Biomaterial Interfaces Division
Room B117-119 - Session BI1+PS-MoM

Microbes and Fouling at Surfaces

Moderators: Kenan Fears, U.S. Naval Research Laboratory, **Sally M. McArthur**, Deakin University, Australia

8:20am **BI1+PS-MoM-1 Amphiphilic Coatings for Marine Low-Fouling Applications***, Axel Rosenhahn,* Ruhr University Bochum, Germany **INVITED**

Manmade materials in contact with ocean water become rapidly colonized by living matter like bacteria, diatoms, barnacles, or mussels. Increased fuel consumption, failure of devices, and substantial maintenance costs are among the penalties associated with marine biofouling. As the historical paradigm to combat fouling by biocide releasing coatings is increasingly challenged by legal restrictions, environmentally benign low-fouling materials for marine applications are intensively explored [1]. While several hydrophilic and hydrophobic materials show promising properties, their combination into amphiphilic coatings unites the best of the two worlds [2]. As hydrophilic compound, zwitterionic materials with different molecular architectures were developed and their structure-function relationship against different fouling organisms have been studied [3]. Amphiphilic coatings based on zwitterionic polymers have been designed and their anti-polyelectrolyte properties have been characterized by several methods including AFM and SPR. Their antifouling properties against a range of marine fouling species and in short term field exposures have been assessed and the results will be discussed under consideration of the interaction of the organic coatings with inorganic particulate matter in the ocean [4,5,6]. Based on the obtained data, design criteria for optimized zwitterionic building blocks for fouling-release technologies will be discussed.

[1] M. Callow, J. Callow, Nature Communications 2011, 2, 244

[2] S. Krishnan, C. Weiman, C. Ober, J. Materials Chemistry 2008, 18, 3405

[3] A. Laschewsky, A. Rosenhahn, Langmuir 2018, 35, 1056

[4] F. Koschitzki, R. Wanka, L. Sobota, J. Koc, H. Gardner, K.Z. Hunsucker, G.W. Swain, A. Rosenhahn, ACS Applied Materials & Interfaces 2020, 12(30), 134148

[5] J. Koc, E. Schönemann, R. Wanka, N. Aldred, A.S. Clare, H. Gardner, G.W. Swain, K. Hunsucker, A. Laschewsky, A. Rosenhahn, Biofouling 2020, 36(6), 646

[6] L. Schardt, A.M. Guajardo, J. Koc, J.L. Clarke, J.A. Finlay, A.S. Clare, H. Gardner, G.W. Swain, K. Hunsucker, A. Laschewsky, A. Rosenhahn Macromolecular Rapid Communications 2021, 43(12), 2100589

9:00am **BI1+PS-MoM-3 Bio-Informed Interface Design and Synthesis to Manipulate Microbial Behavior***, Rong Yang,* Cornell University **INVITED**

Biofilm is often considered detrimental, which needs to be minimized as it can cause infections and fouling in healthcare, food and water manufacturing, and underwater civil and military activities. Nevertheless, we also believe such naturally occurring biofilm can be desirable, upon appropriate programming via precise control over the surface they inhabit, as building blocks for self-actuated and self-repairing “living” coatings. To gain insight into the biointerface, research in the past two decades has unraveled the fundamental thermodynamics and hydrodynamics that have guided the design of numerous antifouling/antimicrobial surfaces. However, the biological effects of insoluble materials remain elusive. Recent advances in vacuum-based synthesis have enabled well-defined material properties at length scales relevant to microbes' biochemical and biophysical activities, enabling a bio-informed materials design approach. Motivated by the unmet needs for antifouling materials and living materials, our recent research has advanced our current understanding of the biointerface in three critical ways: (***i***) leveraging dynamic surface chain reorientation to achieve antifouling at the air-liquid-solid interface, the importance of which has been overlooked in past research; (***ii***) recognizing bacteria to be complex microorganisms with dynamic structure and metabolism and sophisticated chemical communication systems and leveraging the recent breakthroughs in microbiology to guide the design of bio-active polymer coatings; (***iii***) enabling living materials by performing polymerization directly on living organisms, which overcomes the limited tunability of the native microbial extracellular scaffolds and preserves the function and viability of coated organisms by avoiding harmful synthesis conditions. We seek to underscore the importance of understanding detailed microbe-material interactions and provide an outlook on extending the material-bacteria interactions beyond “kill or repel” towards signaling and control.

9:40am **BI1+PS-MoM-5 Using Flow-Cells to Culture Microbial Biofilms for Improved Secondary Ion Mass Spectral Imaging***, Yuchen Zhang,* Oak Ridge National Laboratory, USA*; X. Yu,* Oak Ridge National Laboratory

Bacterial biofilms are a main player in organic processing in the environment. Therefore, characterization and understanding of the biofilm interactions with groundwater and soil components is important in deepening our knowledge in the biosphere and rhizosphere. We present two approaches to prepare the bacterial biofilms suitable for time-of-flight secondary ion mass spectrometry (ToF-SIMS). *Shewanella* MR-1 was used as the model bacteria biofilm due to their known traits in subsurface, surface, and soil microbiology. A mixture of silica, alumina, and iron oxide was used as the model soil system. In the static culture, the bacteria were inoculated in a multi-well cell culture dish at their log phase. Then minerals were added to the culturing well. The mixture of the bacteria biofilms and minerals were scratched off carefully and deposited onto the clean silicon (Si) wafers before ToF-SIMS analysis. Second, we used a microfluidic cell to culture biofilms. We made a modification of the system for analysis at the liquid vacuum interface (SALVI) microfluidics for biofilm attachment in the growth and detection chamber. The mineral components were mixed to the growth media at a ratio of 1:1 by volume as nutrients to support the biofilm’s growth. During static culturing, a series of Si wafers were used to capture the temporal progression of the biofilms and the soil components over days. In dynamic cultures, effluents were collected onto clean Si substrates. The time intervals were chosen based on the growth curve of the strain. Distinctive fatty acids peaks of *Shewanella* biofilms, such as myristic acid (m/z^- 227, $C_{14}H_{27}O_2^-$), palmitic acid (m/z^- 255, $C_{16}H_{31}O_2^-$), and arachidic acid (m/z^- 311, $C_{20}H_{39}O_2^-$), and the biomarker riboflavin peak (m/z^- 241, $C_{12}H_9N_4O_2^-$) are observed in the dynamic results. In contrast, the static results do not provide as much information. This finding indicates that static culture is not optimal for studying biofilms using ToF-SIMS. Our results demonstrate that sample preparation is quite critical in microanalysis of bacteria biofilms, specifically in surface analysis like ToF-SIMS. The microfluidic growth chamber is more flexible in microbial culture and media tuning, both are important in simulating a variety of conditions to understand microbes and soil interactions at the microscale. Additionally, characteristic signals of biofilms are not buried under the mineral components in the dynamic setup, which is imperative in understanding the role of biofilms in soil aggregation and bioremediation occurring at the microbial interface.

10:00am **BI1+PS-MoM-6 Role of Microbial Biofilms in the Settlement of Macrofoulers on Antifouling Marine Coatings***, Sara Tuck, M. Kardish,* US Naval Research Laboratory*; B. Orihuela,* Duke University*; G. Vora,* US Naval Research Laboratory*; D. Rittschof, K. Franz,* Duke University*; K. Fears,* US Naval Research Laboratory

Accumulation of biofouling on submerged surfaces is a foundational problem for maritime transport and human health. Biofouling build-up increases the drag coefficient, fuel consumption, exhaust emissions, and operational costs. Traditionally, biofouling is inhibited by the application of antifouling coatings, the most popular of which, contain copper. Copper-based antifouling coatings can contain up to ~75% CuO, by weight, in attempt to release sufficient levels of copper to deter the settlement of fouling organisms. Despite these high loadings, the efficacy of these antifouling coatings has been declining with the emergence and spread of copper tolerant species. Microbial communities resistant to copper have been found to form mature biofilms on these coatings, which could be altering the interfacial properties to create more favorable conditions for the settlement of a broader biofouling community. To gain an understanding of the mechanisms responsible for the loss in antifouling performance, coated and uncoated polyvinyl chloride panels were submerged at estuarine and marine field test sites and microbial communities were harvested. Collected biofouling communities were cultured and individual species were collected and identified. Copper tolerance was assessed by re-exposing cells to copper-containing coatings and traditional antimicrobial assays to determine susceptibility to an array of biocides. Finally, resistant biofilms were formed on marine coatings to assess the effect of their presence on the settlement of acorn barnacle larvae.

Biomaterial Interfaces Division
Room B117-119 - Session BI2+AS+HC+SS-MoM

Energy Transfer and Light Induced Phenomena in Biologic Systems

Moderators: Morgan Alexander, University of Nottingham, UK, **Tobias Weidner**, Aarhus University, Denmark

10:40am **BI2+AS+HC+SS-MoM-8 Electrochemically Conducting Lipid Bilayers: Q-Lipid-Containing Membranes ShowHigh in-Plane Conductivity Using a Membrane-on-a-Chip Setup**, *U. Ramach,* TU Wien, Austria*; J. Andersson,* IST Austria*; **Markus Valtiner**,* TU Wien, Austria

The light-driven reactions of photosynthesis as well as the mitochondrial powersupply are located in specialized membranes containing a high fraction ofredox-active lipids. In-plane charge transfer along such cell membranes iscurrently thought to be facilitated by the diffusion of redox lipids and proteins.

Using a membrane on-a-chip setup, we show here that redox-active model membranescan sustain surprisingly high currents (mA) in-plane at distances of 25 mm.Wealso showthe same phenomenon in free-standing monolayers at the air-waterinterface once the film is compressed such that the distance between redox centersis below 1 nm. Our data suggest that charge transfer within cell walls hostingelectron transfer chains could be enabled by the coupling of redox-lipids viasimultaneous electron and proton in-plane hopping, similar to conductive polymers.This has major implications for our understanding of the role of lipid membranes,suggesting that Q-lipid-containing membranes may be essential forevolving the complex redox machineries of life.

[1] U. Ramach, J. Andersson, R. Schöfbeck and M. Valtiner, Iscience 26 (2), 2023.

11:00am **BI2+AS+HC+SS-MoM-9 Light Responsive Cyclic Peptide Polymer Nanomaterials**, *O. Atoyebi, M. Beasley, W. Maza, M. Kolel-Veetil, A. Dunkelberger, **Kenan Fears**,* US Naval Research Laboratory

Cyclic peptides are capable of self-assembling into supramolecular peptide nanostructures, via hydrogen bonding along the backbone of the peptide rings. To improve upon this molecular architecture, we designed and synthesized cyclic peptide polymers by covalently linking the cyclic peptides into a linear polymer chain, and demonstrated the conformation of the polymer chain could be transitioned from an unfolded state into rigid, peptide nanorods by varying solution pH. Here we present an alternate way to control the self-assembly via photo-isomerization. We capitalize on azobenzene's photo-actuable nature using a di-carboxylic acid azobenzene to covalently crosslink the cyclic peptide rings into a linear cyclic peptide polymer via terminal amines present in the ring. Self-assembly of the cyclic peptide nanotube occurs by exposing the polymerized cyclic peptide to ultraviolet radiation causing a trans- to -cis transition of the azobenzene and thus assembling the cyclic peptide nanotube. Furthermore, we fluorescence donor/acceptor pairs can be displayed from these materials, at highly controlled separation distances, to alter the optical response of these materials as a function of polymer conformation.

11:20am **BI2+AS+HC+SS-MoM-10 Programmable Biomimetic Light-Harvesting Systems based on Strong Coupling of Synthetic Peptides and Dye-Functionalised Polymer Brushes to Plasmon Modes**, ***Graham Leggett**,* University of Sheffield, UK

Excitation transfer in molecular photonic materials is dominated by incoherent hopping processes; consequently, exciton diffusion lengths are short (~10 nm) placing severe constraints on device design. A grand challenge for the past two decades has been to discover how to achieve efficient long-range transfer of excitation in molecular systems. We have developed a new approach to the design of materials for solar energy capture that combines biomimetic design, inspired by structures used in photosynthesis, with strong light-matter coupling.

Photosynthetic pigment-protein light-harvesting antenna complexes (LHCs) from plants and bacteria are strongly coupled to the localised surface plasmon resonances (LSPRs) in arrays of metal nanostructures leading to the formation of macroscopically extended excited states. Modelling of data indicates that the coupling results from linear combinations of plasmon and exciton states. For example, wild-type and mutant LH1 and LH2 from *Rhodobacter sphaeroides* containing different carotenoids yield different coupling energies; the methods of synthetic biology enable strong light-matter coupling to be programmed.

However, proteins are not suitable for putative applications of molecular photonic materials. Instead, we have designed programmable biomimetic pigment-peptide and pigment-polymer antenna complexes, in which surface-grafted peptide and polymer scaffolds organise excitons within localised surface plasmon resonances to achieve strong light-matter coupling. In these systems, delocalised excited states (plexcitons) extend across at least 1000s of pigments. In synthetic peptide and protein systems, we find that the plasmon mode couples to states not seen under weak-coupling, providing evidence for the formation of macroscopically-extended excited states that facilitate coherent transfer of excitation across long distances. In pigment-polymer systems, the dye concentration in the film can be increased to ~2M, significantly exceeding the concentration of chlorophyll in biological light-harvesting complexes, by optimisation of the polymer grafting density and the dye-scaffold coupling chemistry. Fitting of spectra for these plexcitonic antenna complexes yields Rabi energies up to twice as large as those achieved with biological LHCs. Moreover, synthetic plexcitonic antenna complexes display pH- and temperature-responsiveness, enabling active control of strong plasmon-exciton coupling via regulation of the polymer conformation.

These biomimetic quantum-optical brush systems offer great promise for the design of new types of molecular photonic device.

Nanoscale Science and Technology Division
Room B113 - Session NS1+2D+BI+SS-MoM

Combined Nanoscale Microscopy

Moderators: Adina Luican-Mayer, University of Ottawa, Canada, **Sergei Kalinin**, Oak Ridge National Laboratory

8:20am **NS1+2D+BI+SS-MoM-1 Combined Metrology at the Nanoscale: Advanced Scanning Probe Microscopy to Evaluate Complex Semiconductors**, ***Fernando A. Castro**,* National Physical Laboratory, UK **INVITED**

The performance of semiconductors is strongly affected by spatial variations that can be introduced during manufacturing or due to degradation processes. In addition to the impact of microstructure and defects on electrical and optical properties, complex semiconductors, such as some compound semiconductors, perovskites or 2D materials, can present dynamic changes in properties during operation. Combining metrology methods is critical to better understand and characterise such complex samples as individual methods provide insufficient information. Ideally these combined measurements should be either co-localised or simultaneous in order to reduce uncertainty associated with post process image registration, spatial heterogeneity, or sample contamination. NPL has been developing a suite of spatially resolved measurement methods to understand critical factors that impact semiconductor performance and reliability. In this presentation, we'll focus on nanoscale methods under controlled operational or environmental conditions, including advanced modes of scanning probe microscopy (SPM) such as time-resolved scanning kelvin probe (tr-SKPM) and tip enhanced optical microscopy (TEOS). After introducing the challenges and recent results from the European project PowerELEC, we'll present two examples of how these combined measurements are applied. First, we'll describe the application of SPM to understand degradation mechanisms in state-of-the-art perovskite solar cells (PSCs). Time-resolved SKPM can be used to distinguish the impact of ionic and electronic charges on dynamic processes and in-situ co-localised measurements under controlled environmental conditions can identify nucleation of nanoscale grains on the perovskite film surface at the start of the degradation process, allowing us to link degradation to the local electrostatic environment. The second example will focus on 2D transition metal dichalcogenide (TMD), which present promise for optoelectronic applications but are often limited by Fermi level pinning effects and consequent large contact resistances upon contacting with bulk metal electrodes. A potential solution for near-ideal Schottky–Mott behavior and concomitant barrier height control has been proposed in the literature by contacting TMDs and (semi-)metals in van der Waals heterostructures. We will show how combined nanoscale measurements allows to directly access interface parameters relevant to the Schottky–Mott rule on a local scale and how we use SKPM and TEOS measurements under simulated operational conditions (e.g. electrostatic doping induced Fermi levels) to enable decoupling and quantification of contributions from the interface dipole and electrode work function.

9:00am **NS1+2D+BI+SS-MoM-3 Correlated Functional Imaging of Printed and Ferroelectric 2D Devices for Ubiquitous Sensing and Neuromorphic Computing**, *J. Kim, Z. Zhu, T. Chu, H. Choi, M. Moody,* ***Lincoln Lauhon****,* Northwestern University

The unique properties of 2D materials stimulate the design of devices that exhibit useful new behaviors. However, the correspondence of expected and actual operating principles of devices cannot always be established from simple analysis of temperature-dependent current-voltage characteristics. As a result, the rational optimization of even simple devices such as thin-film transistors, as well as the successful realization of novel neuromorphic devices, benefits from spatially resolved characterization of nanoscale structure and properties to discern the relative contributions of device geometry and 2D material structure and chemistry to device performance. This talk will describe case studies in which Kelvin probe force microscopy (KPFM) and scanning photocurrent microscopy (SPCM) are used to investigate the operating principles of thin-film transistors (TFTs) and source-gated transistors (SGTs) fabricated from MoS_2 and In_2Se_3. In the case of n-type semiconducting 2H MoS_2, model devices constructed from overlapping exfoliated flakes are analyzed to identify factors limiting the performance of printed thin-film transistors (*ACS Nano* 2023, **17**, 575). KPFM analysis is used to isolate the contact, channel, and junction resistances and calibrate a resistor network model of printed thin films. Simulations of the effective mobility and on-current dependence on flake thickness, size, and degree of overlap suggest that the performance of printed TFTs are limited by resistance arising from unpassivated edge states.

In the second use case, KPFM, SPCM, and piezoresponse force microscopy (PFM) are used to pinpoint the origin of resistance modulation in α-In_2Se_3 transistors that exhibit tunable non-volatile channel conductance. Memristive behavior in In_2Se_3 TFTs has been attributed to switching of the channel polarization, but the lack of an obvious threshold for switching raises questions about the evolution of domain structure and the contribution of trap states. Furthermore, the presumed modulation of the Schottky barrier has yet to be confirmed experimentally. We address this gap in understanding through correlated PFM, KPFM, and SPCM measurements. We then fabricate MoS_2-In_2Se_3 transistors with a geometry that induces depletion at the source electrode, i.e. a source-gated transistor, and observe non-volatile switching of the low output current. KPFM, SPCM, and finite element simulations are used to confirm source pinch-off and non-volative multi-level modulation of the effective source resistance. The quantitative correlation of device behaviors with the changes in channel potential at key interfaces usefully constrains the interpretation of the operating principles and builds a foundation for rational design of novel neuromorphic devices and systems.

9:20am **NS1+2D+BI+SS-MoM-4 A Unique New Correlative Microscopy Platform for Combined Nanoscale Microscopy by Combination of AFM and SEM**, ***Chris Schwalb****,* Quantum Design Microscopy GmbH, Germany*; K. Arat,* Quantum Design, Inc.*; H. Alemansour, A. Alipour,* Quantum Design, Inc., Iran (Islamic Republic of)*; A. Amann,* Quantum Design, Inc., Germany*; L. Montes,* Quantum Design, Inc., Colombia*; J. Gardiner,* Quantum Design, Inc.*; H. Frerichs, L. Stuehn, S. Seibert,* Quantum Design Microscopy GmbH, Germany*; S. Spagna,* Quantum Design, Inc.

The combination of different analytical methods into one instrument is a powerful technique for the contemporaneous acquisition of complementary information. This is especially true for the in-situ combination of atomic force microscopy (AFM) and scanning electron microscopy (SEM), two of the most powerful microscopy techniques available. This combination gives completely new insights into the nanoscale.

In this work, we introduce a highly integrated new corelative microscopy platform, the FusionScope, that seamlessly combines AFM and SEM within a unified coordinate system. The self-sensing piezoresistive cantilever technology used for the AFM scanner results in a purely electrical measurement of the cantilever deflection signal. This allows for concurrent, correlated acquisition of both SEM and AFM images at the region of interest. In addition, a three-axis sample stage and a trunnion provide unique experimental capabilities such as profile view – an 80-degree tilt of the combined sample stage and AFM giving full SEM access to the cantilever tip region.

We will present a variety of novel case studies to highlight the advantages of this new tool for interactive, correlative, in-situ nanoscale characterization for different materials and nanostructures. First results will focus on hard-to-reach samples. FusionScope allows for fast and easy identification of the area of interest and precise navigation of the cantilever tip for correlative SEM and AFM measurements. We demonstrate that approach for analysis of blade radius of razor blades and the characterization of lacunae structures on bone surfaces.

In addition, we will present first results for the in-situ characterization of individual nanowires that will be used for energy harvesting applications. The SEM enables the easy location of individual or multiple nanowires, whereas the in-situ AFM allows the characterization of topography, surface roughness, mechanical, and electrical properties of the nanowire.

Based on the broad variety of applications regarding the inspection and process control of different materials and devices, we anticipate that this new inspection tool to be one of the driving characterization tools for correlative SEM and AFM analysis in the future.

9:40am **NS1+2D+BI+SS-MoM-5 Correlative *in-Situ* Nanoscale Microscopy Using AFM and FIB-SEM for Nanomechanical Property Mapping Throughout a 3D Volume**, ***Prabhu Prasad Swain****, M. Penedo, N. Hosseini, M. Kangül, S. Andany, N. Asmari, G. Fantner,* Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland

In this work, we present results obtained with an atomic force microscope (AFM) integrated in a focused ion beam- scanning electron microscope (FIB-SEM). The FIB-SEM is a powerful instrument, capable of automated structural analysis and prototyping at nanometer resolution, while the AFM is a well-established versatile tool for multiparametric nanoscale characterization. Combining the two techniques allows unprecedented *in-situ* correlative analysis at the nanoscale. Nanoprototyping and enhanced multiparametric analysis can be performed without contamination of the sample or environmental changes between the subsequent processing steps. The power of the combined tool lies in the complementarity of the two techniques. The AFM offers nanomechanical property mapping with electrical and magnetic characterization of the sample, while SEM offers elemental analysis and FIB enables thin slicing of the of the sample for block face imaging. This enables 3D tomographic imaging of complex samples mapping composition and mechanical properties throughout the 3D volume. Controlling both these instruments with open-hardware controller (OHC), allows us to perform automated *in-situ* AFM-FIB-SEM characterization. The setup is aimed to provide true 3D correlative information and mapping, with increased resolution for a larger volume. We will demonstrate the capabilities of correlative AFM/SEM/FIB imaging through a series of correlative experiments on polymers, 2D materials, nanowires and rock sediments.

10:00am **NS1+2D+BI+SS-MoM-6 Anisotropic Friction Effects of Perovskite Nanoplatelets on a vdW Substrate**, ***Sidney Cohen****, N. Itzhak, I. Rosenhek-Goldian, O. Brontvein, E. Joselevich,* Weizmann Institute of Science, Israel

Interest in 2D materials can be attributed to their unique properties such as electrical, optical, and mechanical characteristics, which can be harnessed in small devices. Assembly of these materials can be challenging. vdW epitaxy is a promising approach, in which nano-sized crystalline structures are grown on a 2D vdW substrate which has minimal interaction energy, resulting in low strain. The epitaxial growth still provides sufficient interaction to favor specific geometries according to lattice directions. In this presentation, the system is $CsPbBr_3$ platelets grown on vdW $ReSe_2$.This combination is of fundamental and applied interest due to special optoelectronic properties of these 2D-3D mixed semiconductor systems. The mechanism of the nanoplatelet growth leading to their shape and orientation on the surface remains to be fully revealed . Here, we present tribological studies performed by monitoring the force required to push the platelets along the surface. We observed a significant directional effect expressed in the lateral forces required to slide the platelets along the surface. In particular, forces 4-5 times those required to push rectangular platelets along the $ReSe_2$ surface along the long axis were insufficient to move the same platelets along their short axis. STEM images showed that this correlated with commensurability of the two lattice structures.Some of the experiments were performed in an ambient AFM system. Because sliding along the surface can be hindered by atomic steps and defects, unbiased analysis of this effect requires searching for small steps of atomic height along the sliding path. Scanning electron microscopy is a convenient way to search for these defects: thus, comparative experiments were performed in-situ in a combined AFM-SEM system. This combination had the additional advantage of allowing rapid overview of the surface to locate regions of interest.

In the process of evaluating the measurements, those performed in vacuum requiredmuch higher (by as much as an order of magnitude) forces to support pushing along the surface in comparison with comparable

measurements made in the ambient AFM system.These measurements will be presented in the context of the characterization of the 2D substrate and platelet nanostructure as revealed by the two correlative measurement techniques.

Nanoscale Science and Technology Division
Room B113 - Session NS2+2D+BI+EL+SS-MoM

Chemical Identification with Scanning Probe Microscopy

Moderators: Sidney Cohen, Weizmann Institute of Science, Israel, **Harald Plank**, Graz University of Technology

10:40am **NS2+2D+BI+EL+SS-MoM-8 Nanoscale imaging with photo-induced force microscopy***, Eric Potma,* University of California Irvine **INVITED**

Imaging with molecular contrast at the nanoscale is important for a myriad of applications, yet it remains a technical challenge. Over the past two decades, various flavors of optical spectroscopy combined with atomic force microscopy have been developed, each offering hope for a more routine nanospectroscopy technology. One of these approaches is photo-induced force microscopy (PiFM), a non-contact scan probe technique that is sensitive to the light-induced polarization in the material. PiFM has been used to generate molecular maps with 5 nm resolution, based on absorption contrast or on contrast derived from nonlinear optical interactions. Nonetheless, questions remain about the origin of the signal, in particular the possible contribution of forces that result from the thermal expansion of the sample. In this presentation, we will discuss various physical mechanisms that contribute to the PiFM signal and highlight several applications that are unique to the PiFM technique.

11:20am **NS2+2D+BI+EL+SS-MoM-10 Near-field Optical Microscopy Imaging and Spectroscopy at 10nm Spatial Resolution***, Artem Danilov,* Attocube Systems Inc.

Fourier-transform infrared (FTIR) spectroscopy is an established technique for characterization and recognition of inorganic, organic and biological materials by their far-field absorption spectra in the infrared fingerprint region. However, due to the diffraction limit conventional FTIR spectroscopy is unsuitable for measurements with nanoscale spatial resolution. Scattering-type Scanning Near-field Optical Microscopy (s-SNOM) allows to overcome the diffraction limit of conventional light microscopy or spectroscopy enabling optical measurements at a spatial resolution of 10nm, not only at IR frequencies but also in the whole spectral range from visible to terahertz. s-SNOM employs an externally-illuminated sharp metallic AFM tip to create a nanoscale hot-spot at its apex. The optical tip-sample near-field interaction is determined by the local dielectric properties (refractive index) of the sample and detection of the elastically tip-scattered light yields nanoscale resolved near-field images simultaneous to topography.Use of material-selective frequencies in the mid-IR spectral range can be exploited to fully characterize polymer blends or phase change polymers with nanometer-scale domains. Quantification of free-carrier concentration and carrier mobility in doped semiconductor nanowires, analysis of 2D (graphene) nanostructures, or study phase propagation mechanisms in energy storage materials is achieved by amplitude- and phase-resolved near-field imaging. Furthermore, here we introduce correlative tip-enhanced nanoscopy, enables complete collocal vibrational analysis of both IR- and Raman-active modes at the same spatial scale. Our instrument allows for a straight-forward implementation of nano-PL measurements using background suppressing provided by the demodulation of detector signal utilized in nano-FTIR detection scheme. Combining Raman, TERS, nano-FTIR and nano-PL measurements in the same instrument significantly reduces the effort of correlating the resulting datasets, enabling complete optical analysis at nanoscale, which has not been possible so far.

11:40am **NS2+2D+BI+EL+SS-MoM-11 Correlative Nanoscale Chemical, Mechanical and Electrical Property Mapping on a Single AFM-IR Platform***, C. Li, **Martin Wagner**, C. Phillips,* Bruker Nano Surfaces Division

Chemical identification on the nanoscale is a long sought after capability from the inception of AFM. AFM-IR has proven to be uniquely successful in achieving this among all other attempts. It uses a mid-IR laser that is focused onto the AFM tip. Light absorption by the sample results in photothermal expansion that causes a detectable cantilever deflection change of the AFM probe. The obtained IR spectra correlate with conventional FTIR spectroscopy but are associated with sub-10nm spatial resolution. However, a single data set rarely tells the full story and multiplexed analysis is essential to fully understand a material. We use an AFM-IR microscope with image registration and overlay capability to return to the same position on a sample when changing AFM probes, enabling extensive multimodal analysis. Data on a two-component polymer sample PS-LDPE comprising polystyrene and polyethylene reveals nanoIR spectra that correlate well with FTIR, while nanoIR maps at different IR wavenumbers provide the spatial distribution of each component. Further, we show that they are directly correlated at the nanometer level through PeakForce QNM elastic modulus and adhesion maps, as well as work function (surface potential) and dielectric maps with FM-KPFM (frequency-modulated Kelvin probe force microscopy). Many of the properties can be conveniently obtained simultaneously, while others are preferably obtained sequentially in a colocalized manner with the optimal probe choice and parameter settings for each AFM mode. Data on real-world industrial samples is then discussed, e.g. SBR (styrene-butadiene rubber) with carbon-black additives for car tires, exemplifying how ratio-map and multimodal property mapping unravel information not seen through one technique alone. In another use case chemical identification is complemented by nDMA, a mode where viscoelastic nanoscale sample properties are measured that match bulk dynamic mechanical analysis (DMA) data.

Biomaterial Interfaces Division
Room B117-119 - Session BI1-MoA

SIMS and Orbi-SIMS Characterization of Biological and Biomaterials Surfaces

Moderators: Axel Rosenhahn, Ruhr-University Bochum, **Markus Valtiner**, Vienna University of Technology, Austria

1:40pm **BI1-MoA-1 Mixing Things Up to Reduce Mix Ups in Lipid and Fatty Acid Analysis*, Daniel Graham,*** *H. Lei, L. Gamble,* University of Washington

Each ToF-SIMS spectrum can contain a combination of molecular species, fragments of these species, rearranged fragments, cluster ions (combinations of molecules and atoms) and atomic species. The complexity of the spectral information increases with the complexity of the surface being analyzed. This is particularly true when analyzing cells and tissues. Each of these systems contain a rich mixture of molecules including proteins, sugars, lipids and fatty acids. The lipids are typically arranged in well-ordered layers that can contain a wide variety of lipid molecules. While ToF-SIMS has been shown to provide detailed chemical information from the lipids and fatty acids from cells and tissues, this information is complex and can be difficult to uniquely interpret. Recently, it has been shown that the fragmentation pattern in ToF-SIMS spectra contains similar information to an MS/MS experiment and that this information can be used to uniquely identify lipids without doing MS/MS.[1] However, additional work needs to be done to better understand which fragments will show up and whether the relative intensity of these fragments might also encode information about the mixture of molecules which are present.

In order to better understand these complex systems we have taken a reductive approach and started by looking at mixtures of fatty acids. Fatty acids make up a large part of lipids and generate unique signals within ToF-SIMS spectra. This presentation will focus on our work looking at binary mixtures of fatty acids with ToF-SIMS. ToF-SIMS spectra were compared with simulated mixture spectra generated using a custom built graphical user interface (GUI) in Matlab. This GUI allows the user to create spectra of mixtures of two molecules based on the peak intensities of pure component spectra from each chosen fatty acid. Peak areas from the simulated spectra were compared with peak areas from experimental data. It was found that the experimental data deviated from the expected intensities of the simulated spectra. These deviations provide insight into mechanisms that enhance or reduce the yield of certain fatty acid peaks in the mixtures. Insights from these studies will be used to look at increasingly complex surfaces simulating mixtures seen in cells and tissues.

1 T.B. Angerer, D. Velickovic, C.D. Nicora, J.E. Kyle, D.J. Graham, C. Anderton, and L.J. Gamble, *Anal Chem*. **91**, no. 23, pp. 15073–15080, (2019).

2:00pm **BI1-MoA-2 Native State Physicochemical Characterisation of Drug Delivery Hydrogels using Cryo-OrbiSIMS and SEM*, Julie Watts,*** *D. Scurr,* University of Nottingham, UK

Supramolecular hydrogel formulations have the potential to increase topical delivery of active agents and are well suited being biocompatible, with facile gel formation from cationic surfactant bis-imidazolium salts and combination with anionic, cationic or neutral drugs [Limón et. al., Eur J Pharm Biopharm, 2015]. Although the potential of hydrogels for improved topical skin permeation analysis has been demonstrated using time of flight secondary ion mass spectrometry (ToF-SIMS) [Starr et. al., Int. J. Pharm, 2019] the chemistry of the systems themselves have not been chemically characterised in their native state. This is primarily due to ion beam induced fragmentation and limitations of mass resolving power, as well as the obscuring of the spectra of frozen hydrated samples with water fragment ions.

In this work we investigate the application of cryo-OrbiSIMS in the molecular characterisation of supramolecular hydrogels loaded with two different porphyrins (0.1% w/v). Skin permeation studies were performed to evaluate the delivery of 5,10,15,20-Tetrakis(4-hydroxyphenyl)porphyrin (TPPOH) and 5,10,15,20-Tetrakis(4-carboxylatephenyl)porphyrin (TCPP). It was observed that in *ex vivo* porcine skin permeation studies the TPPOH appeared to have permeated the skin whereas the TCPP had not. Gel monomer skin permeation was below detectable levels in all cases. In order to understand this difference in delivery, cryo-OrbiSIMS and SEM were performed to determine if there were any variations in the physicochemical properties of the gels.

In native state gels as well as those loaded with porphyrin, the cryo-OrbiSIMS spectra show the detection of a range of secondary ions attributable to the gel, [M-H]+at m/z 901, TPPOH[M-4H]+ at m/z 677, and TCPP [M-4Na]$^-$ at m/z 788. Ions detected include molecular and fragments ions.The data suggests that the chemistry of the supramolecular gel is confirmed and that the porphyrins have been successfully loaded into the gels and are uniformly distributed. Using a controlled sample sublimation approach to expose the fibrous microstructure of the frozen hydrated gels, cryo-SEM images indicate structural differences between gels with and without porphyrins, with longer, more interconnected fibres present in gels systems without porphyrins. However, the two porphyrin containing systems are comparable, as such the release behaviour is proposed to relate to a difference in their affinity to the gel fibres.

2:20pm **BI1-MoA-3 Molecular Characterization of Cells and Bio-interfaces using SIMS: The Foreign Body Reaction*, Morgan Alexander,*** The University of Nottingham, UK **INVITED**

New biomaterials are necessary to tackle the challenges of medical device centred infection combined with antimicrobial resistance and the foreign body reaction (FBR). Together, these cause unacceptably high rates of device failure, rejection, mortality and morbidity.

Novel polymers have been discovered which reduce bacterial biofilm formation, infection, and control host immune response.[1,2,3] To understand their mode of action and improve these cell-instructive biomaterials requires detailed characterisation of the biointerface that plays a central role in their achieving homeostasis. Recently lipids have been proposed as critical in controlling FBR using ToF SIMS data; [4] this finding is intriguing since it offers an alternative to the prevalent protein adsorption paradigm.

Whilst ToF SIMS is excellent for imaging metabolites present at sufficient abundance, it struggles in identifying endogenous species in complex biological systems due to its relatively poor mass resolving power when faced with myriad possible peak assignments for each secondary ion peak.[5] The 3D OrbiSIMS approach addresses that by combining an OrbiTrap with a time-of-flight SIMS instrument to undertake direct analysis of solid samples.[6] The 3D OrbiSIMS has been able to undertake single cell metabolomics for primary macrophages[7] which are orchestrate the body's response to implanted medical devices. This has been used to help interpret the complex spectra acquired from the tissue interface with novel implanted novel biomaterials.[8] The outlook for this approach in medical device characterisation, and more widely using unbiased assignment procedures for SIMS will be discussed.[9]

1. Immune-Instructive Polymers Control Macrophage Phenotype and Modulate the Foreign Body Response In Vivo **Matter (Cell Press)** Rostam2020
2. Combinatorial hydrogel library enables identification of materials that mitigate the foreign body response in primates **Nature Biotechnology** Vegas2016
3. Combinatorial discovery of polymers resistant to bacterial attachment **Nature Biotechnology** Hook2012
4. Lipid deposition profiles influence foreign body *responses* **Advanced Materials** Schreib 2023
5. Mass Spectrometry and Informatics **Anal Chem** Green2011
6. The 3D OrbiSIMS: Label-free metabolic imaging with subcellular lateral resolution and high mass-resolving power **Nature Methods** Passarelli2017
7. Single cell metabolomics of macrophages using 3D OrbiSIMS: correlations with phenotype **Anal Chem** Suvannapruk 2022
8. Spatially resolved molecular analysis of host response to subcutaneous medical device implantation achieved using the 3D OrbiSIMS *UnderReview.*
9. Molecular formula prediction for chemical filtering of 3D OrbiSIMS Datasets **Anal Chem** Edney2022

3:00pm **BI1-MoA-5 Elucidating of Native Macromolecule Structure in Cryo OrbiSIMS*, Anna Kotowska,*** *M. Alexander, D. Scurr,* University of Nottingham, UK

Analysis of proteins in SIMS has historically been limited due to fragmentation caused by the energetic analysis beam, resulting in only single amino acid secondary ions. In previous work, we successfully demonstrated that the combination of a GCIB with an Orbitrap analyser can return primary structure information from proteins [1]. This was achieved through *de novo* peptide sequencing, with sequence coverage up to 50%.

The presence of water is known to increase ionisation of the sample components, particularly high molecular weight compounds [2]. Analysis of frozen-hydrated samples, spraying water above the sample or using water clusters as primary ion beams have been found to increase the $[M+H]^+$ signals as well as fragments and $[M+Na]^+$ and $[M+K]^+$ adducts [2]. In this work, focusing on macromolecules, this enhancement enabled us to map proteins in human skin and in bacterial biofilm. The additional benefit of analysing large biomolecules in cryogenic conditions is preserving the native state of the molecule, which may enable acquisition of 3D structural information in addition to primary structure.

The extent of chemical information available from cryo-OrbiSIMS analysis is expansive and can be difficult to deconvolute. We have developed a molecular formula prediction (MFP) and level of molecule saturation (double bond equivalents) process to chemically filter multidimensional SIMS data [3]. Chemical filtering is particularly beneficial for the assignment of poorly ionisable molecules (e.g. protein fragments). Here, in addition to filtering protein fragments, we generated a protein fragment database, which facilitates rapid assignment and classification of protein ions and could pave the way for the development of a proteomics-like approach for OrbiSIMS analysis of large biomolecules.

In this work we demonstrate the potential of combining *de novo* sequencing with using cryogenic conditions and advanced data analytics approaches to identify unknown protein samples and obtain structural information from macromolecules.

[1] Anna M. Kotowska *et al.*, *Nat. Comms.*, 2020

[2] Sheraz Née Rabbani *et al.*, *Anal. Chem.,* 2015

[3] Max K. Edney *et al.*, Anal. Chem., 2022

3:20pm **BI1-MoA-6 Comparing Desalination Methods of Bacterial Biofilms for Static ToF-SIMS Analyses*, Gabriel Parker,*** University of Illinois - Chicago*; X. Yu,* Oak Ridge Natinal Laboratory*; A. Plymale, J. Dhas, Z. Zhu,* Pacific Northwest National Laboratory*; L. Hanley,* University of Illinois - Chicago

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is a central technique for imaging of intact bacterial biofilms. Sample preparation in ToF-SIMS is simpler compared with gas chromatography - mass spectrometry (GC-MS) or liquid chromatography mass spectrometry (LC-MS) for biofilm analysis. Nevertheless, sample desalination is crucial to successful measurements from the native environment of biofilms consisting of complex salt and organic matrices. Without desalination, salt and other undesirable signals could dominate biofilm mass spectra and obscure acquisition of useful signals. Matrix effects in high salt environment can also affect the ion yield by enhancing disproportionate ion signals and nonlinear concentration correlations. This work compares desalination methods for ToF-SIMS of planktonic bacterial cells and biofilms on hard surface substrates. *Paenibacillus* sp. 300A biofilms are grown over the course of one week via static cell incubation at room temperature. Two methods of desalination, water submersion (WS) and centrifugal spinning (CS) of bacterial samples, are compared against each other and against samples with no desalination treatment. Water submersion samples are prepared by plating drops of biomaterial solution (planktonic cells or biofilm) onto a substrate, drying the sample, then submerging it in a water bath, and drying again prior to static SIMS analysis. Centrifugal spinning samples are prepared by centrifuging biomaterial, discarding the supernatant, resuspending biomaterial with deionized water, then plating biomaterial solution on substrate and drying under nitrogen prior to SIMS analysis. Results show that non-desalinated samples have the highest salt signal that arises in part from bacteria growth media with signal suppression of biologically relevant ions. By contrast, both WS and CS desalination display well defined peaks with high signal to noise that correspond to metabolites, amino acids, lipids, fatty acids, and salt adducts up to *m/z* 800. WS displays similar peak intensities compared to CS, but in some cases, the signal is higher for WS samples. Overall, experimental results show that the simple WS method for desalination lowers matrix effects in biofilms for ToF-SIMS analysis while keeping the biofilm structure intact. Centrifugal spinning proves to be a reliable method to reduce matrix effects in ToF-SIMS analyses of biofilms.

Biomaterial Interfaces Division
Room B117-119 - Session BI2-MoA
Functional Biomaterials I: Fabrication and Application

Moderators: Pierluigi Bilotto, CEST GmbH, **Caitlin Howell**, University of Maine

4:00pm **BI2-MoA-8 Low Fouling Marine Coatings Based on Nitric Oxide-Releasing Polysaccharide-Based Hybrid Materials*, Samantha Muhring-Salamone,*** *R. Wanka, A. Rosenhahn,* Ruhr University Bochum, Germany

Biofouling describes the undesired accumulation of bioorganisms on surfaces which is a ubiquitous problem and has a severe environmental and ecological impact.[1–3] Increasing restrictions for biocide-releasing coating result in a growing need for environmentally friendly, sustainable, and biodegradable approaches.[1,4,5] Here, we developed a hybrid material coating based on the polysaccharides alginate and heparin and combined them with amine-containing compounds through sol-gel chemistry. The high amine concentration enables the hybrid material to bind nitric oxide when exposed to high pressure NO. The NO binding was characterized by UV-Vis and ATR-IR spectroscopy, and the NO-releasing kinetics by Griess-assays. Dynamic attachment assays with the marine diatom *N. perminuta* revealed a significant reduction in attachment compared to coatings without NO release capabilities. All coatings readily suppressed the attachment of the marine bacterium *C.marina*. The binding of nitric oxide and the release of nitrogen monoxide species was found to be a promising mechanism to add additional fouling-inhibiting functionalities. All building blocks are environmentally friendly, biodegradable, and biocompatible which makes these protective coatings interesting for environmentally benign marine applications.

[1] J. A. Callow, M. E. Callow, *Nat. Commun.***2011**, *2*, 244. [2] V. Eyring, H. W. Köhler, J. Van Aardenne, A. Lauer, *J. Geophys. Res. D Atmos.***2005**, *110*, 171–182. [3] M. P. Schultz, J. A. Bendick, E. R. Holm, W. M. Hertel, *Biofouling***2011**, *27*, 87–98. [4] D. M. Yebra, S. Kiil, K. Dam-Johansen, *Prog. Org. Coatings***2004**, *50*, 75–104. [5] A. Rosenhahn, S. Schilp, H. J. Kreuzer, M. Grunze, *Phys. Chem. Chem. Phys.***2010**, *12*, 4275–4286.

4:20pm **BI2-MoA-9 Underwater Adhesives Through Chemically-Induced Protein Aggregation*, M. Wilson,*** Purdue University*; Q. Lu,* Naval Research Laboratory, Chemistry Division*; K. Nachtrieb, J. Fuller, C. Skogg, E. Yates,* United States Naval Academy*; M. Thum, **Christopher So**,* Naval Research Laboratory, Chemistry Division

The common strategy to develop bioinspired underwater adhesives is the incorporation of specific chemistries into synthetic polymers or proteins. However, many organisms—including barnacles—use amyloid-like materials to produce successful adhesives, relying on the aggregation of proteins rather than extraordinary chemistry to achieve durable underwater bonding. Inspired by such systems, we control the aggregation of a commercially available protein, bovine serum albumin, to develop waterborne adhesives that cure underwater. For this, we investigate the action of added chemicals using gel inversion tests, differential scanning calorimetry, rheometry, and infrared spectroscopy. We find that added chemical constituents influence the unfolding, aggregation kinetics, and final structure of the solid protein material in different ways. Multiple chemicals can be added to a formulation to provide synergistic effect, forming a solid material within minutes at room temperature underwater. These adhesives produce bond strengths comparable to many synthetic bioinspired adhesives when tested by lap shear after exposure to dry and wet conditions. The ease with which these glues can be fabricated paves the way for opportunities with other commercial proteins and curing agents as a new avenue to produce scalable underwater adhesives.

4:40pm **BI2-MoA-10 Analysis of a Pharmaceutical Formulation using Orbitrap-SIMS*, Birgit Hagenhoff,*** Tascon GmbH, Germany*; J. van Rüschen,* University of Muenster, Germany*; D. Breitenstein,* Tascon GmbH, Germany*; A. Pirkl,* IONTOF GmbH, Germany*; G. Winkler,* Tascon GmbH, Germany

Pharmaceutical formulations are subject to high quality standards which must be checked at regular intervals. A pharmaceutical review of the composition of the active ingredients is part of the quality assurance of pharmaceutical companies. For this purpose, also mass spectrometric methods are applied.

Orbitrap-SIMS ("3D-Orbi-SIMS") is a comparably new mass spectrometric technique introduced in 2016 [1]. It is a powerful tool to identify organic as well as inorganic components on the surface of a solid sample.

Furthermore, it allows the detection of the lateral distribution of these analytes with high mass resolving power. To perform Orbitrap-SIMS on a sample, typically no pre-separation of analytes is necessary.

In Orbitrap-SIMS, a primary ion beam is directed at the sample surface, causing the sample to emit secondary ions. These ions are then mass separated and detected by an Orbitrap mass analyzer. By rastering the surface with the primary ion beam, 2D images reveal the lateral distribution of the molecules.

In this study, the application of Orbitrap-SIMS on selected pharmaceutical samples is tested. The focus is set to the mass spectrometric identification of the active agents as well as on the revealing of their lateral distribution in a cross-sectioned tablet.

One type of sample examined was composed of two active ingredients: Hydrochlorothiazide and Candesartancilexetil. Both active agents belong to the group of antihypertensives: Hydrochlorothiazide is a thiazide diuretic, whereas Candesartancilexetil is an angiotensin receptor blocker [2].

Identification was performed by the acquisition of full mass spectra of the sample followed by data evaluation using Principal Component Analysis (PCA). The detected SIMS-induced fragmentation pattern was in line with the fragmentation behaviour of the active agents determined by tandem mass spectrometry.

At last, mass spectrometric imaging of the sample was performed in order to reveal the lateral distribution of the active components within the sample.

The results give a glimpse into the potential of Orbitrap-SIMS to solve analytical questions in pharmaceutical industry.

Sources:

[1] Passarelli MK, Pirkl A, Moellers R et. al. The 3D OrbiSIMS-label-free metabolic imaging with subcellular lateral resolution and high mass-resolving power. Nat Methods. 2017 Dec;14(12):1175-1183.

[2] Carey RM, Moran AE, Whelton PK. Treatment of Hypertension: A Review. *JAMA*. 022;328(18):1849–1861.

Laboratory-Based Ambient-Pressure X-ray Photoelectron Spectroscopy Focus Topic
Room B116 - Session LX+AS+BI+HC+SS+TH-MoA

Laboratory-Based AP-XPS:Surface Chemistry and Biological/Pharmaceutical Interfaces

Moderators: Gregory Herman, Argonne National Laboratory, **Ashley Head**, Brookhaven National Laboratory

1:40pm **LX+AS+BI+HC+SS+TH-MoA-1 The Role of Co-Adsorbed Water in Decomposition of Oxygenates***, H. Nguyen, K. Chuckwu,* ***Líney Árnadóttir,*** Oregon State University **INVITED**

The decomposition of oxygenates in the presence of water finds various applications in chemical processes, such as biomass conversion. The presence of co-adsorbates and solvents affects both the reaction rate and selectivity. In this study, we used NAP-XPS and DFT to investigate the decomposition of acetic acid on Pd(111) as a model system for the decomposition of small oxygenates in the absence and presence of water. The decomposition of acetic acid occurs through two main reaction pathways, decarboxylation, and decarbonylation, forming CO_2 or CO, respectively. Our DFT calculations indicate that the two pathways have similar barriers without water. However, in the presence of water, the decarboxylation path becomes. Similarly, our AP-XPS experiments show an increase in the CO_2/CO ratio as well as a decrease in the CO/acetate-acetic acid and acetic acid/acetate ratios when water is present. The shift in selectivity is not due to a single reaction step, but rather the decreasing barrier in general for OH scissoring and the increasing barrier for C-O scissoring. This shift favors the formation of CO_2, as demonstrated by our microkinetic model.

2:20pm **LX+AS+BI+HC+SS+TH-MoA-3 Integrating First-principles Modeling and AP-XPS for Understanding Evolving Complex Surface Oxides in Materials for Hydrogen Production and Storage***, B. Wood,* ***Tuan Anh Pham,*** Lawrence Livermore Laboratory **INVITED**

Chemical processes occurring at solid-gas, solid-liquid, and solid-solid interfaces critically determine the performance and durability of hydrogen production and storage technologies. While directly probing behavior of these interfaces under actual operating conditions remains challenging, modern surface science approaches such as ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) can provide insight into the evolution of surface chemistry in approximate environments. However, interpretation of these spectra can be complicated: standards for complex surface chemical moieties are often unavailable, and bulk standards can be unreliable. First-principles computations are emerging as an important companion approach, offering the ability to directly compute spectroscopic fingerprints. This has the advantage of aiding interpretation of the experiments, while simultaneously using the experiment-theory comparison to inform construction of more accurate interface models. In this talk, I will show how computation has been combined with laboratory-based AP-XPS measurements to understand the evolving chemistry of complex native surface oxides. Two examples will be drawn from activities within the U.S. Department of Energy HydroGEN and HyMARC consortia, which focus on renewable hydrogen production and materials-based hydrogen storage, respectively. First, I will discuss the application to surface oxidation of III-V semiconductors for photoelectrochemical hydrogen production, which demonstrates transitions between kinetically and thermodynamically controlled oxidation regimes with implications for device performance. Second, I will also show how the same approach has been applied to understand the rate-determining role of surface oxides in the dehydrogenation performance of $NaAlH_4$ for solid-state hydrogen storage.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

3:00pm **LX+AS+BI+HC+SS+TH-MoA-5 Particle Encapsulation on Reducible Oxides Under Near-Ambient Pressures***, F. Kraushofer, M. Krinninger, P. Petzoldt, M. Eder, S. Kaiser, J. Planksy, T. Kratky, S. Günther, M. Tschurl, U. Heiz, F. Esch,* ***Barbara A. J. Lechner,*** TUM, Germany **INVITED**

Catalysts on reducible oxide supports often change their activity significantly at elevated temperatures due to the strong metal-support interaction (SMSI), which induces the formation of an encapsulation layer around the noble metal particles. However, the impact of oxidizing and reducing treatments at elevated pressures on this encapsulation layer remains controversial, partly due to the 'pressure gap' between surface science studies and applied catalysis.

In the present work, we employ near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) and scanning tunneling microscopy (NAP-STM) to study the effect of reducing and oxidizing atmospheres on the SMSI-state of well-defined oxide-supported Pt catalysts at pressures from UHV up to 1 mbar. On a TiO_2(110) support, we can either selectively oxidize the support or both the support and the Pt particles by tuning the O_2 pressure.[1] We find that the growth of the encapsulating oxide overlayer is inhibited when Pt is in an oxidic state. Our experiments show that the Pt particles remain embedded in the support once encapsulation has occurred. On Fe_3O_4(001), the encapsulation stabilizes small Pt clusters against sintering.[2] Moreover, the cluster size and thus footprint lead to a change in diffusivity and can therefore be used to tune the sintering mechanism. Very small clusters of up to 10 atoms even still diffuse intact after encapsulation.

[1] P. Petzoldt, P., M. Eder, S. Mackewicz, M. Blum, T. Kratky, S. Günther, M. Tschurl, U. Heiz, B.A.J. Lechner, Tuning Strong Metal–Support Interaction Kinetics on Pt-Loaded TiO_2 (110) by Choosing the Pressure: A Combined Ultrahigh Vacuum/Near-Ambient Pressure XPS Study, *J. Phys. Chem. C*126, 16127-16139 (2022).

[2] S. Kaiser, J. Plansky, M. Krinninger, A. Shavorskiy, S. Zhu, U. Heiz, F. Esch, B.A.J. Lechner, Does Cluster Encapsulation Inhibit Sintering? Stabilization of Size-Selected Pt Clusters on Fe_3O_4(001) by SMSI, *ACS Catalysis* 13, 6203-6213 (2023).

4:00pm **LX+AS+BI+HC+SS+TH-MoA-8 Applications of NAP XPS in Pharmaceutical Manufacturing: Surface Analysis, Hydrogen Bonds, and Solute-Solvent Interactions***, Sven Schroeder,* University of Leeds, UK **INVITED**

The availability of laboratory-based NAP XPS creates novel interface research opportunities for scientific disciplines and technology areas that deal with materials incompatible with traditional ultra-high vacuum XPS. This is, for example, the case for many organic and/or pharmaceutical materials and formulations, whose characterization by XPS has hitherto been restricted by their vapour pressures. NAP XPS permits for the first time systematic and detailed analysis of the light element photoemission lines (expecially C/N/O 1s) in these materials. In conjunction with elemental analysis by survey XP spectra they provide quantitative information on composition and speciation both in the bulk and at the surfaces of pure

organic solids, in their formulations with other components and in solutions. Especially of interest are studies of the solid/liquid interface with water, which is of high relevance for understanding and controlling drug release profiles from tablets. To illustrate these points I will present various examples of research on pharmaceutical materials. Moreover, near-ambient pressure core level spectroscopy turns out to be an extremely powerful probe for the structure and dynamics of hydrogen bonding and proton transfer in materials, both in the solid state and in solutions. NAP XPS measurements provide unique insight into proton dynamics in noncrystalline solids and liquids, where traditional characterisation by crystallography and nuclear magnetic resonance fails or provides ambiguous information on proton locations.

4:40pm **LX+AS+BI+HC+SS+TH-MoA-10 The Change of DNA and Protein Radiation Damage Upon Hydration: In-Situ Observations by Near-Ambient-Pressure XPS**, ***Marc Benjamin Hahn***, Bundesanstalt für Materialforschung und -prüfung (BAM), Germany **INVITED**

X-ray photoelectron-spectroscopy (XPS) allows simultaneous irradiation and damage monitoring. Although water radiolysis is essential for radiation damage, all previous XPS studies were performed in vacuum. [1] Here we present near-ambient-pressure XPS experiments to directly measure DNA damage under water atmosphere. They permit in-situ monitoring of the effects of radicals on fully hydrated double-stranded DNA. Our results allow us to distinguish direct damage, by photons and secondary low-energy electrons (LEE), from damage by hydroxyl radicals or hydration induced modifications of damage pathways. The exposure of dry DNA to x-rays leads to strand-breaks at the sugar-phosphate backbone, while deoxyribose and nucleobases are less affected. In contrast, a strong increase of DNA damage is observed in water, where OH-radicals are produced. In consequence, base damage and base release become predominant, even though the number of strand-breaks increases further. Furthermore, first data about the degradation of single-stranded DNA binding-proteins (G5P / GV5 and hmtSSB) under vacuum and NAP-XPS conditions are presented.

[1] Hahn, M.B., Dietrich, P.M. & Radnik, J. In situ monitoring of the influence of water on DNA radiation damage by near-ambient pressure X-ray photoelectron spectroscopy. Commun Chem 4, 50, 1-8 (2021). https://doi.org/10.1038/s42004-021-00487-1

Biomaterial Interfaces Division
Room B117-119 - Session BI+AS+PS-TuM

Biomolecules and Biophysics at Interfaces

Moderators: Christopher So, Naval Research Laboratory, **Markus Valtiner**, Vienna University of Technology, Austria

8:00am **BI+AS+PS-TuM-1 Probing Protein Structure on Nanoplastic Surface by Sum Frequency Scattering**, ***Akriti Mishra***, *T. Weidner,* Aarhus University, Denmark

The safe use of nanoparticle protein conjugates in biomedical applications like disease diagnosis, drug delivery, biosensing, etc. depends on the efficacy and stability of these conjugates in body fluids. To date, several analytical techniques like UV-Vis, dynamic light scattering, Fourier transform infrared spectroscopy, circular dichroism, nuclear magnetic resonance, etc. have been used to study the interaction of proteins on nanoparticle surface. Since most of the techniques can not differentiate between the surface bound and the free proteins in solution, it becomes impossible to gather any information about the interfacial proteins. The confirmation of a protein after adsorption on nanoparticle surface can be drastically different from that in solution, which may hamper or amend the activity and function of proteins. Surface sensitive sum frequency scattering (SFS) stands out best in this case since it selectively probes the vibrational modes of the adsorbed analytes on any interface. Sum frequency generation from flat interfaces has been successfully shown to provide rich information about the structure, order, and composition of molecules at the interface. Recently, our group has shown that SFS can effectively probe the structure and orientation of model peptides at nanoscopic oil particle surfaces.1 We will here discuss how also complex human corona proteins can be probed on particle surfaces. We focus on alpha synuclein (aS) interactions with nanoparticles relevant for medical applications and environmental nanoplastics. aS is a 14 kDa intrinsically disordered protein known to form amyloids called Lewy bodies, which can propagate across the neurons to induce Parkinson's disease (PD). Using SFS we follow how aS binds and folds on polymer nanoparticle surfaces. SFS spectra in the amide I region strongly suggest that aS folds into beta sheet and fibrillated structures at the nanointerfaces This is in contrast with flat surfaces, where monomers and helical folds dominate based on reflection SFG experiments.2 We believe, aS binding to the nanoparticles leads to close packing of aS monomers, which leads to the formation of beta sheet and fibrillar type structures.

Fig 1. Schematic of the SFS experiments to follow the binding of aS to polymer nanoparticles particles and the corresponding SFS spectrum

References:

1.) Thaddeus W. Golbeck, Kris Strunge, Adam S. Chatterly, and Tobias Weidner* J. Phys. Chem. Lett. 2022, 13, 10858-62.

2.) Kris Strunge, Tucker Burgin, Thaddeus W. Golbek, Steven J. Roeters, Jim Pfaendtner and Tobias Weidner* Umbrella-like helical structure of alpha-synuclein at the air-water interface observed with experimental and theoretical sum frequency generation spectroscopy, in preprint.

8:20am **BI+AS+PS-TuM-2 The Structure of Alpha-Synuclein at Lipid Interfaces Determined by Experimental and Theoretical Sum Frequency Generation Spectroscopy**, *K. Strunge, K. Pedersen, T. Golbek, M. Brgenhøj, D. Otzen, B. Schiøtt,* ***Tobias Weidner***, Aarhus University, Denmark

The aberrant folding of α-synuclein (αS) into amyloid aggregates is associated with Parkinson's disease. It has been shown that the refolding into oliogomers and harmful fibrils can be catalyzed by lipid-membrane surfaces. Despite the importance of lipid interactions, the 3D-structure of lipid-membrane bound αS, and thereby, the mechanism of the catalysis process, is still not known at the molecular level. Here, we report interface-specific sum-frequency generation (SFG) experiments revealing how monomeric αS binds, folds and orients at anionic lipid membranes. Since SFG is inherently surface specific and unbond proteins are not detected, the experiments can be performed at high αS concentrations, far beyond previous structural studies. To interpret the experimental SFG data and develop a high fidelity structural model of the aS binding motif, we developed an analysis method in which out-of-equilibrium molecular-dynamics (MD) simulations are linked to excitonic amide-I SFG spectra calculations. 10s of thousands of theoretical spectra calculated for frames of extensive MD simulations are evaluated pooled for their experimental fitness to determine the structure of aS binding at low, physiological and pathological aS concentrations. We find that at low and physiological αS concentrations, the protein binds in a flat geometry, while at elevated, pathological concentrations, a transition to an upright αS binding pose occurs. This upright conformation promotes lateral interactions and likely explains how protein concentrations can catalyze the formation of αS amyloids.

8:40am **BI+AS+PS-TuM-3 Lubricant Viscosity Affects the Antifouling Activity of PFPE Based SLIPS Coatings**, ***Onur Özcan***, *J. Karthäuser, R. Kopecz, A. Gelhar, A. Rosenhahn,* Ruhr-Universitat Bochum, Germany

Settlement of organisms on submerged surfaces can enhance the spread of life-threatening infections.[1] Therefore it is desired to identify methods for the prevention of biofilm formation. The omniphobic properties of slippery liquid infused porous surfaces (SLIPS) have been shown to provide outstanding protection against biofouling, icing, corrosion and to be repellent against complex liquids like blood.[2] In this study, we examine the fouling behavior of E. coli, P. fluorescence, and B. subtilis on seven different superhydrophobic perfluoropolyether (PFPE) urethane methacrylate-based SLIPS with varying lubricant viscosities. The polymers were fabricated following our previously published grafting-through protocolby which superhydrophobic micro-structured porous PFPE matrices could be obtained by adding cychlohexanol as pore forming agent to the monomer mixture.[3,4] The coatings were incubated in an excess of seven different lubricants of varying viscosities to obtain SLIPS. In dynamic attachment assays we were able to show the antifouling capabilities of these SLIPS with organism reductions of up to 90% compared to the dry, smooth, and hydrophobic butyl methacrylate references. Our results further revealed critical species-specific settlement on the coatings that depended on the viscosity of the incorporated liquid, highlighting the relevance of the choice of the lubricant in the design of low-fouling SLIPS.

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9:00am **BI+AS+PS-TuM-4 Orientation of the Dysferlin C2A Domain is Responsive to the Composition of Lipid Membranes**, *A. Carpenter,* Oregon State University*; S. Roeters, T. Weidner,* Aarhus University, Denmark*;* ***Joe Baio***, Oregon State University

Dysferlin is a 230 kD protein that plays a critical function in the active resealing of micron-sized injuries to the muscle sarcolemma by recruiting vesicles to patch the injured site via vesicle fusion. Muscular dystrophy is observed in humans when mutations disrupt this repair process or dysferlin is absent. While lipid binding by dysferlin's C2A domain (dysC2A) is considered fundamental to the membrane resealing process, the molecular mechanism of this interaction is not fully understood. By applying nonlinear surface-specific vibrational spectroscopy, we have successfully demonstrated that dysferlin's N-terminal C2A domain (dysC2A) alters its binding orientation in response to a membrane's lipid composition. These experiments reveal that dysC2A utilizes a generic electrostatic binding interaction to bind to most anionic lipid surfaces, inserting its calcium binding loops into the lipid surface while orienting its β-sheets 30–40° from surface normal. However, at lipid surfaces, where PI(4,5)P2 is present, dysC2A tilts its β-sheets more than 60° from surface normal to expose a polybasic face, while it binds to the PI(4,5)P2 surface. Both lipid binding mechanisms are shown to occur alongside dysC2A-induced lipid clustering. These different binding mechanisms suggest that dysC2A could provide a molecular cue to the larger dysferlin protein as to signal whether it is bound to the sarcolemma or another lipid surface.

9:20am **BI+AS+PS-TuM-5 Probing the Interfacial Action of *Thermomyces Lanuginosus* Lipase at Lipid Surfaces with Vibrational Sum Frequency Spectroscopy – from Monolayers to Emulsions**, ***Khezar Saeed***, *K. Strunge, T. Golbek, T. Weidner,* Aarhus University, Denmark

Lipases are a diverse class of biologically important enzymes with a key role in the digestion of dietary fats. The general ability to catalyse triacyl glyceride hydrolysis also enables their application to a wide variety of systems outside of the digestive tract, including transesterification, enantioselective synthesis and as an additive to laundry detergents. Key to their efficacy is the phenomenon of interfacial activation. For lipases this almost universally involves the "opening" of a lid domain upon interaction with a lipid surface, revealing a hydrophobic region containing the active site. The lipase derived from the *Thermomyces lanuginosus* fungus (TLL) is

used extensively on an industrial scale as an additive to laundry detergents. As such significant effort has been expended to genetically engineer improvements to the lipase function, with particular attention paid to this lid region. Gaining a deeper understanding of the interfacial activation mechanisms of such lipases could inform the design of improved enzymes in the future.

The inherent surface sensitivity of vibrational sum frequency generation (VSFG) spectroscopy can provide the required molecular level information to further our understanding of the interfacial activation of TLL. VSFG spectroscopy relies on the selection rules associated with frequency mixing of high power visible and infrared laser beams, resulting in a vibrational spectrum of solely the interfacial region. Three key results are presented here:

(i)The TLL-catalysed reaction at the air/triglyceride/water interface can be monitored by reflection VSFG spectroscopy, showing loss of ester carbonyl modes and appearance of carboxylate stretching modes of the fatty acid products.

(ii)Comparison of experimental and predicted VSFG spectra of the amide I band are used to interpret structural changes in the lid domain of TLL upon interaction with a hydrophobic surface.

(iii)Specially formulated emulsions allow further analysis using our new angle-resolved sum frequency scattering spectrometer, showing the first example of reaction dynamics at a particle surface probed by vibrational sum frequency scattering spectroscopy.

This work highlights the utility of VSFG spectroscopy for studying interfacial reactions. Not only does it offer a label-free method of following surface reactions, but it also provides structural and orientational information on interfacial species when combined with appropriate simulations. Furthermore, the results from the sum frequency scattering spectrometer open the door to studying a whole new class of chemical systems at particle surfaces with as yet unseen levels of molecular detail for such systems.

11:00am **BI+AS+PS-TuM-10 An *in Situ* Look at Interfacial Controls on Nucleation, Self-Assembly, and Crystal Growth in Biomolecular and Biomimetic Systems***, Jim De Yoreo,* Pacific Northwest National Laboratory **INVITED**

From harvesting solar energy to capturing CO_2 to purifying water, living organisms have solved some of the most vexing challenges now faced by humanity. They have done so by creating a vast library of proteins and other macromolecules that can assemble into complex architectures and direct the mineralization of inorganic components to produce materials characterized by a hierarchy of structure. While the high information content contained within the intricate sequences of the proteins is crucial for accomplishing these tasks, self-assembly and mineralization are nonetheless constrained to proceed according to the physical laws that govern all such processes, even in synthetic systems. An understanding of the mechanisms by which biological systems successfully manipulate those laws to create hierarchical materials would usher in an era of materials design to address our most pressing technological challenges. In this talk, I will present the results of recent research using in situ atomic force microscopy and in situ transmission electron microscopy to directly observe interfacial structure, protein self-assembly, and nanocrystal formation in biomolecular and biomimetic systems, including protein-directed nucleation of calcium carbonate and calcium phosphate and mineral-directed nucleation of two-dimensional protein assemblies. The results elucidate the mechanisms by which the interface between biomolecules and materials directs nucleation, self-assembly and crystal growth, leading to unique materials and morphologies. The results reveal the importance of surface charge, facet-specific binding, solvent organization near interfaces, and, more generally, the balance of protein-substrate-solvent interactions in determining how ordered materials emerge in these systems.

11:40am **BI+AS+PS-TuM-12 the Surface Chemistry of Gecko Toe Pads***, **Mette Heidemann Rasmussen**, K. Holler,* Department of Chemistry, Aarhus University, Denmark*; J. Baio,* School of Chemical, Biological and Environmental Engineering, Oregon State University*; C. Jaye, D. Fischer,* National Institute of Standards and Technology, Gaithersburg*; S. Gorb,* Functional Morphology and Biomechanics, Zoological Institute, Kiel University, Germany*; T. Weidner,* Department of Chemistry, Aarhus University, Denmark

Geckos can climb nearly all surface and are able to cling to walls and ceilings using their toe pads. The gecko adhesion mechanism has been debated over the past years. Current models include van der Walls, hydrophobic and acid-base interactions. Even though the adhesion mechanism of the spatulas has been studied in detail, the surface chemistry involved in the gecko adhesion mechanism is unclear. What is the structure of the supporting proteins within the spatula at the very tips of the setae within the gecko toe pad? What is the role of lipids in the adhesion process? Understanding the surface chemistry of the adhesion of the gecko toe pads gives insight into this highly specialized biological interface, and give clues for materials scientists aiming at mimicking the gecko adhesion mechanisms. Using near edge X-ray absorption fine structure (NEXAFS) imaging and spectroscopy we have studied the structure and order of the molecules at the outermost surface layer of gecko toe pads. We show that the keratin molecules within the spatulas are highly organized and adopt a flat, strand-like geometry, which may support the stability and adaptability of gecko setae (1). We will also discuss evidence showing that a nanometer-thin ordered lipid layer is covering the beta proteins (2).

1. Structure of Keratins in Adhesive Gecko Setae Determined by Near-Edge X-ray Absorption Fine Structure Spectromicroscopy. J Phys Chem Lett. 2022 Mar 10;13(9):2193–6.

1. Evidence that gecko setae are coated with an ordered nanometre-thin lipid film. Biology Letters. 18(7):20220093.

12:00pm **BI+AS+PS-TuM-13 All-Atom Simulations of Peptide Aggregation: Understanding and Predicting Biopolymeric Morphologies***, A. Kwansa, A. Cannon,* North Carolina State University*; **Yaroslava Yingling**,* 911 Partners Way, Engineering Building I, Campus Box 7907

The self-assembly and aggregation of partly or completely disordered peptides have emerged as crucial areas of research with broad implications in therapeutics, supramolecular assembly, and functional biomaterials. Understanding the intricate processes underlying the self-assembly and aggregation of these proteins is essential for harnessing their functional properties and expanding their applications. Simulations can be used to isolate the importance of the interplay between aggregate morphology and secondary structure formation. However, most of the simulation's studies investigate either single peptide in solution or several short peptide analogues. We used large-scale all-atom MD simulations to investigate the structure of hydrated peptide aggregates in detail. Two example systems were investigated, reflectin and elastin-like peptides (ELP). Reflectin proteins, found in cephalopods, play a pivotal role in dynamic coloration for camouflage and communication. On the other hand, ELP proteins possess unique thermoresponsive properties, making them attractive for drug delivery systems, tissue engineering, and biomaterial design. We found significant differences between the structure of a single polypeptide in water and the structure of peptide within the aggregate. Overall, the aggregation process is driven by the formation of peptide–peptide interactions whereas the average hydration of peptides remains almost the same between dissolved and aggregated states. Even though the aggregation is driven by hydrophobic interactions, aggregate has no hydrophobic core and contains many water molecules. Overall, our findings provide an insight into the sequence-dependent structure of aggregates and molecular behavior of individual peptides during aggregation.

Biomaterial Interfaces Division
Room B117-119 - Session BI+AS+EM+NS+SE+TF-TuA

Functional Biomaterials II: Sensing and Diagnostics

Moderators: Joe Baio, Oregon State University, **Caitlin Howell**, University of Maine

2:20pm **BI+AS+EM+NS+SE+TF-TuA-1 AVS Nellie Yeoh Whetten Awardee Talk: Detection of SARS-CoV-2 using Surface-enhanced Raman Spectroscopy and Deep Learning Algorithms**, ***Yanjun Yang***[1], University of Georgia; *H. Li,* Chongqing University, China; *L. Jones, J. Murray, D. Luo, X. Chen, H. Naikare, Y. Mosley, R. Tripp,* University of Georgia; *B. Ai,* Chongqing University, China; *Y. Zhao,* University of Georgia

A rapid and cost-effective method to detect the infection of SARS-CoV-2 is crucial in the fight against *COVID-19* pandemic. This study presents three strategies to detect SARS-CoV-2 from human nasopharyngeal swab (HNS) specimens using a surface-enhanced Raman spectroscopy (SERS) sensor with deep learning algorithms. The first strategy is to use DNA probes modified silver nanorod array (AgNR) substrate to capture SARS-CoV-2 RNA. SERS spectra of HNS specimens have been collected after RNA hybridization, and a recurrent neural network (RNN)-based deep learning (DL) model is developed to classify positive and negative specimens. The overall classification accuracy was determined to be 98.9%. For the blind test of 72 specimens, the RNN model gave 97.2% accuracy in the prediction of the positive specimens, and 100% accuracy for the negative specimens. The second strategy is to use a human angiotensin-converting enzyme 2 protein (ACE2) functionalized SERS sensor to capture the intact viruses. Such a method can differentiate different virus variants, including SARS-CoV-2, SARS-CoV-2 B1, and CoV-NL63. A convolutional neural network (CNN) deep learning model for classification and regression has been developed to simultaneously classify and quantify the coronavirus variants based on SERS spectra, achieving a differentiation accuracy of > 99%. Finally, a direct SARS-CoV-2 detection on SiO_2 coated AgNR substrate is tested. SERS spectra of HNS specimens from 120 positive and 120 negative specimens are collected. The HNS specimens can be accurately distinguished as positive or negative with an overall 98.5% accuracy using an RNN-based deep learning model, and the corresponding Ct value can be predicted accurately by a subsequent RNN regression model. In addition, 99.04% accuracy is achieved for blind SARS-CoV-2 diagnosis for 104 clinical specimens. All the detections are accomplished in 25 min. These results indicate that the SERS sensors combined with appropriate DL algorithms could serve as a potential rapid and reliable point-of-care virus infection diagnostic platform.

2:40pm **BI+AS+EM+NS+SE+TF-TuA-2 Wafer-Scale Metallic Nanotube Arrays: Fabrication and Application**, ***Jinn P. Chu,*** National Taiwan University of Science and Technology, Taiwan

This presentation reports on the wafer-scale fabrication of metallic nanotube arrays (MeNTAs) with highly ordered periodicity. Various metals and alloys have been used to prepare MeNTAs via sputtering over a contact-hole array template created in the photoresist. We have used ferrous (stainless steel) and nonferrous (Cu-, Ni-, Al-, and Ti-based) alloys, as well as elemental metals (Cu, Ag, and Au), to form MeNTAs. The proposed nanotubes can be fabricated over a wide range of heights and diameters (from a few hundred nm to 20 μm) in various shapes, including tall cylinders and dishes. In addition, after combining with other nanomaterials (e.g., ZnO nanowires, graphene oxide, or Au nanoparticles), MeNTAs become nanohybrids suitable for many applications. These applications include thermal emitters, triboelectric nanogenerators, SERS-active biosensors, microfluidics, and anti-icing devices.

3:00pm **BI+AS+EM+NS+SE+TF-TuA-3 Low-Cost, Continuous Spectroscopic Monitoring of Chemical and Biological Contamination in Liquids**, ***Liza White***, *C. Howell,* University of Maine

Traditional UV-visible spectroscopic testing of liquids to assess contamination typically involves manual collection and measurement in a dedicated instrument at discreet time intervals. Here, we describe how low-cost, mass-produced diffraction gratings can be used to approach the functionality of traditional UV-visible spectroscopic readouts under continuous flow conditions. We designed and built a flow chamber setup that permitted uninterrupted monitoring of the diffraction pattern as water with different contaminants was passed over it. Various chemical dyes as well as biological contaminants such as bacteria and algae at varying concentrations in water were tested using standard LEDs as a light source. Information was extracted from the diffraction patterns by analyzing changes in the transmitted wavelengths as well as changes in scattering. Our results showed that the system permitted reasonable detection of each of the contaminants tested within a subset of the concentration range of a standard UV-vis instrument. Tests using the toxic dye methylene blue showed accurate detection well below the toxic limit (5 μg/mL), although the limit of detection for *E. coli* was higher at ~10^7 cells/mL. Our results demonstrate how mass-produced diffraction gratings can be used as low-cost detection systems for the continuous detection of contamination in liquids, opening the door for autonomous monitoring for a range of different applications.

3:20pm **BI+AS+EM+NS+SE+TF-TuA-4 Clickable Cerium Oxide Nanoparticles with Gadolinium Integration for Multimodal Micro- and Macroscopic Targeted Biomedical Imaging**, ***Anna du Rietz***, *C. Brommesson, K. Roberg, Z. Hu, K. Uvdal,* Linköping University, Sweden

Multimodal and easily modified nanoparticles enable targeted biomedical imaging at both the macro- and micro level. Computed tomography and magnetic resonance imaging are biomedical imaging techniques used daily in clinical practice all over the world. These non-invasive techniques can identify more medical conditions if contrast and sensitivity are increased. Commonly, targeted imaging is realized by conjugating biomolecular recognition elements such as antibodies to the contrast agent.

Herein, we present a clickable nanoparticle of our own design, consisting of a Cerium oxide nanoparticle core with integrated Gadolinium, coated with polyacrylic acid and functionalized with both a clickable moiety and a fluorophore. Click chemistry is a versatile toolbox of conjugation reactions that can be performed under gentle conditions enabling facile tailoring of the nanoparticles. Results from XRD and TEM studies clearly show that the cores are mono-crystalline and approximately 2 nm in diameter, the hydrodynamic radius of <5 nm is measured by DLS. The soft coat of the nanoparticles is characterized by IR spectroscopy as well as zeta potential measurements. We have verified the presence of azide-groups on the finished particles and the carboxylic groups of polyacrylic acid are firmly bound to the nanoparticle core. The nanoparticles have high colloidal stability even in physiological ionic strength environments with a zeta potential of -48 mV. We have proven direct anchoring of monoclonal antibody cetuximab to the nanoparticles enabling targeting of epidermal growth factor receptor, a common target in many cancer types. Fluorescence spectroscopy and relaxivity measurements were used to evaluate and optimize the properties for future imaging applications of tumors. The nanoparticles provide high MRI contrast with a T_1 relaxivity of 42 $s^{-1}mM^{-1}$ Gd, more than two times higher than currently used contrast agents. The finished antibody functionalized nanoparticles are efficiently purified using size exclusion chromatography, separating them from unbound nanoparticles and antibodies. Finally, the cellular uptake of the nanoparticles was evaluated using fluorescence microscopy as well as live/dead assays. We show that the nanoparticles are taken up by cell lines of head- and neck squamous cell carcinoma, in a lysosomal pattern. The nanoparticles are visualized at the nm scale inside the lysosomes using TEM. In conclusion, we have designed and synthesized a versatile nanoparticle with functionalized capping that enables facile fabrication of tailored nanoprobes for biomedical imaging.

4:20pm **BI+AS+EM+NS+SE+TF-TuA-7 Molecularly Imprinted Polymers (MIPs): Rising and Versatile Key Elements in Bioanalytics**, *J. Völkle, A. Feldner,* Center for Electrochemical Surface Technology, Wiener Neustadt, Austria; *P. Lieberzeit,* University of Vienna, Faculty for Chemistry, Department of Physical Chemistry, Vienna, Austria; ***Philipp Fruhmann***, Center for Electrochemical Surface Technology, Wiener Neustadt, Austria **INVITED**

Molecularly imprinted polymers (MIPs) are specific materials with tailored binding cavities complementary to a specific target molecule. Although the first example of artificial materials with molecular recognition were already described 80 years ago, they experienced a surge of popularity since the late 1990s due to improved synthetic methods and their great potential as recognition element in (biomimetic) sensors. MIPs can achieve similar selectivity and sensitivity as antibodies[1], while their robustness and stability is superior compared to biomolecules. They can also be used under non-physiological conditions, are suitable for long-term storage and accessed by scalable synthetic methods. These properties make them highly promising

[1] **AVS Nellie Yeoh Whetten Awardee**

candidates for a wide range of applications, from biomimetic receptor layers to nanomaterials or artificial antibodies.

Despite this versatility, their design and optimization towards a specific analyte is probably the most challenging task in the development of a sensor. In general, MIP based sensors either rely on electrochemical, mass sensitive or optical transducers and are commonly used as thin film or nanoparticle (nanoMIP). While there is a considerable amount of literature on electrochemical sensors with MIPs available, new developments such as the improvement of conductive MIPs[2], optimized epitope imprinting[3], or the development of novel synthetic techniques such as the solid-phase synthesis of nanoMIPs[4] are highly important for the further development of MIPs in sensing.

For this reason, this presentation will provide an overview about different MIP types, their synthesis, application, and challenges. Furthermore, their potential in future applications with be addressed to give a wholistic impression of the numerous possibilities of this versatile compound class.

References

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#equal contribution

5:00pm **BI+AS+EM+NS+SE+TF-TuA-9 X-ray Fluorescence Analysis of Metal Containing Cytostatics in HeLa Cells using the Ultra-compact Cryo-vacuum Chamber µ-HORST***, **Lejla Jusufagic**, C. Rumancev, A. Rosenhahn, A. Steinbrück, N. Metzler-Nolte,* Ruhr-University Bochum, Germany

Synchrotron-based X-ray fluorescence spectroscopy (XRF) is an excellent method for investigating elemental distributions and metal concentrations in biological systems.[1-4] The method provides a high sensitivity down to the detection of trace elements with high spatial resolution and penetration depth.[3,4] We introduced an ultra-compact cryogenic vacuum chamber called "µ-HORST" at the P06 nanoprobe beamline at PETRA III, DESY to measure 2D-XRF elemental distribution maps and concentrations in cryogenically fixated cells treated with cytostatic metal complexes with varying ligand sphere.[1,2] The cells are grown on silicon nitride membranes and treated with a 10 µM solution of the metal complexes for different durations and all physiological processes were stopped by rapid cryo-fixation. Cryogenic fixation is a non-destructive method that keeps the cells as close as possible to their biologically hydrated state. The frozen cell samples can be transferred into the µ-HORST setup and maintained in a frozen state throughout the nano-XRF measurements. The acquired data show that the concentration of the metal complexes and their intracellular location can be correlated to the one of physiologically relevant ions such as potassium and zinc as well as associated changes in the metal homeostasis. The developed chamber can not only be used for the analysis of intracellular cytostatic metal complexes, but also to the accumulation of antimicrobial metal complexes or of anthropogenic metals in environmental samples.

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5:20pm **BI+AS+EM+NS+SE+TF-TuA-10 Hemocompatibility Analysis of Novel Bioinspired Coating***, **AnneMarie Hasbrook**, R. Faase, M. Hummel, J. Baio,* Oregon State University

Surface-induced thrombosis is a critical concern in medical device development. To minimize thrombosis, current extracorporeal circulation units require systemic anticoagulation. However, systemic anticoagulants can cause adverse effects such as thrombocytopenia, hypertriglyceridemia, and hyperkalemia. To address this issue, we combine the technology of polydopamine (PDA) functionalization with slippery liquid infused porous surfaces (SLIPS) to potentially enhance the biocompatibility of medical devices. PDA readily coats a wide variety of surfaces and can be functionalized with a thiolated fluoropolymer, via Michael Addition, to form a pseudo self-assembled monolayer (pSAM) which serves as the porous surface component of SLIPS. Liquid perfluorodecalin can then be added to complete the SLIPS coating. We hypothesized that the PDA SLIPS coating provides enhanced hemocompatibility due to its omniphobic properties and composition of compounds currently used in medical applications. Surface modifications were confirmed using contact angle and X-ray photoelectron spectroscopy (XPS) which revealed significant changes to the surface chemistry after the addition of each subsequent layer of PDA SLIPS. The coatings were evaluated for thrombogenicity via quantification of Factor XII (FXII) activation under static and dynamic settings, fibrin formation, platelet adhesion, and clot morphology. The PDA SLIPS coating activated 50% less FXII than glass and 100% more FXII than bovine serum albumin (BSA) coated substrates. PDA SLIPS had similar plasma clotting time to BSA and plasma clotted two times slower on PDA SLIPS than on glass. Platelet adhesion was increased two-fold on SLIPS compared to BSA and decreased two-fold on SLIPS compared to glass. PDA SLIPS had approximately 20% higher fiber diameter and 25% lower clot density than glass and was significantly different in fiber diameter and density than BSA.

5:40pm **BI+AS+EM+NS+SE+TF-TuA-11 Signal Enhancement for Gravimetric Biomimetic Detection – Conjugation of Molecularly Imprinted Polymer Nanoparticles to Metal Nanoparticles***, **Julia Völkle**,* CEST GmbH, University of Vienna, Austria*; A. Weiß, P. Lieberzeit,* University of Vienna, Austria*; P. Fruhmann,* CEST GmbH, Austria

Over the past decades, the field of biosensors and -diagnostics has been increasingly dominated by a growing demand for non-centralized point-of-care devices that do not rely on extensive laboratory infrastructure and trained personnel. Recently, the COVID-19 pandemic has emphasized the crucial role of such fast, reliable, and affordable diagnostic tools. Novel, tailor-made nanomaterials are considered a key component for tackling the upcoming challenges of miniaturization and cost-efficiency in the field of biosensing.

One emerging class of such biomimetic nanomaterials are molecularly imprinted polymer nanoparticles (nanoMIPs). nanoMIPs are artificial receptors that can mimic the highly selective binding capabilities of biological recognition units, such as antibodies and enzymes. Unlike their natural counterparts however, they are stable under a wide range of non-physiological conditions, suitable for long-term storage, and can be derived from a straightforward, rapid synthesis procedure without the need for cell culturing or animal experimentation. Thus, they are ideal candidates for the development of sensitive, robust and inexpensive bioanalogous sensors.

While impressive results regarding their high selectivity and low non-specific binding have been reported [1], nanoMIP-based gravimetric (quartz crystal microbalance, QCM) assays are restricted with regards to the achievable limit of detection by their comparatively low overall mass. This project therefore is focused on the synthesis of well-defined nanoMIP-metal nanoparticle (NP) conjugates, which would result in a larger change in mass upon binding of the recognition units to the QCM transducer. Moreover, conjugation to gold-NPs would allow the incorporation of nanoMIPs into other analytical techniques such as lateral flow devices (LFDs). Experiments therefore are focused on the incorporation of suitable functional groups for further conjugation into the nanoMIP polymer network, the surface functionalization of metal NPs with complementary linker moieties and a suitable coupling procedure. In the poster, nanoMIPs selective for various biologically relevant species are coupled to metal NPs and the performance of the conjugates in QCM-based detection is presented in detail and discussed.

[1] Park, et al. „Recent Advances of Point-of-Care Devices Integrated with Molecularly Imprinted Polymers-Based Biosensors: From Biomolecule Sensing Design to Intraoral Fluid Testing". Biosensors 12, Nr. 3 (22. Februar 2022): 136. https://doi.org/10.3390/bios12030136.

Biomaterial Interfaces Division
Room Oregon Ballroom 203-204 - Session BI-TuP
Biomaterial Interfaces Flash Poster Session

BI-TuP-1 Spacer Length Variations in Sulfo- and Sulfabetaines Affecting the Resistance Against Pathogenic Bacteria, ***Regina Kopecz***, *J. Karthäuser,* Ruhr University Bochum, Germany*; E. Schönemann, A. Martínez Guajardo, A. Laschewsky,* University Potsdam, Germany*; A. Rosenhahn,* Ruhr University Bochum, Germany

Zwitterionic polymers are characterized by their positively and negatively charged groups and their overall neutral net charge. The typically highly hydrophilic polymers are classified into several groups. Beside the well-studied phosphatidylcholine-, carboxybetaine-, and sulfobetaine-, also more recently developed sulfabetaine-based polymers were found to form fouling-resistant coatings.[1] Out of the large variety of possible geometric arrangements of zwitterionic functional groups, only very few have been explored. Following recent studies demonstrating the importance of the precise molecular polymer structure of sulfabetaines on their marine fouling resistance[2], we synthesized sulfo- and sulfabetaines with varying chain lengths of inter-charge and backbone spacers to investigate the effect of the structural change on the resistance against proteins and pathogenic bacteria. The study included six different zwitterionic polymers synthesized by free radical polymerization of monomers with varying ethyl, propyl, and a long undecyl backbone-betaine spacer in combination with ethyl, propyl, and butyl inter-charge spacers. All zwitterionic polymers consistently exhibited very good wettability determined by contact angle goniometry. The non-specific attachment of proteins on the different coatings was analyzed by surface plasmon resonance spectroscopy and the resistance against bacterial fouling was determined by dynamic attachment assays with the freshwater pathogens *E. coli*, *P. fluorescens,* and *B. subtilis*. The highest resistance exhibited the combination of propyl backbone betaine spacers with sulfonate functional groups.

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BI-TuP-2 Frequency-Dependent Mechanical Characterization of Hygroscopic Biological Materials, ***Saima Sumaiya***, *B. Sejour, O. Sahin,* Columbia University

Hygroscopic biological materials constitute a significant portion of the biological world, encompassing a diverse range of biomass from wood to bacterial spores. These materials respond to external stimuli by changing their size, shape, and mechanical properties. This responsiveness allows them to play critical roles in important natural processes such as growth of plants, distribution of seeds etc. Apart for their natural significance, these materials have also demonstrated promising applications in fields such as energy harvesting, development of biohybrid devices, and drug delivery. Our recent results show that these hygroscopic materials can exhibit a jamming-driven transition in mechanical properties at short timescales that differs from glassy and poroelastic behaviors (1). To this end, we have developed an atomic force microscopy (AFM)-based setup that can probe the nanomechanical properties of hygroscopic biological materials across a wide range of frequencies. With this setup, we study the frequency-dependent stiffness of the hygroscopic spores of *Bacillus subtilis* under varying load and humidity levels. We perform frequency sweeps over multiple decades and, alternatively, probe response at a single frequency at varying indentation forces. We interpret the response of the spores in terms of amplitude and phase differences between the applied modulation and cantilever response signal. Through this study, we aim to shed light on the jamming-driven transition in hygroscopic bacterial spores.

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BI-TuP-4 Gas Sensing via Conductive Molecularly Imprinted Polymers (cMIPs), ***Adriana Feldner***, CEST GmbH/University of Vienna, Austria*; P. Lieberzeit,* University of Vienna, Austria*; P. Fruhmann,* CEST GmbH, Austria

Molecularly imprinted polymers (MIPs) are synthetic materials that contain binding sites for selectively rebinding the target analyte. [1] Herein, cMIP blends serve as receptor layers on quartz crystal microbalances (QCMs) and chemiresistors. QCMs are mass-sensitive sensors based on the piezoelectric properties of quartz. [2] Chemiresistors can detect volatile organic compounds (VOCs) in the gas phase through thin conductive polymeric films. [3] The analytes in this case are volatile organic compounds (VOCs) that are known breath biomarkers of breast cancer patients. [4] Those sensors could be preliminary work towards applications in non-invasive early detection of diseases via breath analysis. Alternatively, they could serve as a stepping stone to other conductive MIP systems for VOC monitoring purposes

This work presents the results obtained with cMIPs as sensor materials for detecting 2-propanol, heptanal and acetophenone, respectively. MIPs for the detection of 2-propanol are based on polyurethane. For heptanal detection an acrylamide-based MIP was developed. The acetophenone MIP relies on an acrylate-based system. cMIPs were obtained by blending MIPs with a conductive material. The blends were applied to QCMs and chemiresistors. All sensors were tested in gas flow containing the respective analytes.

All described QCMs sensors react to the desired analyte in gas flow with concentration dependency. The cMIPs have also proven suitable for chemiresistors where binding of the analyte leads to a reversible concentration dependent change in the electric resistance. Detailed results for all analytes including selectivity studies with other VOCs will be presented on the poster.

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BI-TuP-7 3d Mass Imaging of Bacterial Biofilm Composition Using Water Cluster Sims, ***Kate McHardy***, *N. Sano,* Ionoptika Ltd., UK*; N. von Jeinsen, D. Ward,* University of Cambridge, UK

Here we present recent work related to the study of biofilms; Microbial communities embedded in a 3D extracellular matrix. The matrix is composed of a complex array of extracellular polymeric substances that contribute to the unique attributes of biofilm lifestyle. Samples of bacteria and the biofilms they evolve are prepared and the growth arrested after a set period, with the resulting sample analysed with two distinct imaging techniques. We present data from water gas cluster ion beam secondary ion mass spectrometry (Water Cluster SIMS) which offers a mass and depth resolution to aid understanding of the spatial composition of the biofilm by visualising the 3D structures within.

One of the key benefits of Water Cluster SIMS is its ability to achieve high depth resolution due to the low kinetic energy of the water clusters which allows for the analysis of surface and subsurface structures with a high degree of precision. The use of water clusters as the primary ion source enhances secondary ion sensitivities of high mass molecules, in addition, it also minimises sample damage and fragmentation of high mass molecules which are common issues with other cluster ion beams. The water cluster beam was used in Ionoptika's J105 Cluster SIMS system with a beam spot size of 1.5um.

The results here show species consistent with biofilms and tracing masses through the sample in 3D, allows the differentiation between known surface features, for example, biofilm components, fixative residue, growth medium and substrate.

Despite the work being at an early stage, a significant step forward has been made in delivering new methods for the study of highly topical bio-samples that are of wide interest and application.

BI-TuP-8 Characterization of Commercial Catheter Surfaces with Bio-Inspired Liquid-Infused Surfaces, ***Evan Leonard***, University of Maine

Hospital-acquired infections (HAIs) affect over 1.7 million patients annually and are often treated with antibiotics, which can contribute to antibiotic resistance. Catheter-associated urinary tract infections (CAUTIs) are the most common type of HAI, resulting in an estimated $390-450 million in treatment and increased length of stay-associated costs annually. Previously, a bio-inspired coating on commercial catheter surfaces has demonstrated the ability to reduce the need for antibiotics by minimizing both protein and bacterial adhesion to the catheter surface as well as the spread of bacteria to other organs. In this work, we treated commercial catheters with the bio-inspired liquid-infused coating to investigate changes

in properties such as length, mass, and French size. Confocal microscopy was used to examine the catheter and coating interface, while material tensile testing was conducted to quantify bulk material properties after coating application. Through the development of liquid-infused treatments for commercial catheters, we aim to create a widely available, cost-effective solution for preventing CAUTI and reducing the need for antibiotic use in patients who need indwelling catheters.

BI-TuP-9 Multi-Component Liquid-Infused Systems: A New Approach to Functional Coatings for Biomaterials, ***Zachary Applebee***, *C. Howell,* University of Maine

Liquid-infused surfaces (LIS) have found utility across the globe due to their diverse applications including bactericidal functionality, ice adhesion prevention, and medical diagnostic equipment enhancement. Recent research has started exploring the broader potential of LIS by incorporating additional components into the liquid matrix. In this work, we present the concept of multi-component liquid-infused systems (MCLIS), in which the coating liquid consists of a primary liquid and a secondary component and review recent examples. At the molecular scale, MCLIS consisting of silicone oils infused with bacterial quorum sensing inhibitor compounds have been shown to stop bacterial biofilms not only from adhering but also from forming. At the nanoscale, MCLIS made from ferrous magnetic nanoparticles within fluorocarbon-based fluids or silicone oil can change their shape upon exposure to magnetic fields, making them useful for the active removal of adherent fouling organisms. Alternatively, MCLIS fabricated by first adding free particulates to the surface of a spherical droplet, then allowing the decorated droplet to be coated with an immiscible liquid, results in a 3D-coated MCLIS system. At the microscale, microdroplet arrays using more than one liquid in a defined pattern have been fabricated and used for high-throughput detection of compounds. By introducing an additional element into the liquid matrix of liquid-infused systems, a diverse spectrum of attributes can be imbued into these materials, creating novel opportunities for applications within the biomedical realm and beyond.

BI-TuP-10 Subcellular Detection of PEBCA Particles in Macrophages: Combining Darkfield Microscopy, Confocal Raman Microscopy, and ToF–SIMS Analysis, ***Elke Tallarek***, Tascon GmbH, Germany*; A. Vennemann,* IBE gGmbH, Germany*; M. Wiemann,* IBe gGmbH, Germany*; D. Breitenstein, B. Hagenhoff,* Tascon GmbH, Germany

The detection of biomedical organic nanocarriers in cells and tissues is still an experimental challenge. Here we developed an imaging strategy for the label-free detection of poly (ethylbutyl cyanoacrylate) (PEBCA) particles. Experiments were carried out with phagocytic NR8383 macrophages exposed to non-toxic and non-activating concentrations of fluorescent (PEBCA NR668 and PEBCA NR668/IR), non-fluorescent (PEBCA), and cabazitaxel-loaded PEBCA particles (PEBCA CBZ). Exposure to PEBCA NR668 revealed an inhomogeneous particle uptake similar to what was obtained with the free modified Nile Red dye (NR668). In order to successfully identify the PEBCA-loaded cells under label-free conditions, we developed an imaging strategy based on enhanced darkfield microscopy (DFM), followed by confocal Raman microscopy (CRM) and time-of-flight secondary ion mass spectrometry (ToF–SIMS). Nitrile groups of the PEBCA matrix and PEBCA ions were used as suitable analytes for CRM and ToF–SIMS, respectively. Masses found with ToF–SIMS were further confirmed by Orbitrap-SIMS. The combined approach allowed to image small (< 1 µm) PEBCA-containing phagolysosomes, which were identified as PEBCA-containing compartments in NR8383 cells by electron microscopy. The combination of DFM, CRM, and ToF–SIMS is a promising strategy for the label-free detection of PEBCA particles.

We thank SINTEF, Norway for providing the samples.

BI-TuP-11 Removal of Free Liquid Layer from Liquid-Infused Silicone Catheters Reduces Silicone Loss into the Environment while Maintaining Adhesion Resistance, ***Chun Ki Fong***, University of Maine*; M. Andersen,* University of Notre Dame*; E. Kunesh, E. Leonard, D. Durand, R. Coombs,* University of Maine*; A. Flores-Mireles,* University of Notre Dame*; C. Howell,* University of Maine

Silicone catheters infused with silicone liquid are an effective alternative to antibiotic coatings in reducing the adhesion and dissemination of bacteria. However, free silicone liquid on the surface of catheters *in vivo* can be lost into the host system, potentially causing complications. To reduce the potential for liquid loss, free silicone liquid was removed from the surface of liquid-infused catheters and the effects on protein and bacterial adhesion were explored. Absorption of the surface liquid from fully saturated catheter surfaces removed the most if not all of the free liquid layer but preserved the slippery properties. As anticipated, significantly less oil could be forcibly removed from the surface of the samples with the free silicone liquid removed than samples that retained their liquid layer. Tests using the catheter infection-associated protein fibrinogen and bacterium *Enterococcus faecalis* revealed no significant differences in adhesion between the material with or without the free liquid layer. To better understand what point infusing liquid saturation becomes important to resisting adhesion, catheter samples were infused to between 5–100% of maximum liquid uptake values then tested for their ability to resist adhesion by fibrinogen and *E. faecalis*. The results revealed that samples infused with ~80% of their performed statistically similarly to fully infused materials. Together, the results suggest that eliminating free liquid layers through either mechanical means or partial infusion can reduce oil loss from liquid-infused catheters into the host system while preserving functionality, improving the safety of liquid infusion as alternatives to antibiotic coatings in catheters.

Biomaterial Interfaces Division
Room Exhibit Halls A-B Booth 1003 - Session BI-WeA

Biointerphases: Emerging Young Scientists Focus Session (ALL INVITED)

Moderators: Caitlin Howell, University of Maine, **Tobias Weidner**, Aarhus University, Denmark

2:20pm **BI-WeA-1 Mycelium's Dynamic Functionality Across Material Systems: Insights and Research Challenges***, **Wenjing Sun,*** EPFL, Switzerland
The surge in using fungal mycelium as a sustainable material aligns with global sustainability goals. Mycelium exhibits diverse functionality that varies across different forms of materials. This presentation explores past research, emphasizing differences in mycelium's roles and properties based on material types, fungal species, hypha types, and growing conditions. We also address research challenges in this domain.

2:40pm **BI-WeA-2 Breaking Protein-Membrane Chemistry to Understand the Molecular Origins of Adult-Onset Muscular Dystrophies***, **Andrew Carpenter**, J. Baio,* Oregon State University
Dysferlinopathies are a class of adult-onset muscular dystrophies related by a similar disruption to the dysferlin mediate membrane repair of damaged muscle sarcolemmas. Dysferlin possesses a modular structure with 7 C2 domains, where the N-terminal C2A domain is believed to carry out the initial steps of the membrane repair process. Missense mutations within the C2A domain, as well as outside the domain, have been identified in patients with dysferlinopathies suggesting these mutations are disrupting the proper membrane repair function of dysferlin. In this talk we describe our recent progress towards understanding of how dysferlin interacts with cellular membranes and the impact missense mutations exert on this normal function. We utilize vibrational sum-frequency spectroscopy to identify several dysferlin C2A binding mechanisms at biomimetic membrane surfaces and test how missense mutations alter the normal membrane binding function. Further work that will be discussed extends our studies beyond the C2A domain to study how interactions between multiple C2 domains at membrane surfaces contributes to the full-length dysferlin-membrane membrane repair function.

3:00pm **BI-WeA-3 Understanding Adsorption, Adhesion, and Cohesion Phenomena at the Solid/Liquid Interface***, **Pierluigi Bilotto**,* Centre for Electrochemistry and Surface Technology GmbH, Austria*; D. Barragan,* University of Calabria, Italy*; L. Mears, M. Valtiner,* TU Wien, Austria*; B. Zappone,* CNR/University of Calabria, Italy
Marine invertebrates such as mussels and barnacles exhibit an impressive ability to adhere in sea water onto wave-swept rocks, moving ship hulls, submerged metal infrastructures and even anti-adhesive Teflon coatings. On one hand, marine biofouling is a concern for maritime industries, aquaculture, water, and waste treatment industries, as it increases the weight and drag of ships and infrastructures and accelerates surface degradation (corrosion). On the other hand, biofouling is a source of inspiration to solve an outstanding challenge in surface and material science: How to control adsorption (on one surface), adhesion (between two different surfaces) and cohesion (between two equal surfaces) underwater. A large body of literature has been devoted to the aromatic amino acid 3,4-dihydroxy-L-phenylalanine (DOPA), which is exceptionally abundant in mussel adhesive proteins. DOPA is able to bind to a wide variety of substrates and create protein cross-links in salty water using a diverse array of molecular interactions. However, it is becoming increasingly clear that DOPA is neither necessary nor sufficient to ensure underwater surface-attachment and tissue cross-linking. [1] Surface forces apparatus (SFA) and atomic force microscopy (AFM) are preferential tools to investigate forces at the solid/liquid interface when electrolytes are in play. [2] During this talk, I will review our current understanding on the role of DOPA in mussel adhesion, [3] and show our preliminary results in employing tropocollagen type I and type III nanofibrils as model systems to reveal adhesion, adsorption, and cohesion of macromolecules on different substrates. The expected outcomes of this project will shed light on a possible collagen-based biocompatible and biodegradable adhesive.

[1]P. Bilotto, C. Labate, M. P. De Santo, K. Deepankumar, A. Miserez, and B. Zappone, *Adhesive Properties of Adsorbed Layers of Two Recombinant Mussel Foot Proteins with Different Levels of DOPA and Tyrosine*, Langmuir **35**, 15481 (2019).

[2]P. Bilotto, A. M. Imre, D. Dworschak, L. L. E. Mears, and M. Valtiner, *Visualization of Ion|Surface Binding and In Situ Evaluation of Surface Interaction Free Energies via Competitive Adsorption Isotherms*, ACS Phys. Chem. Au **1**, 45 (2021).

[3]L. L. E. Mears, J. Appenroth, H. Yuan, A. T. Celebi, P. Bilotto, A. M. Imre, B. Zappone, R. Su, and M. Valtiner, *Mussel Adhesion: A Fundamental Perspective on Factors Governing Strong Underwater Adhesion*, Biointerphases **17**, 058501 (2022).

3:20pm **BI-WeA-4 Plasma and Beyond: Expanding the Horizons of Naturally-derived Polymers as Biomaterials Through Surface Modification***, **Morgan Hawker,*** California State University Fresno **INVITED**
Naturally-derived polymers hold important utility in biomedical materials, ranging in applications from suturing to biosensors to tissue engineering scaffolds to drug delivery vehicles. Naturally-derived polymers are advantageous for use in biological settings owing to their non-immunogenic nature and favorable mechanical properties. Several naturally-derived polymers also degrade via enzymatic hydrolysis into non-toxic byproducts in vivo. All biomedical applications, however, require specific interactions between the naturally-derived polymer and biological species. These polymers universally lack the necessary surface cues required to facilitate such precise interactions. Thus, further modification is required to tailor naturally-derived polymer surface properties and enhance their applications as biomaterials. Although synthetic wet-chemical approaches have been used to this effect, these strategies introduce complex processing conditions that pose challenges to naturally-derived polymers (e.g., high temperatures and solvents).

Plasma treatment represents a promising alternative to control how naturally-derived polymer constructs interact with biological environments. This talk will highlight several recent thrusts toward better understanding fundamental interactions between plasma and three different naturally-derived polymers. In the first thrust, we seek to evaluate water vapor and nitrogen gas plasma-treated silk fibroin stability upon aging to better understand the shelf life of plasma-modified silks. Water contact angle goniometry findings demonstrate remarkable stability of modified silk materials after aging for 42 days under both ambient and elevated temperatures. In the second thrust, we explore immobilizing three different antioxidants on chitosan films via plasma activation. This thrust aims to target oxidants in burn wounds to enhance healing, and 2,2-diphenyl-1-picrylhydrazyl assay results demonstrate promising antioxidant activity for all modified surfaces. In the final thrust, we describe efforts in coating commercially-available wound dressing materials with an antibacterial film using plasma-enhanced chemical vapor deposition (contrasting pulsed and continuous power conditions). Surface analyses reveal differences in surface chemistry and wettability for plasma-treated dressings compared to untreated dressings. Collectively, these projects demonstrate how plasma modification can be harnessed to enhance the utility of naturally-derived polymers in the biomedical space.

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