Biomaterial Interfaces
Room 321 - Session BI2-TuM

Biomaterials and Nanomaterials Fabrication II

Moderator: Christopher So, Naval Research Laboratory

9:15am **BI2-TuM-6 Tuning Biopolymer Surface Wettability through Plasma Copolymerization*, Morgan Hawker****, Alexzandria Kubik, Mackenzie Jackson, Kristina Closser,* California State University, Fresno

Plasma, the fourth state of matter, is a partially ionized gaseous mixture and versatile tool for controlling interactions at biointerfaces. Polymers are ubiquitous biomaterials and tailoring how the polymer device interfaces with the biological environment is paramount to controlling its function. For example, promoting favorable cell-surface interactions is needed for tissue engineering devices, whereas preventing bacterial attachment is favorable to prevent infection at the device surface. Plasma-enhanced chemical vapor deposition is a versatile technology to control interactions at the biomaterial/biological environment interface through adding a conformal protective film that encases the polymeric device below. The film is obtained through interfacing a polymer substrate with the plasma (partially ionized gas mixture). Plasma species such as radicals and cations undergo gas-phase reactions, and products from those reactions form the conformal film. Plasma copolymerization is a related strategy that utilizes a mixed feedgas of two or more plasma precursors, whereby conformal coating surface properties can be controlled by simply varying the feedgas composition.

This study reports a previously unexplored combination of plasma precursors – pentane and acrylic acid – to deposit coatings with tunable chemistry and wettability on silk fibroin constructs. Five pentane/acrylic acid feedgas compositions were utilized, ranging from 100%, 75%, 50%, 25%, and 0% pentane by pressure. Plasma deposited coating properties were evaluated through water contact angle goniometry and x-ray photoelectron spectroscopy. Coating static water contact angle values were tunable between >90 degrees to <55 degrees depending on the feedgas composition, which correlated to surface chemical composition. Plasma diagnostics and density functional theory were used to evaluate plasma precursor fragmentation, providing further insights into plasma/surface interactions. This library of plasma-modified silk-based materials can be used to design biomaterial surfaces that are optimally situated for the intended biomedical setting.

9:30am **BI2-TuM-7 Capture of Rare Earth Metals Using Bio-Inspired Polymeric Materials*, Gillian Kropp****, Kailey Richard, Kenan Fears, Okhil Nag,* U.S. Naval Research Laboratory

Rare earth metals, largely comprised of lanthanides, are essential materials for a wide range of applications, including electronics, imaging and diagnostic technology, and energy systems. However, in nature these metals are found dispersed at low concentrations and mixed with other metals, making them challenging to locate, extract, and chemically isolate. Therefore, developing materials with high selectivity and tuneability is crucial to the separation and extraction of these lanthanides. Peptoids are a class of biomimetic molecules that are expanding the landscape of materials used for therapeutics, diagnostics, and metal chelation. In fact, with the development of new synthetic and automated strategies, peptoid-based materials are highly versatile and tunable. Our goal is to leverage this tuneability to design, synthesize, and characterize materials for selective rare earth metal extraction.

11:00am **BI2-TuM-13 Watching Enzymes Work at Interfaces: Orientation, Activation and Catalysis of Lipases and Nerve-Agent Hydrolases*, Tobias Weidner****,* Aarhus University, Denmark

Enzymes only function at an interface if they arrive folded, correctly oriented, and with the active site accessible. Yet the standard tools of structural biology are blind to the few nanometers where this is decided. We use vibrational sum-frequency generation (SFG) spectroscopy, combined with spectral calculations based on crystal structures (our ViSCa toolbox), to determine the secondary structure, in-situ orientation and catalytic state of enzymes directly at hydrophobic surfaces, and we connect these structural results to measured turnover.We first illustrate the approach with Thermomyces lanuginosus lipase (TLL), a workhorse of detergent and biofuel technology whose activity depends on a helical "lid" that swings open at a hydrophobic interface. Amide I SFG spectra recorded at the air/water interface, compared with calculated spectra for libraries of protein orientations, identify the lid-open state and show that the enzyme contacts the surface through a loop region well away from the lid and active site. Following the ester carbonyl and carboxylate stretching modes in real time lets us watch interfacial lipolysis as it happens. Extending this to glycosylation variants shows that the lid-open conformation is retained regardless of glycan content, while high-mannose glycosylation broadens the distribution of orientations and increases interfacial disorder, a route to tuning enzyme presentation without mutating the protein.We then apply the same framework to a problem with a very different motivation: the destruction of organophosphorus nerve agents. Current protective filters rely on activated carbon, which traps rather than destroys the agent and eventually saturates. Diisopropyl fluorophosphatase (DFPase) from Loligo vulgaris hydrolyses sarin, soman and tabun, but a surface-bound enzyme is only useful if it is deposited in a pose that leaves the active site available. We show that SFG can be used as the design tool for exactly this: by reading out the secondary structure and the tilt and twist of DFPase on hydrophobic supports, and by tracking the chiral polarization combinations (PSP, SPP) that report on the organization of the adsorbed film, we identify deposition conditions that yield an ordered layer in a productive binding pose. AFM confirms a uniform film, and ATR-FTIR shows that the resulting surfaces hydrolyse diisopropyl fluorophosphate to the far less toxic diisopropylphosphate, with activity retained over repeated cycles and after drying and storage for weeks.Together these studies show that interface-sensitive spectroscopy can both explain and guide the design of working immobilized biocatalysts.

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