Biomaterial Surfaces & Interfaces
Room Naupaka Salon 4 - Session BI-TuM2

Novel Biomaterials

Moderator: Michael Grunze, Max Planck Institute for Medical Research

10:20am **BI-TuM2-8 Moving Towards Intracellular and Enzyme Catalyzed Molecule Synthesis with Mesoporous Materials**, ***Brian Trewyn,*** Colorado School of Mines

As we think about advanced medicine and new biomolecule synthesis, we need to turn to cells and biological systems where drugs and precursors to new consumer goods can be synthesized. We are investigating mesoporous silica nanomaterials (MSN), functionalized with a series of catalytic active sites (inorganic and biological) that are physisorbed and covalently tethered to the pore surface and external surface of the MSN. Because catalytic active sites can be cytotoxic to viable cells, we are investigating pore properties that can be tuned and modified so single site, nanoparticle, and enzymatic catalytic sites can be active in the pores and not interfere with the health of the cell.

Our initial effort into this grand plan has been a tandem system initially using two independent metal nanoparticles to catalyze the oxidative esterification of allyl alcohol. Using separate gold nanoparticle (Au NP) and palladium nanoparticle (Pd NP) catalysts we studied the initial oxidation of the alcohol followed by ester formation to allyl acrylate. Our next generation tandem system finds us replacing the first step of the reaction (Pd NP catalyzed oxidation of allyl alcohol) with an enzyme, alcohol dehydrogenase and conducting the tandem reaction in aqueous buffer at ambient conditions. Future directions of including tethered organometallic catalysts in syntheses conducted in biological and biological simulated environments will be shared.

10:40am **BI-TuM2-9 QCM-D Characterization of Competitive Plasma Protein Adsorption on Low-Fouling Fluoropolymers for Thromboresistant Biomaterials**, ***Sherry Liu,*** *B. Ratner,* University of Washington

Blood-contacting medical devices have classically suffered from endogenous protein fouling that initiate coagulation and inflammation pathways, often leading to fatal thromboembolic complications. The temporal turnover of adsorbed plasma proteins forms the basis for materials-induced thrombosis: human serum albumin (HSA), a platelet-inert and mobile protein, forms an initial passivating layer but is rapidly displaced by fibrinogen (Fg), which is surface-activated to mediate platelet recruitment and initiate fibrin clot formation. Herein, we employ quartz crystal microbalance with dissipation (QCM-D) to monitor competitive HSA:Fg adsorption on a selected panel of superhydrophobic low-fouling fluoropolymers (FPs): poly(vinylidene difluoride) (PVDF), poly(vinylidene difluoride)-*co*-poly(hexafluoropropylene) (PVDF-HFP), and our custom plasma-polymerized C_3F_6 (ppC_3F_6). Across all FPs, ppC_3F_6 demonstrates the greatest HSA:Fg adsorption affinity ratio. Comparing Sauerbrey vs. Voigt mass models, ppC_3F_6 exhibits an uncharacteristic viscoelasticity for the HSA adlayer attributed to hydrophobic-induced reorganization and partial coupling of the hydration layer at the protein-bulk fluid interface. Additionally, binary protein exposure reduced the equilibrium areal mass (R_{max}) compared to the pure Fg condition across all FPs, indicating that HSA competes with Fg for nonspecific binding spots and is retained on the surface at different equilibrium coverages for prolonged periods. Finally, longer HSA residence time on the surface reduces total Fg adsorption upon sequential exposure, suggesting that time-dependent denaturation and packing of HSA on a surface following adsorption increases resistance to Fg displacement. Ultimately, our observations for ppC_3F_6 are attributed to its unique fluorochemistries and superhydrophobic properties created through the plasma polymerization process, while the hydration shells are subject to further study due to existing evidence that they deter cellular adhesion. With QCM-D-enabled characterization of protein adlayers, we hope to identify the optimal FP surface modifications that encourage favorable protein surface compositions and mitigate downstream thrombus formation.

11:00am **BI-TuM2-10 Hierarchical Surface Restructuring for Next Generation Implantable Neural Interfacing Applications**, ***Shahram Amini,*** University of Connecticut, Pulse Technologies Inc.*; S. Shahbazmohamadi,* University of Connecticut

Selective and targeted stimulation of neurons in close proximity to implantable electrodes is an essential prerequisite for successful application of neural interfacing devices. Additionally, the trajectory for further refinement of neural interfacing devices is in large part predicated on increased miniaturization of electrodes that enables higher spatial resolution, precision, and reliability. To achieve miniaturization, the geometric surface area of the electrodes must be reduced while the electrochemical surface area is increased. Therefore, availability of highly electroactive electrode materials or surfaces capable of improving the electrodes' electrochemical performance is paramount as it ensures delivery of enough charge across the electrode/tissue interface for stimulation as well as low impedance at the interface for sensing and recording purposes. In the past two decades, several surface treatment technologies e.g. coatings, thin films, nanomaterials, and also physical and electrochemical techniques have been vastly investigated. Despite varying degrees of improvement in electrochemical performance, most of these techniques are still facing several challenges and shortcomings, e.g. poor performance and durability, manufacturing, scalability and commercialization challenges. In this research, we introduce, for the first time, an innovative, tunable, scalable and commercially viable electrode surface treatment technology known as hierarchical surface restructuring targeted for use in next generation neural interfacing applications. In this work, we demonstrate how ultra-short pulse lasers are utilized to hierarchically restructure the surface of electrodes to create ultra-high-surface-area electrodes. In-vitro electrochemical studies such as cyclic voltammetry and electrochemical impedance spectroscopy were used to show unprecedented improvement in electrochemical performance of these electrodes compared to their untreated electrode counterparts.

11:20am **BI-TuM2-11 Blood Compatibility Assessment of Biomaterial Surface Chemistries to Reduce the Intrinsic Coagulation Pathway Activation**, ***Kyung-Hoon Kim,*** *B. Ratner,* University of Washington

Implantable biomedical devices play critical roles for patients in need of sustainable treatment. However, surface thrombus formation is still a significant complication for blood-contacting surfaces, as it can cause lethal problems. Countless attempts have been made over the past decades to overcome this challenge. However, there is still no perfect blood compatible surface yet. One efficient approach to resolve this issue is to propose different strategies depending on the hemodynamic shear rates. A single mechanism does not govern the blood coagulation of high and low shear hemodynamic flow. The low shear condition is governed by an intrinsic pathway triggered by Factor XII adsorption and activation at the surface. On the other hand, high shear is dominantly affected by an extrinsic pathway initiated by platelet aggregation. We have investigated the blood compatibility regarding an intrinsic pathway by studying diverse biomaterial groups to understand better how each molecular event of clotting varies over different surface chemistries. Two promising categories of biomaterial surface have been tested based on two different hypotheses. The zwitterionic carboxybetaine surface is one of the popular blood-compatible surfaces due to its ultralow protein fouling properties. Fluoropolymer, a popular class of biomaterial used in vascular graft, is another historical surface for improved blood compatibility. The RFGD plasma polymerized hexafluoropropylene (ppC3F6) surface has demonstrated unique properties for preferential albumin tight binding since albumin is hypothesized as a benign protein to reduce the surface blood coagulation. The tight binding of albumin can reduce the factor XII adsorption, resulting in less activation of the intrinsic coagulation pathway.

The zwitterionic polymer outperformed all the surface groups tested, demonstrating low thrombin generation, extended clotting time, low factor XII adsorption, and low factor XIIa activity. Besides, ppC3F6 also demonstrated second-best performance in reducing the intrinsic pathway activation compared to commercial fluoropolymers and other medical polymers. We will further investigate the various ppC3F6 surfaces with varying fluorocarbon ratios, including the CF2:CF3 portion, to discover the potential rules that can contribute to the mitigation of intrinsic pathway activation and improve the understanding of how fluorocarbon chemistry can affect the surface-blood interaction. The result of this study will offer varying strategies for reducing the factor XII-triggered surface thrombus formation, aiming to enhance the blood compatibility at the low shear hemodynamic flow condition.

11:40am **BI-TuM2-12 Innate Immune Response an Integral Part of Acorn Barnacle Surface Adhesion**, ***Kenan Fears,*** *J. Schultzhaus,* US Naval Research Laboratory

Understanding the adhesion mechanisms of marine hard foulers (e.g., barnacles and tubeworms) is of critical importance to the global maritime communitiy due to the pervasiveness of these organisms, coupled with the desire to transition away from toxic antifouling paints that have a deleterious ecological impact. Often, the biochemical processes that are crucial for the attachment and survival of hard foulers occur at buried

interfaces, which further complicates analysis. He we use confocal laser scanning microscopy protocols for imaging the adhesive interface of a model hard fouler, acorn barnacles (*Amphibalanus (=Balanus) amphitrite*), using multiple fluorescent probes to simultaneously label up to four different biochemistries. Time lapse imaging reveals cellular and extracellular processes related to cuticle development, biomineralization, and surface adhesion. More importantly, the presence of a lipidaceous secretion that phase-separates once it is exposed to seawater. This secretion oxidizes and detaches surface-adhered biofilms ahead of barnacle growth and cement deposition, and also facilitates the remodeling of the cement matrix to fill voids that may exist between the base of the barnacle and the underlying substrate. Enzymes present in this secretion generate hypochlorite ions (i.e., bleach) to oxidize organic matter at the adhesive interface and defend against microbial attack. Protein sequence analysis reveals that peroxidase enzymes found in cement collections are highly conserved across the barnacle tree of life, which includes stalked, calcareous-based, and membranous-based barnacles. However, we did not observe this surface-cleaning secretion in two membranous barnacles, *Chthamalus fragilis* and *Elminius modestus,* suggesting it is a more recent evolutionary trait.

Author Index

Bold page numbers indicate presenter