Biomaterial Interfaces
Room 117 - Session BI1-MoM

Biomolecules and Biophysics at Interfaces

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

8:15am **BI1-MoM-1 Molecular Modeling of Peptide and Protein-Based Materials: Role of Surface and Interface on Structure and Function***, **Yaroslava Yingling**,* North Carolina State University **INVITED**

Borrowing the structure and function of proteins to design novel multifunctional materials offers a potential solution for pressing technological needs and various applications. However, integration of proteins or peptides with synthetic materials requires a deeper understanding of properties and processes at the bio-material interfaces. We use molecular modeling for the detailed examination of proteins or peptides as they interact with material surfaces or interfaces revealing critical insights into binding dynamics, structural changes, orientation shifts, and conformational alterations. These molecular interactions are key to engineering materials that are not only stable and biocompatible but also capable of retaining specific biological functions. We specifically examine the interaction of proteins and peptides with heterogeneous material interfaces, such as graphene oxide and silica, elucidating how these interactions impact the protein structure. We also incorporated functional peptides into supramolecular structures, such as micelles, that would mimic protein functions from natural metalloproteins and phosphate-binding functionalities and explore the role of core-corona interface by altering the chemical nature of the core on the retention of protein function and structure, the influence of molecular tails on properties and secondary structures, and the adsorption behaviors of phosphate and zinc ions. Overall, we show that atomic-level understanding of the properties and processes at the protein-material interface is crucial for designing advanced materials that enhance functionality and performance across diverse applications.

8:45am **BI1-MoM-3 Crowding Accelerates Molecular Aging in Protein Droplets***, M. Brzezinski, P. Argudo, J. Michels,* Max Planck Institute for Polymer Research, Germany*; **Sapun Parekh**,* University of Texas at Austin

Protein liquid-liquid phase separation (LLPS) is a process in which a homogeneous mixture of proteins in a solvent self-assembles, upon certain stimuli, into a protein-rich and protein-depleted phase. In a simple two-component system, the protein-rich phase is called a protein condensate or droplet phase, and the protein-depleted phase is the continuous phase. Recent work has shown that many intrinsically disordered proteins (IDPs) undergo two-component phase separation in vitro due to a myriad of weak interactions. LLPS can be further enhanced by crowding agents. Crowders help to tune effective volume fractions to more “convenient” ratios, which results in a broader window of suitable parameters for obtaining phase separation. Moreover, with use of crowding agents, LLPS has been shown to occur not only for IDPs, but also for folded proteins. So, how do crowding agents affect LLPS of proteins? Depending on the affinity of the crowder for the protein, segregative and associative phase separation can be distinguished. In the following work, we present a systematic approach to quantifying LLPS influenced by crowding agents for an IDP and folded protein. We use fluorescence recovery after photobleaching (FRAP) to quantify material properties and coherent anti-Stokes Raman spectroscopy (CARS) to quantify molecular composition and secondary structure, and theory to demonstrate molecular aging in crowded condensates. We find that crowding accelerates aging in condensates and that folded proteins can phase separate and show molecular aging as well. These results have implication for studying transitions from condensates to fibrils over time.

9:00am **BI1-MoM-4 Self-Healing Nanotubes Consisting of Cyclic Peptides Conjugated by Azobenzene Derivatives***, **Olufolasade Atoyebi**, M. Beasley, W. Maza, M. Thum, C. Pyles, S. Tuck, A. Dunkelberger, M. Kolel-Veetil, K. Fears,* US Naval Research Laboratory

Cyclic peptides are capable of self-assembling into supramolecular peptide nanotube structures, via hydrogen bonding along the backbone of the peptide rings. Research from our lab has improved upon the synthesis of the self-assembled peptide nanotubes by covalently linking the cyclic peptides into a linear polymer chain that transitions from the unfolded structure to the peptide nanotube by varying the pH of the solution. Here we present an alternate way to control the self-assembly from the linear polymer chain to the rigid peptide nanotube via photo-isomerization. We capitalize on azobenzene’s photo-actuable nature using a di-carboxylic acid azobenzene to covalently crosslink the cyclic peptide rings (KVVKVV) via the two primary amines displayed by each ring. When the azobenzene crosslinker is in its thermally-relaxed, *trans* conformation, the cyclic peptide polymer adopts a rigid, nanotube conformation. When excited by UV light (320 nm), the *trans* to *cis* transition of the azobenzene crosslinker disrupts hydrogen bonding between adjacent rings, causing the polymer to unfold. Atomic force microscopy (AFM) shows that the polymer chain re-fold into rigid nanotube when the azobenzene crosslinkers return to the trans conformation, either by stimulation by visible light (420 nm) or thermal relaxation. This work introduces a novel class of intrinsically self-healing nanomaterials that can be used as reinforcement agents for a wide variety of industrial and biological materials.

9:15am **BI1-MoM-5 Anti-Biofouling Polymer Coatings with Statistical Amphiphilicity and Improved Environmental Sustainability***, **Rong Yang**[1],* Cornell University **INVITED**

Biofouling caused by bacterial biofilms is found in nearly every ecosystem on earth, ranging from ship hulls to membranes for separations and to bioimplants and live tissues (e.g., auditory bullae). It drives up energy consumption and causes dangerous infections. The need for economical, safe, and environmentally sustainable anti-biofouling coatings has motivated our recent investigations into a new class of copolymers with statistical amphiphilicity, demonstrating exceptional biofouling deterrence. Such amphiphilic copolymers simultaneously present hydrophilic and hydrophobic moieties mixed at a molecular level. As such, they are uniquely positioned to reduce biofouling at the air-liquid-solid three-phase interface, where bacterial biofilms are rampant via facile side-chain reorientation. However, their synthesis has challenged common solution-based techniques due to the need for a common solvent for the precursors that present disparate solubility. To overcome that challenge, my group has leveraged an all-dry polymer synthesis technique, namely initiated Chemical Vapor Deposition (iCVD), which has led to several synthesis pathways toward anti-biofouling coatings with statistical amphiphilicity. Our recent effort has focused on improving the environmental sustainability of this class of polymers by replacing the fluorine-bearing hydrophobic side chains with siloxanes or antimicrobial enzymes, which led to improved fouling deterrence. The iCVD method enables polymer synthesis and coating formation in a single step and on virtually any substrate. It has been scaled up to produce functional polymer coatings in a roll-to-roll configuration, pointing to rapid translation of the amphiphilic coatings to reduce the environmental and economic impact of biofouling.

9:45am **BI1-MoM-7 Aqueous Underwater Adhesives Made from Multiple Agricultural Proteins***, **Zachary Lamberty**, C. So,* U.S. Naval Research Laboratory

Underwater adhesion, *i.e.* binding to wet surfaces, is a major challenge for medical adhesives, marine repair, and for the durability of shoreside structures. The majority of industrial and academic solutions utilize hydrophobic solvents or polymers to exclude water from the bond area with the goal of obtaining a dry-like contact.However, many organisms have evolved methods of adhering in adverse underwater environments using water-borne protein adhesives. Not only are aqueous adhesives generally less toxic than their organic counterparts, but the water-soluble precursor components are believed capable of diffusing through interfacial water layers, vastly increasing the true contact area of the bond. Inspired by the tenaciously sticky barnacle, we have designed an aqueous two-part adhesive from common agricultural byproduct proteins. Upon mixing, the protein will denature and aggregate, forming a hydrogel. Overtime these proteins rearrange into β-sheet rich amyloid fibers, lending the material strength and allowing it to remain water-insoluble for long periods. We have previously demonstrated this adhesive system using Bovine Serum Albumin (BSA) proteins, with underwater-deposited bond strengths of 0.6 – 0.8 MPa on metal oxide or polymer substrates. Here I will demonstrate that similar principles can be applied to make underwater adhesives from bovine α-lactalbumin (αLa), an abundant milk protein. αLa adhesives can be deposited underwater like BSA adhesives, with bond strengths of 0.52 - 0.09 MPa on polycarbonate after 1 week aging in artificial sea water. Interestingly, unfolded αLa proteins are stabilized by the denaturant urea, remaining liquid for hours in air but rapidly solidifying when deposited in solution as the denaturant diffuses away. This offers unique advantages, including greatly reduced sag and the ability to densify the material to improve cohesive strength. By understanding and controlling the aggregation and densification process we aim to develop tunable, easily

[1] **BID Early Career Researchers Award**

deployable underwater adhesives made from non-toxic, domestically sourced agricultural proteins.

10:00am **BI1-MoM-8 How Is the Hydrophobic Force Modified by an Oscillation Frequency in Saline Conditions?**, *C. Wagner, P. Stöcher, M. Valtiner,* ***Laura Mears,*** Vienna University of Technology, Austria

Hydrophobic interactions can occur in many biorelevant systems, including hydrophobic side chains as part of many amino acids, drug molecules and surfaces used to support and control the adhesion of cells. Several of Stephanie Allen's works involve such hydrophobic amino acids [1] or surfaces [2] and their characterisation with atomic force microscopy (AFM). In this contribution we set our work on the hydrophobic force in the context of biointerfaces. There have been many investigations over the years regarding the mechanism behind the hydrophobic force and over how long a range it can be felt [3]. We present a detailed set of AFM force measurements of hydrophobic SAM modified surfaces, with varying salt concentration and oscillation frequency (0-2kHz). We observe dynamic changes in the force curve characteristics with both salt concentration and oscillation frequency. The changes lead to a reduction of the average force with increasing applied frequency, while multiple distinct characteristic curves are present and enhanced by certain conditions. We also notice changes in the range of the force away from the surface. Altogether, the results we will present bring new insight into the mechanism of hydrophobic interactions. Further they open the opportunity for discussion of how the addition of oscillations could, perhaps, be used in biorelevant applications to modify the hydrophobic forces directly.

[1] L. Niu, Xi. Chen, S. Allen, and S. J. B. Tendler, *Langmuir*, **2007**, 23, 14, 7443–7446.[2] S. Allen, S.D.A. Connell, X. Chen, J. Davies, M.C. Davies, A.C. Dawkes, C.J. Roberts, S.J.B. Tendler, P.M. Williams, *Journal of Colloid and Interface Science*, **2001**, 242, 2, 470-476.[3] W. A. Ducker and D. Mastropietro, Current Opinion in Colloid & Interface Science, **2016**, 22, 51–58.

Biomaterial Interfaces
Room 117 - Session BI2-MoM
Functional Materials

Moderators: Kenan Fears, U.S. Naval Research Laboratory, **Rong Yang**, Cornell University

10:30am **BI2-MoM-10 Customizing Naturally-Derived Polymers Using Plasma-Enhanced Chemical Vapor Deposition**, ***Morgan Hawker,*** California State University, Fresno

Naturally-derived polymers are the fastest-growing biomaterials because they are non-immunogenic and are able to recapitulate a range of biological tissues through bulk mechanical property tuning. This remarkable materials class includes silk, collagen and cellulose, all of which have high potential for use as tissue engineering implants, biosensors, and drug delivery devices. One drawback is that naturally-derived polymers are bioinert, exhibiting non-specific interactions with proteins, cells, bacteria, enzymes, and other biological species. Another possible drawback in some applications includes fixed degradation kinetics which may not match the rate required for a given application. Plasma-enhanced chemical vapor deposition (PECVD) is a useful strategy to address both drawbacks, providing a chemically customizable coating that can control interfacial interactions while also modulating degradation.

This talk will highlight our recent work on plasma-enhanced chemical vapor deposition approaches to modify different naturally-derived polymers. First, an acrylic acid and pentane plasma copolymerization strategy has been developed to control silk film wettability. We demonstrate that silk film wettability decreases with increasing pentane in the feedgas, with impressive static water contact angle tunability between 50° and 100°. High-resolution XPS findings provided additional insight into changes in surface chemical composition for coatings deposited with varying proportions of monomers in the feedgas. Second, PECVD coatings were deposited on commercially-available cellulosic wound dressings using a 1,8-cineole precursor. Pulsed and continuous power conditions were utilized with the goal of preserving the 1,8-cineole monomer structure because of the molecule's well-documented antibacterial properties. Although surface analysis revealed minimal difference between films deposited under different powers, films unexpectedly exhibited differing performance when interfaced with *Streptococcus pneumoniae*. Last, novel PECVD systems currently under development in our lab will be presented. One goal of employing new precursors is to develop additional antibacterial coating systems that are stable in aqueous environments. Each of these systems is poised to enhance naturally-derived polymer utility in biomedical contexts through controlling interfacial interactions.

10:45am **BI2-MoM-11 Vascularized Polymers: Optimizing Support Systems for Biotic/Abiotic Living Materials**, *E. Leonard, S. Zier,* ***Caitlin Howell,*** University of Maine

Large-scale detection of and active response to changing conditions at interfaces is a promising pathway to facilitating the long-term growth and stability of the biotic component of biotic/abiotic living materials. In Nature, one method of both detecting and actively responding to environmental changes is by using vascular networks as intermediaries that transport signals and materials from one location to another. In this work, we explore various methods of embedding vascular networks into abiotic polymeric matrices that use widely available fused filament deposition model (FDM) 3D printing. We test each method for the efficacy of diffusion to and from the interface, as well as how well it can be used in both hydrophobic and hydrophilic abiotic polymers. Our goal is to create detection-and/or-response systems to support the growth of biotic systems located at abiotic polymer interfaces in a low-cost, easily scalable manner, paving the way for the creation of durable and adaptable biotic/abiotic living materials.

11:00am **BI2-MoM-12 Preserving the Hydrophilicity of Biodegradable Films Post-Plasma Treatment: Impact of Aging Environment on Hydrophobic Recovery**, ***Mina Abdelmessih,*** *M. Hawker,* California State University, Fresno

Polylactic acid (PLA) and chitosan (CS) are biopolymers with vast potential in the biomedical field. Their biodegradability and non-toxicity *in vivo* makes them useful as tissue engineering scaffolds. The slower degradability of PLA is suitable for slower-healing bone tissues, while the faster degradability of CS is suitable for faster-healing soft tissues. Nevertheless, both polymers are inherently hydrophobic, which would potentially restrict the cell adhesion desirable for tissue engineering applications. There is some evidence that hydrophilic surfaces are preferable for cell adhesion and growth. Previous studies display the promise of utilizing radio-frequency nitrogen plasma treatment in increasing the surface hydrophilicity of PLA and CS. In addition, nitrogen plasma treatment polymers have been shown to exhibit improved surface cell adhesion properties. Many plasma treated polymers, including PLA and CS exhibit a phenomenon known as hydrophobic recovery, where the polymers partially retain their original hydrophobic properties with age. Hydrophilicity loss in treated PLA and CS is detrimental, especially in applications that require cell adhesion. Methods of preventing this phenomenon in PLA and CS are widely unexplored.

This work explored the impact of various aging conditions (storage in vacuum, cold temperature, and air) on the surface hydrophilicity of nitrogen-plasma-treated PLA and CS following treatment. Films were prepared as model substrates using the solvent-casting method. The films were treated in a RF plasma reactor under optimized parameters (power, pressure, and treatment time). After treatment, the films were aged in the different aging environments for two weeks. Throughout the aging period, multiple surface analyses were conducted on samples exposed to the various preservation environments, including untreated samples as controls. Surface wettability analysis utilizing water contact angle goniometry displayed that vacuum aged samples possess the least hydrophobic recovery in comparison to the other aging conditions. Additionally, surface chemical composition was examined using x-ray photoelectron spectroscopy. Expanding these treatment preservation methods to PLA and CS has potential to positively impact their use as scaffolds in the biomedical field.

11:15am **BI2-MoM-13 3-D Atomic Layer Infiltrated Metal Oxide Barriers for Thin-Film Active Microelectrode Arrays**, ***Martin Niemiec,*** *K. Kim,* University of Connecticut

A recent trend in neural interfaces is a shift away from rigid devices comprised of materials such as silicon and metals toward thin and flexible material classes such as polymers. While such devices show more favorable biointegration over chronic timescales, they are often plagued by issues of reliability, stemming from poorer resistance to the permeation of moisture and ions as compared to traditional materials. As such, the incorporation of ultrathin barrier layers of inorganic materials deposited by atomic layer deposition (ALD) or chemical vapor deposition (CVD) is an area of interest. Most ALD and CVD processes incorporate wafer-grown inorganic barriers,

depositing metal oxides above and below the polymeric layers, followed by via opening using established microfabrication techniques. However, the etching step can leave unprotected polymer sidewalls, leaving a significant path for permeation, and the high stiffness mismatch between the polymer and inorganic film often leads to interfacial delamination. Herein, we describe a technique and its advantages for the fabrication of mechanically reliable thin-film barrier encapsulated polymeric active microelectrode arrays with three-dimensional all-side atomic layer infiltration using a modified liftoff process. Unlike barriers grown on-wafer, the metal oxides infiltrate all sides of the polymer array at once and leave no exposed sidewalls vulnerable to moisture. Secondly, the gradual stiffness transition at the polymer-inorganic barrier interface can reduce delamination and improve flexibility. Finally, the modified liftoff process allows ALD via opening on freestanding devices. We have demonstrated such devices previously in a completely encapsulated form, without active microelectrodes. Here, the combination of active electrodes with our three-dimensional coating is achieved via a modified liftoff process utilizing ultrasonication to remove the metal oxide over the microelectrodes, without removing it elsewhere. Because the inorganic barrier is deposited after insulation via opening, our devices feature the additional benefit of via sidewall encapsulation with a protective barrier, thereby decreasing the chances of side-permeation and delamination initiation at the microelectrode. The encapsulation (~10nm Al_2O_3, ~25nmTiO_2) can provide water vapor transmission rates less than 1 mg m-2day-1 at 85% RH (see supplement). Ongoing accelerated aging tests will offer insights as to the effectiveness of our encapsulation on preserving functionality under implanted conditions, with initial trials showing functionality up to ~20 days at 87°C (roughly 640 days at 37°C).

11:30am **BI2-MoM-14 Injectable Siloxane Sponges for on-Site Treatment and Rapid Hemostasis**, *P. Sarkar,* ***Kausik Mukhopadhyay,*** University of Central Florida

Hemorrhage is one of the main causes of preventable civilian death and on the battlefield. According to a report by the USAMRDC in 2022, nearly 50% of combat deaths have been due to exsanguinating hemorrhage. Of those, about half could have been saved if timely, appropriate care had been available. This underscores the need to develop appropriate FDA-approved hemostatic treatments. While external wound injury can be treated mostly by visual inspection, internal hemorrhages are often much more intractable. The need to treat trauma wounds requires an immediate solution that can be applied by individual soldiers in the field swiftly and efficiently. In our current study, we report a silicone-based hemostatic bandage system that is both antibacterial and self-expanding. The two-component hemostatic system chemically reacts in situ to form a stretchable foam that generates autogenous pressure on the wound to control bleeding. It can be easily administered with a dual-syringe device, and when the components interact on delivery, hydrogen peroxide decomposition is catalyzed by silver oxide, releasing oxygen to expand the siloxane matrix into a rigid ‘foam’ within seconds. This foam or sponge then acts as a 'tamponade' arresting further bleeding. The adhesive properties of the foam render them optimal for wound-dressing applications and the presence of silver oxide imparts antibacterial effects against both Gram-positive and Gram-negative strains of bacteria. Optimization of the constituents allows control over system temperature and porosity. Support data include studies on rheology, adhesion, and in-vitro assays. To further assess the efficacy of the foam, a unique mannequin system capable of simulating a deep abdominal wound has been employed. The objective of this novel hemostatic agent is to provide the injured party with a means to rapidly stagnate or arrest bleeding from external and internal wounds in a manner superior to those currently available. This unique formulation presents an easy and economical approach to a hemostatic bandage system with spontaneous self-expanding properties, capable of remaining functional in inclement weather conditions.

Biomaterial Interfaces
Room 117 - Session BI-MoA

Microbes at Interfaces

Moderators: Axel Rosenhahn, Ruhr-University Bochum, **Rong Yang**, Cornell University

1:30pm **BI-MoA-1 The Role of Surface/Interface Phenomena in The Antibacterial Action of Nano- and Microscale Gallium Oxide and Gallium Hydroxide**, ***Yuri M. Strzhemechny***, *D. Johnson, J. Brannon,* Texas Christian University*; P. Ahluwalia,* Harmony School of Innovation Fort Worth*; T. McHenry, M. Smit, D. Kalluholematham,* Texas Christian University*; Z. Rabine,* Wayne State University*; P. Jodhka,* Tarrant County College Northwest

Worldwide trend of increasing antibiotic resistance has spun interest in alternative antibacterial agents such as metal oxide particles. Whereas the antibacterial action of many such oxides is well established, the mechanism of this activity is largely unknown. Cytotoxicity could be mediated via such mechanisms as production of reactive oxygen species, release of toxic cations, interactions disrupting cell walls and causing osmotic stress. Targeted applications of oxide antibacterials are also hindered by a lack of understanding of the role and nature of the local bacterial environment in mediating/hindering antibacterial interactions. Surface defects in nano- and micro-crystals strongly affect performance of metal oxides in applications, necessitating elucidation and control of those defects. The beta polymorph of gallium oxide (β-Ga_2O_3) in nano- and microcrystalline form is attracting a significant research interest due to potential applications in biological therapeutics, optoelectronics, and catalysis. In our studies, we employ nano- and microparticles of β-Ga_2O_3 synthesized via a simple bottom-up hydrothermal method, which yields, as a first step, a GaOOH precursor, which then undergoes calcination to bear the final product. Such growth method, through variation of growth parameters, allows production of particles with tunable morphology and controllable relative abundances of surfaces with desired polarities. To address the nature of interactions between β-Ga_2O_3 and GaOOH crystal surfaces, cellular membranes and bacterial growth media we perform detailed systematic studies of the optoelectronic and physicochemical properties of both GaOOH and β-Ga_2O_3 samples and then evaluate their impact of on the antibacterial action of these samples. We are especially interested in the influence of surface defects and particle morphologies on the antimicrobial efficiency of the studied oxides. The biological assays with *Escherichia coli* and *Staphylococcus aureus* are used to examine the antibacterial action and also to run pre- and post-assay comparative studies of the oxide specimens themselves. For the latter we employ a variety of characterization techniques, such as electron microscopy, energy-dispersive X-ray spectroscopy, time and wavelength dependent surface photovoltage, temperature-dependent photoluminescence spectroscopy, Fourier-transform infrared spectroscopy, etc. We find in our samples a strong correlation between the growth parameters, particle morphologies, crystal surface characteristics, and antimicrobial properties.

1:45pm **BI-MoA-2 Microbially-Induced Corrosion of Synthetic Granite and Dike Glass by Paenibacillus Polymyxa SCE2 Using ToF-SIMS**, ***Gabriel Parker***, University of Illinois Chicago*; A. Plymale, J. Hager, J. Dhas, Z. Zhu,* PNNL*; L. Hanley,* University of Illinois - Chicago*; X. Yu,* ORNL

Microbially-induced corrosion (MIC) is an important topic that focuses on material degradations over extended periods. Soil microbes are often associated with MIC of foreign objects interacting within the rhizosphere. *Paenibacillus polymyxa* SCE2 is a facultative anaerobic microbe found in soil. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is a powerful mass spectrometry imaging technique that provides insights into the surface characteristics by its spectral, two-dimensional (2D) imaging, and depth profiling capabilities of biointerphases. Herein, ToF-SIMS was used to detect surface changes on synthetic granite and synthetic dike glass coupons that were treated with *Paenibacillus polymyxa* SCE2 over extensive periods of time. Confocal laser scanning microscopy (CLSM) was used to verify bacterial coverage across the granite and dike glass surfaces after three and seven months' growth in a static cell. ToF-SIMS spectral analysis shows detection of glass component related ions, such as *m/z* 276.84, 380.81, 418.77, 607.62, 693.48, and 721.51. Also, ions that are indicative of extracellular polymeric substance (EPS) components were observed, such as *m/z* 241.22, 255.23, 269.25, 297.15, 311.16, and 325.18.Clusters of un-identified peaks are detected in the biofilm treated glass coupons, which are speculated to reflect EPS components as they incorporated into the glass to form colonies, resulting in MIC. ToF-SIMS analysis results show that granite glass has more "corrosion related" peaks than the dike glass.The observed surface compositional and morphological differences between the two types of glass are hypothesized to be related to the glass surface hydrophobicity and ultimately its affinity to biofilms.

2:00pm **BI-MoA-3 Titanium Oxynitride Thin Films Deposited in a Custom-Built ALD Reactor with Real-Time Residual Gas Probing to Enhance the Photocatalytic Activity of Polymethylmethacrylate (PMMA) and Induce Antimicrobial Activity on Its Surface**, ***Harshdeep Bhatia***, University of Illinois - Chicago*; B. Nagay, V. Barão,* University of Campinas (UNICAMP), Brazil*; G. Jursich, C. Sukotjo, C. Takoudis,* University of Illinois - Chicago

Titanium oxynitride is a novel material researched for its visible light photocatalytic activity (PCA). Polymethylmethacrylate (PMMA) is a common organic biomaterial used in the dental industry which is used in conditions where they are highly susceptible to microbial biofilm formation. In this study, Atomic Layer Deposition (ALD) was used to deposit a thin layer of titanium oxynitride on 3D printed PMMA disks. The reactor used tetrakis(dimethylamino) titanium(IV) as the titanium precursor and ammonia (NH_3) as the nitriding agent; the system was custom-designed and controlled using a Python program. A common single board computer controlled the solenoid valves connected to the pneumatic valves. The Python program could deposit a single or a bilayer of oxide and nitride and control the ALD valves manually. A Chemical Vapor Deposition (CVD) mode is also possible for faster film growth. In addition, a residual gas analyzer (RGA) was connected to the downstream to study the outgassed products from the reactor in real time. The operating pressure for the ALD reactor was 1.6 Torr while for the RGA was $1x10^{-6}$ Torr. After deposition, thickness was measured on the reference silicon sample using Spectroscopic Ellipsometry while the composition was measured using X-ray Photoelectron Spectroscopy. Post-deposition, PCA of the PMMA surfaces were also determined using the degradation of a standard methylene blue solution after irradiation by three different light sources. A similar approach was used to test the antibacterial and antifungal effect under light irradiation. Cell viability tests were also performed to test the biocompatibility of the film.

2:15pm **BI-MoA-4 Isolation and Identification of Copper-Tolerant Fouling Communities**, ***Sara Tuck***, *M. Kardish,* US Naval Research Laboratory*; B. Orihuela,* Duke University*; G. Vora,* US Naval Research Laboratory*; K. Franz,* Duke University*; K. Fears,* US Naval Research Laboratory

Biofouling, the accumulation of unwanted organisms on submerged assets, is a fundamental problem in maritime transport and human health. Biofouling build-up increases fuel consumption, exhaust emissions, and operational costs in addition to facilitating the transfer of environmental and pathogenic bacteria from one location to another. Conventionally, biofouling is inhibited by the application of antifouling coatings, the most popular of which are copper based. In biological systems, copper is tightly regulated and, in an attempt, to exploit this, antifouling coatings contain up to 75% CuO by weight. Despite these high loadings, the efficacy of these coatings is rapidly 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 of antifouling performance, coated and uncoated polyvinyl chloride panels were submerged at estuarine and marine field test sites and microbial communities were isolated. Biofouling communities were harvested from three test sites and individual species were cultured, isolated, and identified. Copper tolerance was assessed by re-exposing these cells to copper-containing coatings and traditional broth microdilutions.

2:30pm **BI-MoA-5 Surface-Cleaning Mechanisms Used by Acorn Barnacles (Amphibalanus Amphitrite) to Prevent Microbial Colonization at Their Adhesive Interface**, *Q. Lu, E. McGhee, W. Hervey, D. Leary, C. Spillmann,* ***Kenan Fears***, US Naval Research Laboratory

Barnacles have long been admired, or hated, for their robust underwater adhesives that allow them to tenaciously adhere to surfaces and endure harsh marine environments. Previously, we revealed that acorn barnacles evolved a remarkable surface cleaning fluid that removes microorganisms ahead of expansion of their base and the deposition of a new ring of cement. This process involves the secretion of a lipidaceous material that phase separates in seawater, into a phenolic laden gelatinous phase that presents a phase rich in lipids and reactive oxygen species to the seawater interface. Biofilms in close proximity to this material rapidly oxidize and lift

off the surface as the secretion advances. Proteomics analysis of the adhesive interface reveals the presence of a haloperoxidase, a class of enzyme known to participate in the innate immune response of a wide variety of organisms, which converts chlorine ions to hypochlorite ions (bleach) in the presence of hydrogen peroxide. We performed agar well diffusion assays the assess the susceptibility of marine and terrestrial micro-organisms to hydrogen peroxide with and without the presence of a haloperoxidase. While yeast cells (*P. larentii*) where shown to be quite susceptible to hypochlorite ions at low doses, the oxidation of biofilms of marine bacterium (*V. natrigens* and *M. atlanticus*) by hypochlorite ions did not result in significant cell death. Confocal microscopy of different barnacle species revealed that the surface cleaning mechanisms employed by acorn barnacles is not ubiquitous to all barnacle species. Microbial colonies were present in the basal region of barnacle species in which the secretion of this surface cleaning fluid was not observed, in stark contrast to barnacle with this surface cleaning fluid. Knowledge of these processes could enhance the efficiency of synthetic underwater adhesives and lead to novel environmentally benign antifouling technologies.

2:45pm **BI-MoA-6 BioSAXS - a Tool to Enrich and De-Risk Antimicrobial Drug Development***, **Axel Rosenhahn**, C. Rumancev, A. Gräfenstein,* Ruhr University Bochum, Germany*; K. Hilpert,* University of London, UK **INVITED**
Antimicrobial resistance is a worldwide threat to modern health care. Low-profit margin and high risk of cross-resistance resulted in a loss of interest in big pharma, contributing to the increasing threat. Strategies to address the problem are starting to emerge. Novel antimicrobial compounds with novel modes of action are especially valued because they have a lower risk of cross-resistance. Up to now determining the mode of action has been very time and resource consuming and will be performed once drug candidates were already progressed in preclinical development. BioSAXS is emerging as a new method to test up to thousands of compounds to classify them into groups based on ultra-structural changes that correlate to their modes of action. BioSAXS experiments in gram-negative E. coli and a correlation with transmission electron microscopy have demonstrated that using conventional and experimental antimicrobials a classification of compounds according to their mode of action was possible. Further work showed that the approach can also be used for gram-positive bacteria (S. aureus) and the effects of novel antimicrobial peptides on both types of bacteria were studied. Preliminary experiments will be presented that show that BioSAXS can also be used to classify antifungal drugs, demonstrated on Candida albicans. The data will be discussed in view of the perspective of how BioSAXS can accelerate and enrich the discovery of antimicrobial compounds from screening projects with a novel mode of action and hence de-risk the development of urgently needed antimicrobial drugs.

Biomaterial Interfaces
Room 117 - Session BI1-TuM

Characterization of Biological and Biomaterial Surfaces I: Celebration of Stephanie Allen

Moderators: Morgan Hawker, California State University, Fresno, **Sapun Parekh**, University of Texas at Austin

8:00am **BI1-TuM-1 Biointerfacial Characterisation of Implanted Medical Devices with OrbiSIMS*, Morgan Alexander,*** University of Nottingham, UK

The 3DOrbiSIMS hyphenation of ToF SIMS with an OrbiTrap™ makes meaningful analysis the molecules in complex biological samples and bio-interfaces formed on materials feasible. [1,2] Critically, the mass resolving power and mass accuracy has rendered routine peak assignment with deviations below 2 ppm. The large spectral data files with thousands of peaks that arise from biological samples requires automated untargeted analysis to make the most of this information. These have been enabled by the methodology for molecular formula prediction (MFP) assignment adapted to SIMS by Edney et al. [3]

I will illustrate how this enables us to investigate the bio-interface for implanted medical devices, to shed light on their failure mechanisms. The importance of the lipids and other metabolites is revealed in the analysis of tissue sections. Subsequent analysis of the bio interfacial deposit at the surface of extracted devices sheds light on the complexity of this process. [4,5] Understanding medical implant fibrosis by biointerfacial OrbiSIMS analysis [Bin Sabri unpublished]

References

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2. The 3D OrbiSIMS: Label-free metabolic imaging with subcellular lateral resolution and high mass-resolving power. Passarelli et al. (2017) *Nature Methods*.
3. Molecular formula prediction for chemical filtering of 3D OrbiSIMS Datasets. Edney et al (2022) *Anal Chem.*
4. Single-cell metabolic profiling of macrophages using 3D OrbiSIMS: Correlations with phenotype. Suvannapruk et al. (2022) *Anal Chem*
5. Spatially resolved molecular analysis of host response to medical device implantation using the 3D OrbiSIMS highlights a critical role for lipids. Suvannapruk et al. (2024) *Advanced Science*.

8:15am **BI1-TuM-2 Insights into the Chemistry of Wheat Leaves and their Uptake of Agrochemicals using OrbiSIMS*, M. Khan,*** University of Nottingham, UK*; C. Whitehouse, T. Powell,* Syngenta, UK*; C. Roberts, **David Scurr,*** University of Nottingham, UK

The estimated size of the global agrochemicals market in 2022 amounted to USD 227.9 billion with a projected increase to USD 234.27 billion in 2023 [Market Analysis Report 2018-2022]. The notable increase in agrochemical usage observed worldwide can be attributed to the economic benefits that to farmers through the safeguarding of crops against invasive species, including the improvement in quality and quantity of harvests. Limited knowledge of the *in-situ* chemical composition of wheat leaves and the permeation mechanisms of pesticides into skin and leaf tissues constrains research and development of new products.

OrbiSIMS has been recently demonstrated as a powerful tool for skin research, providing label-free insight into the 3D permeation profiles of endogenous and exogenous compounds. Previous work [Starr et. al., *PNAS*, 2022] investigated the molecular composition of the *stratum corneum* and tracking the permeation of an active agent. Our study expands the use of OrbiSIMS to investigate the native chemistry of wheat leaves, particularly the plant cuticle as the primary diffusion barrier. The study reveals the distribution of a fungicide formulation through both wheat leaves and skin, offering insights into its diffusion in relevant biological matrices.

The molecular architecture of wheat leaves was first probed, with a focus on the cuticle. *In-situ* analysis provided novel insights into the localisation of endogenous species, including fatty acids, aldehydes, phospholipids, flavones and vitamins. Depth profiling revealed depth-dependent variations in leaf structure, with fatty acids and aldehydes associated with the cuticle and epicuticular waxes exhibiting a prominent concentration at the leaf surface. Conversely, flavones and vitamins were predominant in the epidermis.

Exogenous compounds were identified in skin and wheat leaves, alongside endogenous species. The investigation focused on the impact of exposure time and concentration on agrochemical permeation across skin and wheat leaves. *In-situ* analysis provided the detection and tracking of the entire formulation, even at 100 ppm. Cyproconazol exhibited enhanced permeation with prolonged exposure time and higher concentrations in both matrices. Co-formulants showed varied localization patterns, with carrier solvents resembling the permeation of cyproconazole and emulsifiers remained primarily at the surface.

8:30am **BI1-TuM-3 Imaging 3D Cell Culture Systems*, Sally McArthur,*** Deakin University, Australia

Imaging three dimensional cell and tissue systems is central to our fundamental understanding of tissue engineered materials. We need to be able to look at the cell morphology, scaffold architecture and their specific interactions. By combining a range of tools we have explored how biomaterials and cells interact in 3D and the reproducibility of 3D cell culture systems. This talk is submitted as part of the celebration of Prof Stephanie Allen's career.

8:45am **BI1-TuM-4 SIMS for Label-Free in situ Analysis of Glycosaminoglycans*, Li Jennifer Lu,*** University of Nottingham, UK*; J. Hippensteel,* University of Colorado - Anschutz Medical Center*; K. Grobe,* University of Münster, Germany*; C. Gorzelanny,* University Medical Center Hamburg - Eppendorf, Germany*; A. Kotowska, D. Scurr, A. Hook,* University of Nottingham, UK

Glycosaminoglycans (GAGs) are linear polysaccharide chains with many varied roles in physiology, including embryonic patterning and modulation of blood vessel permeability. Despite their biological importance, their *in-situ* analysis is limited by a lack of analytical tools with which to study their complex structure. Here we present the development of secondary ion mass spectrometry (SIMS) for *in-situ* GAG analysis [1], allowing for simultaneous spatial and compositional analysis. Initially, a list of characteristic ions for different GAG types was identified using high mass resolution analysis using an Orbi-trap mass analyser of a library of reference GAGs. These GAG-derived ions were validated using a range of biosynthetic enzyme knockout cellular models. This approach has been used to spatially assess the distribution of varied GAG types within complex tissues, including a sepsis model and to explore embryogenesis within *Drosophila*. Additionally, the depth profiling capability of SIMS enables 3D imaging of GAG ions within samples. This demonstrated ToF-SIMS as a powerful analytical tool to spatially analyse (at near optical resolution) GAG type and composition within a single analysis across multiple biological sample types.

References

1. Hook, A.L., Hogwood, J., Gray, E. et al. High sensitivity analysis of nanogram quantities of glycosaminoglycans using ToF-SIMS. Commun Chem 4, 67 (2021).

9:00am **BI1-TuM-5 Tribochemical Nanolithography – Fast, Simple Biomolecular Nanopatterning with 23 nm Resolution at Speeds of up to 1 mm s-1*, O. Siles-Brugge, C. Ma, A. Meijer, Graham Leggett,*** University of Sheffield, UK

Films formed by the adsorption of (methoxyheptaethylene glycol) nitrophenylethoxycarbonyl-protected aminopropyltriethoxysilane (OEG-NPEOC-APTES) on silica are highly resistant to the adsorption of proteins. On exposure to UV light, the photocleavable protecting group is removed allowing the immobilization of biomolecules.

We have discovered that the same result can be achieved using an AFM probe at a load of ca. 100 nN in the absence of UV light. A FWHM of 23 nm can be achieved at a writing rate of 1 mm s^{-1}. The FWHM increases with load, reaching 90 nm at a load of 10 μN. At larger loads than this an abrupt transition occurs to a regime dominated by mechanical abrasion, yielding broader features. However, for control films that do not contain photo-removable protecting groups, lithographic modification was not observed at loads below 10 μN.

We hypothesize that at low loads the AFM probe causes selective cleavage of the same C-N bond in the carbamate group that is cleaved during UV irradiation. Consistent with this, we found that patterned surfaces can be derivatized with nitrilotriacetic acid (NTA) functional groups, enabling coupling of His-tagged green fluorescent protein (GFP) to the surface.

Confocal fluorescence microscopy confirms that GFP attaches to nanolines, but is released when the samples are treated with imidazole, which disrupts the interaction between NTA and the His tag on the protein, consistent with site-specific binding.

The effect of compression on the nitrophenyl protecting group was explored using density functional theory (DFT). Our results indicate that compression of the nitrophenyl group causes substantial changes in its electronic structure. In particular, the energy of the main energetic barrier in the photodeprotection scheme, the initial S_0 to S_1 transition, is greatly reduced, so that deprotection may occur at near IR wavelengths. Hence, application of the AFM probe facilitates deprotection by low energy photons, while UV photons are required in the absence of a mechanical deformation.

The methodology may also be applied to the fabrication of polymer nanostructures. Tribochemical nanolithography of nitrophenylpropyloxyoxycarbonyl protected aminopropyl triethoxysilane (NPPOC-APTES) films yields amine-functionalised nanolines that are functionalized with bromine initiators and used to grow surface-grafted polymer brushes. Polymer chains grafted to the smallest nanolines are collapsed, because they have a high free volume and because adsorption to the surrounding surface is energetically favourable. However, as wider structures are formed, the chains repel each other and begin to swell away from the surface.

9:15am **BI1-TuM-6 Nanoprobe X-Ray Fluorescence Analysis of Frozen-Hydrated Biological Samples - from 2D to 3D**, ***Axel Rosenhahn***, *C. Rumancev, L. Jusifagic, A. Gräfenstein,* Ruhr University Bochum, Germany

The accumulation of metals and the homeostasis of ions in biological cells and tissue is of fundamental relevance for a wide range of environmental, biological, and medical processes. Synchrotron-based nanoprobe X-ray fluorescence analysis provides a unique combination of metal analysis with high spatial resolution, a high penetration depth, and high sensitivity down to trace concentrations. In the last years we developed several endstations for the analysis of cryogenically prepared biological samples at the P06 beamline at Petra III. Cryopreservation is the gold standard if cells are meant to be analyzed in a preserved state that is as close as possible to their natural, hydrated state. In particular for highly soluble ions, such as potassium, cryopreservation is the only way to obtain accurate concentrations. The new technique has been used to analyze the stress response of cells to the presence of Huntingtin aggregates, which are currently hypothesized to be responsible for the consequences of the corresponding disease. Also, the intracellular distribution of different metal-based cytostatic compounds has been analyzed and compared to the cellular stress response as reflected by changes in the intracellular potassium level. In addition to the 2D imaging experiments, a new tomography setup has been developed that allows cross-sectional imaging of biological samples to image metal distributions. A novel self-absorption correction during the tomographic reconstruction has been implemented that compensates artefacts especially for light elements due to the limited photon-escape depth.

9:30am **BI1-TuM-7 Harnessing Plasmon-Enhanced Fluorescence for Ultrasensitive and Minimally-Invasive Bio-Diagnostics**, ***Srikanth Singamaneni,*** Washington University in St. Louis **INVITED**

Detection, imaging, and quantification of low-abundant biomolecules within biological fluids, cells, and tissues is of fundamental importance but remains extremely challenging in biomedical research as well as clinical diagnostics.We have designed and synthesized an ultrabright fluorescent nanoconstruct, termed “plasmonic-fluor”, as an “add-on” bio-label to dramatically improve the signal-to-noise ratio of a wide variety of existing fluorescence bioassays without altering or complicating the conventional assay workflow or read-out devices.We demonstrate that these novel nanoconstructs can be readily utilized in a broad range of bioanalytical methods, including fluorophore-linked immunosorbent assays, multiplexed bead-based immunoassays, lateral flow assays, immuno-microarrays, flow cytometry, and immunocytochemistry, to attain more than 1000-fold improvement in the limit-of-detection and dynamic range.Harnessing plasmonic-fluors, we also demonstrate minimally-invasive and ultrasensitive quantification of target protein biomarkers in interstitial fluid through microneedle-assisted *in vivo* sampling and subsequent on-needle analysis.With the microneedle patch, we demonstrate minimally-invasive evaluation of cocaine vaccine efficiency and longitudinal monitoring of inflammatory biomarker levels in mice.

Biomaterial Interfaces
Room 117 - Session BI2-TuM
Characterization of Biological and Biomaterial Surfaces II

Moderators: Morgan Hawker, California State University, Fresno, **Sapun Parekh**, University of Texas at Austin

11:15am **BI2-TuM-14 Native Supported Lipid Bilayers: A Bioanalytical Tool to Study and Detect Viruses**, ***Marta Bally***, *H. Pace,* Umea University, Sweden **INVITED**

Cellular membranes are complex dynamic structures consisting of a lipid bilayer containing a multitude of biomolecules, including a variety of lipids, proteins and carbohydrates. Systematic investigations of biomolecular processes at the cell surface call for the development of bioanalytical platforms capable to recapitulate, in vitro and under well-controlled experimental conditions, this compositional complexity while maintaining the membrane´s basic physico-chemical properties (e.g. membrane fluidity). In this context, we present native supported lipid bilayers (nSLBs), two-dimensional fluid planar bilayers produced from purified cellular plasma membranes and mounted on a solid support as a promising tool. [1,2] These cell-free systems provide the compositional complexity of nature, yet they are free from metabolic feedback loops. They are a snapshot of the membrane’s composition at the moment of cell lysis, providing hundreds of experiments with the exact same membrane composition. They further allow for optimal instrumental accessibility, being compatible with a broad range of surface-sensitive biosensing tools.

In our work, we take advantage of nSLBs to characterize virus- membrane interactions [2]. The combination of nSLBs with total internal reflection fluorescence microscopy allows us to quantitatively assess the attachment, detachment, and diffusion behavior of individual virus particles at the cell membrane and to address a variety of fundamental questions related to viral attachment and entry. Specifically, this experimental approach was used to (i) study how SARS-CoV-2 changes its interaction with the plasma membrane when evolving and mutating [3], (ii) investigate the role of a cellular factor in modulating HSV-1 interactions at the cell surface [4] and (iii) to study how different carbohydrate moieties modulate the dynamics of norovirus-membrane interactions [5].

Taken together, our research contributes to a better understanding of the mechanisms regulating the interaction between a virus and the surface of its host. Such insights will without a doubt facilitate the design of more efficient antiviral drugs or vaccines.

[1] Pace at al., Analytical Chemistry, **87(18)** (2015)

[2] Peerboom, N. et al., ACS Infect. Dis. **4 (6)**, (2018)

[3] Conca, D. et al., Biorxiv (2024), https://doi.org/10.1101/2024.01.10.574981

[4] Liu, L. et al., Biorxiv (2023) ¸https://doi.org/10.1101/2023.02.10.526562

[5] Pace, et al., In manuscript.

11:45am **BI2-TuM-16 Force Probe Techniques for Probing Biologic and Lipid Bilayer Interactions Under Physiological Conditions**, ***Markus Valtiner***, *L. Mears, I. Peters,* TU Wien, Austria

Quantification of biologic interactions - from single molecular to macroscopic interfaces - is essential for understanding function in living systems. We will provide a short overview of force probe techniques (AFM, SFA, and optical tweezers) and will then discuss lipid bilayer interactions, and single molecular interaction measurements (under potential control) in detail. These are essential to a vast range of biological functions, such as intracellular transport mechanisms. Surface charging mediated by concentration dependent ion adsorption and desorption on lipid headgroups alters electric double layers as well as van der Waals and steric hydration forces of interacting bilayer and molecules. Two examples will be discussed:

First, we characterized the interaction between single hydrophobic molecules quantitatively using atomic force microscopy, and demonstrated that single molecular hydrophobic interaction free energies are dominated by the area of the smallest interacting hydrophobe. The interaction free energy amounts to 3–4 kT per hydrophobic unit. Also, we find that the transition state of the hydrophobic interactions is located at 3 Å with respect to the ground state, based on Bell–Evans theory.

Further, we directly measure bilayer interactions during charge modulation in a symmetrically polarized electrochemical three-mirror interferometer

surface forces apparatus. We quantify polarization and concentration dependent hydration and electric double layer forces due to cation adsorption/desorption. Results demonstrate that exponential hydration layer interactions effectively describe surface potential dependent surface forces due to cation adsorption at high salt concentrations. Hence, electric double layers of lipid bilayers are exclusively dominated by inner Helmholtz charge regulation under physiological conditions. These results are important for rationalizing bilayer behavior under physiological conditions, where charge and concentration modulation may act as biological triggers for function and signaling.

We will finally provide an outlook on combining all force probe techniques with electrochemical potential modulation.

Biomaterial Interfaces
Room West Hall - Session BI-TuA

Future of Biointerface Science Collection (ALL-INVITED SESSION)

Moderators: Kenan Fears, U.S. Naval Research Laboratory, **Tobias Weidner**, Aarhus University, Denmark

2:45pm **BI-TuA-3 Adsorption of Cytochrome C on Different Self-Assembled Monolayers:the Role of Surface Chemistry and Charge Density**, ***Shengjiang Yang,*** School of Chinese Ethnic Medicine, Guizhou Minzu University, Key Laboratory of Guizhou Ethnic Medicine Resource Development and Utilization, China*; C. Peng,* School of Chemistry and Chemical Engineering, Guangdong Provincial Key Lab for Green Chemical Product Technology, South China University of Technology, China*; J. Liu,* Key Laboratory for Green Chemical Process of Ministry of Education, School of Chemical Engineering and Pharmacy, Wuhan Institute of Technology, China*; H. Yu, Z. Xu,* School of Chemistry and Chemical Engineering, Guangdong Provincial Key Lab for Green Chemical Product Technology, South China University of Technology, China*; Y. Xie,* Guangdong Provincial Key Laboratory of Electronic Functional Materials and Devices, Huizhou University, China*; J. Zhou,* School of Chemistry and Chemical Engineering, Guangdong Provincial Key Lab for Green Chemical Product Technology, South China University of Technology, China **INVITED**

Contradictory results regarding cytochrome c (Cyt-c) adsorption onto different self-assembled monolayers (SAMs) have been reported. In this work, the adsorption behavior of Cyt-c on five different SAMs (i.e., CH_3-SAM, OH-SAM, NH_2-SAM, COOH-SAM and OSO_3^--SAM) were studied by combiningparallel tempering Monte Carlo and molecular dynamics simulations. The results show that Cyt-c binds to the CH_3-SAM through a hydrophobic patch (especially Ile81)and undergo a slight reorientation, while the adsorption on the OH-SAM is relatively weak.Cyt-c cannot stably bind to the 7% protonated NH_2-SAM even under a relatively high ionic strength condition, while a higher surface charge density (SCD, 25% protonated) promotes its adsorption. The preferred adsorption orientations of Cyt-c on the negatively charged surfaces are very similar, regardless of the surface chemistry and SCD. As the SCD increases, more counterions are attractedto the charged surfaces, forming distinct counterion layers.The secondary structure of Cyt-c is well-kept when adsorbed on all these SAMs.The deactivation of redox properties for Cyt-c adsorbed on the CH_3-SAM and highly negatively charged surface (OSO_3^--SAM) is due to the confinement of heme reorientation and the farther position of the central iron to the surfaces.This work may provide insightful guidance for the design of Cyt-c-based bioelectronic devices and controlled enzyme immobilization.

3:00pm **BI-TuA-4 Spatiotemporal Control of Cellular Signaling Cues in 3D Biointerfaces for Tailored Cellular Functionality**, ***Sadegh Ghorbani,*** Stanford University*; D. Sutherland,* Aarhus University, Denmark **INVITED**

A promising research direction in the field of biological engineering is the development of programmable three-dimensional (3D) biointerfaces designed to support living cell functionality and growth in vitro, offering a route to precisely regulate cellular behaviors and phenotypes for addressing therapeutic challenges. While traditional two-dimensional (2D) biointerfaces have provided valuable insights, incorporating specific signaling cues into a 3D biointeractive microenvironment at the right locations and time is now recognized as crucial for accurately programming cellular decision-making and communication processes.The incorporation of advanced biomaterials, capable of responding to cellular cues and environmental changes, offers unique opportunities for creating these 3D environments. Emerging technologies, including nucleic acid nanotechnology (e.g., DNA origami, aptamers) and click chemistry, along with smart biomaterials, could further enhance the capabilities of these 3D biointerfaces. These tools allow for the submicrometer spatial organization of biomolecules over time, enabling the selective addition, removal, or shielding of signaling components through strand displacement or conformationally switched constructs. Leveraging these innovative tools also allows cell-membrane engineering, thereby enabling the precise organization of cells in appropriate spatial and temporal contexts to promote the formation of multicellular arrangements enhancing overall functionality. Developing cell-focused environments using 3D biointerfaces that deliver specific spatial and temporal signals can replicate complex biological functions into a finite set of growing cellular organizations. Additionally, they provide insights into the hierarchical logic governing the relationship between molecular components and higher-order multicellular functionality. The functional live cell-based microenvironment engineered through such innovative biointerfaces has the potential to be used as an in vitro model system for expanding our understanding of cellular behaviors or as a therapeutic habitat where cellular functions can be reprogrammed.

3:15pm **BI-TuA-5 Exploring the Dynamics of Proteins, Nucleic Acids, and Their Interplay by Coherent Anti-Stokes Raman Spectroscopy**, ***Pablo G. Argudo,*** *M. Brzezinski,* Max Planck Institute for Polymer Research, Germany*; W. Chen, B. Dúzs, A. Samanta, A. Walther,* Johannes Gutenberg University, Germany*; S. H. Parekh,* The University of Texas at Austin **INVITED**

The comprehension of proteins and nucleic acid chains, along with their interactions, is vital in contemporary biochemistry and molecular biology. These molecules can induce biological phase separation, resulting in the formation of membraneless organelles (MLOs) within cells. Consequently, understanding their structure is key, as it directly influence their ultimate behaviour. Moreover, external factors or interactions can directly impact their characteristics and final function, as evidenced in degenerative diseases like amyotrophic lateral sclerosis (ALS) or frontotemporal dementia (FTD).

In this context, we present the employment of Coherent Anti-Stokes Raman spectroscopy (CARS) as an appropriate method to characterize the changes happening over time in condensates. By examining the fingerprint region of nucleic acids, we can determine the biological interactions taking place. In designed DNA condensate model systems, ssDNA to dsDNA hybridization or salt effects can be monitored in the final assembled conformation. For proteins, their secondary structure can be elucidated, ranging from an ordered α-helix or β-sheet to a disordered random coil. Finally, protein-RNA interactions can be also characterized, as for TDP-43 low complexity domain (TDP43-LCD) and RNA. While introducing further complexity, the Raman shifts observed in specific regions of the formed condensates can indicate the RNA's effect on the protein, including secondary structure control.

Electronic Materials and Photonics
Room 114 - Session EM+2D+BI+QS+TF-TuA

Advances in Photonic Materials and Devices

Moderators: Leland Nordin, University of Central Florida, **Philip Lee**, University of Kentucky

2:15pm **EM+2D+BI+QS+TF-TuA-1 New Materials for Metamaterials: Electrochemical Materials and Switchable Chiral Nanostructures**, ***Vivian Ferry,*** University of Minnesota **INVITED**

Alternative materials for metasurfaces enable new properties and lay the foundation for advantage applications. This talk will discuss two strategies for new, tunable metasurfaces. The first part of the talk will discuss the use of electrolyte gating to control the optical properties of materials, focusing on $La_{1-x}Sr_xCoO_{3-d}$ (LSCO) as an exemplary case. We fabricate electric double layer transistors using LSCO and an ion gel, and under application of positive gate voltage gating facilitates the formation and migration of oxygen vacancies, and a transition from a perovskite phase to an oxygen-vacancy-ordered brownmillerite phase. This is accompanied by substantial change in optical properties, as measured with spectroscopic ellipsometry. The talk will discuss how LSCO can be incorporated with metasurfaces to produce tunable optical response. The second part of the talk will discuss chiral metamaterials, and particularly novel materials comprised of nanopatterned, light emitting nanocrystals with simultaneous control over both directionality and polarization state.

2:45pm **EM+2D+BI+QS+TF-TuA-3 Optoelectronic Nanowire Neuron**, ***Thomas Kjellberg Jensen,*** Lund University, Sweden*; J. E. Sestoft,* Niels Bohr Institute, Denmark*; D. Alcer, N. Löfström, V. Flodgren, A. Das,* Lund University, Sweden*; R. D. Schlosser, T. Kanne Nordqvist,* Niels Bohr Institute, Denmark*; M. Borgström,* Lund University, Sweden*; J. Nygård,* Niels Bohr Institute, Denmark*; A. Mikkelsen,* Lund University, Sweden

Three different semiconductor nanowires are combined into a single optoelectronic artificial neuron. In general, artificial neurons sum and weight input signals, and output a signal according to a non-linear function which may be sigmoid-shaped (a generalized artificial neuron is shown in Fig. 1a). Figure 1b schematically shows the artificial neuron realized using nanowires. Here, neural excitation/inhibition is achieved by balancing inputted light across two pin-diode nanowires outputting a summed voltage measured by a nanowire-based field-effect transistor (FET).

The false-colored electron microscope image shown in Figure 1c depicts the fabricated nanowire neuron. In Figure 1d we show the current measured across the FET nanowire as a function of laser beam position, demonstrating the excitatory and inhibitory behavior. Selectively illuminating the excitatory nanowire diode, the change in conductance follows a sigmoidal curve as a function of linearly increasing light intensity (Figure 1e) – the necessary non-linear part of a neural network. Taken together, these properties provide the device with the basic functionalities needed for a neuromorphic computing node [1,2]. Future measurements will explore the time-domain effects.

Our artificial neuron provides a promising future platform for combining diverse materials with low power consumption and significantly reduced circuit footprint, this way addressing critical limitations for future-proofing photonics-based applications in neuromorphic computing.

REFERENCES:

[1] D. O. Winge, S. Limpert, H. Linke, M. T. Borgström, B. Webb, S. Heinze, and A. Mikkelsen, "Implementing an insect brain computational circuit using III-V nanowire components in a single shared waveguide optical network", *ACS Photonics*, vol. 10, pp. 2787-2798, 2020.
[2] D. Winge, M. Borgström, E. Lind, and A. Mikkelsen, "Artificial nanophotonic neuron with internal memory for biologically inspired and reservoir network computing"*, Neuromorph. Comput. Eng.*, vol. 3, no. 034011, 2023.

3:00pm **EM+2D+BI+QS+TF-TuA-4 Modulation of Optical and Plasmonic Properties of Epitaxial and Precision Titanium Nitride Thin Films***, I. Chris-Okoro,* North Carolina A&T State University*; S. Cherono,* North Carolina A & T State Uni*; C. Martin,* Ramapo College of New Jersey*; V. Craciun,* National Institute for Laser, Plasma, and Radiation Physics, Romania*; S. Kim, J. Mahl, J. Yano,* Lawrence Berkeley National Laboratory*; E. Crumlin,* Lawrence Berkeley Lab*; D. Kumar,* North Carolina A & T State Uni*;* ***Wisdom Akande****,* North Carolina A&T State University

The present study arises from the need for developing negative-permittivity materials beyond commonly employed plasmonic metals (e.g., Au, Ag), which are often incompatible (i.e., low melting point, mechanically soft, chemically unstable) with real operating environments. This work reports a pulsed laser-assisted synthesis, detailed structural characterization using x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), x-ray absorption spectroscopy (XAS), Rutherford Backscattering spectroscopy (RBS), and plasmonic properties of three sets of TiN/TiON thin films. The first two sets of TiN films were grown at 600 and 700 °C under a high vacuum condition (≤2 ×10^{-7} Torr). The third set of TiN film was grown in the presence of 5 mTorr of molecular oxygen at 700 °C. The purpose of making these three sets of TiN/TiON films was to understand the role of film crystallinity and the role of the oxygen content of TiN films on their optical and plasmonic properties. The results have shown that TiN films deposited in a high vacuum are metallic, have large reflectance, and high optical conductivity. The TiN films, grown in 5 mTorr, were found to be partially oxidized with room temperature resistivity nearly three times larger than those of the TiN films grown under high vacuum conditions.

The optical conductivity of these films was analyzed using a Kramers-Kronig transformation of reflectance and a Lorentz-Drude model; the optical conductivity determined by two different methods agrees very well. The good agreement between the two methods is indicative of a reliable estimate of the absolute value of reflectance in the first place. The existence of significant spectral weight below the interband absorptions is shared between two Lorentzians, one around 250 cm^{-1} and one around 2,500 cm^{-1}. We discuss here the dependence of the two bands on the deposition conditions and their effect on the plasmonic performances of TiN/TiON thin films, in particular on the surface plasmon polariton (SPP) and localized surface plasmon resonance (LSPR) quality factors.

This work was supported by the NSF PREM on the Collaborative Research and Education in Energy Materials (CREEM) via grant # DMR-2122067 and the DOE EFRC on the Center for Electrochemical Dynamics And Reactions on Surfaces (CEDARS) via grant # DE-SC0023415.

3:15pm **EM+2D+BI+QS+TF-TuA-5 Nano-Focusing and Characterization of the OAM Beam Through an Optical Fiber Using Plasmonic Nanostructure***, Rohil Kayastha, W. Zhang, B. Birmingham,* Baylor University*; Z. Gao,* Texas A&M University*; J. Hu,* Baylor University*; R. Quintero-Torres,* UNAM, Mexico*; A. V. Sokolov,* Texas A&M University*; Z. Zhang,* Baylor University

Optical vortex beam has been used in many applications such as nanoscale imaging, telecommunication, sensing, and so on due to its unique azimuthal phase distribution. Many of these applications utilize optical fibers as a sensor or to propagate the beam to transmit data and information. The vortex beam carrying an orbital angular momentum (OAM) has a phase singularity giving the beam a doughnut intensity profile. Due to its helical wavefront nature, the vortex beam carrying OAM has also been used to distinguish the enantiomers of the chiral molecule. However, coupling efficiency remains a problem due to the size mismatch of the beam and the molecule. Our work uses vortex fibers with plasmonic nanostructures to nano-focus the vortex beam to enhance the coupling between light and chiral matter. To achieve this goal, characterization of vortex beam in free space and through vortex fiber (a polarization-maintaining ring core optical fiber), and fabrication of nanostructure on fiber facet were performed.

Generation and propagation of OAM beams were characterized in free space and through a vortex fiber. The free-space OAM beam was coupled and transmitted successfully through the vortex fiber with a pure and stable output beam. The helicity characterization and polarization analysis of the free-space and fiber-coupled output vortex beams showed consistent polarization and OAM. The direction of the phase front was maintained after propagation of the OAM through the vortex fiber, as observed from the spiral interference pattern. Nano-focusing of the OAM beam using nanostructure on the fiber facet was observed from the simulation. The circular array of plasmonic nanobars was fabricated on the fiber facet core, and the far-field image of the output OAM beam was observed after transmission through the fiber with the nanostructure. The near-field image of the nano-focused OAM beam on the fiber will be investigated using a near-field scanning optical microscope (NSOM). The focusing of the OAM beam on a fiber facet with the nanostructure could enhance the coupling efficiency of the beam with chiral molecules. The nano-focused OAM on the fiber could be used as a scanning and sensing probe for single-molecule chirality detection.

4:00pm **EM+2D+BI+QS+TF-TuA-8 Templated Block Copolymer Network Thin Films as 3D Chiral Optical Metamaterials: Connecting Finite-Difference Time-Domain and Self-Consistent Field Theory Simulations***, E. McGuinness, B. Magruder, P. Chen, K. Dorfman, C. Ellison,* ***Vivian Ferry****,* University of Minnesota

Optical metamaterials, whose properties depend not only on material selection but also the spatial arrangement of the material, provide access to interactions with light that are not present in bulk materials alone. Block copolymer self-assembly is a scalable method for creating 3D spatially periodic nanoscale structures to act as metamaterial templates. The gyroid morphology, whose curved, percolating structure is composed of triply connected struts, possesses chiral elements such as helices in bulk and chiral structures at certain surface terminations. As a result of their chirality, when templated with a plasmonic material, gyroids exhibit circular dichroism (CD) with applications in anti-counterfeit as well as molecular and protein sensing. While many optical simulations of gyroids assume a perfect cubic structure, most applications utilize thin films whose processing results in distortions such as compression normal to the substrate or surface rearrangements due to interactions with interfaces. Distorted gyroids, as well as the growing library of additional network structures possible from block copolymer self-assembly, are increasingly challenging to model from a purely mathematical basis and require better basis in physical reality. Combining the output of polymer self-consistent field theory (SCFT) with finite-difference time-domain (FDTD) optical simulations enables the exploration of thermodynamically equilibrated structures for both distorted gyroids and expanded network geometries. This presentation will investigate the CD response of compressed double gyroid thin films as well as that of newly hypothesized network structures such as H^{181}. In the first example, compression of (110) oriented silver double gyroid thin films yields a switching phenomenon from left to right circularly polarized light preferential absorption, offering the potential for dynamic systems (**Figure 1a**). Mechanistically, this behavior depends both on the surface and sub-surface structures of the compressed double gyroids. In the second example, (001) oriented silver templated thin films of the newly computationally uncovered H^{181} structure are shown to support a broadband visible light CD response (spanning 200 nm) with a g-factor (CD normalized to average absorption) of at least 0.14 across that entire wavelength range (**Figure 1b**). Overall, this work moves the optical simulations of metamaterials from block copolymers closer those physically realized, introducing additional opportunities for engineering their optical response.

4:15pm **EM+2D+BI+QS+TF-TuA-9 Solution Processing of Optical Phase Change Materials**, ***Brian Mills,*** Massachusetts Institute of Technology*; R. Sharma, D. Wiedeman,* University of Central Florida*; C. Schwarz,* Ursinus College*; N. Li,* Massachusetts Institute of Technology*; E. Bissell,* University of Central Florida*; C. Constantin Popescu,* massachusetts Institute of Technology*; D. Callahan,* Charles Stark Draper Laboratory, Inc.*; P. Banerjee, K. Richardson,* University of Central Florida*; J. Hu,* Massachusetts Institute of Technology

Chalcogenide optical phase change materials (O-PCM) serve as the functional material in a variety of non-volatile photonic devices, from reconfigurable metasurface lenses to tunable integrated photonic resonators. Although a handful of high figure of merit O-PCMs have been identified and implemented in prototype devices, the space of O-PCM composition remains relatively unexplored, precluding the possibility of application specific choices in material composition that optimize device performance. This is due, in large part, to the lack of time and cost efficient methods for O-PCM thin film deposition and characterization, for which vacuum chamber deposition is the most common method. In this work, we present the first implementation of a solution processing approach for O-PCM film synthesis and deposition, providing evidence of the method's viability in creating high quality, functioning O-PCM films with close adherence to target stoichiometry. This method serves as a robust platform for materials exploration of O-PCM composition and allows for the identification of candidate O-PCM, as well as an understanding of the effect of compositional changes in O-PCM optical and cycling properties.

4:30pm **EM+2D+BI+QS+TF-TuA-10 Effects of Ce Concentration on the Microstructural, Optical, and Luminescence Properties in Ce:GAGG Ceramic Phosphors**, ***William Bowman,*** *S. Lass,* University of Central Florida*; F. Moretti, W. Wolszczak,* Lawrence Berkeley National Laboratory*; R. Gaume,* University of Central Florida

Efficient luminescence and optical quality are necessary phosphor attributes for applications such as down-conversion layers in photovoltaics and computed tomography. Cerium-doped gadolinium aluminum gallium garnet (Ce:GAGG) is highly applicable for these purposes. It has been shown in other garnet hosts such as Ce:YAG and Ce:LuAG that Ce concentration alters both the luminescence and optical properties of the materials. In the case of Ce:GAGG single crystals and Ce concentrations lower than 1 at%, radioluminescence decay constants decrease by increasing the Ce concentration while light yield reaches a maximum at 0.3 at%. For Ce:GAGG ceramics, the effect of Ce concentration on these properties has not been systematically investigated. There is at current no work on determining the solid solubility limit of Ce in GAGG, which is critical in controlling the development of secondary phases and subsequent optical quality.

This study aims to investigate the effects of Ce concentration on the microstructural, optical, and luminescence properties of GAGG optical ceramics with dopant concentrations in the 0.1at% to 10at% range. Transmission of the material increases with increasing Ce concentration up to 5.0at%. At the same time, the optical and luminescence properties of these samples show a complex evolution upon Ce concentration, highlighting the complex interplay among optical characteristics of the samples, concentration-related luminescence quenching phenomena, and charge carrier trapping defects.

This material is based upon work supported by the U.S. Department of Homeland Security under Grant Award Number 20CWDARI00038-01-00. The views and conclusions contained in this document are those of the authors and should not be interpreted as necessarily representing the official policies, either expressed or implied, of the U.S. Department of Homeland Security.

4:45pm **EM+2D+BI+QS+TF-TuA-11 Solution Based Processing of $Ge_2Sb_2Se_4Te_1$ Phase Change Material for Optical Applications**, ***Daniel Wiedeman,*** *R. Sharma, E. Bissel, P. Banerjee,* University of Central Florida*; B. Mills, J. Hu,* Massachusetts Institute of Technology*; M. Sykes, J. Stackawitz, J. Lucinec, C. Schwarz,* Ursinus College*; K. Richardson,* University of Central Florida

Chalcogenide based phase change materials are important for creating novel optical and photonic devices, improving on current devices for future applications. Solution processing, via dip coating, spin coating, or drop-casting, is a low-cost, high-throughput alternative method of depositing thin films, which allows for greater composition diversity. In this work, we performed a detailed systematic study of the solution derived drop-casted film of Ge2Sb2Se4Te1 alloy in an ethylenediamine and ethanedithiol mixture. The composition, morphology and structural properties of the films were analyzed by employing scanning electron microscopy, energy dispersive X-ray spectroscopy, Raman spectroscopy, and X-ray diffraction. Our findings provide insight into a potential route for scalable $Ge_2Sb_2Se_4Te_1$ films.

5:00pm **EM+2D+BI+QS+TF-TuA-12 Multi-Dimensional p-WSe_2/n-Ga_2O_3 Enhancement-Mode Phototransistors for Stand-Alone Deep-Ultraviolet Sensing**, *J. Kim,* ***Soobeen Lee,*** Seoul National University, South Korea

β-Ga_2O_3 is an ultra-wide bandgap (UWBG) semiconductor with a bandgap of 4.9 eV, resulting in a high breakdown field of approximately 8 MV/cm and a high Baliga's figure-of-merit. β-Ga_2O_3 is a promising material for deep-ultraviolet (DUV) photodetector (PD) applications due to its direct bandgap of 4.9 eV, excellent thermal stability, and high absorption coefficient. Self-powered β-Ga_2O_3 PDs can be realized through p-n heterojunction (HJ) field-effect transistor architectures, exhibiting normally-off operation owing to the depletion region in the β-Ga_2O_3 channel. With intrinsic n-type conductivity caused by unintentional doping and challenges in p-type doping, fabricating self-powered β-Ga_2O_3 PDs necessitates combining β-Ga_2O_3 with p-type semiconductors such as transition-metal dichalcogenides (TMDs), nickel oxide, or silicon carbide. Tungsten diselenide (WSe_2), one of the TMDs, stands out as a promising material with a high monolayer mobility of approximately 180 $cm^2V^{-1}s^{-1}$. Their dangling-bond-free surfaces provide an advantage in forming sharp interfaces with other materials in HJs. Moreover, efficient p-type doping of WSe_2 is achieved via charge transfer by utilizing the high electron affinity of its self-limiting oxide, sub-stoichiometric tungsten oxide (WO_{3-x}), which is used as a dopant.

In this work, we introduce normally-off p-WSe_2/n-β-Ga_2O_3 phototransistors and demonstrate their self-powered operation under 254 nm light. p-Type WSe_2 was realized through charge transfer doping of WO_{3-x} formed by O_3 treatment, and the p-type doping effect of this oxide was confirmed through electrical characteristics. The cross-sectional structure of the fabricated p-WSe_2/n-β-Ga_2O_3 phototransistors was analyzed, and the electrical and optical properties were evaluated before and after WSe_2 oxidation. The device demonstrated a responsivity of 2 A/W under 254 nm light without an external bias, surpassing the performance of previously reported p-n HJ-based β-Ga_2O_3 PDs. Furthermore, we investigate the enhanced optoelectronic performance of multi-dimensional β-Ga_2O_3 phototransistors with plasmonic metal nanoparticles. In this presentation, we will discuss the potential of the self-powered multi-dimensional DUV β-Ga_2O_3 PDs with improved performance and their prospects in practical applications.

This work was supported by Korea Institute for Advancement of Technology (KIAT) grant funded by the Korea Government (P0012451, The Competency Development Program for Industry Specialist) and the Korea Research Institute for defense Technology planning and advancement (KRIT) grant funded by Defense Acquisition Program Administration (DAPA) (KRIT-CT-21-034, and KRIT-CT-22-046).

Biomaterial Interfaces
Room Central Hall - Session BI-ThP
Biomaterial Interfaces Poster Session

BI-ThP-1 Optimizing Regenerative Cell Infiltration in Vascular Grafts: Enhanced Strategies to Engineer Pore Microstructures During Fabrication, ***Aurora Battistella,*** University of Colorado at Boulder

Introduction: In tissue engineering, the goal is to create scaffolds that seamlessly integrate into the human body, guiding native tissue regeneration while slowly degrading. A crucial aspect of this process is achieving scaffold infiltration of functional cells. The initial phase centered on the material aspect, particularly different polymer behaviors, including degradation rates. Production methods represent another modifiable parameter to fine-tune the device structure, especially its porosity. Additionally, post-fabrication techniques can refine the microstructure and enhance interaction with the human body. The investigation originated with a control group, PCL+PEG-NB coaxially electrospun and air-dried. Ultimately, four groups were created by systematically altering one or more parameters and examined to assess their impact.

Methods: Coaxial electrospinning was used to achieve a strong core (PCL/PLCL) surrounded by a functionalized sheath (PEG-NB). The mixed condition was fabricated by directly blending sheath and core solutions for electrospinning. Samples were air-dried or freeze-dried. Surface topography, including fiber structure and porosity, was investigated by SEM. Uniaxial tensile testing was adopted to determine the impacts of different parameters on the mechanical properties of the graft. The groups were implanted subcutaneously and explanted at various time points (1, 4, and 16 weeks). Histological and fluorescent analyses were performed to visualize tissue morphology and cellular penetration.

Results: Freeze-dried samples demonstrate higher Young's Modulus and higher porosity, and, consequently, increased cell infiltration than their air-dried counterparts. PLCL shows faster degradation and higher cell infiltration than PCL. However, PLCL was mechanically weaker and had a less rigid structure than PCL. Mixed fibers also displayed increased degradation compared to the control and were shown to be slightly weaker in tensile tests.

Conclusions: Through systematic experimentation, we have uncovered the benefits of freeze-drying in enhancing scaffold porosity and cell infiltration, while also highlighting the importance of selecting polymers with suitable degradation rates. Work is still ongoing to determine optimal fabrication parameters. Moving forward, these insights may help to guide the development of advanced vascular grafts with improved regenerative capabilities, paving the way for more effective clinical applications in tissue engineering.

BI-ThP-2 Mass-Manufactured Surface Textures Enable Low-Cost Large-Volume Water Analyte Detection and Location Tracking, ***Liza White,*** *C. Howell,* University of Maine

Timely detection of aqueous analytes is critical for agriculture, aquaculture, industry, and municipalities. Currently, testing methods are limited to small volumes and discrete, one-location samples. In this work, we show that an industrially manufactured nanotextured diffraction surface can provide aqueous analyte information across multiple locations over time. Specifically, the aqueous solution can be scanned by changing the location or angle of the light source and detector. By positioning the diffraction surface behind or below an aqueous matrix, the analyte's 3D spatial information and approximate size are determined. The identification and quantification of the analyte can also be determined based on the measurement of light absorbance and transmittance unique to the chemical or biological components of the analyte. The novel development of a sensor capable of large-volume scanning and analyte location detection is beneficial in numerous aqueous sensing capabilities, potentially transforming aqueous analyte monitoring methods.

BI-ThP-3 Low Fouling Amphiphilic Zwitterionic Carboxybetaine/Perfluoropolyether Methacrylate Polymer Coatings, ***Onur Özcan,*** *F. Koschitzki, R. Wanka, M. Krisam, A. Rosenhahn,* Ruhr University Bochum, Germany

Amphiphilic polymer systems have proven to be an effective and non-toxic approach to combat the challenges of biofouling.[1,2] We manufactured a variety of amphiphilic polymers consisting of carboxybetaine methacrylate (CBMA) and perfluoropolyether (PFPE) urethane methacrylate. These polymers were anchored to chemically functionalized substrates by photoinduced grafting-through polymerization.[1] Highly hydrated hydrogels may create a diffuse interphase and thus promote silt incorporation.[3] We were able to show that low amounts of PFPE already reduce silt uptake substantially. Captive bubble contact angle (CBCA) goniometry revealed that the polymer networks possess enough orientational freedom to quickly rearrange upon immersion in water. Dynamic diatom and bacteria accumulation assays revealed enhanced antifouling performances in most of the amphiphilic mixtures compared to the solely hydrophobic compound PFPE. We were further able to identify individual CBMA/PFPE compositions where the synergistic effect of hydrophilic and hydrophobic contents had the strongest impact on their marine anti-fouling and fouling-release properties.

[1] F. Koschitzki, R. Wanka, L. Sobota, J. Koc, H. Gardner, K. Z. Hunsucker, G. W. Swain, A. Rosenhahn ACS Appl. Mater, Interfaces 2020, 12, 34148-34160. [2] A. J. Ruiz-Sanches, A. J. Guerin, O. El-zubir, G. Dura, C. Ventura, L. I. Dixon, A. Houlton, B. R. Horrocks, N. S. Jakubovics, P. Guarda, G. Simeone, A. S. Clare, D. A. Fulton Prog. Org. Coat. 2020, 140, 105524 – 105533. [3] J. Koc, T. Simovich, R. Schoenemann, A. Chilkoti, H. Gardener, G. W. Swain, K. Hunsucker, A. Laschewsky, A. Rosenhahn Biofouling 2019, 35, 454-462

BI-ThP-4 Pore Size Impact on Oil-Release and Fouling Resistance of Macroporous Oil-Infused PDMS Systems, ***Regina Kopecz,*** *S. Böer, Z. Tiris, A. Rosenhahn,* Ruhr University Bochum, Germany

Since their invention, SLIPS have been known for their self-repairing properties, pressure stability, repellency of water and complex fluids, and low-fouling properties. We created a series of environmentally benign, non-fluorinated liquid paraffin-infused PDMS sponge systems with varying porosities including a thin interfacial PDMS membrane for controlled oil-release kinetics. Different pore volumes and varying interfacial roughness were fabricated by sugar and salt templating. The obtained porous polysiloxane networks were investigated using water contact angle goniometry, scanning electron microscopy, and light microscopy. The macroporous sponge systems revealed excellent oil-uptake and an oil-release between 3% and 14% of initial oil-loading during incubation in MilliQ water for seven days depending on the pore size. The resistance against bacterial fouling by dynamic attachment assays with the freshwater model organisms *Pseudomonas fluorescens*, *Escherichia coli*, and *Bacillus subtilis* was investigated. We found a correlation between bacterial adhesion and the porosity of the interface for the individual bacterial strains. As the porous polymer networks can be fabricated in any shape, they are promising low-fouling bulk materials for a wide range of applications in medicine.

BI-ThP-5 Advancing Catheter Care: Liquid-Infused Catheters as a Novel Approach to Combat CAUTIs, ***Zachary Applebee,*** *C. Howell,* University of Maine

Catheter-associated urinary tract infections (CAUTIs) pose a significant challenge in healthcare settings, leading to reduced patient outcomes, extended hospital stays, and increased healthcare costs. Although the current standard of care is to use systemic antimicrobials, there is growing concern that such treatment is contributing to the rise of antimicrobial resistance. Recently, liquid-infused catheters, in which a thin layer of biocompatible oil is used on the catheter surface, have emerged as a promising solution to reduce CAUTIs without the use of antimicrobials. In this work, we explore aspects of the use of liquid-infused catheters, including the potential for the liquid coating to be lost to the host as well as the integration of bioactive anti-inflammatory compounds into the coating. Our goal is to develop this novel technology further so that it can be translated into the clinic, helping to reduce CAUTIs without the need for antimicrobial treatment.

BI-ThP-6 Developing an Effective Coating Process for Nanoscale Cellulose Fibrils on Biodegradable Substrates, ***Sandro Zier,*** *D. Bousfield, C. Howell,* University of Maine

Bio-derived materials show the potential to replace plastic packaging with similar functionality while also having the advantage of biodegradability and recyclability. Cellulose, the most abundant polymer in the world, can be mechanically ground to have nanoscale dimension which provide good oil/grease and gas barrier properties. However, coating cellulose nanofibrils (CNF) as a thin film onto biodegradable substrates such as paper in a single step comes with significant challenges due to the unique way in which the CNF fibers interact with water. To overcome this challenge, we first simulated CNF coating onto paper to further understand the physics behind the process. We then developed a novel technique that uses a vacuum system to reduce the amount of water associated with the CNF as it is being

coated. We found that unlike previous attempts to coat CNF in a single step, which resulted in non-uniform layers, use of our method resulted in a smooth, continuous coating with anywhere between 12 and 28 g/m^2. Tests on gas permeability revealed the CNF coatings could decrease the amount of air that could pass through by ~500x, a critical result for plastic replacement products that serve to keep oxygen and other gasses away from the contents of the package. Finally, analysis of the ability of the CNF coatings to resist oil and grease showed an increase of ~10 times compared to uncoated controls. Our results show that by using our method, nanoscale cellulose fibrils can be effectively coated as a one-step process, preserving their unique properties and laying the foundation for their adoption as plastic replacements.

BI-ThP-7 The Surface Enhancement of Electro-Spun Polycaprolactone (PCL) Using Room Temperature Atomic Layer Deposition of Magnesium Oxide for Use as a Novel Resorbable Membrane for Dental and Corneal Surgery, ***Harshdeep Bhatia,*** University of Illinois - Chicago*; F. Esmaeilabadi,* Northern Illinois University*; C. Sukotjo, C. Takoudis,* University of Illinois - Chicago*; S. Vahabzadeh,* Northern Illinois University

Polycaprolactone is a popular biomaterial used for dental and corneal surgery. Recently MgO ALD at room temperature has been used to enhance the surface of resorbable membranes. In this study, electro-spun polycaprolactone was coated with different film thickness of magnesium oxide and tested for surface properties and cell proliferation. The ALD was performed at room temperature using a commercial ALD reactor, ALD150 LE. The source of Mg was bis(ethylcyclopentadienyl) Mg(eCp)$_2$ while ozone was used as the oxidizing agent. The composition and thickness of the as-deposited film were characterized by X-ray photoelectron spectroscopy and spectroscopic ellipsometry, respectively. The surface was also viewed using a scanning electron microscope. The water contact angle was measured right after deposition and 24-hour after deposition. A cell proliferation study was also performed to determine if the film had any toxic effects on cells.

BI-ThP-8 Label-Free High-Resolution Molecular Imaging of Sex Steroid Hormones in Zebrafish by Water Cluster Secondary Ion Mass Spectrometry (Cluster SIMS), *N. Sano,* Unit B6, Millbrook Cl Chandler's Ford, UK*; E. Lau, J. von Gerichten,* University of Surrey, UK*;* ***Kate McHardy,*** *P. Blenkinsopp,* Ionoptika, Ltd., UK*; M. Al Sid Cheikh, M. Bailey,* University of Surrey, UK

Sex steroid hormones are essential biomolecules for vertebrates and are involved in the maintenance of pregnancy, development of secondary sexual characteristics and diseases such as osteoporosis and breast cancer. Visualising the distribution of steroids contributes to further understanding of disease. However, analysis of steroids is difficult; their low polarity leads to poor ionisation efficiency, meaning they need to be derivatised for conventional analyses. Furthermore, the steroid signals overlap with a MALDI matrix background.

Water Cluster SIMS is a high-sensitivity mass spectrometry technique for imaging complex-mixture materials without derivatisation or the use of matrix. We demonstrate imaging of sex steroid hormones in zebrafish (an ideal vertebrate model organism) with a Water Cluster SIMS instrument.

An adult female zebrafish was prepared for this work. It was embedded while fresh in 0.75% HPMC and 0.25% PVP embedding media to facilitate sectioning. The whole block was flash-frozen in a dry-ice and isopropanol bath. The sample was sectioned to 20 µm at -25 °C and thaw-mounted onto a conductive indium-tin-oxide (ITO) coated glass. The section was dried while frozen in a vacuum desiccator, and then directly analysed without any matrix application for the analysis. The Cluster SIMS analyses were then performed with the J105 SIMS Cluster SIMS (Ionoptika Ltd), using a 70 keV $(H_2O)n$ beam, where n is in the range of 15,000-35,000, and also separately with a 40 keV C_{60} beam. High-resolution images were acquired with a pixel size of < 1 micron.

Water Cluster SIMS uses a high-energy beam of ionised clusters of water to sputter and ionise molecules from a surface. It is far less damaging and generates far fewer fragment ions than traditional ToF SIMS, but retains many of the benefits of that technology such as high-spatial-resolution imaging. As a result, detailed images of the distribution of sex steroid hormone molecules in the zebrafish are visible. Preliminary data shows that it is possible to map the chemical distribution of steroids in the ovary area. In addition, we also detected lipid ions related to the embryo or oocyte around the ovary area as unique distributions.

BI-ThP-9 Fouling Inhibition by Replenishable Plastrons on Microstructured, Superhydrophobic Carbon-Silicone Composite Coatings, ***Louisa Vogler,*** *E. Manderfeld, A. Rosenhahn,* Ruhr University Bochum, Germany

Superhydrophobic surfaces (SHS) exhibit the outstanding ability to retain stable air layers underwater (the so-called plastron), making them resistant to the adhesion of marine organisms and therefore counteracting the detrimental impact of marine biofouling without the use of toxic substances.[1] Since the longevity of such plastrons is limited, we recently established an approach to replenish plastrons on submerged surfaces by Joule heating by only 1-2 °C.[2] In this work mechanically stable, conductive carbon-silicone composite coatings with replenishable plastrons were fabricated by 3D printing. For the fabrication, a striped, an intersected striped, and a hierarchically-shaped mold were used.[3] Characterization of the differently structured coatings was carried out by scanning electron microscopy, water contact angle goniometry as well as dynamic attachment assays against the marine diatom *Navicula perminuta*. We demonstrated that the resulting microstructured, superhydrophobic coatings revealed a plastron formation when being submerged in water, which greatly reduced the adhesion of diatoms on such surfaces by up to 84 %. Furthermore, plastron replenishment and growth of the conductive coatings were accomplished by Joule heating.[3]

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BI-ThP-10 iCVD Polymer Thin Film Bio-Interface-Performance Based on Functional Groups and Aerohydrogels, ***Torge Hartig,*** *J. Paulsen, W. Reichstein, M. Hauck,* Kiel University, Germany*; M. Taale,* Universität Heidelberg, Germany*; T. Strunskus,* Kiel University, Germany*; C. Selhuber-Unkel,* Universität Heidelberg, Germany*; A. Amin,* National Research Centre, Giza, Egypt*; R. Adelung,* Kiel University, Germany*; B. Freedman,* Harvard University*; F. Schütt, F. Faupel, S. Schröder,* Kiel University, Germany

Interactions of biological species with polymer surfaces are dependent on various factors such as roughness, surface functional groups, wetting, residual liquids and defects. In conventional wet chemical polymers these different influences on the bio-interface cannot be examined independently. Initiated Chemical Vapor Deposition (iCVD) is an all-dry technique used to deposit ultrathin polymer films, which are defect-free and surface-conformal. Via iCVD polymer surfaces can be tailored precisely in monomer-composition, enabling the isolated examination on the bio-interface performance based on functional groups. The influence of the functional groups was examined regarding human fibroblasts, cancer cells and respiratory viruses, including in silico analysis of the interaction of key protein structures with the defined surfaces.

Furthermore, the iCVD conformal coatings are used to fabricate freestanding aerohydrogels. For this tetrapodal ZnO is coated dry-chemically and etched wet-chemically to create a freestanding polymer thin film scaffold with >99% empty space. The compressive properties of the well-defined aerohydrogels can be tailored by the gas phase composition and resulting crosslinking during the iCVD process. The aerohydrogels are used in 3D cell culture application for muscle cells.

BI-ThP-11 Bacterial Co-Culture Methods to Enhance Growth Rates in Mycelial Biomaterials, ***Lindsay Pierce,*** *M. Tajvidi, C. Howell,* University of Maine

Mycelia, the hair-like projections that make up the majority of fungal tissue, are gaining attention as a non-toxic, low-cost replacement for chemical adhesives and binders in bio-composite materials. However, the growth of fungal mycelia is a slow process which can take up to several weeks to complete. In this work, we explore the use of bacterial co-culture as a natural method to increase the growth rate of fungal mycelia in bio-composites made of wood particulates. In nature, fungi co-exist and compete with bacteria for space and resources, and previous work has demonstrated that the presence of some species of bacteria can enhance the rate of mycelial spread in response to competition pressure. We adapt these observations to mycelial bio-composites, examining the effect of the extract of a range of species in 3D constructs. Our results show how the use of bacterial co-culture methods can help to enhance the growth rate of mycelial biomaterials, potentially reducing the manufacturing time of these all-natural materials.

BI-ThP-12 Vascularization to Enhance Growth Rates in Mycelial Biomaterials, ***Anna Folley***, *M. Tajv, C. Howell,* University of Maine

Wood bio-composites are of increasing interest as sustainable building materials; however, they are frequently manufactured using hazardous chemicals as particle binders, which reduces their value as eco-friendly products. Fungal mycelia, the fine threads that make up most fungal biomass are a natural alternative to chemical binders, yet their slow growth is one of the major limiting factors in their widespread adoption. In Nature, living organisms use vascular systems to enhance growth rates by delivering nutrients and other essential materials to tissue. Here, we work to develop an internal vascular network for wood bio-composites in an effort to increase the delivery of oxygen and moisture to the fungal mycelial, enhancing the rate of growth. We use modeling to determine the optimal arrangement of vascular channels which maximizes delivery throughout the composite structures while minimizing the impact on strength. We then use 3D printing of specialized molds to create the vascularized bio-composites, testing the rate of growth both with and without active moisturized airflow through the channel network. Our results show how the use of an internal vascular system in wood composite biomaterials can be used to enhance the growth rate of fungal mycelial as a binder, lowering the barriers to wider adoption of this approach for eco-friendly building materials.

BI-ThP-13 Self-Assembled Multifunctional Thin Films with Cerium Dioxide Nanoparticles, ***Daniela Topasna***, *A. Psczulkoski, M. Albertson, S. Harris,* Virginia Military Institute

This study investigated multifunctional ionic self-assembled monolayers thin films composed of cerium dioxide nanoparticles and polymer. Samples of films werefabricated using different molarities, substrates, and layer compositions. Various characterization techniques and tests, such as optical spectroscopy, SEM, EDS, and temperature tests, reveal useful optical and antibacterial properties of these films, with potential applications in biomedicine, remote sensing, or consumer industry.

BI-ThP-14 Electroanalytical Investigation of Preferred Crystal Growth of Piezoelectric Gamma Glycine Biocrystals from Solution-Organic Film Interfaces, ***Bijay Dhungana***, *C. Neal,* University of Central Florida*; X. Wang,* University of Wisconsin-Madison*; S. Seal,* University of Central Florida

Materials with piezoelectric properties, capable of inter-converting mechanical and electrical energy, hold promise as actuators, transducers, sensors, and energy harvesters in modern devices. Due to economic and application-specific constraints for traditional piezoelectric materials, biomaterials with advantages such as biocompatibility, biodegradability, renewable sourcing, and low cost are being studied for wearable and implantable energy-harvesting devices and tissue engineering frameworks. Developing corresponding manufacturing methods is crucial for effective, reliable future production. The presented study utilizes a combination of electroanalytical methods to characterize the nucleation and preferred growth of piezoelectric γ-phase glycine biocrystals at a molecular film interface. Herein, a self-assembled monolayer (SAM)-modified gold electrode surface was utilized to induce the preferred growth of γ-phase over non-piezoelectric polymorphic structures (α,β) through formation of an initial SAM-aqueous glycine coordination structure. We first assess interaction between SAM films and glycine in aqueous solutions electrochemically by focusing on adsorption behavior determined as transient, charging currents and changes in open circuit potential. Continuous measurements of potential change were complemented by linear sweep voltammetry measurements, to characterize SAM-glycine interface character/strength, and electrochemical impedance spectroscopy (EIS), to reflect changes in the growing crystal layer character. Results from these studies were fit to relevant models (adsorption isotherms and equivalent circuit diagrams, respectively) which were then interpreted in relation to physicochemical processes mediating crystal formation behaviors. Conclusions drawn from these studies provide necessary insights into the biocrystallization process for future manufacturing processes of environmentally friendly piezoelectric materials.

BI-ThP-15 Towards a Biomimetic Approach to Transition Metal Sensing in Water, ***William Maza***, *K. Fears,* US Naval Research Laboratory

Nature has evolved to express biological molecules displaying extremely high affinities for transition metals. For example, siderophores are known to bind Fe^{3+} with binding affinities exceeding 10^{20} M^{-1}. The core structure of a number in this class of biomolecules is comprised of a cyclic peptide ring. However, the cost of expressing and isolating these molecules makes their commercialization prohibitively expensive and impractical. Here we demonstrate that cyclic peptides that demonstrate reasonable affinities for transition metals can be synthesized at an appreciable scale. Moreover, we further demonstrate that by including the intrinsic naturally fluorescent amino acid tryptophan in the structure of the cyclic peptide we can use fluorescence spectroscopy to determine the presence of transition metals in water. The α- and β-K_3W_3 cyclic peptides discussed here display different affinities for both Ni^{2+} and Zn^{2+}. In both cases, the α-K_3W_3 bind more tightly to the transition metals compared to the β-K_3W_3 by a factor of nearly two in the case of Ni^{2+} and a factor of four for Zn^{2+}.

BI-ThP-16 Optical Tweezers for Electrochemically Manipulated Force Measurements, *J. Appenroth, I. Peters, M. Valtiner,* ***Laura Mears***, Vienna University of Technology, Austria

Force measurements can vary in magnitude dramatically depending on the number of individual bonds or interactions that take place. Optical tweezers offer a highly sensitive measurement of forces during binding events of either just a few or even single molecules. In order to bring two molecules together optical tweezers commonly use two beads decorated with the relevant molecules. These beads are either in the optical trap or immobilized by suction to a micropipette or other such mechanism. However this change in geometry compared to techniques such as atomic force microscopy (AFM), may impact the comparability of results with AFM. While AFM is an incredibly flexible technique with many different in situ environmental changes, the force sensitivity is approx. an order of magnitude less than optical tweezers. We have taken inspiration from scanning probe microscopy to overcome some of the environmental limitations of the optical tweezers to include a gold STM tip. This tip can be modified in a similar way to AFM tips and can also form part of a three-electrode electrochemical cell. Here, we present some of our first results with the system on biorelevant molecules. The electrochemical manipulation allows the probability of a binding event to occur to be increased by changing the surface potential of the tip or the oxidation state of any molecules bound to it. This is particularly useful in the context of using force measurements to determine the free energy of a bond using Jarzynski's equality. In that calculation unbinding events with small values in the Gaussian distribution of forces carry more weight than the larger values. Therefore, we hope our changes to the optical tweezer set up can further our understanding of single molecule interactions and the application of Jarzynski's equality.

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