Biomaterial Surfaces & Interfaces
Room Naupaka Salon 4 - Session BI-MoM2

Biofunctional Surfaces and Coatings
Moderator: Buddy D. Ratner, University of Washington

10:20am **BI-MoM2-8 Structure in Lipid Films: From Biophysical Models to Drug Delivery***, **Christine DeWolf**,* Concordia University, Canada **INVITED**
Our understanding of the role of lipid membrane has evolved a long way from the Singer and Nicolson model of a fluid mosaic in which the bilayer served simply as a two-dimensional liquid providing a hydrophobic environment for membrane proteins. While inherently dynamic, membranes exhibit a wide polymorphism of co-existing structures that play important roles in cellular processes. Lipid films (monolayers and bilayers) are frequently used as models to understand and probe structural changes upon interaction with proteins, enzymes, drugs, drug delivery vehicles and foreign bodies such as pollutants and chemicals. Moreover, the understanding of such interactions and how they influence biomolecular conformation and structure, enables us to design lipid-based surface coatings that confer functionality (from simple biocompatibility to triggered drug delivery) to nanoparticles and other solid surfaces. Our work focuses on understanding the composition-structure-function relationships that govern such functionality suing a surface analysis approach that encompasses lateral and vertical structure on both the molecular and meso-/microscopic scales and employs a combination of surface x-ray scattering (GIXD, GIXOS, X-ray reflectivity), imaging (AFM, Brewster angle microscopy and imaging ellipsometry) and spectroscopic (IRRAS) techniques. The power of these methods for elucidating the inter-relationships between the structure and organization of biomembranes and their functional properties will be shown using examples of Langmuir films as model membranes. A focus of the talk will be on lipid-nanoparticle interactions. On one hand, nanoparticles can be considered pollutants or contaminants as their impacts on cellular components, including the cell membrane itself, are not well established. This will be exemplified by examining the impact of inhaled nanomaterials on the functional properties of pulmonary surfactant membranes, a lipid-protein film coating the air-alveolar surface. On the other hand, nanocarriers which are comparable in size to many cellular components and easily internalized, cause unique interactions with cells and therefore offer an intriguing route for the encapsulation and delivery of difficult to deliver drugs. In this case the nanoparticle-lipid membrane interactions have to be tuned to minimize deleterious effects and in fact using a lipid coating can not only provide the necessary biocompatibility but also to enhance the delivery of drugs using nanocarriers via a carefully selected coating composition.

11:00am **BI-MoM2-10 Ways to Synthesize Silicone Nanobodies with Complex Shape and Their Applications as Coatings***, K. Chen, **Stefan Seeger**,* University of Zurich, Switzerland
One-dimensional (1-D) silicone micro- and/or nanostructures such as filaments, wires, fibers and tubes have attracted significant attention due to their remarkable application capabilities in a large range of material and surface science /1/. The chemical synthesis is surprisingly simple and based on the Droplet-Assited-Growth and Shaping process (DAGS)/2/. Here, we demonstrate a novel, extraordinarily simple and efficient *dynamic* DAGS synthesis strategy allowing for the one-step synthesis and in situ control of the shape of nanostructures. We demonstrate bamboo-shaped silicone nanorods (SNRs) obtained by the repetitive dynamic regulation of growth conditions, concomitant with the periodic purging and injection of precursors. The new resulting nanostructures endow these newly designed SNRs with a specific number of segments and a highly regular arrangement. This approach allows the silicone micro- and/or nanorods to be customized with different heights and different segment numbers tailor-made to the requirements for various properties. With this method, various properties can be controlled, for example mechanical stiffness and water repellence. The obtained SNR coatings exhibit for example stable water-resistance under both static and dynamic wetting conditions, robust chemical and mechanical durability, and excellent performance in buoyancy promotion, self-cleaning and water harvesting. Notably, the properties are obtained by fluorine-free compounds, are very environmentally friendly, and are based on a very simple, solvent-free one-step procedure accomplishable at room temperature and normal pressure. The well-structured ultra-long rods can also be fabricated with an ultrahigh aspect ratio (~ 176), still standing straight upwards and regular even the they consist of flexible and soft silicone material /3/. Finally, the presentation will give insight in new applications which are accessible due to the precise control of the nanstructures' shape.

/1/ G. Artus, S. Jung, J. Zimmermann, H. P. Gautschi, K. Marquardt, S. Seeger, EP1644450A2 [http://www.google.ch/patents/EP1644450A2?hl=de&cl=zh]**(2003)**, *Adv. Mater. (***2006)**,18,* 2758, J. Zhang, S. Seeger, *Angew. Chem.***(2011)** 50, 6652, Stojanovic, S. Olveira, M. Fischer, S. Seeger, *Chem.Mat.*, *25*, 2787**(2013),** X. Zhang, S. Seeger, *Small*, 15(34) 1901822 (**2019**)

/2/ G Artus, S Olveira, D Patra, S Seeger, *Macromol.Rapid Comm*. **2017,** *38, 1600558*

/3/ K Chen, S Liu, Y Lau, S Seeger, *Small*, in press (**2022**)

11:20am **BI-MoM2-11 Isolation and Label-Free Detection of Circulating Tumour Cells by Fluidic Diffraction Chips with a Reflective Laser Beam System***, F. Lin,* National Taiwan University of Science and Technology, Taiwan*; H. Hsu,* National Defense Medical Center, Taiwan*; **Jem-Kun Chen**,* National Taiwan University of Science and Technology, Taiwan
A photonic crystal (PC) based line array of poly(methacrylic acid) (PMAA) brushes was grafted from a photoresist template using a trench array. The array was functionalised with anti-epithelial cell adhesion molecule antibodies (EpY). A laser beam was employed to analyse the two-dimensional (2D) and three-dimensional (3D) reflective signals of PCs at an incidence angle of 45◦. The EpY-tailed PMAA PC possessed an optical feature with a characteristic diffraction effect along two laser input configurations including the SII configuration, in which the projection of the laser beam on the plane of the SPM chip was parallel to the strips, and the ST configuration, in which they were perpendicular. A fluidic diffraction chip based on the EpY-tailed PMAA PC with 1-μm resolution was fabricated to examine the ability to detect circulating tumour cells (CTCs) along the ST configuration. The CTCs attached on the EpY-tailed PMAA PC, resulting in the change in the diffraction intensity. Dependence of change degree of the diffraction intensity exhibited a linear range of concentration of CTC from 0 to 64 cells and a limit of detection of 5 cells in 3 mL. CTC detection using both fluidic diffraction chips and a commercial IsoFlux system was carried out in clinical trials, including three healthy donors and 12 patients at various stages of colorectal cancer for comparison. Our platform provides a simple label-free method with high accuracy for rapid CTC counting, which has great potential in clinical treatment applications.

11:40am **BI-MoM2-12 Designer Silk: Plasma-Based Strategies to Customize Surface Properties of Silk Fibroin Films***, **Morgan Hawker**,* California State University, Fresno
Silk fibroin (silk) materials have promise for use in the biomedical space owing to their incredible mechanical properties. Compared to other naturally-derived polymers, silk exhibits remarkable tensile strength because of a unique antiparallel β sheet secondary structure. Additionally, silk is favorable for use in biological settings because it is non-immunogenic and degrades via enzymatic hydrolysis into non-toxic byproducts *in vivo*. Silk can be fabricated into a range of architectures to mimic biological settings, including films, porous networks, and microparticles. These aspects illustrate silk's utility in areas including biosensors, tissue engineering, and drug delivery. All biomedical applications, however, require silk to interact with biological species in specific ways. As with most polymers, silk lacks the necessary surface cues required to facilitate precise interactions with biological species. Thus, further modification is required to tailor silk materials' surface properties and enhance their efficacy as biomaterials.

Low-temperature plasma (LTP) modification represents a relatively unexplored but highly promising area for silk construct modification. LTP processing negates the use of solvents and high temperature conditions associated with wet chemical modification. Moreover, LTP treatment can be conducted with a range of precursors, translating to a myriad of attainable surface chemistries. In this talk, I will highlight three LTP approaches our group recently investigated to modulate silk film surface properties. For example, we utilized LTP strategies to enhance silk film hydrophilicity using N_2 and H_2O(g) precursors. After N_2 and H_2O(g) LTP treatments, water contact angles (WCAs) decreased by ~35° and ~50°, respectively. Notably, all LTP-modified constructs exhibited minimal hydrophobic recovery after 6 weeks of aging. In addition, we have developed plasma-enhanced chemical vapor deposition approaches to modulate silk film surface properties. We utilized LTP copolymerization, where feedgas composition was tuned using two unique precursors: acrylic acid (to produce thin films with polar functional groups on the silk surface) and pentane (to produce thin films with non-polar functional groups on the silk surface). WCA goniometry and x-ray photoelectron spectroscopy were utilized to evaluate wettability and changes in surface chemistry following

LTP treatment, respectively. We elucidated that surface properties depend on both feedgas composition and position of the film in the LTP reactor. In sum, LTP represents a promising avenue to customize silk surface properties for use in biomedical contexts.

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