment of the charge compensator to the ions and particles in solution and the high pH conditions improve the driving force for metal deposition. Si(100) native oxide was hydroxylated and terminated with a self-assembled amine layer (4 mM (3-aminopropyl)-trimethoxysilane in methanol). Metal films were deposited by suspending samples in a bath made by dissolving Cu(II) chloride in ethylene glycol (reducing agent), and adding 1-butyl-3-methylimidazolium tetrafluoroborate as a charge compensator. The Cu particle ion shell is attracted to the positively charged amine groups at high pH depositing a thin metal film that is both continuous and cohesive. Annealing the coupons at 200ºC in nitrogen promoted electrically conductive film formation. Electron microscopy images of the coated substrates showed a 80-95 nm thick film of 3 nm diameter particles. Four-point probe measurements of the films yielded electrical conductivities in the range 10^6-10^7 S/m (10-80% of bulk conductivty). The surface plasmon resonance (SPR) peak of the Cu nanoparticles in the bath and film was at 585 nm. Light scattering measurements and transmission electron microscopy (TEM) images yielded a size distribution of 3.1±1.56 nm. Scanning electron microsopy (SEM) images at various angles in relation to the films were taken to examine film morphology and thickness. Spectroscopic ellipsometry (SE) data were modelled with bulk, nanophase d-band transition, and SPR absorbances. The SE agreed well with UV-VIS results for the SPR and shows an increasing contribution from d-band transitions with increasing ionic liquid concentration. SEM and Fourier transform infrared (FTIR) spectroscopy were used to determine film thicknesses and chemistry.

2:40pm **EL+AS+BI+EM-ThA2 Using Plasmonic Effects to Design Ellipsometric Targets with Sub-Angstrom Resolution**, ***Samuel O'Mullane***, SUNY Polytechnic Institute, *J. Race*, *N. Keller*, Nanometrics, *A.C. Diebold*, SUNY Polytechnic Institute

For traditional ellipsometric targets, slightly changing the thickness of a layer or the index of refraction of a material results in a similarly small change in the observed spectra. If structures are designed to allow for plasmonic coupling, a slight change in those same parameters results in wildly different spectra. Specifically, localized plasmonic resonances in metallic grating structures allow for extraordinary sensitivity to parameters such as CD, sidewall angle and pitch.

Existing metallic grating structures are arrays of long, thin lines of copper that can be described using one dimension. The typical resolution for ellipsometric CD measurements on these structures ranges from nanometers to Ångströms. Because there is no confining second dimension, localized plasmons cannot be produced.

In order to obtain sub-Ångström resolution, additional structural modifications are required. This is achieved by adding a second metallic grating perpendicular to the original grating forming a cross-grating structure. Note that the added pitch and linewidth are an order of magnitude larger than the original parameters. This results in fully localized plasmonic resonances so that parameter variation on the order of tens of picometers could be detected through ellipsometric measurements. Making use of conical diffraction further increases the sensitivity to structural changes due to increased anisotropy.

These conclusions are the result of rigorous coupled wave-analysis (RCWA) simulations which were confirmed via finite element method (FEM) simulations. With both RCWA and FEM agreement, experimental confirmation is expected.

3:00pm **EL+AS+BI+EM-ThA3 Enhanced Temperature Stability of Slanted Columnar Thin Films by ALD Overcoating**, ***Alyssa Mock***, *D. Sekora*, *T. Hofmann*, *E. Schubert*, *M. Schubert*, University of Nebraska - Lincoln

The demand for thermally stable nanostructures continues to increase as nanotechnology becomes ever more prevalent in both commercial and research applications. The high surface area of nanostructured thin films is susceptible to degradation under extreme temperatures. Scanning electron microscopy (SEM) and Mueller Matrix Generalized Ellipsometry (MMGE) were used to observe optical and structural properties of a glancing angle deposited cobalt slanted columnar thin film (SCTF) over increased annealing temperature. We show that the use of atomic layer deposition (ALD) to conformally passivate the SCTF surface provides both physical scaffolding and thermal protection during the annealing process up to 475°C as no changes in the SEM or MMGE results were present.

3:20pm **EL+AS+BI+EM-ThA4 Vector Magneto-Optical Generalized Ellipsometry on Heat Treated Sculptured Thin Films: A Study of the Effects of Al_2O_3 Passivation Coatings on Magneto-Optical Properties**, ***Chad Briley***, *A. Mock*, University of Nebraska-Lincoln, *D. Schmidt*, National University of Singapore, *T. Hofmann*, *E. Schubert*, *M. Schubert*, University of Nebraska-Lincoln

We present the vector magneto-optical generalized ellipsometric (VMOGE) response[1] and model dielectric function (MDF) anisotropic hysteresis calculations[2] of ferromagnetic slanted columnar thin films under the effects of heat treatment up to 475° C. Directional hysteresis magnetization scans were performed with an octu-pole vector magnet at room temperature on Cobalt slanted columnar thin film samples grown by glancing angle deposition with and without Al_2O_3 conformal passivation overcoating done by atomic layer deposition. Analysis of the measured Mueller matrix ellipsometric data through a point-by-point best match model process determine the magneto-optical (MO) dielectric tensor. Three dimensional rendering of the anti-symmetric off-diagonal elements of the MO dielectric tensor displays anisotropic magnetic response of the thin film with the hard axis along the long axis of the columns. Data analysis reveals the preservation of anisotropic magneto-optical properties of the thin film with the passivated coating as compared to the non-passivated coating due to oxidation effects from heat treatment.

[1)] D. Schmidt, C. Briley, E. Schubert, and M. Schubert, Appl. Phys. Lett. **102**, 123109 (2013).

[2)] C. Briley, D. Schmidt, T. Hofmann, E. Schubert, and M. Schubert, Appl. Phys. Lett. **106**, 133104 (2015).

4:00pm **EL+AS+BI+EM-ThA6 Spectroscopic Ellipsometry for Critical Dimensions Analysis**, ***Vimal Kamineni***, GLOBALFOUNDRIES, *D. Dixit*, *S. O'Mullane*, SUNY Polytechnic Institute, *G. Iddawela*, *A. Vaid*, GLOBALFOUNDRIES, *A.C. Diebold*, SUNY Polytechnic Institute **INVITED**

In this talk an overview of the current applications of spectroscopic ellipsometry (SE) towards measuring the shape of nanostructures will be presented. The transition of the semiconductor industry from planar to 3D transistors has expanded the applications of ellipsometry. Ellipsometry measurements on the periodic nanoscale structures enable a diffraction based measurement technique referred to as scatterometry. The critical dimensions can be extracted by means of a regression on the diffracted light using rigorous coupled wave analysis (RCWA). RCWA is a Fourier-space method used to generate the optical response by slicing the periodic structure of interest and matching the boundary conditions to compute EM modes. This method is inherently dependent on *a priori* knowledge of the dielectric function of the materials that construct the nanostructures as well as the shape of the nanostructure obtained from reference metrology. Furthermore, time-to-solution is one of the main drawbacks of developing scatterometry applications due to the dependency on developing a robust model and for validating the model with reference metrology measurement. To address these challenges new methods such as signal response metrology (SRM) encompassing machine-based statistical learning and virtual reference metrology have been proposed. [1,2] These methods will be reviewed along with their benefits and limitations when applied to advanced 3D transistor structures. In addition, application of Mueller matrix ellipsometry measurements on strained grating structures (SiGe/Si) and block copolymer structures to determine the impact of strain and defectivity (bridging defects, wiggles, LER, etc.) on anisotropy coefficients will be presented, respectively. [3,4] Additionally, hybrid approaches will be proposed in conjunction with complementary/supplementary metrology methods (CD-SEM, HRXRD and CD-SAXS). [5-7]

[1] S. Pandev et al., SPIE Proc. 9424 (2015).

[2] A. Vaid et al., SPIE Proc. 9424 (2015).

[3] G. R. Muthinti et al., SPIE Proc. 8681 (2013).

[4] D. J. Dixit et al., Journal of Micro/Nanolithography, MEMS, and MOEMS 14, 021102 (2015).

[5] A. Vaid et al., SPIE Proc. 8324 (2012).

[6] A. C. Diebold et al., Proceedings of SPIE 8681, 86810I (2013).

[7] Charles Settens et al., Journal of Micro/Nanolithography, MEMS, and MOEMS 13, 041408 (2014)

4:40pm **EL+AS+BI+EM-ThA8 Structural and Ellipsometric Analysis of the Topological Insulator Bi_2Se_3, *Avery Green***, SUNY Polytechnic Institute

Topological Insulator (TI) materials have been the subjects of increasing scientific interest in the last decade. Their spin-momentum locked Dirac cone surfaces and insulating bulks have resulted in new directions in physics research and new spintronic devices. Though these materials have been thoroughly described in theory, the experimental realization and measurement of these surface states has been problematic, due to various crystalline defects. Theory predicts that TI surface states are protected against local defects, but it is essential to study the effects of global perturbations caused by surface oxidation, stoichiometric aberrations, and significant structural defect densities. The aim of this study is to measure the time-dependent dielectric function of the Bi_2Se_3 surface and bulk in air, using a dual rotating compensator spectroscopic ellipsometer. These data are backed up with various metrological measurements (AFM, cross-sectional TEM, EDS) to confirm surface topology and oxide thickness. This analysis of optical properties and oxide formation will, in the future, be used to optimize the Bi_2Se_3 flake thickness identification process, and provide a control for further necessary structural analysis, as stated above.

5:00pm **EL+AS+BI+EM-ThA9 Visible Luminescence in the VLS Grown Self Ga Doped ZnS Nanostructures**, ***Arshad Bhatti***, *H. Hussain, M.A. Johar, S. Rehman, M.A. Shehzad, M.A. Hafeez*, COMSATS Institute of Information Technology, Pakistan

ZnS is a wide band gap semiconductor and thus offers fascinating opportunities for tailoring and tuning its bandgap states for photonic devices in visible region of the spectra. Ga introduced a strong red luminescence in ZnS. VLS mechanism was employed to synthesize ZnS nanowires using Ga as a catalyst and dopant simultaneously. The thickness of Ga ultrathin film was varied from 0.5 nm to 5 nm to observe the effect of Ga droplet size on the formation, lifetime and activation energies of defect states in the band gap. It was expected that Ga^{3+} would replace Zn^{2+} sites and dope ZnS, in addition, an impurity phase of Ga_2S_3 was also observed, whose content showed strong dependence of Ga thickness. It also shrunk the crystallinity of ZnS due to varied size of Ga^{3+}(76 pm) ions replacing Zn^{2+} (88 pm), which was observed in the shifts of major XRD reflections of ZnS. Incorporation of Ga introduced strong impurity states in the band gap of ZnS. It also affected the intrinsic defect states of ZnS, namely Zn and S vacancies (Please refer to Figure 1, which also shows the de-convoluted band gap broad band). In the PL spectra, blue (440 nm), yellow (560 nm), orange (600 nm) and red (680 nm) bands were attributed to S vacancies, Ga related defects, donor-acceptor recombination and Ga_2S_3, respectively. Photoluminescence excitation spectroscopy revealed strong absorbance at corresponding energies. A strong correlation of these states was observed in the temperature dependent PL measurements due to presence in their presence in the vicinity as the activation energies of these states matched the energy differences of corresponding states. The conductivity measurements also complimented the optical results. Time resolved PL demonstrated the lifetime of these states was between 0.5 ns to 1.5 ns and had somewhat significant effect of dopant concentration. Finally, Ga doped ZnS showed extremely efficient IR sensitivity.

Figure 1: The room temperature PL spectra of Ga doped ZnS nanowires synthesized with varied thickness of Ga: (a) 0.5 nm, (b) 1.0 nm, (c) 3.0 nm, and (d) 5.0 nm. The broad band between 450 nm to 750 nm has been de-convoluted to show contribution of various defect states (as mentioned in the Figure). These states were identified from the PLE spectrum.

5:40pm **EL+AS+BI+EM-ThA11 Can Front-Surface Metal Mirrors Be Protected from Oxidation by Vacuum Applied Polymer Films?**, ***David Allred***, *R.S. Turley*, Brigham Young University, *R.T. Perkins*, Utah Valley University

We have used variable-angle, spectroscopic ellipsometry to monitor secular changes in multilayers consisting of chemically active thin films, such as aluminum, deposited on dielectric-coated silicon wafers and protected by various vacuum-applied barrier layers. Ultrathin barrier layers included polymers such as parylene and rarely, sputtered inorganic films, such as silicon. Applications include the measurements of the oxidation of evaporated aluminum for use as a mirror in the VUV (vacuum ultraviolet) and the determination of the optical constants of materials such as Y_2O_3 potentially useful in VUV and XUV (extreme ultraviolet) optics.

Surface Modification of Materials by Plasmas for Medical Purposes Focus Topic
Room: 211D - Session SM+AS+BI+PS-ThA

Plasma Processing of Biomaterials and Biological Systems

Moderator: David Graves, University of California, Berkeley, Jean-Michel Pouvesle, GREMI CNRS/Université d'Orléans

2:20pm **SM+AS+BI+PS-ThA1 Matching Plasma Sources with Intended Biomedical Outcomes: Open Questions in Modeling of Plasma Surface Interactions**, *W. Tian*, University of Michigan, *S.A. Norberg*, US Military Academy - West Point, *A.M. Lietz*, University of Michigan, *N.Yu. Babaeva*, Joint Institute for High Temperatures, ***Mark Kushner***, University of Michigan **INVITED**

Plasma surface modification of materials for biomedical applications typically involves atmospheric pressure plasmas in the form of dielectric barrier discharges (DBDs) or atmospheric pressure plasma jets (APPJs). In many cases, APPJs operate similarly to DBDs with an ionization wave (IW) propagating through a rare-gas dominated gas channel. The intersection of the IW with the surface being treated, for example tissue, in both DBDs and APPJ produces locally large fluxes of ions, UV/VUV photons and electric fields onto the surface. These fluxes are collectively *hard fluxes* due to the higher levels of activation energy they represent. Remote DBDs and APPJs where the plasma plume does not intersect the surface produce *soft fluxes*, dominated by neutral reactants. The character and ratios of *hard-to-soft fluxes* and their compositions are functions of flow dynamics, ambient conditions (e.g., humidity) and pulse power waveforms. In many biomedical applications, the tissue is covered by a liquid (or the intended surface is liquid as in plasma activated water). In these cases, plasma produced activation energy, radicals and ions must penetrate through the plasma-liquid interface, where liquid phase mechanisms then determine the reactants to the tissue. From one perspective, significant advances have been made in modeling these processes and furthering our understanding. From another perspective, there are still significant open questions that models need to address, including the manner of coupling of the gas phase plasma and liquid, gas induced fluid dynamics, long term evolution of the liquid chemistry, reactions at the surface of the tissue and control schemes to minimize variability. A brief overview of progress in modeling plasma modification of biomaterials will be provided followed by examples of the authors' modeling works for APPJs and DBDs intersecting with model tissues and liquids.

3:00pm **SM+AS+BI+PS-ThA3 Plasma Processing of Biomimetic and Sintered Calcium Phosphates for Bone Regeneration and Repair**, ***Cristina Canal***, Technical University of Catalonia, Spain **INVITED**

Large bone defects caused by trauma, osteoporotic fractures, infection and tumour or cysts resection pose a great clinical and socio economic problem. Bone grafting materials respond to the need generated by over 2 million bone grafting procedures that are performed every year worldwide. As an alternative to autografts or xenografts, different biomaterials have been proposed, yet with partial success since different aspects remain yet to be improved.

In this context, the use of low pressure (LP) and atmospheric pressure (AP) plasmas opens new opportunities in the field of bone biomaterials. It is the aim of this talk to provide an overview on the strategies undertaken in our group to enhance diverse features of bone biomaterials and to enhance bone therapies.

The examples discussed here include biomimetic hydroxyapatite (HA) and β-tricalcium phosphate (β -TCP) as the most clinically used calcium phosphate (CaP) ceramics for bone regeneration. Some of the points of improvement include increasing their mechanical strength, or using them as local dosage forms for the delivery of drugs, to aid in different therapies, such as combating infection or fighting cancer.

For instance, we have investigated LP plasmas with the aim of expanding the use of biomimetic CaPs to load-bearing sites. Although composites have been defined, their performance is not yet optimal, possibly due to insufficient adhesion between the matrix and the reinforcing agent. Oxygen

and argon plasmas have been employed in the surface modification of polylactide fibers to improve the adhesion at the interface between them and biomimetic CaPs with interesting results.

In a different approach we have focused on modulating drug delivery from bone biomaterials. Both AP and LP plasmas are of interest with views on different medical applications and in the design of advanced biomaterials with controlled drug release properties. Different strategies are considered with that aim, such as using either plasma functionalization with AP plasma jet to modulate the interactions of the drug with the CaP surface or employing LP plasma polymerization on CaP scaffolds as a strategy to control the drug release. Lastly, AP plasmas are in the limelight due to their wide potential in the medical field, and here we will discuss some recent findings for application in bone therapies and regeneration.

Acknowledgements

Spanish Government is acknowledged for support through Project MAT2012-38438-C03-01, co-funded by the EU through European Regional Development Funds, and Ramon y Cajal fellowship of CC. The European Commission is also acknowledged through funding in FP7/2007-2013 under the Reborne project (no. 241879).

4:00pm **SM+AS+BI+PS-ThA6 Plasma Processing of Biomaterials and Biomedical Devices**, *H.J. Griesser, T.D. Michl, S.S. Griesser, M. Jasieniak, H.H. Mon,* ***Bryan Coad***, University of South Australia **INVITED**

Gas plasmas have attracted considerable attention over more than 40 years as a convenient method for changing the surface chemical composition of biomaterials and thereby alter and control the interfacial interactions between biomedical devices and contacting "biology" such as protein solutions, blood, cells and tissue, and bacterial biofilm growth. Plasma technologies are already in use on a large industrial scale in several biomedical device companies; for example 30-day contact lenses use a thin plasma coating to confer wettability and low fouling to silicone-based contact lens materials. Bio-interfacial interactions are very short range, and hence it is sufficient to apply ultrathin coatings (< 20 nm thick). Plasma techniques are ideally suited because process control is straightforward and the resultant surface modifications or coatings tend to have a high degree of uniformity and reproducibility compared with other, solution based coating methods. On the other hand, the complex chemical composition of plasma gas phases prevents fine control of chemistry to the extent achievable by conventional chemical approaches. Detailed surface analysis is essential.

Plasma approaches are useful to produce coatings designed to combat the problem of bacterial and fungal biofilm growth on biomedical devices, which leads to infections and delayed healing. One approach is the use of organochlorine plasma polymer coatings, which are highly effective at contact killing. Other, cytocompatible approaches comprise the use of plasma polymer coatings that release NO or available antibiotics such as levofloxacin. A different approach entails the covalent immobilization of a monolayer of antimicrobial molecules onto a thin plasma polymer interlayer whose function is to provide good adhesion and reactive surface chemical groups that can be used to attach antibiotics. Such covalently grafted monolayers have given excellent deterrence of attachment and biofilm formation of bacteria and pathogenic fungi.

4:40pm **SM+AS+BI+PS-ThA8 Organs on a Chip – Biointerfaces in Stem Cell Research**, ***Kevin Healy***, University of California at Berkeley **INVITED**

Highly regulated signals in the stem cell microenvironment such as ligand adhesion density, matrix stiffness and architecture, and growth factor presentation and concentration have been implicated in modulating stem cell differentiation, maturation, tissue formation, and ultimately function. My group has developed a range of materials systems and devices to study and control stem cell function and their self-organization into three-dimensional microtissues (e.g., 'organs on a chip'). These systems are being developed for screening molecular therapies and patient specific medicine via *in vitro* disease specific tissue models. Examples of how biointerface science is important in these applications will be highlighted. The benefits of our approach include: 1) robust and reproducible platform embodies precision microengineering to create better microtissue environments; 2) precise delivery of molecules (e.g., drugs) in a computationally predictable manner; 3) ability to model human cardiomyopathy; and, 4) cost efficient and high content characterization of cardiac tissue drug response.

5:20pm **SM+AS+BI+PS-ThA10 Effect of the Radical Species for Gene Transfection by Discharge Plasma Irradiation**, ***Yoshihisa Ikeda***, *M. Jinno*, Ehime University, Japan

Gene transfection is a technique of deliberately introducing nucleic acids into cells in order to give them specific characteristics. In practice, this can be achieved in three different ways: chemical method, physical method and the viral vector method.

One of the physical methods that uses discharge plasma irradiation was invented by Satoh, who is one of the authors, and his group in 2002. Since this technique is free from adverse effect associated with viruses, there are no risks as the others mentioned above. The plasma irradiation on genes and cells induces the transfection process in which the genes and cells are exposed to discharge current, charged particles and chemically reactive species.

The authors investigated the factors for plasma gene transfection by changing protocols and looked at the time periods the factors become effective. The results is that transfection rate drops to 1/10 of the standard protocol when the charged particles and chemically reactive species genes are washed out from the wells by PBS solution 60s after plasma irradiation. Since the life times of the charged particles delivered from plasma to the plasmid solution is less than 60s, the direct effect of the charged particles causing transfection finishes before wash out process. This means that nearly 1/10 of transfections occur during plasma irradiation and that the last 9/10 of transfections occur after plasma irradiation is stopped. This second stage transfection is mainly caused by the residual chemically reactive species, however, plasma irradiation stress to cells and plasmids also induces transfection., i.e. possibly charging effect and oxidation stress induce bio-chemical process of the cells in addition to the chemical reactions on the cell membrane and plasmid induced by chemically reactive species such as radicals.

5:40pm **SM+AS+BI+PS-ThA11 Nonlinear Optical Spectroscopic Observation of Plasma-Treated Bio-Specimen**, ***Kenji Ishikawa***, *R. Furuta, K. Takeda,* Nagoya University, Japan, *T. Nomura, T. Ohta,* Meijo University, Japan, *H. Hashizume, H. Kondo,* Nagoya University, Japan, *M. Ito,* Meijo University, Japan, *M. Sekine, M. Hori*, Nagoya University, Japan

Applications of nonequilibrium atmospheric pressure plasma (NEAPP) to the medical field have been reported in recent years. However, a mechanism of interactions between NEAPP and living cells has not been yet elucidated comprehensively. Our strategy for elucidation of plasma-biomaterial interactions is to observe reactions *in situ* at real time. By applying nonlinear optical spectroscopic techniques, the vibrational sum-frequency-generation (SFG) and multiplex coherent anti-Stokes Raman scattering (CARS) microscopy, which are a beneficial tool for addressing best sensitivity at surface and interface, have been used in this study. By using SFG, we have explored topmost surface modification after the interaction between plasma and biopolymeric materials. For the NEAPP-induced reactions on budding yeasts as an eukaryotic cell model, a two-dimensional mapping of budding yeasts treated by the plasma using the CARS microscopy was observed with fluorescence label-free contrasts of chemical vibrational nature. The biomedical imaging of cell membranes, intracellular organelles, nucleus and so forth, was revealed to decompose intracellular membrane by exposure of plasma-generated chemically reactive species, especially for induction of lipid peroxidation. These results will be useful for understanding the plasma induced reactions in the plasma medicine.

Scanning Probe Microscopy Focus Topic
Room: 212A - Session SP+BI+NS+SS+TF-ThA

Probing Material Growth on the Surface
Moderator: Chuanxu Ma, Oak Ridge National Laboratory

2:20pm **SP+BI+NS+SS+TF-ThA1 Tailoring the Growth of Organic Thin Films via Chemical Reactions at the Molecular Scale**, ***Pengpeng Zhang***, Michigan State University **INVITED**

Control of highly ordered organic molecular thin films with extended π systems is currently of intense interest for integrating molecules into modern electronics due to their tunable nature. Selection of molecules and substrates can lead to desired transport properties such as charge transfer, charge injection, exciton diffusion, etc., at the heterointerface, which is crucial to the development of organic and molecular electronics. However, achieving large-scale molecular ordering remains a significant challenge that requires a thorough understanding of the growth mechanism. I will discuss our recent discovery of the anisotropic crystalline step-flow growth of the prototypical metal phthalocyanine molecules on the deactivated Si(111)-B surface. I will then address the growth mechanism and show that the molecular ordering and molecular orientation can be effectively controlled through selective orbital coupling between the molecule and substrate. Finally, I will illustrate an abnormal temperature dependent growth evolution and discuss the associated mechanism.

This research is funded by the U.S. Department of Energy (DOE) Office of Science Early Career Research Program (DE-SC0006400) through the Office of Basic Energy Sciences.

3:00pm **SP+BI+NS+SS+TF-ThA3 Investigation of Initial Stages of Oxidation of Ni-Cr and Ni-Cr-Mo alloys by Scanning Tunneling Microscopy and Spectroscopy**, ***Gopalakrishnan Ramalingam****, *P. Reinke*, University of Virginia

Ni-Cr alloys are excellent candidates for use in highly corrosive environments due to the formation of a protective Cr_2O_3 layer. Molybdenum is a common alloying addition as it improves the resistance to localized corrosion and prevents the breakdown of the oxide layer. While the effect of Mo addition on corrosion resistance is well known, the underlying mechanisms at the atomic scale and the role of electronic structure changes due to Mo addition are poorly understood. In the current work, we have used STM/STS to investigate the initial stages of oxidation of Ni, Cr and Ni-Cr (10-25wt.% Cr) alloy thin films and subsequently, the effect of Mo addition (2-10 wt.%) on the oxidation behavior. The alloy thin films are grown on MgO(001) substrates using two recipes that yielded smooth films: (a) deposition at 100 °C and subsequent anneal at 300 °C for 2 hours, and (b) deposition at 400 °C with no post-growth annealing. While recipe (a) yielded smooth Ni films, co-deposition of Ni and Cr resulted in the formation of secondary Ni_2Cr phases. Alloy films grown using recipe (b) did not result in secondary phases and are optimal for oxidation studies of alloy films. STM/STS data of the oxidation (30 L of O_2) of a pure Ni thin film at 200 °C reveal preferential oxidation of some terraces compared to others and indicates a dependence of oxidation rate on the crystallographic orientation of the terrace. dI/dV maps of a Cr surface after 10 L oxidation at 200 °C shows the presence of a bandgap (1.32 eV) throughout the surface and indicates the growth of a uniform oxide layer. In the case of Ni-13wt.%Cr binary alloy, a 25 L exposure (at $1x10^{-8}$ mbar) at 300 °C results in a complete loss of step structure with a fully formed oxide layer as shown by STS spectra. A bandgap of 1.42 eV is observed throughout the surface and this value is less than the bulk bandgap of all possible oxide species (NiO, Cr_2O_3 or mixed). We will present the results of the initial stages of oxidation (<3 L) of the pure Ni thin films and discuss the differences in the oxidation processes due to the addition of 8-25 wt.% Cr. The progression from chemisorption regime (at low temperatures) to the oxide nucleation regime will be shown for different alloys by performing room temperature O_2 exposures and post-exposure annealing cycles and the effect of alloying additions on this transition will be discussed. Preliminary data on the changes in the atomic and electronic structure of the thin film and oxidation behavior due to the addition of Mo will be presented.

4:00pm **SP+BI+NS+SS+TF-ThA6 Growth and Properties of Skyrmionic Nanowires and Thin Film**, ***Zheng Gai***, Oak Ridge National Laboratory, *J. Yi, S. Tang,* University of Tennessee, Oak Ridge National Laboratory, *D. Mandrus*, University of Tennessee **INVITED**

Magnetic skyrmion lattice, a vortex-like spin texture recently observed in chiral magnets, is of great interest to future spin-electronic data storage and other information technology applications. The combined effect of a large ferromagnetic exchange and a weak DM interaction is to twist the magnetization into a long-period spiral that can be tens to hundreds of nanometers in length. As these spirals are only weakly bound to the underlying lattice in cubic systems, they can be readily manipulated with modest applied fields. The skyrmion lattice in MnSi appears in a small region (known as the A phase) of the H-T phase diagram in bulk samples, but in 2D samples like thin films the skyrmion phase is much more robust. If skyrmion ordering can persist in one-dimensional MnSi nanowires and 2D films, then these systems are very promising for spintronics applications as the magnetic domains and individual skymions could be manipulated with small currents. We have systematically explored the synthesis of single crystal MnSi nanowires via controlled oxide-assisted chemical vapor deposition and observed a characteristic signature of skyrmion magnetic ordering in MnSi nanowires. The SiO_2 layer plays a key role for the high yield, correct stoichiometric and crystalline growth of the B20 MnSi nanowires. A growth phase diagram was constructed. For the thin films, an unique growth receipt was developed for the growth of high quality of thin films. The structure and magnetic properties of the films at different thickness were studied.

4:40pm **SP+BI+NS+SS+TF-ThA8 Sulfur-induced Structural Motifs on Cu(111) and Au(111) Surfaces**, ***Holly Walen‡***, Iowa State University, *D.-J. Liu,* Ames Laboratory, *J. Oh, H. Lim,* RIKEN, Japan, *J.W. Evans,* Iowa State University, *C.M. Aikens,* Kansas State University, *Y. Kim,* RIKEN, Japan, *P.A. Thiel*, Iowa State University

The interaction of sulfur with copper and gold surfaces plays a fundamental role in important phenomena that include coarsening of surface nanostructures, and self-assembly of alkanethiols. Here, we identify and analyze unique sulfur-induced structural motifs observed on the (111) surfaces of these two metals. We choose very specific conditions: very low temperature (5 K), and very low sulfur coverage (≤ 0.05 monolayers, ML). In this region of temperature-coverage space, which has not been examined previously for these adsorbate-metal systems, the effects of individual interactions between metals and sulfur are most apparent and can be assessed extensively with the aid of theory and modeling. Furthermore, at this temperature diffusion is minimal and relatively-mobile species can be isolated. The primary technique is scanning tunneling microscopy (STM).

On Cu(111), at 0.004 ML S, we find unexpected heart-shaped Cu_2S_3 complexes on the terraces, made up of intersecting linear S-Cu-S units. With supporting density functional theory (DFT) and reaction-diffusion equation analysis, we propose that these hearts are a viable candidate for S-enhanced mass transport of Cu on Cu(111) at higher temperature. As S coverage increases (up to 0.05 ML), a diverse group of Cu-S structures develops which includes concatenated hearts, and eventually the known ($\sqrt{43}$ x $\sqrt{43}$)R±7.5° reconstruction[1-2]. Analysis of the step edges of Cu(111) indicates that S decorates the step edges preferentially (relative to the terraces) and that the complexes observed on terraces originate at the step edges.

In contrast, no metal-sulfur complexes are observed on Au(111) under similar conditions (0.03 ML). Instead, we observe striking $\sqrt{3}$R30° rows made up of S adatoms. Using DFT and *ab-initio* Monte Carlo analysis, we construct and test a lattice gas model. This analysis shows that these short rows of S adatoms form because of a complex set of through-metal interactions: a linear three-body attraction, as well as long-range pairwise interactions (up to 5*a*) between S atoms.

These experimental observations for Cu(111) and Au(111) surfaces—made under essentially-identical conditions—together with extensive DFT analyses, allow comparisons and insights into factors that favor the existence of metal-sulfur complexes, vs. chemisorbed atomic sulfur, on metal terraces.

[1] E. Wahlström, I. Ekvall, H. Olin, S. A. Lindgren, and L. Wallden, Phys. Rev. B **60** 10699 (1999).

[2] E. Wahlström, I. Ekvall, T. Kihlgren, H. Olin, S. A. Lindgren, and L. Wallden, Phys. Rev. B **64** 155406 (2001).

5:00pm **SP+BI+NS+SS+TF-ThA9 Surface Strain-Modulated Binding of Adsorbates on TiO_2(110)**, *D.V. Potapenko*, ***Richard Osgood, Jr.***, Columbia University

Mechanical elastic strain is commonly present in nanostructured materials and it has been found to change chemical and electronic properties in a broad range of solids. Systematic study of reactivity-strain relationship on surfaces is difficult because of the fact that only very low values of strain (~0.1%) are achievable through mechanical deformation of macroscopic samples. We have developed a method of preparation of nano-scale strain fields on TiO_2 rutile(110) surface by low energy (1keV) Ar ion bombardments combined with specific thermal treatment. Titanium oxide is a brittle material regarded as a prototypical photocatalyst with numerous applications in the areas of solar energy utilization. Subsurface Ar clusters, which are formed through our preparation procedure, cause 5 – 25 nm wide surface deformations with the tensile strain values as high as 4 %. Surface distributions of various molecular and atomic adsorbates on TiO_2(110) have been studied with atomically resolved STM imaging. Our results indicate significant strain-related variations in the surface binding properties. In this presentation we will concentrate on surface hydroxyl groups (OH) as a mobile adsorbate. We derive the O-H binding energy from the statistical analysis of the adsorbate distribution. Then we demonstrate a roughly linear relationship between the values of surface strain and the O-H binding energy.

5:20pm **SP+BI+NS+SS+TF-ThA10 STM/STS Investigation of Organic Charge Transfer Complex TTF-TCNQ on Noble Metal Surfaces at 4.3K**, ***Seokmin Jeon***, *P. Doak, P. Ganesh, B. Sumpter,* Oak Ridge National Laboratory, *J.I. Cerda,* Instituto de Ciencia de Materiales de Madrid, Spain, *P. Maksymovych*, Oak Ridge National Laboratory

TTF-TCNQ (TTF = tetrathiafulvalene; TCNQ = 7,7,8,8-tetracyanoquinodimethane) is a prototypical organic charge-transfer complex providing with a metallic conductivity (up to 900 ohm-1cm-1 at 300K). It also represents a broad class of organic electronic compounds that exhibit strong electron correlations and a rich gamut of phase transitions involving charge ordering, Mott and Peierls metal-insulator transitions and superconductivity, etc. Despite decades of research in this area, quantitative understanding of this compound is still elusive and their low-dimensional form is barely explored. We investigated ultrathin films of TTF-TCNQ on silver surfaces using scanning tunneling microscopy/spectroscopy (STM/STS) at 4.3 K. TTF-TCNQ forms self-assembled molecular lattices on noble metal surfaces with a few different TTF-to-TCNQ ratios depending on evaporation condition. Among them the islands with 1 to 1 stoichiometric ratio are found ubiquitously in less dependent on the evaporation condition. Structures of the monolayer islands are elucidated

*** Morton S. Traum Award Finalist**

from sub-molecular resolution STM topography images. Single-point conductivity spectroscopy and conductivity mapping elucidate new electronic states which do not stem from their molecular orbital states are spatially located in the void areas of the TTF-TCNQ molecular lattices. We propose the *sp*-derived metal surface states are confined in the molecular lattices. Due to small periodicity of the lattice, the band minimum of the *sp*-derived metal surface states is shifted by as much as 1eV. This shift is much more significant than the ones normally observed in organic self-assemblies. As a result, we can also infer the height of the potential barrier within a 1D potential well model, which in turn is directly related to strong molecular dipole associated with large charge transfer and bent molecular geometry due to metal-molecule interactions.

Acknowledgement: A portion of this research (SJ, PD, PG, BS, PM) was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

Tribology Focus Topic
Room: 230B - Session TR+AS+BI+NS-FrM

Nanoscale Wear and Biotribology

Moderator: J. David Schall, Oakland University

8:20am **TR+AS+BI+NS-FrM1 2D or not 2D? The Impact of Nanoscale Roughness and Substrate Interactions on the Tribological Properties of Graphene**, ***James Batteas***, Texas A&M University **INVITED**

Control of friction and wear is a ubiquitous challenge in numerous machined interfaced ranging from biomedical implants, to engines, to nano- and micro-scaled electromechanical systems (MEMS) devices. While lubricant additives are one approach to the development of surface coatings that can impede wear and reduce friction, in some cases, such approaches are simply not amenable and the development of ultrathin films are required. Recently, the robust mechanical properties of graphene has made it a material of interest as a means of modifying surface frictional properties. While graphene can readily adapt to surface structure on the atomic scale, when deposited on substrates with nanoscopic roughness (~ 10 – 20 nm rms as is common in many machined interfaces) a conformal coating cannot be fully formed due to competition between adhesion to substrate nanoscopic asperities and the bending strain of the graphene. This often leaves a mixture of supported and unsupported regions which respond differently to applied load and shear strain. Here we describe a combination of AFM nanomechanical and confocal Raman microspectroscopy studies of graphene on silica surfaces with controlled nanoscopic roughness to examine the how this impacts the frictional properties of graphene. Composite interfaces where graphene is supported on self-assembled alkylsilane monolayers will also be described along with the synergistic influence of such mixed interfaces on the frictional properties of the surface.

9:00am **TR+AS+BI+NS-FrM3 Atomic–Scale Wear and Wear Reduction Mechanisms Elucidated by *In Situ* Approaches**, *R.W. Carpick,* University of Pennsylvania, ***Tevis Jacobs***, University of Pittsburgh **INVITED**

As technologies shrink to nanometer length scales, tribological interactions play an increasingly dominant role. A lack of fundamental insight into the origin of friction and wear at the nanoscale hinders the advancement of such technologies. Furthermore, macroscopic tribological applications often involve contact between nanostructured materials or at nanoscale asperities, due to surface roughness. Observing and understanding the nanoscale mechanisms at play is inhibited by the hidden nature of the buried interface and the challenge of performing observations at the nanometer scale. Recent advances in *in situ* methods are enabling tribological mechanisms at previously inaccessible interfaces to be studied with unprecedented resolution and sensitivity. We will discuss the application of two *in situ* experimental methods to develop new physical insights into tribological processes. The first approach addresses contact and wear phenomena at the atomic scale by *in situ* sliding in a transmission electron microscope [1], and the second addresses the generation of tribofilms from anti-wear additives using atomic force microscopy while immersed in additive-infused oil [2].

References:

[1] Jacobs, T.D.B. and Carpick, R.W. “Nanoscale Wear as a Stress-Assisted Chemical Reaction,” Nature Nanotech., 8, 2013, 108-112.

[2] Gosvami, N.N., Bares, J. A., Mangolini, F., Konicek, A.R., Yablon D.G., and R. W. Carpick. “Mechanisms of Antiwear Tribofilm Growth Revealed In Situ by Single Asperity Sliding Contacts,” Science, 348, 2015, 102-106.

9:40am **TR+AS+BI+NS-FrM5 Influence of Polysaccharide Conformation on Friction and Adhesion**, ***Rowena Crockett***, Empa, Switzerland **INVITED**

The friction behavior of the polysaccharide dextran has been investigated on surfaces coated with PLL-dextran brushes as well as randomly orientated covalently attached chains in aqueous solution. It was found that while there was a strong dependence of friction on load for the dextran brushes, the randomly orientated chains showed a more constant friction coefficient. Polysaccharides play an important role in bioadhesion, but are also used in the mining industry to assist in the separation of minerals. Despite the high adhesion associated with polysaccharides, investigations showing that they can be used to achieve low friction have also been reported. It was proposed that this transition from low friction to high adhesion is achieved as a result of hydrogen bonding. That is, as the load increases, water is forced out of the contact and the number of hydrogen bonds between the polysaccharide and surface increase, inducing a transition to high adhesion.

10:20am **TR+AS+BI+NS-FrM7 Tribological Rehydration of Cartilage: A New Insight into an Old Problem**, ***David Burris***, *A.C. Moore*, University of Delaware **INVITED**

The bulk of cartilage lubricity is due to its multi-phasic structure and the pressurization of interstitial fluid during loading. Unfortunately, the same pressure gradients that support load and lubricate the contact also drive fluid from the tissue over time. This observation led McCutchen, the researcher responsible for the discovery of this unusual lubrication mechanism, to ponder how the joint prevented the loss of interstitial fluid over time. He proposed that articulation intermittently exposes the loaded zone to the bath, thus allowing the tissue to imbibe fluid. It wasn’t until 2008 that Caligaris and Ateshian showed that interstitial pressure can be maintained if the contact migrates across cartilage more quickly than the diffusive speed of fluid in the tissue; because the joint involves a migrating contact, they proposed that this discovery resolved any uncertainty about how the joint maintains lubrication. However, joints spend only a fraction of the day articulating and the majority of the day exuding fluid in static compression. If the migrating contact simply prevents the loss of fluid by moving quicker than the fluid can respond, we contend that it cannot explain long-term maintenance of interstitial fluid in the joint; there must be an active uptake mechanism in which articulation drives fluid back into the cartilage surface at a rate that outpaces exudation. This paper explores the origins of this mechanism and in doing so uncovers several phenomena that cannot be explained by existing theory. Contrary to existing theory, we show that stationary contacts are able to sustain fluid pressures in a manner similar to the migrating contact. Furthermore, we demonstrate active recovery of interstitial fluid in a stationary contact without exposing the loaded zone to the bath. The results demonstrate that sliding alone, even at sub-physiological speeds, forces fluid back into the cartilage at rates that outpace exudation rates. The results suggest that interstitial or weeping lubrication is the primary lubrication mechanism in the joint and that hydrodynamic effects prevent the loss of this mechanism in the long-term.

11:00am **TR+AS+BI+NS-FrM9 Biomimetic Aspects of Lubrication with Polymer Brushes and Gels**, *C. Mathis, L. Isa,* ***Nicholas Spencer***, ETH Zürich, Switzerland

The role of the solvent is crucial in lubrication with polymer brushes and gels. Firstly it is important in maintaining the structure of the brush or gel layer in an unloaded state. Under loading, however, a new phenomenon becomes crucial, namely the Darcy flow of the solvent through the porous system. This aspect brings in a new set of properties to consider: the viscosity of the solvent determines the rate at which the solvent is forced through the porous network, and the sliding speed determines the extent to which the solvent is expelled from beneath the contact. The very act of expulsion of solvent is actually a process that bears a portion of the load. This phenomenon is well known in cartilage, and has been dubbed "fluid load support". This presentation will illustrate the ways in which this biomimetic approach can be utilized to protect polymer brushes and gels from wear, thus increasing their attractiveness as applicable lubricating systems, and will describe the approaches that can be used to quantify the process.

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Jacobs, T.D.B.: TR+AS+BI+NS-FrM3, **31**
Jasieniak, M.: SM+AS+BI+PS-ThA6, 28
Jaye, C.: BI-WeM10, 18
Jensen, B.D.: TF+AS+BI-WeA11, 23
Jeon, N.L.: BI-WeA3, **19**
Jeon, S.: SP+BI+NS+SS+TF-ThA10, **29**
Jia, H.: BI-WeA10, 20; MN+BI-TuA9, **13**
Jinno, M.: SM+AS+BI+PS-ThA10, 28
Jocham, D.: BI-WeA2, 19
Johar, M.A.: EL+AS+BI+EM-ThA9, 27
Johnson, A.: BI-WeA9, 20
Juthani, N.: BI-TuA2, 10

— K —

Kamineni, V.M.: EL+AS+BI+EM-ThA6, **26**
Kawakami, T.: BI-TuP12, 15
Keller, N.: EL+AS+BI+EM-ThA2, 26
Kelley, M.J.: AS+BI-TuA8, 9
Kelso, S.: BI-TuA2, 10
Kieda, C.: SM+AS+BI+PS-ThM1, 24
Kiguchi, T.: BI-TuP11, 15
Kikuchi, H.: IS+SS+NS+BI+VT+MN+AS-WeA12, 22
Kim, P.: BI-TuA2, 10
Kim, Y.: SP+BI+NS+SS+TF-ThA8, 29
Kjoller, K.: BI+AS-MoM6, 1
Klein, E.: BI+AS-MoM5, 1
Knoll, A.J.: PS+BI+SM-TuM11, 7
Koitaya, T.: IS+SS+NS+BI+VT+MN+AS-WeA12, 22
Kondeti, V.S.S.K.: PS+BI+SM-TuM10, 7
Kondo, H.: SM+AS+BI+PS-ThA11, 28
Kovalenko, Y.: BI-TuA2, 10
Kumar, S.: BI-WeM3, **17**
Kummel, A.C.: BI+AS-MoA9, 5
Kushner, M.J.: SM+AS+BI+PS-ThA1, **27**
Kyung Lee, W.: BI+AS-MoM6, 1

— L —

La Spina, R.: BI+AS-MoM9, 2
Lai, J.: BI+AS-MoM8, 2
Lalor, J.: PS+BI+SM-TuM12, 7
Lamas, J.: BI-WeA8, 20
Lanceros-Méndez, S.: BI-TuA3, 10
Langer, R.: BI-TuA11, 11
Lao, D.: AS+BI-TuA11, 10
Latour, R.A.: BI-WeM5, **17**
Leal-Taixe, L.: BI-TuA10, 11
Leary, D.: BI-WeM11, 18
Lee, C.M.: SM+AS+BI+PS-ThM4, 24
Lee, W.H.: MN+BI-TuA8, **12**
Lee, Y.T.: SM+AS+BI+PS-ThM3, **24**
Leggett, G.J.: BI-WeA9, **20**
Li, C.: SM+AS+BI+PS-ThM3, 24
Li, J.: IS+SS+NS+BI+VT+MN+AS-WeA10, 22; IS+SS+NS+BI+VT+MN+AS-WeA9, 21
Li, L.: BI-WeM6, **17**
Li, N.: BI-WeA8, 20
Li, O.L.: BI-TuP11, 15
Li, X.: BI-WeM5, 17
Li, Y.: BI+AS-MoA10, 6
Liang, E.: BI-WeA7, **19**
Liberman, A.: BI+AS-MoA9, 5
Liedberg, B.: BI-TuA10, 11
Lietz, A.M.: SM+AS+BI+PS-ThA1, 27
Lim, H.: SP+BI+NS+SS+TF-ThA8, 29
Lim, J.S.: MG+BI+MS+NS+TF-MoM8, 3
Lin, J.: BI-TuA2, 10
Lindhorst, K.: TF+AS+BI-WeA8, 23
Liu, D.-J.: SP+BI+NS+SS+TF-ThA8, 29
Liu, J.: BI-WeM11, 18
Liu, S.: BI-WeM1, 17
Lo, M.: BI+AS-MoM6, 1
López, G.P.: BI-WeM6, 17
Luan, P.: PS+BI+SM-TuM11, **7**
Lubinevsky, H.: BI+AS-MoM5, 1
Lund, J.M.: TF+AS+BI-WeA11, 23
Lutolf, M.: BI-TuP2, 14

— M —

MacCallum, N.: BI-TuA2, 10
Mah, E.: BI-WeA7, 19
Maksymovych, P.: SP+BI+NS+SS+TF-ThA10, 29
Maleschlijski, S.: BI-TuA10, 11
Mandal, H.: TF+AS+BI-WeA9, 23
Mandrus, D.: SP+BI+NS+SS+TF-ThA6, 29
Mann, M.N.: BI-TuA9, 11; PS+BI+SM-TuM13, **8**
Martins, P.M.: BI-TuA3, 10
Martirez, J.M.: MG+BI+MS+NS+TF-MoM8, 3
Mathis, C.: TR+AS+BI+NS-FrM9, 31
Matthews, T.: AS+BI-TuA7, **9**
Mattrey, R.: BI+AS-MoA9, 5
Medalsy, I.: BI-TuP17, 16
Mehregany, M.: MN+BI-TuA3, **12**
Messersmith, P.B.: BI-TuP1, 14
Michl, T.D.: SM+AS+BI+PS-ThA6, 28
Milosavljevic, V.: PS+BI+SM-TuM12, **7**
Miyamoto, S.: SM+AS+BI+PS-ThM12, 25
Miyashita, T.: BI-TuP13, **15**
Mo, C.: BI-WeM6, 17
Mock, A.: EL+AS+BI+EM-ThA3, **26**; EL+AS+BI+EM-ThA4, 26
Mon, H.H.: SM+AS+BI+PS-ThA6, 28
Mooney, D.: BI-TuA11, 11
Moore, A.C.: TR+AS+BI+NS-FrM7, 31
Morrish, F.M.: BI+AS-MoA5, 5
Motley, J.: BI+AS-MoA10, 6
Mueller, T.: BI-TuP17, 16
Mukai, K.: IS+SS+NS+BI+VT+MN+AS-WeA12, 22
Murthy, N.S.: BI-WeM5, 17
Muscat, A.J.: EL+AS+BI+EM-ThA1, 26
Myoui, A.: SM+AS+BI+PS-ThM12, 25

— N —

Nagatsu, M.: SM+AS+BI+PS-ThM5, **24**
Nascente, P.A.P.: TF+AS+BI-WeA7, **22**
Nash, J.A.: BI-TuP14, 16
Nemr, C.: BI-TuA2, 10
Newton, M.A.: BI-TuP9, **15**
Niemeyer, T.C.: TF+AS+BI-WeA7, 22
Nomura, T.: SM+AS+BI+PS-ThA11, 28
Norberg, S.A.: SM+AS+BI+PS-ThA1, 27

— O —

O'Mullane, S.: EL+AS+BI+EM-ThA6, 26
Oehrlein, G.S.: PS+BI+SM-TuM11, 7
Oh, J.: SP+BI+NS+SS+TF-ThA8, 29
Ohta, T.: SM+AS+BI+PS-ThA11, 28
Ojea, I.: BI+AS-MoM9, 2
Okada, M.: SM+AS+BI+PS-ThM5, 24
Okamoto, T.: BI-TuP13, 15; BI-TuP5, 14
O'Mullane, S.: EL+AS+BI+EM-ThA2, **26**
Osgood, Jr., R.M.: SP+BI+NS+SS+TF-ThA9, **29**

— P —

Patel, A.: BI-TuA11, 11
Paul, M.: AS+BI-TuA7, 9
Paven, M.: BI+AS-MoA4, 4
Pegalajar-Jurado, A.: BI-TuA9, **11**; PS+BI+SM-TuM13, 8; SM+AS+BI+PS-ThM13, 25
Pehrsson, P.E.: BI+AS-MoM6, 1
Pelster, A.: AS+BI-TuA3, 9
Perkins, R.T.: EL+AS+BI+EM-ThA11, 27
Petersen, K.: MN+BI-TuA1, **12**
Petrovykh, D.Y.: BI-TuA3, **10**
Pinto, I.M.: BI-TuA3, 10
Pittenger, B.: BI-TuP17, **16**
Poespawati, N.R.: SM+AS+BI+PS-ThM5, 24
Potapenko, D.V.: SP+BI+NS+SS+TF-ThA9, 29
Pouvesle, J.-M.: SM+AS+BI+PS-ThM1, **24**
Purnamaningsih, R.W.: SM+AS+BI+PS-ThM5, 24

— R —

Race, J.: EL+AS+BI+EM-ThA2, 26
Rakowska, P.D.: AS+BI-TuA12, 10
Ramalingam, G.: SP+BI+NS+SS+TF-ThA3, **29**
Raman, R.: BI-TuA4, **10**
Raman, S.: BI-WeA1, 19; BI-WeM13, 18
Rappe, A.M.: MG+BI+MS+NS+TF-MoM8, **3**
Rastogi, S.: BI-WeA8, 20
Ratner, B.D.: BI+AS-MoA3, 4; PS+BI+SM-TuM1, **7**
Rehman, S.: EL+AS+BI+EM-ThA9, 27
Reinke, P.: SP+BI+NS+SS+TF-ThA3, 29
Richter, R.P.: BI+AS-MoA7, **5**
Ridou, L.: SM+AS+BI+PS-ThM1, 24
Rieth, L.W.: TF+AS+BI-WeA9, 23
Robert, E.: SM+AS+BI+PS-ThM1, 24
Robinson, R.: BI+AS-MoA6, 5
Rosenhahn, A.: BI-TuA10, **11**
Rosenhahn, B.: BI-TuA10, 11
Rossi, F.J.: BI+AS-MoM9, 2; TF+AS+BI-WeA1, **22**
Roy, A.: AS+BI-TuA7, 9
Roy, S.K.: MN+BI-TuA7, 12
Rubinstein, M.: BI-WeM6, 17
Russell, Jr., J.N.: BI+AS-MoM6, 1

— S —

Saidi, W.A.: MG+BI+MS+NS+TF-MoM8, 3
Saito, N.: BI-TuP11, 15
Sakudo, A.: SM+AS+BI+PS-ThM5, 24
Saldana-Greco, D.: MG+BI+MS+NS+TF-MoM8, 3
Saldin, L.T.: BI+AS-MoA3, 4
Sánchez-Domínguez, M.S.D.: BI-TuP7, 14
Sánchez-Vázquez, M.S.V.: BI-TuP7, 14
Sauer, V.T.K.: MN+BI-TuA7, 12
Schilke, K.F.: BI-TuA4, 10
Schillers, H.: BI-TuP17, 16
Schmidt, D.: EL+AS+BI+EM-ThA4, 26
Schmüser, L.: BI+AS-MoA4, **4**
Schubert, E.: EL+AS+BI+EM-ThA3, 26; EL+AS+BI+EM-ThA4, 26
Schubert, M.: EL+AS+BI+EM-ThA3, 26; EL+AS+BI+EM-ThA4, 26
Scurr, D.: BI-TuP2, 14
Seah, M.P.: AS+BI-TuA12, 10
Sekine, M.: SM+AS+BI+PS-ThA11, 28
Sekora, D.: EL+AS+BI+EM-ThA3, 26
Semetey, V.: BI-WeM12, 18
Sen, R.: AS+BI-TuA4, 9
Sendra, G.H.: BI-TuA10, 11
Seog, J.: PS+BI+SM-TuM11, 7
Sharma, R.: TF+AS+BI-WeA9, 23
Shaw, J.: BI-TuP17, 16
Shehzad, M.A.: EL+AS+BI+EM-ThA9, 27
Shepelenko, M.: BI+AS-MoM5, 1
Silva, A.R.: BI-TuA3, 10
Slade, A.: BI-TuP17, 16
Smallwood, C.: IS+SS+NS+BI+VT+MN+AS-WeA1, 20
Smith, J.: BI-TuA11, 11
So, C.: BI+AS-MoA2, **4**; BI-WeM11, 18
Sousa, C.: BI-TuA3, 10
Spampinato, V.: BI+AS-MoM9, 2
Spencer, N.D.: TR+AS+BI+NS-FrM9, **31**
Spinner, M.: BI-WeM10, 18
Stayton, P.S.: BI+AS-MoM8, 2
Stine, R.: BI+AS-MoA2, 4
Stock, P.: BI-WeA1, 19; BI-WeM2, **17**
Sugimoto, S.: SM+AS+BI+PS-ThM12, 25
Sui, X.: IS+SS+NS+BI+VT+MN+AS-WeA3, **21**; IS+SS+NS+BI+VT+MN+AS-WeA4, 21
Sumpter, B.: SP+BI+NS+SS+TF-ThA10, 29
Syme, D.B.: TF+AS+BI-WeA11, 23

— T —

Takeda, K.: SM+AS+BI+PS-ThA11, 28
Takei, H.: BI-TuP12, 15; BI-TuP13, 15; BI-TuP5, 14
Tan, K.: IS+SS+NS+BI+VT+MN+AS-WeA10, 22; IS+SS+NS+BI+VT+MN+AS-WeA9, **21**
Tanatsugu, Y.: SM+AS+BI+PS-ThM4, 24
Tang, H.: BI-WeA10, **20**; MN+BI-TuA9, 13
Tang, L.: BI-WeA8, 20
Tang, S.: SP+BI+NS+SS+TF-ThA6, 29
Tathireddy, P.: TF+AS+BI-WeA9, 23
Taylor, A.J.: BI+AS-MoA3, **4**
Taylor, M.: BI-TuP2, **14**

Terfort, A.: TF+AS+BI-WeA8, **23**
Thiel, P.A.: SP+BI+NS+SS+TF-ThA8, 29
Thonhauser, T.: IS+SS+NS+BI+VT+MN+AS-WeA10, 22; IS+SS+NS+BI+VT+MN+AS-WeA9, 21
Tian, W.: SM+AS+BI+PS-ThA1, 27
Tian, W.C.: MN+BI-TuA8, 12
Trogler, W.: BI+AS-MoA9, 5
Truong, A.: PS+BI+SM-TuM10, 7
Tsargorodska, A.: BI-WeA9, 20
Tu, Q.: BI-WeM6, 17
Turley, R.S.: EL+AS+BI+EM-ThA11, 27
Tyler, B.J.: AS+BI-TuA3, **9**

— U —

Utzig, T.: BI-WeA1, 19; BI-WeM13, **18**; BI-WeM2, 17

— V —

Vaid, A.: EL+AS+BI+EM-ThA6, 26
Vaish, A.: BI+AS-MoM10, 2
Valsesia, A.: TF+AS+BI-WeA1, 22
Valtiner, M.: BI-WeA1, **19**; BI-WeM13, 18; BI-WeM2, 17
Vanderah, D.: BI+AS-MoM10, 2
Vanfleet, R.: TF+AS+BI-WeA11, 23
Venkatasubramanian, A.: MN+BI-TuA7, **12**
Vieker, H.: BI-TuP13, 15; BI-TuP5, 14
Viswan, A.: SM+AS+BI+PS-ThM5, 24
Vollmer, D.: BI+AS-MoA4, 4

— W —

Wahl, K.: BI+AS-MoA2, 4; BI-WeM11, **18**
Walen, H.: SP+BI+NS+SS+TF-ThA8, **29**
Walker, M.: BI+AS-MoM10, **2**
Walper, S.: BI+AS-MoA2, 4
Wang, H.: IS+SS+NS+BI+VT+MN+AS-WeA10, 22; IS+SS+NS+BI+VT+MN+AS-WeA9, 21
Wang, J.: BI+AS-MoA9, **5**
Wang, YC.: BI+AS-MoA1, **4**
Wei, P.K.: MN+BI-TuA8, 12
Weidner, T.: BI+AS-MoA4, 4; BI-TuP3, 14; BI-WeM10, 18
Weiner, S.: BI+AS-MoM5, 1
White, L.J.: BI+AS-MoA3, 4
Wilson, J.T.: BI+AS-MoM8, 2
Winter, B.: IS+SS+NS+BI+VT+MN+AS-WeA7, **21**
Wu, S.: BI-WeA7, 19

— Y —

Yee, A.: BI-WeA7, 19
Yeh, P.Y.: BI-TuA1, 10
Yi, J.: SP+BI+NS+SS+TF-ThA6, 29
Yingling, Y.G.: BI-TuP14, **16**; BI-WeA8, 20
Yoneda, S.: BI-TuP5, **14**
Yoshikwa, H.: SM+AS+BI+PS-ThM12, 25
Yoshinobu, J.: IS+SS+NS+BI+VT+MN+AS-WeA12, **22**
Yoshiomoto, S.: IS+SS+NS+BI+VT+MN+AS-WeA12, 22
Young, L.: BI-TuA11, 11
Yu, C.: SM+AS+BI+PS-ThM4, **24**
Yu, J.: AS+BI-TuA11, 10; BI-WeM1, **17**; IS+SS+NS+BI+VT+MN+AS-WeA4, 21
Yu, X.-Y.: AS+BI-TuA11, 10; BI-WeM1, 17; IS+SS+NS+BI+VT+MN+AS-WeA3, 21; IS+SS+NS+BI+VT+MN+AS-WeA4, 21

— Z —

Zauscher, S.: BI-WeA8, **20**; BI-WeM6, 17
Zelzer, M.: BI-TuP2, 14
Zhang, J.: IS+SS+NS+BI+VT+MN+AS-WeA4, 21
Zhang, P.P.: SP+BI+NS+SS+TF-ThA1, **28**
Zhou, Y.: AS+BI-TuA11, 10; BI-WeM1, 17; IS+SS+NS+BI+VT+MN+AS-WeA3, 21; IS+SS+NS+BI+VT+MN+AS-WeA4, 21
Zhu, J.F.: TF+AS+BI-WeA10, **23**
Zhu, Z.: AS+BI-TuA11, **10**; BI-WeM1, 17; IS+SS+NS+BI+VT+MN+AS-WeA3, 21; IS+SS+NS+BI+VT+MN+AS-WeA4, 21
Zuilhof, H.: AS+BI-TuA4, **9**
Zuluaga, S.: IS+SS+NS+BI+VT+MN+AS-WeA10, **22**; IS+SS+NS+BI+VT+MN+AS-WeA9, 21
Zurek, E.: MG+BI+MS+NS+TF-MoM10, **3**