

## Biomaterial Interfaces Division

### Room 101B - Session BI-WeA

#### Microbes and Fouling at Surfaces

**Moderator:** Caitlin Howell, University of Maine

3:00pm **BI-WeA-3 Gaede-Langmuir Award Lecture: From Description to Prediction of Biointerphase Reactions, Michael Grunze<sup>1</sup>**, Max Planck Institute for Medical Research, Germany; *H Kreuzer*, Dalhousie University, Canada

**INVITED**

Many experiments in Biointerphase Research aim to determine the number of cells or organisms adsorbing on a surface. In order to discriminate between physisorbed and settled cells, a rinsing step is applied when the sample is removed from solution. However, no information is obtained which shear flow is required to overcome the activation barrier of detachment to remove the cell. In this lecture I want to address the question to what extent we can use the formalism derived in gas phase adsorption and desorption experiments to describe the analog reactions in solution quantitatively and predictably? Predictive models would help to advance microfluidic based diagnostics and contribute to the design of environmental benign anti-fouling surfaces.

Recent experiments and theoretical work to understand adsorption and detachment of small (cell size) objects from a surface under shear flow will be discussed with reference to the formalism used in basic gas phase adsorption/desorption experiments. In the most basic experiments, the probability that a molecule will adsorb or desorb is measured as a function of pressure, temperature, and coverage. Monolayer adsorption of a gas is described by the Langmuir isotherm (or its derivatives if interactions between the molecules need to be considered) and desorption by an Arrhenius type equation to determine the activation energies.

The kinetic equation used in gas phase experiments can be modified to describe adsorption and detachment of particles from a surface under shear flow, where temperature is replaced by shear force to determine activation energies. The shear force is ramped up in a programmable way, and by fitting the experimental data with a rate equation gives highly reproducible results from which the activation energy of detachment of these particles can be derived. The activation energy values determined from these experiments will be discussed in the context of separately measured adhesion energies of these particles in an aqueous environment to derive a mechanistic understanding for attachment and detachment of small objects in laminar shear flow.

4:20pm **BI-WeA-7 Unraveling Complexities at the Adhesive Interface of Acorn Barnacles, Kenan Fears, C So, D Leary, H Ryou, J Schultzhans, C Wang**, US Naval Research Laboratory; *B Orihuela, D Rittschof*, Duke University Marine Laboratory; *C Spillmann, K Wahl*, US Naval Research Laboratory

**INVITED**

Marine macro-foulers (e.g. barnacles, tubeworms, mussels) create robust underwater adhesives capable of attaching themselves to almost any material. While proteomic analysis has provided insight into the chemical composition of these natural adhesives, developing synthetic analogs that mimic their performance remains a challenge due to an incomplete understanding of adhesion processes. Through the use of in vivo confocal microscopy with multiple fluorescent probes, we have identified that acorn barnacles (*Amphibalanus (= Balanus) amphitrite*) secrete a phase-separating surfactant mixture to clean and protect the surface ahead of growth and cement deposition. This mixture consists of a phenolic laden gelatinous phase that holds a phase rich in lipids and reactive oxygen species at the seawater interface. This secretion oxidizes and lifts off adhered biofilms surrounding the barnacle base as it expands. These findings show barnacles repurpose phenolic chemistries ubiquitous to adhesives and cuticles as part of their own antifouling strategy. The discovery of this critical step in underwater adhesion represents a missing link between natural and synthetic adhesives, and provides new directions for the development of environmentally-friendly biofouling solutions.

5:00pm **BI-WeA-9 Ultra Low Fouling Zwitterionic Coatings – Influence of Molecular Architecture on Fouling Inhibition, Axel Rosenhahn, J Koc**, Ruhr-University Bochum, Germany; *S Bauer*, Ruhr-Universität Bochum, Germany; *J Finlay, A Clare*, Newcastle University; *E Schoenemann*, University of Potsdam; *A Laschewsky*, University of Potsdam

Zwitterionic polymers are promising ultra-low fouling coating materials. While their outstanding properties are undisputed, a precise understanding of how the molecular architecture leads to optimized polymer function is still missing. Here we compare the influence of different anionic groups using a range of self-assembled monolayers and compare it against a series of photocrosslinkable zwitterionic polymers. In all cases, the intramolecular arrangement was varied in order to determine if the spacing between the oppositely charged moieties, the nature of the charged group, and the backbone affect their non-fouling properties. A comparison of self-assembled monolayers consisting of mixed, oppositely charged thiols and custom designed zwitterionic thiol compounds showed that in particular sulfate groups showed promising properties and an horizontally adjacent arrangement was preferred. As approach towards polymeric coatings, zwitterionic methacrylates were co-polymerized with benzophenonemethacrylates to obtain a photocrosslinkable polymer. We applied the polymers by spin-coating and subsequent photocrosslinking. All coatings were characterized by AFM, IR, and XPS prior to biological testing and protein resistance was characterized by SPR. The antifouling activity against marine biofilm formers, algae, and invertebrate larvae was determined in laboratory assays. On the basis of the obtained data, design criteria for optimized zwitterionic components for fouling-release technologies will be discussed.

5:20pm **BI-WeA-10 Biomimetic Surfaces on Chitosan Membranes with Enhanced Antibacterial Properties Produced by Directed Plasma Nanosynthesis, Camilo Jaramillo, A Civantos, J Allain**, University of Illinois at Urbana-Champaign

First reported in the late 1950s, antibiotic-resistant bacteria have become an issue of major concern<sup>1</sup>. This has motivated the study of other mechanisms to provide interfaces with antibacterial activity, including surface chemistry, surface topography and other physicochemical properties<sup>2</sup>. Among these mechanisms, the physico-mechanical effects have also attracted attention. An example of this concept can be found in natural nanostructured surfaces. The nanopatterned surface of the cicada wings has been observed to possess very effective bactericidal activity, via a chemistry-independent mechanism<sup>3</sup>. Chitosan, a biodegradable and non-toxic biopolymer with antibacterial properties, has been used for wound treatment, drug delivery and biosensing applications<sup>4</sup>. These properties make it an attractive material to be used in biointerfaces. Following the same concept of the cicada wings, nanopatterned silicon surfaces coated with CS showed enhanced antibacterial activity, when compared to uncoated Si surfaces<sup>5</sup>.

In previous works from our group, we had shown that Directed Plasma Nanosynthesis (DPNS) can induce the formation of nanofeatures on the surface of chitosan. In this work, we further study the effects of DPNS on the formation of nanopatterns on the surface of different chitosan membranes are further studied, using angle of irradiation as a control parameter. Additionally, the biocidal action of the modified surfaces is studied by running in vitro tests with *E. coli*. SEM images were used to evaluate the nanofeatures induced on the surfaces, as well as their effects on the incubated bacteria. Studying the antibacterial activity of these nanopatterned surfaces constitutes a step towards elucidating the mechanisms of antibacterial activity based on physico-mechanical effects.

References:

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2. Bazaka, K. *et al.* Anti-bacterial surfaces: natural agents, mechanisms of action, and plasma surface modification. *RSC Adv.***5**, 48739–48759 (2015).
3. Ivanova, E. P. *et al.* Natural bactericidal surfaces: Mechanical rupture of pseudomonas aeruginosa cells by cicada wings. *Small***8**, 2489–2494 (2012).
4. Bano, I., Arshad, M., Yasin, T., Ghauri, M. A. & Younus, M. Chitosan: A potential biopolymer for wound management. *International Journal of Biological Macromolecules***102**, 380–383 (2017).
5. Tripathy, A. *et al.* Impact of Bioinspired Nanotopography on the Antibacterial and Antibiofilm Efficacy of Chitosan. *Biomacromolecules* [acs.biomac.8b00200](https://doi.org/10.1021/acs.biomac.8b00200) (2018). doi:10.1021/acs.biomac.8b00200

<sup>1</sup> Gaede Langmuir Award Winner

# Wednesday Afternoon, October 24, 2018

5:40pm **BI-WeA-11 How Do Geobacter Aggregates Communicate: New Understanding from In Situ Liquid SIMS**, *Wenchao Wei*, *R Komorek*, Pacific Northwest National Laboratory; *C Yang*, *F Liu*, Yantai Institute of Coastal Zone Research; *Z Zhu*, *X Yu*, Pacific Northwest National Laboratory

We developed a vacuum compatible microfluidic interface, System for Analysis at the Liquid Vacuum Interface (SALVI), to enable direct observations of liquid surfaces and liquid-solid interactions using time-of-flight secondary ion mass spectrometry (ToF-SIMS) and a variety of spectroscopy and microscopy characterization techniques. SALVI was recently applied to investigate biological interfaces in living biofilms and co-cultured microbial communities [1, 2]. In this talk, a more complex microbial communities consisting of syntrophic *Geobacter metallireducens* and *Geobacter sulfurreducens* was investigated using ToF-SIMS [3]. As a surface technique, in situ liquid SIMS provides direct measurement of initial attachment of the co-cultured aggregates. Our 3D imaging results give spatial distribution of amino acid fragments and lipids, indicative of the role of proteins and lipids played in the co-cultured aggregate formation. The planktonic cells seem to show strong evidence of hydrogen transfer in liquid by the direct observations of lipid fragments with the addition of water and hydrogen. This pheromone indicates that higher direct electron interspecies transfer may exist in co-culture aggregates whereas hydrogen transfer is dominant in planktonic cells. More interestingly, distinct water distribution is observed between co-cultured aggregates and planktonic cells, indicating the change of hydrogen bonding as a result of the complex microbial syntrophic community communication. Our results demonstrate that interfacial chemistry involving living microbial systems can be studied from the bottom up based on microfluidics, potentially providing more important understanding in system biology.

**Key words:** microfluidics, biofilm, co-cultured aggregate, electron transfer, EPS, ToF-SIMS

#### References:

1. X. Hua et al., In situ molecular imaging of hydrated biofilm in a microfluidic reactor by ToF-SIMS, *Analyst*, 139 (7), 1609-1613, 2014.
2. W. Wei et al., Characterization of syntrophic *Geobacter* communities using ToF-SIMS, *Biointerfaces*, 12 (5), 05G601, 2017.
3. Y. Ding et al., In situ molecular imaging of the biofilm and its matrix, *Analytical Chemistry*, 88 (22), 11244-11252, 2016

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