

## 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.

## 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

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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**

Poly(lactic 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 Substrate-independent Vapor Deposition of Superhydrophobic Coating with Hierarchical Roughness to Reduce Bioadhesion, C. Huang, Jessie Mao, Oklahoma State University**

Superhydrophobic surfaces offer effective resistance against the adhesion of biomolecules like bacteria and proteins. This property holds promise for their application in medical devices, aiming to mitigate complications such as infections and thrombosis. Hierarchical roughness plays a pivotal role in enhancing superhydrophobicity by providing multiple scales of surface features, which collectively contribute to increased water repellency and reduced adhesion of biomolecules. Traditional fabrication of topographical roughness requires specific substrates or solvent-based processing, which could raise concerns regarding biotoxicity. We constructed topographical roughness using an initiated chemical vapor deposition (iCVD) method that is applicable independent of substrate material and geometry. We studied how the processing parameters affect the formed surface topography and the bio-adhesion properties. In addition, surfaces with hierarchical roughness were created by varying the vapor deposition parameters *in situ*. The hierarchically roughened surface demonstrated superhydrophobicity, with more than 80% reduction in the adhered bacteria and a 98.8% decrease in the surface fibrin clotting, as compared with the homogeneously rough surface. This iCVD technique presents a novel avenue for attaining superhydrophobicity on medical devices to reduce device-related adverse events.

**11:30am BI2-MoM-14 Injectable Siloxane Sponges for on-Site Treatment and Rapid Hemostasis, Pritha Sarkar, K. 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.

**11:45am BI2-MoM-15 3-D Atomic Layer Infiltrated Metal Oxide Barriers for Thin-Film Active Microelectrode Arrays, Martin Niemiec, 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<sub>2</sub>O<sub>3</sub>, ~25nm TiO<sub>2</sub>) can provide water vapor transmission rates less than 1 mg m<sup>-2</sup>day<sup>-1</sup> 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).

## Biomaterial Interfaces

### Room 117 - Session BI-MoA

#### Microbes at Interfaces

**Moderators:** Axel Rosenhahn, Ruhr-University Bochum, Germany, 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. Jadhka, 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 ( $\beta$ -Ga<sub>2</sub>O<sub>3</sub>) 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  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> 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  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> 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  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> 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 unidentified 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<sub>3</sub>) 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<sup>-6</sup> 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

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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 to 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*) were 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.

## Biomaterial Interfaces

### Room 117 - Session BI1-TuM

#### Characterization of Biological and Biomaterial Surfaces I

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

#### 8:30am BI1-TuM-3 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 et 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.

#### 9:00am BI1-TuM-5 Machine Learning-Enhanced Point of Care SERS Detection Of SARS-CoV2 Variants using Handheld Raman Spectrometer, Sneha Senapati, J. Singh, Indian Institute of Technology Delhi, India

The rapid evolution of SARS-CoV-2 and its emerging variants necessitates advanced diagnostic techniques for effective pandemic management. On-field detection of disease-causing pathogens is one of the primary health concerns. This study introduces a Machine Learning (ML)-enhanced surface-enhanced Raman scattering (SERS) methodology for the precise differentiation of distinct SARS-CoV-2 strains and sub-strains in clinical samples. Glancing angle deposition (GLAD), a physical vapor deposition technique, was utilized to create Ag nanorods (AgNR), which were then employed as extremely pure SERS substrates. The characterization of AgNR substrates were performed using FESEM, AFM, HRTEM, EDX, XRD, UV-Vis and contact angle. Our research targets the detection of four different strains of SARS-CoV2: Wildtype, Kappa, Delta, and Omicron, including their respective sub-strains (BA.1, BA.2, BA.5, and XBB). Using pristine AgNR arrays and a handheld Raman spectrometer, discernible spectral variations were observed. Despite the clarity in isolated cultured strains of viruses, clinical validation using nasopharyngeal swabs from positive samples presented complexities due to spectral overlaps. By harnessing the unique molecular vibrational patterns elucidated by Raman spectroscopy, SERS offers heightened sensitivity. But problems came up because of the small

differences in spectral patterns between closely related SARS-CoV-2 variants found in clinical samples. To address this, machine learning (ML) algorithms were integrated to discern intricate patterns from SERS data, enhancing differentiation capabilities. Through the integration of gradient boost (GB) and support vector machine (SVM) models of ML within the SERS framework, our approach achieved an accuracy of 89% and 94%, respectively, in identifying targeted variants from nasal swabs of human patients. This integrated ML-SERS approach not only enhances detection efficacy but also offers cost-effective on-site detection capabilities and disease prediction ability. The demonstrated precision underscores the methodology's potential in future variant identification and pandemic surveillance.

#### 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: Celebration of Stephanie Allen

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

11:00am BI2-TuM-13 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-

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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

1. Mass spectrometry and informatics: distribution of molecules in the PubChem database and general requirements for mass accuracy in surface analysis. FM Green, IS Gilmore, MP Seah (2011) *Analytical Chemistry*.
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*.

11:15am **B12-TuM-14 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).

11:30am **B12-TuM-15 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.

11:45am **B12-TuM-16 Tribochemical Nanolithography – Fast, Simple Biomolecular Nanopatterning with 23 nm Resolution at Speeds of up to 1 mm s<sup>-1</sup>**, *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<sup>-1</sup>. 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<sub>0</sub> to S<sub>1</sub> 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.

## 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  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-d}$  (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. Cheron, 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; **Dhananjay Kumar**, North Carolina A & T State Uni

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 ( $\leq 2 \times 10^{-7}$  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  $250 \text{ cm}^{-1}$  and one around  $2,500 \text{ cm}^{-1}$ . 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.

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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**, *Emily McGuinness, B. Magruder, P. Chen, K. Dorfman, C. Ellison, V. 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<sub>2</sub>Sb<sub>2</sub>Se<sub>4</sub>Te<sub>1</sub> 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 Ge<sub>2</sub>Sb<sub>2</sub>Se<sub>4</sub>Te<sub>1</sub> 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<sub>2</sub>Sb<sub>2</sub>Se<sub>4</sub>Te<sub>1</sub> films.

5:00pm **EM+2D+BI+QS+TF-TuA-12 Multi-Dimensional p-WSe<sub>2</sub>/n-Ga<sub>2</sub>O<sub>3</sub> Enhancement-Mode Phototransistors for Stand-Alone Deep-Ultraviolet Sensing**, *J. Kim, Soobeen Lee*, Seoul National University, South Korea

$\beta$ -Ga<sub>2</sub>O<sub>3</sub> 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.  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> 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  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> PDs can be realized through p-n heterojunction (HJ) field-effect transistor architectures, exhibiting normally-off operation owing to the depletion region in the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> channel. With intrinsic n-type conductivity caused by unintentional doping and challenges in p-type doping, fabricating self-powered  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> PDs necessitates combining  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> with p-type semiconductors such as transition-metal dichalcogenides (TMDs), nickel oxide, or silicon carbide. Tungsten diselenide (WSe<sub>2</sub>), one of the TMDs, stands out as a promising material with a high monolayer mobility of approximately 180 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>. Their dangling-bond-free surfaces provide an advantage in forming sharp interfaces with other materials in HJs. Moreover, efficient p-type doping of WSe<sub>2</sub> is achieved via charge transfer by utilizing the high electron affinity of its self-limiting oxide, sub-stoichiometric tungsten oxide (WO<sub>3-x</sub>), which is used as a dopant.

In this work, we introduce normally-off p-WSe<sub>2</sub>/n- $\beta$ -Ga<sub>2</sub>O<sub>3</sub> phototransistors and demonstrate their self-powered operation under 254 nm light. p-Type WSe<sub>2</sub> was realized through charge transfer doping of WO<sub>3-x</sub> formed by O<sub>3</sub> treatment, and the p-type doping effect of this oxide was confirmed through electrical characteristics. The cross-sectional structure of the fabricated p-WSe<sub>2</sub>/n- $\beta$ -Ga<sub>2</sub>O<sub>3</sub> phototransistors was analyzed, and the



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electrical and optical properties were evaluated before and after WSe<sub>2</sub> 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  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> PDs. Furthermore, we investigate the enhanced optoelectronic performance of multi-dimensional  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> phototransistors with plasmonic metal nanoparticles. In this presentation, we will discuss the potential of the self-powered multi-dimensional DUV  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> 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 Exhibit 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 Kopeck, 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<sup>2</sup>. 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)<sub>2</sub> 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<sub>2</sub>O)<sub>n</sub> beam, where n is in the range of 15,000-35,000, and also separately with a 40 keV C<sub>60</sub> 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.<sup>[1]</sup> 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.<sup>[2]</sup> 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.<sup>[3]</sup> 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.<sup>[3]</sup>

[1] G. B. Hwang, K. Page, A. Patir, S. P. Nair, E. Allan, I. P. Parkin, *ACS Nano* **2018**, *12*, 6050., [2] T. Simovich, A. Rosenhahn, R. N. Lamb, *Adv. Eng. Mater.* **2020**, *22*, 1900806., [3] E. Manderfeld, L. Vogler, A. Rosenhahn, *Adv. Mater. Interfaces* **2024**, *2300964*, 1.

**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.

# Thursday Evening, November 7, 2024

## **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 were fabricated 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  $\gamma$ -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  $\gamma$ -phase over non-piezoelectric polymorphic structures ( $\alpha, \beta$ ) 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  $\text{Fe}^{3+}$  with binding affinities exceeding  $10^{20} \text{ M}^{-1}$ . 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  $\alpha$ - and  $\beta$ - $\text{K}_3\text{W}_3$  cyclic peptides discussed here display different affinities for both  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$ . In both cases, the  $\alpha$ - $\text{K}_3\text{W}_3$  bind more tightly to the transition metals compared to the  $\beta$ - $\text{K}_3\text{W}_3$  by a factor of nearly two in the case of  $\text{Ni}^{2+}$  and a factor of four for  $\text{Zn}^{2+}$ .

**Bold page numbers indicate presenter**

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Abdelmessih, M.: BI2-MoM-12, **2**  
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 Crumlin, E.: EM+2D+BI+QS+TF-TuA-4, **7**

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Quintero-Torres, R.: EM+2D+BI+QS+TF-TuA-5, **7**

— R —

Rabine, Z.: BI-MoA-1, **3**  
 Reichstein, W.: BI-ThP-10, **11**  
 Richardson, K.: EM+2D+BI+QS+TF-TuA-11, **8**;  
 EM+2D+BI+QS+TF-TuA-9, **8**  
 Rosenhahn, A.: BI1-TuM-6, **5**; BI-ThP-3, **10**;  
 BI-ThP-4, **10**; BI-ThP-9, **11**  
 Rumancev, C.: BI1-TuM-6, **5**

— S —

Sano, N.: BI-ThP-8, **11**  
 Sarkar, P.: BI2-MoM-14, **2**  
 Schröder, S.: BI-ThP-10, **11**  
 Schütt, F.: BI-ThP-10, **11**  
 Schwarz, C.: EM+2D+BI+QS+TF-TuA-11, **8**;  
 EM+2D+BI+QS+TF-TuA-9, **8**  
 Scurr, D.: BI2-TuM-14, **6**  
 Seal, S.: BI-ThP-14, **12**  
 Selhuber-Unkel, C.: BI-ThP-10, **11**  
 Senapati, S.: BI1-TuM-5, **5**  
 Sharma, R.: EM+2D+BI+QS+TF-TuA-11, **8**;  
 EM+2D+BI+QS+TF-TuA-9, **8**  
 Siles-Brugge, O.: BI2-TuM-16, **6**  
 Singamaneni, S.: BI1-TuM-7, **5**  
 Singh, J.: BI1-TuM-5, **5**  
 Smit, M.: BI-MoA-1, **3**  
 Spillmann, C.: BI-MoA-5, **3**  
 Stackawitz, J.: EM+2D+BI+QS+TF-TuA-11, **8**  
 Strunskus, T.: BI-ThP-10, **11**  
 Strzhemechny, Y.: BI-MoA-1, **3**  
 Sukotjo, C.: BI-MoA-3, **3**; BI-ThP-7, **11**  
 Sykes, M.: EM+2D+BI+QS+TF-TuA-11, **8**

— T —

Taale, M.: BI-ThP-10, **11**  
 Tajv, M.: BI-ThP-12, **12**  
 Tajvidi, M.: BI-ThP-11, **11**  
 Takoudis, C.: BI-MoA-3, **3**; BI-ThP-7, **11**  
 Thum, M.: BI1-MoM-4, **1**  
 Tiris, Z.: BI-ThP-4, **10**  
 Topasna, D.: BI-ThP-13, **12**  
 Tuck, S.: BI1-MoM-4, **1**; BI-MoA-4, **3**

— V —

V. Sokolov, A.: EM+2D+BI+QS+TF-TuA-5, **7**  
 Vahabzadeh, S.: BI-ThP-7, **11**  
 Valtiner, M.: BI2-TuM-15, **6**  
 Vogler, L.: BI-ThP-9, **11**  
 von Gerichten, J.: BI-ThP-8, **11**  
 Vora, G.: BI-MoA-4, **3**

— W —

Wang, X.: BI-ThP-14, **12**  
 Wanka, R.: BI-ThP-3, **10**  
 White, L.: BI-ThP-2, **10**  
 Wiedeman, D.: EM+2D+BI+QS+TF-TuA-11, **8**;  
 EM+2D+BI+QS+TF-TuA-9, **8**  
 Wolszczak, W.: EM+2D+BI+QS+TF-TuA-10, **8**

— Y —

Yano, J.: EM+2D+BI+QS+TF-TuA-4, **7**  
 Yingling, Y.: BI1-MoM-1, **1**  
 Yu, X.: BI-MoA-2, **3**

— Z —

Zhang, W.: EM+2D+BI+QS+TF-TuA-5, **7**  
 Zhang, Z.: EM+2D+BI+QS+TF-TuA-5, **7**  
 Zhu, Z.: BI-MoA-2, **3**  
 Zier, S.: BI2-MoM-11, **1**; BI-ThP-6, **10**

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