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Bio-Lithography: A Novel Process for Modification and Patterning of Supported Lipid Bilayers using Lipopolysaccharide, a Biological Aphiphile
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Biological cell membranes are highly organized, multi-component systems that carry out complex energy and information processing. Supported lipid bilayers (SLBs) have shown great promise as model membranes but generating biologically-relevant complexity is challenging using existing membrane patterning techniques. Here we demonstrate an unconventional method that allows the controlled formation and patterning of complex membrane arrangements. Lipopolysaccharide (LPS) is a membrane-inserting amphiphile and an immunogenic protein. We recently reported that LPS can insert into and destabilize fluid-phase SLBs, leading to the formation of voids [Adams et al. (2014) Biophys J. 106, 2395]. We noted that the fluidity and continuity of the remainder of the SLB was maintained. In the current study, we exploit this effect of LPS to generate SLBs containing voids that can be backfilled to introduce desired functional components. This ‘biochemical-assisted lithography’ procedure was used to generate hierarchically organized membrane domains and microscale 2-D array patterns of domains. These domains could be formed using proteins, gel-phase lipids or even synthetic polymers. Alternatively, the voids could be healed by introducing new fluid-phase lipids. Significantly, this technique can be used to repeatedly modify membranes allowing iterative control over membrane composition. This approach expands our toolkit for functional membrane design, with potential applications for enhanced materials templating, biosensing and mimicking biological processes. Furthermore, we present fundamental insights into the interaction of lipids and other amphiphiles, demonstrating that line tension and alky chain packing effects can direct the organisation of a membrane-inserted amphiphile into geometric patterns.

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The Bacterial Spore as an Energy-Rich Adaptive Material
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Stimuli responsive materials are in high demand for myriad applications within the fields of biomedicine, adaptive-architecture, robotics, and alternative energy. The non-pathogenic bacterial spores of Bacillus subtilis have the ability to swell as much as 12% in response to humidity gradients. Within the spore unique biomaterials drive this dynamic response, resulting in energy densities greater than 10 MJ·m⁻³, more than a hundred times the potential of existing synthetics. We hypothesize that the spore’s cortex, a protective layer surrounding the genetic core, is largely but not solely responsible for this peculiar water-responsive behavior. To evaluate the spore’s constituent biomaterials we developed AFM techniques that assay individual spores during a thermodynamic cycle of varied applied force and relative humidity. This method resulted in energy density and strain profiles for multiple spore variants and structural mutants. Electron microscopy (FIB SEM) was then used to ascribe radial dimensions to biomaterial layers within the spore. Quantifying precise substructural contributions to the spore’s hydromechanics will allow for in vitro optimization of composite spore biomaterials and may even facilitate artificial synthesis in the future. The bacterial spore’s inherent ability to form monolayers and superior performance in highly efficient energy conversion and actuation qualifies it as an intriguing material worthy of broad development.
and exceptional biocompatibility should prove valuable for bionanofluidic and cellular interface applications. 2462-Pos Board B599

Titration Properties and pH-Dependent Aggregation of Chitosan Brian H. Morrow 1, Gregory F. Payne 1, Jana K. Shen 1. 1Department of Pharmaceutical Sciences, University of Maryland, Baltimore, MD, USA, 2Fischell Department of Bioengineering, University of Maryland, College Park, MD, USA. Chitosan is a polysaccharide consisting of N-acetyl-glucosamine and glucosamine units, prepared by the deacetylation of chitin. Glucosamine contains an ionizable primary amine, rendering chitosan water-soluble at low pH and insoluble at pH above ~6.5. This pH dependent solubility can be exploited to make hydrogels used for coatings and sensors. We have used constant-pH molecular dynamics (CpHMD) to investigate the pH dependence of chitosan. Starting from a stable aggregate of neutral chitosan, we performed replica exchange simulations over a pH range 4.0-8.5. The aggregate remains stable at high pH and dissociates at low pH, as expected. Interestingly, the transition occurs cooperatively at around pH 6.5, in a remarkable agreement with experiment. The calculated bulk pKa was found to be similar to the transition pH, again in agreement with experiment. The role of electrostatic interactions and aggregation-induced desolvation in the protonation equilibria of the amine groups was also examined. This work provides atomic-level insight into the pH-dependent behavior of chitosan which may aid in the design and development of various chitosan-based materials. 2463-Pos Board B600

Using Spores of Bacillus to CreateEVaporation-Driven Engines Xi Chen 1, Davis W. Goodnight 1, Zhenghan Gao 1, Ahmed-Hamdi Cavusoglu 1, Nina Sabharwal 1, Michael DeLay 1, Adam Driks 1, Ozgur Sahin 1, 2. 1Department of Biological Sciences, Columbia University, New York, NY, USA, 2Department of Physics, Columbia University, New York, NY, USA, 3Department of Chemical Engineering, Columbia University, New York, NY, USA, 4Department of Biomedical Engineering, Columbia University, New York, NY, USA, 5Department of Microbiology and Immunology, Loyola University Chicago, Maywood, IL, USA. Biological organisms harness energy from natural evaporation by using their inherent structures which are able to capture and stretch water molecules in response to the chemical potential gradient of water. A tree is a simple example, where water is continuously transported to the top, sometimes one hundred meters above the ground, due to evaporation occurring at the leaves. These stimuli-responsive biomaterials could possibly exhibit high energy densities for efficient energy converters and actuators. Bacillus spore is a water-responsive biomaterial that has a large energy density, high reversibility, and fast response to variations in relative humidity (RH). Here, we present hybrid spore/plastic biomaterials that can be used for high strain actuation and energy harvesting from evaporation. We fabricated the spore/plastic hybrid biomaterials by periodically coating alternating sides of ultrathin polyimide tapes with bacterial spores. The resulting structure curved into an approximately sinusoidal shape with a low RH nearby, and achieved a large linear displacement at both ends of the tape. By exchanging less than 5% water by weight, these hybrid biomaterials produced a large actuation strain of ~200 % and a fast response (~1s) due to changes of RH. The actuation displacement and force can be easily scaled up by assembling these hybrid biomaterials in series and parallel. Using these packaged hybrid biomaterials, we created two types of evaporation-driven engines that convert evaporation energy to oscillatory and rotary motion. When we placed these engines near wet surfaces, they start and run autonomously and produce work continuously. We demonstrated that the mechanical work is sufficient to power a light source and drive a miniature device. 2465-Pos Board B602

Field Effect Transistors Based on Semiconductive Microbiologically Synthesized Chalcogenide Nanofibers Ian R. McFarlane 1, Julia R. Lazzari-Dean 1, Mohamed Y. El-Naggar 1, 2. 1Physics and Astronomy, University of Southern California, Los Angeles, CA, USA, 2Chemistry, University of Southern California, Los Angeles, CA, USA. Microbial redox activity offers a potentially transformative approach to the low-temperature synthesis of nanostructured inorganic materials. Diverse strains of the dissimilatory metal-reducing bacteria Shewanella are known to produce photoactive filamentous arsenic sulfide nanofibers by reducing arsenate and thiosulfate in anaerobic culture conditions. We present in situ microscopic observations and measure the thermally activated (79 K/ mol) pre- cipitation kinetics of high yield (504 mg per liter of culture, 82% of theoretical maximum) extracellular AsS 2 nanofibers produced by Shewanella sp. strain ANA-3, and demonstrate their potential in functional devices by constructing field effect transistors (FETs) based on individual nanofibers and photoelectro-chemical cells based on macroscopic mats. The use of strain ANA-3, which possesses both respiratory and detoxification arsenic reductases, result in significantly faster nanofiber synthesis than other strains previously tested, mutants of ANA-3 deficient in arsenic reduction, and when compared to abiotic arsenic sulfide precipitation from As(III) and S 2-. Detailed characterization by electron microscopy, energy-dispersive X-ray spectroscopy, electron probe micro-analysis, and Tauc analysis of UV-Vis spectrophotometry show the biogenic precipitate to consist primarily of amorphous As 2 S 3 nanofibers with an indirect optical band gap of 2.37 eV. X-ray diffraction also reveal the presence of crystalline As 2 S 3 minerals that, until recently, were thought to form only at higher temperatures and hydrothermal conditions. The nanoscale FETs enable a detailed characterization of the charge mobility (~10 cm 2 V s) and gating behavior of the heterogeneously doped nanofibers. We also present a characterization of detected photocurrent. These studies indicate that the biotransformation of metalloids and chalcogens by bacteria enables fast, efficient, sustainable synthesis of technologically relevant chalcogenides for potential electronic and optoelectronic applications. 2466-Pos Board B603

Nanomechanical Deformation Behavior of Amyloid Fibrils Bumjoo Choi 1, Sangwoo Lee 1, Kilho Eom 2. 1Yonsei University, Wonju, Korea, Republic of, 2Sungkyunkwan University, Suwon, Korea, Republic of. Amyloid fibrils playing a role in disease expression have recently been found to exhibit excellent mechanical properties, which are highly correlated with the biological functions of amyloid fibrils. It has not yet fully understood how amyloid fibrils formed by aggregation of mechanically weak protein chains can exhibit remarkable mechanical properties. In this work, we study the nanomechanical deformation behavior of amyloid fibrils using steered molecular dynamics simulations. It is shown that the length scale of amyloid fibrils is a key factor in determining the nanomechanical deformation mechanisms of amyloid fibrils and their resulting nanomechanical properties. It is attributed to the competition between shear and bending deformations, which depends on the length scale of amyloid fibrils. The length-dependent elastic property of amyloid fibrils has been elucidated based on Timoshenko beam model. Our study sheds light on the importance of the length scale of amyloid fibrils for understanding their nanomechanical properties.