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

Biomolecules and Biophysics and Interfaces & Flash Session

Moderators: Markus Valtiner, Vienna University of Technology, Austria, Tobias Weidner, Aarhus University, Denmark

2:20pm **BI+AS-TuA1 Electrochemical Surface Reactivity of Catechol Derivatives: Competitive Adsorption and Ion Effects**, ***Laila Moreno Ostertag***, *L.L.E. Mears, D. Dworschak, M. Valtiner,* Vienna University of Technology, Austria

Catechols are molecules well known for their participation in important biological processes such as neurotransmission and bioadhesion. Their adhesive properties are of great interest for the development of biocompatible glues and coatings. In particular, L-3,4-dihydroxyphenylalanine (L-DOPA) has been found to play a defining role in the attachment of mussel feet to organic and inorganic surfaces in wet environments. Its electrochemistry has been widely studied, but the possibilities of many other catechols in this field remain largely unexplored, as is the effect of diverse ionic media in which their properties could be improved.

By using several electrochemical techniques and comparing to a well-known model system, we have obtained an understanding of the redox mechanisms involved in the interaction of these molecules at a metallic interface. Reaction parameters such as diffusion coefficients and reaction constants have been determined in different ionic media.

This fundamental insight allows us to set catechols in the context of their role within interfacial phenomena. Our approach enables the elucidation of free energies that characterize the energy landscape of adhesion processes at electrified interfaces, which can then bridge the gap between bulk electrochemistry and single-molecular surface-force analysis techniques. Full energy pathways can be drawn based on combined results and lead to a wide range of possibilities in the development of catechols for specific applications.

2:40pm **BI+AS-TuA2 Direct Observation of Lysozyme Interaction with a Curved Lipid Membrane Surface by Sum Frequency Scattering Vibrational Spectroscopy**, ***Thaddeus Golbek***, Aarhus University, Denmark, Denmark; *H.I. Okur, S. Kulik, J. Dedic, S. Roke,* École Polytechnique Fédérale de Lausanne (EPFL), Switzerland; *T. Weidner,* Aarhus University, Denmark

Highly ordered protein aggregates play a large role in many neurodegenerative and non-neuropathic disorders including type II diabetes, Alzheimer's, Parkinson's, prion, and Huntington's disease. Even though a causative link between the formation of protein aggregates and server diseases has been established, the molecular level-details of protein aggregation and cell membrane disruption are still underdeveloped. One of the most characterized proteins that has been used to model protein aggregation is hen egg-white lysozyme. While lysozyme has been extensively studied at model surfaces, it has not been well studied on curved, more realistic, surfaces. In order to observe lysozyme at a curved surface we applied sum frequency scattering (SFS) vibrational spectroscopy to probe the interface between the protein and the curved lipid model cell membrane surface. The model cell membrane was built upon 10% 1,2-dimyristoyl-*sn*-glycero-3-phospho-(1'-rac-glycerol) (DMPG) and 90% 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine (DPPC) lipid nanodroplet emulsions, were the oil is *n*-hexadecane. SFS studies at the protein-lipid interface demonstrate that binding of lysozyme induces increased lipid monolayer order. An increase in acyl chain order determined by the ratio of the CH_3 symmetric and CH_2 asymmetric peak amplitudes and lipid head group orientation change from about 0˚ to greater than 60˚, determined by the increase is phosphate head group signal, suggests that lysozyme inserts into the lipid layer causing lipid dehydration and reorientation. The amide I SFS spectrum lysozyme interacting with the model cell lipid monolayer is also studied to observe the folding and ordering of the protein. Altogether, we demonstrate the use of lipid monolayer nanodroplet emulsions as a platform to study protein membrane interactions in solution, which excludes air form the model further increasing biomimetic modeling potential using SFS.

3:00pm **BI+AS-TuA3 Iron Speciation at Aqueous Surfaces**, ***Heather Allen***, Ohio State University **INVITED**

Ion pairing and speciation in the condensed phase and at the aqueous surface is presented for mono and multi-valent ions including iron and phosphate systems. We present new evidence of iron (III) surface prevalence at both the water and glycerol surfaces. Understanding surface water solvation structure using polarized Raman and vibrational sum frequency generation spectroscopy are also discussed.

4:20pm **BI+AS-TuA7 Identifying the Molecular Mechanisms that Mediate Cell Membrane Repair by Sum Frequency Generation Spectroscopy**, *T.W. Golbek,* Oregon State University; *S.J. Roeters, T. Weidner,* Aarhus University, Denmark; *C.P. Johnson,* ***Joe Baio***, Oregon State University

Movement in everyday life places stress on sarcolemma which creates small tears in the muscle cell membrane. Mutations in this multi-domain dysferlin protein render it unable to repair the membrane and this phenomena is related to diseases such as specific forms of muscular dystrophy. Of particular importance is the moment after the release of calcium from tears in the muscle cell membrane, whereby the release of calcium triggers the C2A domain of dysferlin to dock with a lipid vesicle. Mutations mapped to this domain cause loss of binding ability of the C2A domain. This is the first step of muscle cell membrane repair, therefore there is a crucial need to understand the geometry of dysferlin C2A at a membrane interface as well as cell membrane lipid reorientation when compared to a variant. Here we describe a comparison between the wild type dysferlin C2A and a mutation to the conserved aspartic acids on the domains binding loops. To identify both the geometry and the cell membrane lipid reorientation, we applied sum frequency generation (SFG) vibrational spectroscopy and coupled it with simulated SFG spectra to observe and quantify the interaction. A model cell membrane was built with phosphotidylserine and phosphotidylcholine. Observed changes in surface pressure demonstrate that calcium bridged electrostatic interactions govern the initial interaction of the C2A domains docking with a lipid membrane. SFG spectra taken from the amide I region for wild type and variant contain features near 1642 cm^{-1}, 1663 cm^{-1}, and 1675 cm^{-1} related to the C2A domains beta-sandwich secondary structure indicates that the domain binds in a specific orientation. Mapping simulated SFG spectra to the experimentally collected spectra indicated that both wild type and variant domains have nearly the same orientation to the membrane surface. However, examining the ordering of the lipids that make up a model membrane using SFG, we find that the wild type clusters the lipids as seen by the ratio of the CD3 and CD2 symmetric intensities increases by 170% for the wild type and by 120% for the variant. This study demonstrates and highlights the capabilities of SFG to probe with great detail biological mutations in proteins at cell membrane interfaces.

4:40pm **BI+AS-TuA8 Fishing Manganese out from Cellulose: Impact of Coupling Desferrioxamine B to Stainless Steel Beads on the Circular Economy of Paper and Pulp Industry**, ***Jeff Wilkesman***[1], Mannheim University of Applied Sciences, Germany; *K. Mörtter, I. Sommer, P.M. Kunz,* Mannheim University of Applied Sciences, Deutschland

Important as an essential trace element with abundant applications, manganese (Mn) is rising attention due to its aesthetic, operational and health problems at higher concentration in the paper and water industry. When oxygen-containing paper bleaching chemicals (O_2, O_3, H_2O_2 or peracids) are used, the presence of heavy metals like Mn causes problems in the pulp processing, increasing the consumption of the bleaching chemicals and deteriorating pulp quality, including pulp darkening. An effective way to remove Mn from pulp is employing chelators, although its effectiveness is influenced by the overall water chemistry and concomitant contaminants. Successful chelation of Mn usually occurs at pH<8, otherwise highly oxidized species would form, precipitating insoluble Mn(III/IV) oxide minerals, and binding strongly to the pulp. Though the environmentally critical EDTA is used in the paper industry to chelate heavy metals, friendlier and greener alternatives are sought, like desferrioxamine B (DFOB) or E (DFOE), which are linear trihydroxamic acid siderophores produced by bacteria to acquire primarily Fe(III), but also Mn(II/III). Advantages of employing siderophores are its commercial availability, high solubility and stability over a wide pH range. The coupling of DFOB to ~3-4 mm stainless steel beads as solid support was performed. The beads were incubated overnight with several cellulose suspensions to allow formation of the Mn-DFOB complex (log *K* ~29.9). Control assays were performed using EDTA. After treatment, cellulose suspensions originally containing

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~30–40 mg Mn/kg, were submitted for Mn(II), Mn(III) analysis, employing the TCPP [Tetrakis(4-carboxyphenyl)porphyrin] method. Total Mn content was also determined by Inductively Coupled Plasma (ICP). Preliminary results show an approximate 80% reduction of Mn content from the cellulose suspension, though experimentation is still carried on; DFOE is planned to be also analyzed. Mn was recovered by decoupling from DFOB by metal exchange and the beads were reused for further activation with DFOB. This removal alternative resulted in a feasible, easy, greener and economical procedure, leading for improvement in the paper industry. Still, the most expedient option comprising circular economy statements based on sustainable management parameters (cost-effectiveness, performance, simplicity) must be deeper explored. Clearly, further research regarding Mn(II/III) formation and removal will help the water and paper industry, by developing better methods to diminish Mn oxide deposits in pipe networks and optimizing the paper bleaching process, ultimately reducing significant operational costs.

5:00pm **BI+AS-TuA9 The Hybrid Nano-biointerfaces Between Gold, Graphene Oxide and Angiogenin for Wound Repair**, ***Diego La Mendola***, University of Pisa, Italy; *L.M. Cucci, G. Villaggio, C. Satriano,* University of Catania, Italy

Angiogenin (ANG) is a member of the ribonuclease family and a physiological constituent of the human plasma. Ang is a potent angiogenic factor regulating a wide range of responses, such as angiogenesis, cell proliferation, cell migration, and pro-survival effects. ANG has been shown related to many pathophysiological processes, including cancers, neurodegeneration, inflammation and regeneration of damaged tissues. In this work, we investigated a hybrid obtained by the assembly of ANG to gold nanoparticles and graphene oxide nanosheets, to exploit the synergic effects of antioxidant AuNP and antimicrobial GO, respectively. Au-GO-ANG were characterized by UV-visible spectroscopy, to correlate the changes in the plasmonic peak as well as in the π-->π* transitions to the protein interaction with Au and GO, respectively. QCM-D measurements on supported lipid bilayers, as model of cell membranes, pointed to a stronger interaction of the AuNP-Ang systems in comparison with the uncoated nanoparticles. The developed systems promoted fibroblasts migration and wound closure. Confocal microscopy cell imaging evidenced dynamic processes at the level of cytoskeleton and sub-cellular compartments. The results reveal a promising multifunctional platform for wound care treatment and tissue regeneration.

5:20pm **BI+AS-TuA10 Improved Antibacterial Sandwich system for Urological Purposes**, ***Sara Bröskamp***, *G. Franz,* Munich University of Applied Sciences, Germany; *D. Jocham,* University Hospital of Schleswig-Holstein, Germany

In the anaerobic environment of kidneys and bladder which even lack the permanent presence of weak but always toxic oxidative reagents (like ClO_2^-) it is obvious that no Ag^+ ions can be generated by oxidation of a metallic silver film. However, it is well known that the antibacterial impact of Ag^+ ions which can act as a single ion is much higher than the effect of neutral silver nanoparticles [1]. In our efforts to define an effective membrane which is deposited on the interior and exterior surfaces of tubes which exhibit an aspect ratio of more than 100 (balloon catheters) we introduce a significantly improved coating which makes use of the soft oxidation of already deposited silver layers by a microwave or RF plasma [2]. This procedure not only improves the antibacterial effect but also extends the active time of the catheters. The silver oxide on top of the base silver layer which is deposited on an originally hydrophobic surface of an organic polymer by a well-known process is eventually topped by an organic layer of comparable thickness [3,4]. This coating with even thickness on the interior of the tubes has been extensively improved by a device which counteracts the decreasing vapor density of the film-building species by a well-definded temperature gradient [5]. In the case of ureteral stents, we make use of the series of drainage holes along the catheter which act as adjacent sources for the film-building monomer. This layer controls the antibacterial activity which can be effectively tuned by its porosity [6]. The oxidation of the silver also effectively prevents sulfidation by S-containing amino acids (cysteine) which can be present in the kidneys of patients. The silver release rate has been measured by atomic absorption spectroscopy (AAS).

[1] Heidari Zare, V. Juhart, A. Vass, G. Franz, and D. Jocham; Biointerphases 12, 011001 (2017).

[2] G. Franz, S. Bröskamp, K. Resch, W. Hiemeyer, D. Jocham; German patent disclosure DE 10 2019 001 994.6, Mar 26, 2019.

[3] G. Franz, F. Schamberger, A. Kutschera, S. Seyedi, D. Jocham, German patent disclosure DE 102012023349.3, Nov. 29, 2012.

[4] G. Franz, F. Schamberger, H. Heidari Zare, S.F. Bröskamp, and D. Jocham; Beilstein J. Nanotechn. 8, 1982 (2017). [5] S. Bröskamp, D. Redka, A. Möhlmann, G. Franz, and D. Jocham; AIP Advances 7, 075005(2017).

[6] F. Schamberger, A. Ziegler, and G. Franz, J. Vac. Sci. Technol. B30, 01801 (2012).

5:40pm **BI+AS-TuA11 Quantitative Characterization of Piezoelectric Property in Biological System via Piezoresponse Force Microscopy**, ***Jinha Kwon***, *D.G. Kim, H. Cho,* The Ohio State University

Piezoresponse force microscopy (PFM) is a variant of scanning probe microscopic technique based on atomic force microscopy (AFM) that allows imaging of piezoelectric material domains with high resolution. This is achieved by keeping a sharp conductive probe in contact with a piezoelectric material and applying an alternating current (AC) directly to the sample through the probe, which results in deflection of the probe detected through photodiode detector. PFM has been successfully applied to many biological materials such as teeth [1], bone [2], seashell [3], and collagen fibrils [4]. Although biological samples are commonly vulnerable to high voltage input, previous studies used a high voltage input more than 10V to induce a piezoelectric strain large enough to be captured by an AFM tip [5]. Moreover, previous works did not carefully scrutinize the effect of substrate's conductivity and the contribution of parasitic electrostatic forces between the tip and sample, which should be precisely examined to obtain the quantitative piezoelectric properties of sample. In this study, we used type I collagen fibril which has weak piezoelectricity around 1 pm/V. The collagen fibril was aligned to the probe perpendicularly and AC voltage was applied to the fibril through the conductive AFM tip which was carefully calibrated in both vertical and lateral directions. In order to amplify its piezoresponse signal with a small electrical input, we utilized the contact resonance of an AFM cantilever. We also carefully examined the effect of substrate's conductivity by comparing piezoelectric response of the collagen on bare and gold-coated glass slides. Moreover, the contribution of electrostatic forces to the PFM results were investigated while they are varied by applying different DC offsets simultaneously to compensate the electrostatic force. Finally, the piezoelectric property of the collagen was calculated by fitting the measured piezoresponse vs. applied voltage graph. As a result, the piezoelectric properties of a single collagen fibril were precisely characterized in both vertical and shear directions and its heterogeneous nature within a fibril was revealed.

[1] S.V. Kalinin, B.J. Rodriguez, J. Shin, S. Jesse, V. Grichko, T. Thundat, A.P. Baddorf, A. Gruverman, Bioelectromechanical imaging by scanning probe microscopy: Galvani's experiment at the nanoscale, Ultramicroscopy. 106 (2006) 334–340.

[2] M. Minary-Jolandan, M.-F. Yu, Shear piezoelectricity in bone at the nanoscale, Appl. Phys. Lett. 97 (2010) 153127.

[3] T. Li, K. Zeng, Nanoscale piezoelectric and ferroelectric behaviors of seashell by piezoresponse force microscopy, J. Appl. Phys. 113 (2013) 187202.

[4] M. Minary-Jolandan, M.-F. Yu, Nanoscale characterization of isolated individual type I collagen fibrils: polarization and piezoelectricity, Nanotechnology. 20 (2009) 085706.

[5] D. Denning, J.I. Kilpatrick, E. Fukada, N. Zhang, S. Habelitz, A. Fertala, M.D. Gilchrist, Y. Zhang, S.A.M. Tofail, B.J. Rodriguez, Piezoelectric Tensor of Collagen Fibrils Determined at the Nanoscale, ACS Biomater. Sci. Eng. 3 (2017) 929–935.

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