Biomaterial Interfaces Division
Room A120-121 - Session BI+AS-MoA

Cutting Edge Bio: Bio-Nano, Bio-Energy, 3D Bio

Moderators: Heather Canavan, University of New Mexico, Jordan Lerach, ImaBiotech Corp.

1:40pm **BI+AS-MoA-1 Emulsion-templated Asymmetric Vesicles**, ***Laura Arriaga***, University of Madrid, Spain **INVITED**

A vesicle is a naturally existing or an artificially prepared aqueous droplet stabilized by an amphiphilic membrane that ensures retention of hydrophilic ingredients within its core. This amphiphilic membrane typically comprises two leaflets, which have either identical or different compositions. While membranes comprising two compositionally identical leaflets exhibit lateral asymmetries or domains if prepared from mixtures of amphiphilic molecules capable of phase separation, membranes comprising compositionally different leaflets are asymmetric in the transversal direction. Moreover, internal vesicle asymmetries can be induced through the phase separation of sufficiently concentrated polymer solutions encapsulated in the vesicle cores. All these types of asymmetry dictate vesicle properties, making them more suitable than symmetric vesicles for a wide range of applications, especially to appropriately mimic biological cells. However, the utility of these vesicles depends critically on the degree of control achieved over their properties in the fabrication process. Here, we address the adequacy of emulsion droplets with well-controlled topologies, fabricated with exquisite control by microfluidic technologies, as vesicle templates. In particular, we describe a first strategy to fabricate vesicles with symmetric membranes exhibiting lateral domains and internal asymmetries using double emulsion drops as templates [1,2], and a second strategy to form vesicles with asymmetric membranes using triple emulsion drops as templates [3]. These strategies efficiently encapsulate ingredients within the core of the vesicles or their membranes and yield vesicles with monodisperse sizes and controlled degrees of asymmetry.

[1] L.R. Arriaga, S. Datta, S.-H. Kim, E. Amstad, T. Kodger, F. Monroy, D.A. Weitz. Ultra-thin shell double emulsion templated giant unilamellar lipid vesicles with controlled microdomain formation. Small 10, 950-956 (2014).

[2] J. Perrotton, R. Ahijado-Guzman, L.H. Moleiro, B. Tinao, A. Guerrero-Martinez, E. Amstad, F. Monroy, L.R. Arriaga. Microfluidic fabrication of vesicles with hybrid lipid/nanoparticle bilayer membranes. Soft Matter 15, 1388-1395 (2019).

[3] L.R. Arriaga, Y. Huang, S.-H. Kim, J.L. Aragones, R. Ziblat, S.A. Koehler, D.A. Weitz. Single-step assembly of asymmetric vesicles. Lab Chip 19, 749-756 (2019).

2:20pm **BI+AS-MoA-3 Antimicrobial Cyclic Peptide Polymer Nanopores**, ***Kenan Fears***, *L Estrella,* US Naval Research Laboratory

We present a new class of bioinspired nanomaterials that are stabilized by a combination of covalent and hydrogen bonds. Prior work by others has shown that cyclic peptides can self-assemble to form supramolecular assemblies through backbone-backbone hydrogen bonding. To improve upon this molecular architecture, we develop a synthesis route to polymerize cyclic peptides and form a linear polymer chain that can transition between a rigid nanorod and a “soft” unfolded conformation. For a cyclic peptide polymer containing amine-terminated side chains on each ring, we demonstrate self-assembly can be triggered in aqueous solutions by varying the pH. We measure the elastic modulus of the rigid nanorods to be ca. 50 GPa, which is comparable to our molecular dynamics (MD) prediction (ca. 64 GPa). Our results highlight the uniqueness of our molecular architecture, namely their exemplary toughness (up to 3 GJ m^{-3}), in comparison to other cyclic peptide-based assemblies. Finally, we demonstrate the amphiphilic cyclic peptide nanopores are capable of inserting into the membrane of both gram-negative and gram-positive bacteria, and causing their deaths by disrupting their osmotic pressure.

2:40pm **BI+AS-MoA-4 ToF-SIMS Analysis of the Distribution of *p*-Hydroxybenzoate in Wood**, ***Robyn E. Goacher***, Niagara University; *Y Mottiar,* University of British Columbia, Canada

The progress towards a green bio-based economy depends in part on our ability to chemically modify lignocellulosic plant matter. Possible targets for such chemical modifications include ester-linked pendant groups that occur on lignin in some plant species. The lignin in poplar and willow is known to contain 1-10% of *p*-hydroxybenzoate (-*p*HB) moieties, although little is known about the function of these -*p*HB groups. To understand the function of -*p*HB, it is important to understand the distribution of -*p*HB among different cell types. Previous work with ultraviolet microscopy suggests that -*p*HB is present only in fibers and not in vessels. The goal of this work is to provide a more specific analysis of the spatial distribution of -*p*HB in wood by using surface-sensitive chemical imaging. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was used to image cross-sections of mature Lombardy poplar, juvenile (greenhouse-grown) Lombardy poplar and mature DUKE-5 willow. Lombardy poplar is known to contain higher levels of -*p*HB than the DUKE-5 willow. Samples were analyzed prior to and after solvent extraction to remove spectral interferences from small molecule extractives, which have similar chemical composition to -*p*HB and lignin. A milk alkaline hydrolysis was also performed to cleave ester-linked -*p*HB from lignin in order to confirm identification of certain peaks within the mass spectra as characteristic of -*p*HB. Multivariate statistical analysis was used to aid in the data interpretation. The process of identifying peaks that arise from -*p*HB will be discussed, and chemical images of the localization of -*p*HB will be presented. This data contributes to our understanding of how -*p*HB is distributed in wood. These insights may shed light on the role of ester-linked moieties in lignin and will hopefully advance the use of -*p*HB as a biotech target.

3:00pm **BI+AS-MoA-5 Feeling the Force; Probing the Cues that Influence Stem Cell Behaviour**, ***Stephanie Allen***, School of Pharmacy, The University of Nottingham, UK **INVITED**

There is considerable research activity directed towards understanding the basic biology of stem cells and controlling their mechanisms of self-renewal and differentiation into functional tissue types. Much of the current research involves genetic and/or biochemical approaches to control proliferation and differentiation. Over the last decade, studies using biophysical approaches, including our own, have begun to impact on this understanding, revealing that physical signals and cues elaborated by neighbouring cells and the surrounding extra-cellular matrix, are also fundamental to controlling stem cell fate (1-4). For many emerging approaches/applications, including those that aim to create functioning tissues through the 3D patterning of stem cells, an understanding of such physical cues is therefore vital.

Despite this importance relatively few studies have still attempted to investigate and quantify the physical interactions between stem cells and/or the effects of applied stimuli. This talk aims to provide an overview of our recent research in this area, that aims to address this knowledge gap by utilizing force measurement approaches (including optical tweezers and atomic force microscopy). The presentation will include results from a current project where we are employing AFM-based single molecule force measurement approaches to provide new insights into the role of cadherins on mouse embryonic stem cells (mESCs).

(1) Discher *et al Science* 324 :1673-1677 (2009)

(2) Lanniel *et alSoft Matter.* 7, 6501-6514 (2011)

(3) Lanniel *et alThin Solid Films* 519, 2003-2010 (2011)

(4) Kirkham *et alScientific Reports*, 5, No. 8577 (2015)

4:20pm **BI+AS-MoA-9 Angstrom-Resolved Characterization of Electrochemical Interfaces in Real Time during Polarization**, ***Markus Valtiner***, Vienna University of Technology, Austria

Electrochemical solid|liquid interfaces are critically important for energy conversion, biosensing and biodegradation processes. Yet, a real-time visualization of dynamic charging processes at electrified solid|liquid interfaces with close to atomic resolution is extremely challenging.

I will discuss a unique real-time atomistic view into dynamic charging processes at electrochemically active metal interfaces using white light interferometry in an electrochemical surface forces apparatus. This method allows simultaneous deciphering of both sides of an electrochemical interface; the solution and the metal side; with microsecond resolution under dynamically evolving reactive conditions that are inherent to technological systems in operando. The real-time capability of this approach reveals significant time lags between electron transfer, oxide reduction/oxidation, and solution side reaction during a progressing electrode process. In addition, the developed approach provides detailed insight into the structure of the electric double layer under varying charging conditions. I will also discuss how we can complementary use high resolution in-situ AFM imaging to further characterize ion layering at charged surfaces.

The presented work may have important implications for designing emerging materials utilizing electrified interfaces and may apply to bio-electrochemical processes, signal transmission and pore charging.

4:40pm **BI+AS-MoA-10 New Electrochemical Methods for Probing Metalloenzymes*, Alison Parkin,*** University of York, UK **INVITED**

Large amplitude Fourier transform alternating current voltammetry (FTacV) is being developed as a new tool for probing electron-transfer processes in metalloenzymes. We can probe non-innocent active site ligand chemistry in molybdenum enzymes and based on our new insight into the rates and energetics of electrons entering/exiting an iron sulfur cluster we have been to rationally re-design a hydrogen enzyme to increase the catalytic efficiency and hydrogen production. This talk will describe these studies and detail our solutions to the challenges in efficient data analysis and protein-electrode wiring.

Author Index

Bold page numbers indicate presenter