Biomaterial Interfaces Division
Room 318 - Session BI+AS+PS-MoM

Biomolecular Interfaces and Underwater Adhesion

Moderator: Morgan Alexander, University of Nottingham, UK

8:20am **BI+AS+PS-MoM-1 Supported Lipid Bilayers as Model Systems to Understand Molecular Interactions at Complex Solid/Liquid Interfaces***, **Pierluigi Bilotto**,* Centre for Electrochemistry and Surface Technology, Austria*; L. Mears, M. Valtiner,* Vienna University of Technology, Austria

Generating a detailed molecular understanding of complex, simultaneous inter actions at reactive and/or dynamic solid|fluid interfaces is a challenge across disciplines, and has intrigued researchers for decades.[1, 2] Whether it is, for example, in medical adhesives, friction of articular cartilage,[3] or the adhesion of organisms in seawater,[2] complex macroscopic properties at crowded biologic solid|liquid interfaces are mediated by large numbers of individual nanoscale interactions.[4] Exactly this complex competition and molecular structuring at interfaces are central to a multitude of interfacial phenomena, such as membrane transport,[5] membrane conductance, [6,7] cellular adhesion [8] and adhesion regulation in the marine environment. [9]

In our previous works, we characterised a lipid-based model system (LMS) in terms of its stability and bending properties by employing atomic force microscopy and surface forces apparatus. [10] Then, we further modified its outer face with amine-terminating polymers to investigate the specific electrostatic interaction between the amine and a negatively charged mica surface. Then, we examined how interaction forces are affected by the electrolyte concentration, funding a direct exponential like decay between adhesion and electrolyte concentration. Specifically, we found a decrement of 90% in adhesion in a 1M sodium chloride environment. These fundings suggested the presence of a competing mechanism which was confirmed by a kinetic model at the interface involving two competing Langmuir isotherms. Finally, we could estimate ion/surface interaction energies from the experimentally recorded interaction force measurements.[11]

In the talk we will discuss these works and present the new research opportunities coming out from these results.

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(5) Gage, P. W.; Quastel, D. M. J. The Journal of Physiology 1966, 185, 95–123

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8:40am **BI+AS+PS-MoM-2 Recombinant Lubricin Improves Anti-Adhesive, Wear Protection and Lubrication of Collagen II Surface***, H. Yuan,* Tianjin University, China*; **Laura Mears**,* Vienna University of Technology, Austria*; R. Su,* Tianjin University, China*; M. Valtiner,* Vienna University of Technology, Austria

Lubrication in articular joints is regulated by a number of biomolecules including the collagen of the cartilage, lubricin and lipids in the synovial fluid. Camptodactyly-arthropathy-coxa vara-pericarditis syndrome (CACP) is a joint disease, which causes a lack of lubricin, leading to failed lubrication as well as abnormal deposition at cartilage surfaces. Injection of recombinant lubricin (R-LUB) is a promising way to treat the disease. Here, the protein adsorption and lubrication behavior of type II collagen (COL II), mimicking the cartilage surface, upon R-LUB injection were followed by a surface plasmon resonance spectroscopy and surface forces apparatus. The results indicated R-LUB can bind well on COL II surface and the layer of COL II/R-LUB complex exhibited a much lower nonspecific adsorption of BSA (3.25 ng/cm^2) and LYS (0.26 ng/cm^2) compared to those of the COL II layer (32.7 ng/cm^2, 7.26 ng/cm^2), respectively. Normal force measurement demonstrated there were repulsive forces between the COL II/R-LUB complex and different surfaces with $-COO^-$, $-NH_3^+$ and $-CH_3$ groups. Likewise, COL II had a high coefficient of friction ($\mu \sim 0.48$) with surface damage at 2 μm/s and wear pressure of 1.56 MPa. In contrast, the coefficient of friction of COL II/R-LUB complex was dramatically decreased to ∼0.014-0.13 with surface damage at 13 μm/s, the complex even shows an ultralow coefficient of friction of 0.008 at the lowest loading <3 mN. Furthermore, R-LUB modification boosts the strength of the surface against abrasive wear (damage) of 11.96 MPa, which was 7.7 times higher than that of COL II alone. Hence, R-LUB may act as an anti-adhesive and lubrication layer adsorbed on COL II surfaces to develop strong steric-repulsive interactions and lubrication to prevent direct surface contact. Our results provide fundamental insights into the adsorption and lubrication behavior for understanding biological lubrication, especially using R-LUB for CACP disease treatment.

9:40am **BI+AS+PS-MoM-5 Hyaluronic Acid-Dopamine Conjugate for Facile Deposition onto Collagen I with Enhancing Anti-Adhesion and Lubrication***, H. Yuan,* Tianjin University, China*; L. Mears, M. Valtiner,* Vienna University of Technology, Austria*; **Rongxin Su**,* Tianjin University, China

Collagen I matrix (COL I) has been applied clinically for repairing damaged cartilage, but it has poor protein resistance and insufficient lubrication performance, which seriously affects the repairing performance for cartilage. Hyaluronic acid (HA) has good anti-adhesive and lubrication properties, and seems to be a potential candidate to improve treatment with COL I, but it cannot be immobilized onto the collagen surface. Inspired by mussels, dopamine (DA) was chemically grafted to HA to form the HADA conjugate, which could firmly adhere to the surface of COL I by dopamine oxidation and reacted with amine from COL I. The protein resistance and lubrication properties of COL I and HADA-modified COL I (COL I/HADA) surfaces were followed by quartz crystal microbalance with dissipation and surface force apparatus techniques. The optimal modified time of HADA on COL I surface was 8 h. The nonspecific adsorption of bovine serum albumin (BSA) and lysozyme on COL I/HADA were reduced to 1/25 and 1/42 of that on COL I. COL/HADA also displayed very good resistant to high concentrations of BSA. Upon HADA modification, the interaction force between COL I and the surfaces with positive and negative charges sharply decreased from 2-6 mN/m to 0, demonstrating that the COL I/HADA surface had a strong anti-adhesion property. The coefficient of friction of COL I (∼0.65) was quite high displaying poor lubricating ability, while that of COL I/HADA reduced to ∼0.16. Upon HADA modification, the wear occurred at a shear rate of 14 μm/s, and the surface resistance to abrasive wear (damage) was greatly improved to 9.7 MPa, about 12 times higher than the COL I surface. These results indicated that HADA-modified COL I is a promising anti-adhesive and lubricating joint repair material, especially in the field of osteoarthritis treatment.

10:00am **BI+AS+PS-MoM-6 Anti-Fouling Properties of Amphiphilic Zwitterionic Hydrogels**, ***Lisa Schardt**,* Ruhr University Bochum, Germany*; A. Martínez Guajardo,* University of Potsdam, Germany*; J. Koc,* Ruhr University Bochum, Germany*; J. Clarke, J. Finlay, A. Clare,* Newcastle University, UK*; H. Gardner, G. Swain, K. Hunsucker,* Florida Institute of Technology*; A. Laschewsky,* University of Potsdam, Germany*; A. Rosenhahn,* Ruhr University Bochum, Germany

Hydrogels exhibit excellent biocompatibility and resistance against nonspecific attachment of organisms most likely due to their stable hydration shell.[1] Zwitterionic polymers like the sulfobetaine N-(2-methacryloxy)-ethyl-N,N-dimethylammoniopropansulfonate (SPE) are promising candidates foranti-fouling coatings. However, due to low mechanical strength, their performance in the field is limited.[2] N-butyl methacrylate (BMA) was added in amounts between 0 and 50% to copolymers containing SPE and the photocrosslinker 2-(4-benzoylphenoxy)ethyl methacrylate (BPEMA) to tune the hydrophilicity of the resulting hydrogel properties. The rearrangement of the polymer upon immersion in seawater was characterized by under-water contact angle goniometry. The swelling and resistance against mineral particles were measured with surface plasmon resonance (SPR) and sediment immersion tests. Biological anti-fouling experiments were performed using *Ulva linza* and field tests. Upon immersion in saltwater, the polymer chains rearranged to form hydrophilic surfaces and the degree of swelling depended on the salt concentration. The incorporation of BMA successfully altered the mechanical properties of the coatings resulting in a lower silt uptake. At the same time, the amphiphilicity did not hamper the anti-fouling performance in laboratory assays and a decrease of the settlement was observed in field tests.[3]

[1] A. Laschewsky, *Polymers*, **2014**, 6, 1544-1601.

[2] J. Koc, *Biofouling*, **2019**, 4, 454-462.

[3] L. Schardt, *Macromolecular Rapid Communications*, **2021**, 2100589.

10:40am **BI+AS+PS-MoM-8 Mussel Adhesion: A Fundamental Perspective on Factors Governing Strong Underwater Adhesion***, L. Mears, J. Appenroth, A. Celebi, A. Imre, H. Yuan,* TU Wien, Austria*; P. Bilotto,* CEST Centre for Electrochemistry and Surface Technology, Austria*; R. Su,* Tianjin University, China*; **Markus Valtiner,*** TU Wien, Austria

Tuning interfacial electrochemistry is central to the principle of the strong underwater adhesive of mussels. Here we critically discuss recent progress in the field, and we discuss how interfacial electrochemistry can vary interfacial forces by a concerted tuning of surface charging, hydration forces and tuning of the interfacial ion concentration. Mussel foot proteins contain a number of different functional groups, with much focus directed towards the catechol moiety. Therefore, we discuss some of our recent results in the area of adhesion of different functional groups in a saline environment. We also present new data from electrochemical surface force apparatus experiments that explore the difference in adhesion for oxidized and reduced forms of the catechol functional group against a mineral, mica, in different environments. These results raise interesting questions about the role of the catechol group. We propose new paths into understanding and utilizing redox-proteins and derived polymers for enhancing underwater adhesion in a complex salt environment.

11:00am **BI+AS+PS-MoM-9 Bioinspired Underwater Adhesives Using Amyloids from Commonplace Proteins***, M. Wilson,* NRC Post-doctoral Fellow sited at the Naval Research Laboratory, Chemistry Division*; M. Beasley,* NRC post-doc sited at the Naval Research Laboratory, Chemistry division*; K. Fears,* Naval research laboratory, Chemistry Division*; E. Yates,* US Naval Academy, Chemistry Department*; **Christopher So**[1]**,*** Naval Research Laboratory, Chemistry Division

Barnacles adhere permanently underwater using proteins that are delivered as a liquid, triggered to assemble, and cure as a bulk amyloid material in extreme seawater environments. More cosmopolitan than most other fouling organisms, barnacles rely on these materials to remain stuck at frigid ocean depths, as well as on hot intertidal coasts. We have previously been successful in designing sequences that can mimic the natural glue chemistry and structure, however bridging the gap between natural sequences and materials of practical use remains a challenge. Here, we mimic protein aggregation from the barnacle with unmodified food proteins as model systems and fabricate adhesives by curing them at the adhesive joint. We use temperature and time to control protein assembly and define the relationship between biophysical state and adhesive strength. Using thermal processing, we fabricate adhesives that approach the underwater lap shear strength of commercial marine and contemporary bioinspired chemistries. Though we observe differences in adhesive behavior between the examined proteins and their aggregation state, the presence of amyloids improves underwater performance across all proteins studied. We show that commonplace proteins can be delivered as a liquid, triggered to cure with chemistry or heat, and form strong underwater adhesives at the contact. The aggregation of commonplace proteins is therefore a viable pathway in creating strong underwater adhesives which, like the organisms that use them, can operate in extreme underwater conditions.

11:20am **BI+AS+PS-MoM-10 Incorporation of Antimicrobial Cyclic Peptides in Polymeric Materials***, D. Regan, Q. Lu, D. Barlow, **Kenan Fears,*** US Naval Research Laboratory

Polymeric coatings are used universally to protect structural materials and extend their operational lifetime. Microbial growth on these coatings, if unmitigated, present health risks and can diminish the protective performance of the coatings. For example, fungi have been linked to the degradation of aircraft surface coatings which can lead to corrosion of the underlying metals. After bans on heavy metal mixtures within surface treatments, a commercial void remains for a solution to prevent biodegradation of material surfaces. Building on the advancements within cyclic peptide synthesis, we test the antimicrobial activity of alpha and beta conformations of cyclic peptides against microorganisms of medical and industrial interest. Minimum inhibitory concentration (MIC) and microbial growth assays showed that cyclic peptides exhibited broad spectrum activity against gram-positive and gram-negative bacteria, yeasts, and algae. Furthermore, the cyclic peptides were mixed into a commercial polyester polyurethane coating, Irogran, and exposed to cultured isolates of biodegrading yeasts. For both cyclic peptide-Irogran blends, zero colony forming units were detected after a one-week exposure. These findings demonstrate how synthesized cyclic peptides retain their antimicrobial activity after incorporation into polymeric surface coatings to prevent the growth of problematic microorganisms.

11:40am **BI+AS+PS-MoM-11 Tuning Amphiphilicity of Alginic Acid-Based Polyelectrolyte Multilayers to Enhance Marine Fouling Resistance***, **Jana Karthäuser**, T. Gnanasampanthan, S. Spöllmann, R. Wanka, H. Becker, A. Rosenhahn,* Ruhr University Bochum, Germany

Polysaccharides are among other naturally occurring polymers commonly used in fouling-resistant coatings for both marine and medical applications. The anionic polysaccharide alginic acid (AA) is a non-toxic, eco-friendly, and readily accessible biopolymer that is widely used for biomedical purposes because of its high water-binding capacity. Thus, alginic acid is an interesting and promising building block to produce marine antifouling coatings. Unfortunately, in seawater, the biopolymer loses its antifouling efficacy due to the complexation of bivalent ions. An approach to overcome the susceptibility of charged polysaccharides, such as AA, is the blocking of the carboxylate groups by hydrophobic functional groups. The incorporation of amphiphilic moieties additionally changes the physicochemical properties of the coating and enables the tuning of fouling-resistant properties.[1]Layer-by-layer assembly of polyelectrolytes is a versatile and common technique to produce highly defined and reproducible coatings. The use of different or differently modified polyelectrolytes with opposite charges enables the charge-driven assembly.[2] To introduce amphiphilicity, different degrees of carboxyl groups of alginic acid were modified with pentafluoropropylamine. The influence of the amphiphilicity on the physicochemical characteristics of the modified alginic acid itself as well as of the coatings, when used alternately deposited with polyethyleneimine in multilayers, were investigated. Subsequently, the different degrees of modification of the AA-containing coatings with respect to the non-specific attachment of proteins by surface plasmon resonance spectroscopy and marine fouling organisms by attachment assays were examined in more detail and revealed an improved fouling resistance with increasing amphiphilicity.

1. Bauer, S. *et al.* Resistance of Amphiphilic Polysaccharides against Marine Fouling Organisms. *Biomacromolecules***17**, 897–904 (2016).

Gnanasampanthan, T. *et al.* Effect of Multilayer Termination on Nonspecific Protein Adsorption and Antifouling Activity of Alginate-Based Layer-by-Layer Coatings. *Langmuir***37**, 5950–5963 (2021).

Gnanasampanthan, T. *et al.* Amphiphilic Alginate-Based Layer-by-Layer Coatings Exhibiting Resistance against Nonspecific Protein Adsorption and Marine Biofouling. *ACS Appl. Mater. Interfaces***14**, 16062–16073 (2022)

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[1] **BID Early Career Researchers Award**

Biomaterial Interfaces Division
Room 318 - Session BI+AS+HC+SS-MoA

Bioinspired Materials and Applications

Moderators: Sally M. McArthur, Deakin University, Australia, **Tobias Weidner**, Aarhus University, Denmark

1:40pm **BI+AS+HC+SS-MoA-1 Bioinspired Approaches to Prevent Microbes and Fouling on the Surface of Membranes***, R. Shah, T. Goodwin, **Jessica Schiffman,*** University of Massachusetts Amherst **INVITED**

The reliability and ease of operation of membrane-based water purification systems has led to their increased use in water and wastewater treatment. However, water and energy are mutually dependent critical resources; to produce clean water requires energy and the production of energy requires large volumes of water. Unfortunately, when microorganisms and other foulants accumulate on the surface of membranes and block their pores, more energy is required to operate the separation process even though its productivity is significantly reduced. The overall goal of this talk is to illustrate how bioinspired approaches can be used to enhance the properties of ultrafiltration membranes. Our first approach will demonstrate how we controlled the deposition of the bioinspired "glue" dopamine in order to fabricate ultrafiltration membranes with retained selectivity and pure water flux. Molecules for polymerization were immobilized on the membrane's surface yet prevented from attaching to the membrane's pores due to a backflow of nitrogen gas achieved using simple in-house constructed equipment. If time allows, I will provide an overview of our recent exploration into how pitcher plant inspired immobilized liquids can dramatically increase the fouling resistance of membranes that have consistent flux over at least ten cycles of operation. Biofouling during membrane-based operations is a major challenge and we suggest that there are numerous bioinspired approaches that can address this problem.

2:20pm **BI+AS+HC+SS-MoA-3 Antibiotic-Free Liquid Layers Decrease Bacterial Adhesion on Catheters In Vivo***, C. Fong,* University of Maine*; M. Andersen, A. Flores Mireles,* Notre Dame*; **Caitlin Howell,*** 5737 Jenness Hall

The rise of antibiotic resistance is one of the greatest global public health challenges of our time. Although new antibiotics continue to be discovered, the pace is slowing while the rate of discovery of new antibiotic-resistant organisms continue to grow at an alarming rate. New, non-chemical approaches are needed which can reduce bacterial surface attachment and growth without leading to further resistance. Over millions of years, Nature has developed several ways to mechanically direct or stop bacterial growth, leading to materials-based antibacterial mechanisms which are elegant, effective, and difficult for bacteria to overcome. One of these approaches, immobilized liquid layers, functions via the use of a mobile, dynamic, and sacrificial physical barrier between the bacteria and the surface which they may contaminate. *In vitro* proof-of-concept experiments using urinary catheters— one of the most common and infection-prone medical devices—liquid layers were found to reduce bacterial adhesion by 99% compared to untreated controls. In tests *in vivo*, the system performed beyond expectations, reducing not only bacterial adhesion but overall surface protein contamination as well. The results provide hope that continuing to engineer materials-based approaches to stop bacterial adhesion and growth can help us to stay ahead of antibiotic resistance.

2:40pm **BI+AS+HC+SS-MoA-4 Discovery of Cell Instructive Materials for Next Generation Medical Devices: Exploring Microtopography and 3D Shapes***, **Morgan Alexander,*** University of Nottingham, UK

The polymer biomaterials found in the clinic today are dominated by materials that have been chosen largely on the basis of their availability and mechanical properties. It would be desirable to design our way forward from this situation to new and better biomaterials chosen for positive interactions with surrounding cells and tissues. Unfortunately, our understanding of the interface between most materials and biology is poor. Only in isolated cases is there a good understanding of cell-material surface interactions and fewer still where material-tissue interactions are well characterised and understood.

This paucity of information on the mechanism of biomaterial interactions within the body acts as a roadblock to rational design. Consequently, we have taken a high throughput screening approach to discover new bio-instructive polymers from large chemical libraries of synthetic monomers presented as micro arrays. [1,2] This approach, akin to engineering serendipitous discovery, has resulted in novel materials which we have taken all the way from the lab to the clinic.

More recently we have extended our approach to explore the opportunities offered by micro topography and 3D shape manipulation to provide bio-instructive cues topography to immune cells, stromal cells and pathogenic bacterial cells. To do this we have developed and adopted a range of high throughput screening platforms, including theTopoChip[3], ChemoTopoChip [4] and used 3D printing to produce the ArchiChip [5]. The talk will focus on these topographic platforms and our findings, in particular novel topographies that reduce bacterial biofilm formation and provide beneficial host cell responses which has the potential to reduce infection in medical device implantation.[6]

References

[1] Combinatorial discovery of polymers resistant to bacterial attachment Hook et al. **Nature Biotechnology** 30 (9), 868-875 (2012).

[2] Materials for stem cell factories of the future Celiz et al. **Nature Materials** 13 (6), 570-579 (2014).

[3] Immune modulation by design: using topography to control human monocyte attachment and macrophage differentiation Vassey et al. **Advanced Science** 7 (11), 1903392 (2020).

[4] Discovery of synergistic material-topography combinations to achieve immunomodulatory osteoinductive biomaterials using a novel in vitro screening method: The ChemoTopoChip Burroughs et al. **Biomaterials** 271, 120740 (2021).

[5] Innate Immune Cell Instruction Using Micron-scale 3D Objects of Varied Architecture and Polymer Chemistry: The ChemoArchiChip Vassey et al. under review.

[6] Micro topographical instruction of bacterial attachment, biofilm formation and in vivo host response Romero et al. under review.

3:00pm **BI+AS+HC+SS-MoA-5 Development of a Method for Visualizing Nanometer-Scale Three-Dimensional Structures of Chromosomes by Three-Dimensional Atomic Force Microscopy***, **Ryohei Kojima**, K. Miyazawa, K. Teramae,* Kanazawa University, Japan*; T. Sumikama,* PRESTO, JST, Japan*; M. Meguro,* Research Center for Experimental Modeling of Human Disease, Kanazawa University, Japan*; K. Imadate,* Osaka University, Japan*; N. Okano,* Kanazawa Unversity, Japan*; S. Horike,* Research Center for Experimental Modeling of Human Disease, Kanazawa University, Japan*; K. Hirahara,* Osaka University, Japan*; T. Fukuma,* Kanazawa University, Japan

Three-dimensional atomic force microscopy (3D-AFM) is capable of obtaining 3D force images at solid-fluid interface in sub-nanometer scale. In the previous research, 3D-AFM visualized molecular-scale hydration and flex molecular structures of bio samples such as lipid and DNA. As a next step, it is required to visualize 3D complex structures with high order molecular organizations.

In this research, we developed 3D-AFM for visualizing 3D folded structures of human chromosomes. Chromosome (Fig. 1a) is composed of 3D folded structures that has important roles for genetic transfer. However, nanometer-scale 3D folded structures of human chromosomes have not been well understood yet. It is expected that 3D-AFM contributes to chromosome study, but it is difficult to measure inside of 3D folded structures of chromosomes by conventional conical tip without damage of samples by tip scanning. To visualize 3D folded structures of chromosome by 3D-AFM, we fabricated a carbon nanotube (CNT) tip (length > 500 nm, diameter < 20 nm) to penetrate chromosomes by 3D-AFM. By using the conventional tip and home-made CNT tip (Fig. 1c(i)-d(i)), we performed 3D-AFM of human chromosomes, and obtained 3D frequency shift (Δf) image (Fig. 1b). We extracted single Δf curves from the 3D Δf images obtained with Si tip and CNT tip, respectively (Fig. 1c(ii)-d(ii)). Δf curve using CNT tip shows oscillatory profile until 500 nm in depth from the surface of the chromosome in contrast to the Δf curve using Si tip. This result suggests that the obtained 3D Δf image using CNT tip reflects structures inside chromosome. Based on this research, applications of 3D-AFM will be expanded for visualizing 3D structures of biological samples in various research fields.

3:20pm **BI+AS+HC+SS-MoA-6 Mass-Manufactured Surface Textures Kill Bacteria as Part of Low-Cost Water Purification Devices***, **Liza White**, C. Howell,* University of Maine

Water purification and disinfection, particularly of turbid water, is a significant and growing need worldwide. Pulsed electric field (PEF) devices can be used to inactivate pathogens in water; however, manufacturability, power consumption, cost, and portability remain significant hurdles. Through leveraging paper industry technology in Maine, we have optimized electric field generation using custom textured film in a roll-to-roll manufacturing process to act as the functional part of portable PEF water purification devices. Specifically, we used commercially produced textured release paper as a substrate for the film electrodes and explored different types of metal coating to reduce the overall power consumption, cost, and manufacturability. CAD and modeling software was then used to simulate various textures to determine the optimal texture to focus the electric field while keeping a low total current density, and a custom texture was designed. The mass-manufactured textured materials were cut into singular flow cells and were sputter-coated with various metals and assembled. The flow cells were connected to a pulsed generator that pulsed a square wave at 15 µs at a frequency of 100 Hz with a voltage of 100 V. Water with a known concentration of bacteria was pushed through the flow cells at a rate of 200 µL/minute. The outlet sample was collected, and bacterial reduction was calculated. These tests demonstrated that mass-manufactured surface textures could function as part of a low-cost PEF water purification device. The development of low-cost PEF water purification devices based on surface texture will help provide more accessible clean water in the face of growing water shortages.

4:00pm **BI+AS+HC+SS-MoA-8 Nature-inspired Materials for Energy and Environmental Sustainability***, **Tak Sing Wong**,* The Pennsylvania State University **INVITED**

With an evolutionary history of 3.95 billion years and over 8 million species on earth, natural organisms have often served as blueprints for the design of highly functional engineered materials. In particular, natural species have demonstrated how different micro/nanoscale surface architectures can yield an array of distinct interfacial functions. Understanding the fundamental principles behind these natural surfaces will aid the design of multifunctional materials for a range of energy and sustainability applications. In this talk, I will discuss a number of specific examples showcasing our recent biologically inspired technologies which take inspirations from insects to plants. These examples include the development of anti-fouling and self-cleaning surfaces inspired by the slippery rims of the *Nepenthes* pitcher plants, as well as the fabrication of ultra-antireflective coatings inspired by the leafhopper-produced brochosomes. Perspectives on how nature-inspired materials may impact future applications in energy and sustainability will be discussed.

4:40pm **BI+AS+HC+SS-MoA-10 Programmable Biomimetic Light-Harvesting Systems: Quantum-Optical Control of Light-Matter Interactions***, A. Lishchuk, E. Csanyi, **Graham Leggett**,* University of Sheffield, UK

The absorption of light by molecules leads to the formation of excitons (electron-hole pairs). Control of excitons is essential for many new and emerging technologies, but the inefficient dynamics and short diffusion lengths (~ 10 nm) of excitons in molecular systems limit their utilisation.Theory suggests that exciton diffusion lengths could be enhanced by several orders of magnitude in the strong light-matter coupling regime. However, design principles for the production of photonic materials that exploit strong coupling are lacking. We have found that photosynthetic light-harvesting complexes (LHCs) from plants and bacteria are strongly coupled to localised surface plasmon resonances (LSPRs) in arrays of metal nanostructures, yielding macroscopically extended excited states that enable coherent, non-local excitation transfer and the creation of bespoke optical states not found under weak coupling. However, proteins are not suitable for putative applications of molecular photonic materials. Inspired by photosynthetic LHCs, we demonstrate the fabrication of programmable plexcitonic antenna complexes, in which polymer scaffolds organise excitons within localised surface plasmon resonances to achieve strong light-matter coupling, yielding delocalised excited states (plexcitons) that extend across at least 1000s of pigments. In our plexcitonic antenna complexes, poly(amino acid methacrylate) scaffolds grown from gold nanostructures by atom-transfer radical polymerisation (ATRP) organise excitons (transitions in chlorophylls) within LSPRs to achieve strong light-matter coupling, yielding Rabi energies up to twice as large as those achieved with biological LHCs. The energies of the resulting delocalised excited states (plexcitons) are programmed by varying the degree of polymerisation, scaffold packing density and chlorophyll loading. Steric hinderance in fully-dense PCysMA brushes limits binding of bulky chlorophylls, but the chlorophyll concentration can be increased to ~2M, exceeding that in biological light-harvesting complexes, by controlling the grafting density and polymerisation time. Moreover, synthetic plexcitonic antenna complexes display pH and temperature responsiveness, facilitating active control of strong plasmon-exciton coupling. These biologically-inspired metamaterials offer great promise for the design of new types of molecular photonic device.

5:00pm **BI+AS+HC+SS-MoA-11 Microfluidic QCM with Ultrahigh Q-Factor: A New Paradigm for Acoustic Biosensing?***, Y. Zhao,* Duke University*; Z. Parlak,* Qatch LLC.*; M. Yu,* Duke University*; D. French,* Qatch LLC.*; W. Aquino, **Stefan Zauscher**,* Duke University

Acoustic thickness shear mode transducers, such as the quartz crystal microbalance (QCM), can provide high throughput biomolecular detection for diagnostics with minimal sample preparation. A QCM's resonance frequency change (Δf) is generally related to the mass change (Δm) due to analyte binding on the sensor surface. If equipped with dissipation monitoring, a QCM's dissipation (D or ΔD) is related to the viscoelastic properties of the surface-bound analyte. Although current QCM sensors are simple and robust devices, they generally require high sample volumes and suffer from low sensitivity/resolution due to fluid damping.

We show that by adding microfluidic channels onto QCM sensors, we can strongly couple small amounts of liquid within the channels to the sensor, thereby largely eliminating fluid damping. This coupling eliminates dissipation effects during shear excitation and thus dramatically increases the quality factor (Q-factor) of the sensor and allows for accurate measurement of changes in fluid density, and therefore also for biomolecular mass measurements in liquid environments.

The abrogation of damping effects arises from the almost lossless coupling of the liquid to the side walls of the channels, which results in an in-plane pressure wave. We found that if the wavelength of the pressure wave is considerably longer than the channel width, the liquid inside the channels is strongly coupled to the channel walls and thus damping is suppressed. Since viscous effects are largely eliminated, the microfluidic QCM (µ-QCM) is also insensitive to temperature-induced viscosity changes. With a high Q-factor, direct data interpretation, pure mass sensitivity and temperature insensitivity, and small device size, the µ-QCM provides a new paradigm for acoustic biosensing.

We used Finite Element Analysis (FEA) to test our hypothesis that the in-plane pressure wave generated by the channel side walls is responsible for the enhanced performance of the µ-QCM. Furthermore, we conducted a nondimensional analysis to reveal the most important parameters, including channel dimensions, crystal thickness, and fluid viscosity/density, and how they affect the dissipation. This knowledge can be easily extended to other acoustic bio-transducers to improve their sensitivity/resolution.

Finally, we show the design and microfabrication of µ-QCM devices, and their testing with a range of liquids with known viscosity and density, to demonstrate the high Q-factor of µ-QCMs and to demonstrate the latter's ability to sense density changes (unencumbered by viscosity) in small (~nL) sample volumes.

Nanoscale Science and Technology Division
Room 304 - Session NS2+AP+BI-MoA
Fabrication and Operation of Nano-Systems

Moderator: David Czaplewski, Argonne National Laboratory

4:00pm **NS2+AP+BI-MoA-8 Control of Color Centers in Diamond using Photonic and Phononic Crystals***, **Kazuhiro Kuruma**,* Harvard University **INVITED**

Color centers in diamond are one of the promising solid-state quantum emitters for the realization of on-chip quantum network. In particular, SiV centers have been investigated owing to their optically accessible spins as well as large and stable zero phonon line emission in photonic nanostructures. The integration of the SiV centers into the nanostructures such as photonic crystal nanocavities has been demonstrated as an efficient spin-photon interface for various quantum applications [1]. However, SiV centers need operations at mK temperatures [2] or under static strain [3] to achieve a long spin coherence time. I will show another potential approach using phononic crystals as a way to enable the realization of a long spin coherence time at higher temperatures[4]. Our efforts aimed at efficient control of the SiV spins using diamond optomechanical cavities will also be discussed [5]. Finally, I will present our works on the integration of tin-vacancy (SnV) centers, alternatives to SiV centers for operations at higher temperatures, into free-standing photonic crystal nanocavities [6].

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4:40pm **NS2+AP+BI-MoA-10 Scalable Preparation of Intrinsically Chiral Metal Surfaces for Enantioselective Processes***, **Nisha Shukla**, A. Gellman,* Carnegie Mellon University, USA

Chiral surfaces are critical components of enantioselective heterogeneous processes such as those used to prepare enantiomerically pure pharmaceuticals. While the majority of chiral surfaces in practical use are based on achiral materials whose surfaces have been modified with enantiomerically pure chiral adsorbates, there are many inorganic materials with valuable surface properties that could be rendered enantiospecific, if their surfaces were intrinsically chiral.

This work discusses recent developments in the fabrication of intrinsically chiral surfaces exhibiting enantiospecific adsorption, surface chemistry and electron emission. We propose possible paths to the scalable fabrication of high-surface-area, enantiomerically pure surfaces and discuss opportunities for future progress.

5:00pm **NS2+AP+BI-MoA-11 Wrinkle-Induced, Scale-Dependent Mechanical Properties in Nanometer Thick Films***, **Jian Zhou**, N. Moldovan, L. Stan, J. Wen, D. Jin,* Argonne National Lab*; D. Lopez,* Pennsylvania State University*; D. Czaplewski,* Argonne National Lab

Micro- and nano-electromechanical (MEMS/NEMS) devices have relied heavily on materials typically used in electronic devices. The majority of MEMS/NEMS devices are fabricated with a top-down approach to take advantage of the corresponding highly reproducible fabrication processes associated with silicon related materials. As a natural extension, as devices move into the nanoscale regime, new materials are introduced using the same fabrication paradigms used for electronics: ultra-flat surfaces, controlled stresses, simply defined materials properties, with precision 2-dimensional or 2+ dimensional definition using lithographic techniques. New materials, such as 2D materials, began to be incorporated with great promise. However, creating 2D material films that behave like traditional silicon-related films has become challenging due to their unconventional growth/deposition techniques. A typical method for depositing a 2D film is through a transfer process, which struggles to create flat, low stress, thin films. This has led to films that have variations in properties, as observed in large deviations in values reported for parameters such as Young's modulus.

In this work, we explore the variation in properties of films as they become more 2+dimensional textured versus being ultra-flat. We measure the response of resonators fabricated from both ultra-flat and wrinkled films. The ultra-flat films follow expected behaviors with small deviations in resonant frequency and bending rigidity. However, the wrinkled films have a frequency response that is highly variable, up to 45 times that found in flat films. Additionally, we find that the increased rigidity and distribution of values is scale-dependent. As we vary the in-plane dimensions of the resonant structures, we find that the characteristic values scale with the structure dimension. This matches very well with a theoretical model proposed to describe thermal fluctuations in thin films. This opens a new paradigm for device design that allows a single film to have multiple elastic properties based solely on the patterning size. Going forward, we see this being an interesting tool in the design of devices made from single nanometer-thick films.

Biomaterial Interfaces Division
Room 318 - Session BI1+AS+EM+NS+SE+TF-TuM

Bioanalytics, Biosensors and Diagnostics

Moderators: Caitlin Howell, University of Maine, **Laura Mears**, TU Wien, Austria

8:00am **BI1+AS+EM+NS+SE+TF-TuM-1 Understanding and Employing Adhesion Forces in Microfluidic Channels for Cell Separation***, **Avi Gupta**, F. Chrit, A. Liu, A. Alexeev, T. Sulchek,* Georgia Institute of Technology, USA

Rapid advancements in microfluidic technologies during the past few decades have significantly aided advancements in the field of BioMEMS. These technologies can facilitate development of easily scalable tools that can be translated to point-of-care healthcare products. Researchers have capitalized on these tools to create differential separation techniques that rely on adhesion forces. The adhesive interactions play a significant role in governing the trajectory of cells in microfluidic channels as well as the reliability of these devices, however, a concise model explaining cell interactions with chemically coated surfaces is yet to be developed. This research describes studies using microfluidic flow at different flow regimes to study dynamic cell adhesion. APTES, P-selectin, and Pluronic were used as models for non-specific adhesion, specific adhesion, and adhesion-free surfaces, respectively. A microfluidic device with slanting ridges was used to provide forced contact and to visualize the effect of these chemistries on cell trajectories using a microscope and a high-speed camera. Parameters of the channel that were studied include ridge angle, gap size, channel width, and flow rate. It was found that adhesive forces modulate the interaction time of cells during contact points with the slanting ridges. At an average flow velocity of 3.1 cm/sec we observed higher interaction time for APTES coatings and lower for Pluronic coatings. Higher adhesion on APTES coated surface of the channel leads to more deflection of cells towards the streamlines leading them to go opposite to the ridge direction. In contrast, lower surface adhesion on Pluronic coated surface made cells deviate along the ridge perpendicular to streamlines. Narrow channel widths and acute ridge angles helped in exaggerating the differences in trajectories of cells going along or under the ridge. Atomic force microscopy (AFM) was used to quantify the adhesion forces. This knowledge was used to develop a predictive model employing Lattice Boltzmann techniques along with Morse potential and Bell model to represent interaction between cells and device surface. This improved understanding of adhesion forces in microfluidic devices opens new avenues for developing separation techniques that don't employ specific molecules like P-selectin but rely upon the inherent geometry and surface interaction of the cells with a microfluidic channel.

8:20am **BI1+AS+EM+NS+SE+TF-TuM-2 Wafer-Scale Metallic Nanotube Arrays with Highly Ordered Periodicity for SERS Application***, **Jinn Chu**,* National Taiwan University of Science and Technology, Taiwan

This paper reports on the wafer-scale fabrication of ultrahigh sensitivity SERS substrates using metallic nanotube arrays (MeNTAs) with highly ordered periodicity. Various metals and alloys have been used to prepare MeNTAs via sputtering over a contact-hole array template created in photoresist. These include ferrous (stainless steel) and nonferrous (Cu-, Ni-, Al-, and Ti-based) alloys, as well as elemental metals (Cu, Ag, and Au). The proposed nanotubes can be fabricated over a wide range of heights and diameters (from a few hundred nm to 10 µm) in a variety of shapes, including tall cylinders and dishes. In addition, over this is deposited a uniform coating of Au nanoparticles to form a high-sensitivity AuNP@MeNTAs 3D-SERS substrate. Systematic micro-Raman spectroscopic analysis reveal that the fabricated array could function as a SERS-active substrate with crystal violet (CV) and folic acid as analytes (a minimum detection limit of 10^{-13} M CV). Enhancement factor of 1.06×10^{9} is obtained from our triangular Ag MeNTA. This work is the first to fabricate wafer-scale metallic nanotube arrays with SERS properties, which represents an important step toward realizing the large-scale fabrication of ultrasensitive SERS-active materials.

8:40am **BI1+AS+EM+NS+SE+TF-TuM-3 Customizing Silk Film Surface Properties Using Plasma-Enhanced Chemical Vapor Deposition***, A. Devore, G. Reyes, **Morgan Hawker**,* California State University, Fresno

Silk fibroin (silk) is a naturally-derived polymer with high utility in biomedical contexts, notably in tissue engineering. Silk bulk properties can be tuned to mechanically match a range of biological environments, including soft and hard tissues. As with other naturally-derived polymers, silk constructs degrade via surface-mediated enzymatic hydrolysis into non-toxic amino acid byproducts. Because tissue engineering relies on the underlying scaffold to degrade as the healthy tissue forms, controlling silk scaffold degradation kinetics is essential to maximize silk's utility. Notably, prior work to control silk degradation kinetics relies on either altering silk matrix properties (i.e., manipulating the secondary structure), or through creating silk-containing blends such as copolymers. Although both strategies effectively control degradation, doing so is often at the expense of mechanical properties. Any mechanical mismatch induced through controlling degradation can hinder scaffold function. Developing a strategy to program silk degradation - without altering bulk mechanical properties - is required to enhance their efficacy as biomaterials.

This talk will highlight recent efforts to develop a radio-frequency plasma-enhanced chemical vapor deposition (PECVD) approach with the potential to modulate silk degradation. The long-term objective of this work is to control the rate of surface-mediated enzymatic hydrolysis by customizing silk surface properties. Surface properties are thought to be paramount in controlling silk construct/enzyme interactions, so tuning silk film surface properties using PECVD was a logical first step. Silk films were first dropcasted, and were then subjected to PECVD. Plasma 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). Plasma polymerization using mixed precursor conditions was also explored. Contact angle goniometry was utilized to evaluate the wettability of all plasma-modified and control silk films. Changes in surface chemistry were evaluated using high-resolution x-ray photoelectron spectroscopy. Collectively, findings demonstrated that surface properties depend on both feedgas composition and position of the silk film in the plasma reactor. In sum, PECVD represents a promising approach to customize silk surface properties.

9:00am **BI1+AS+EM+NS+SE+TF-TuM-4 Biopotential Sensing Using Flexible, Reusable Smart Textile-Based Dry Electrodes***, **Jitendra Pratap Singh**,* Physics Dept IIT Delhi, India

Biopotential signals are used to assess organ function and make diagnoses. Biopotential electrodes are used to monitor and record biopotentials by acting as an interface between biological tissue and electrical circuits. The accurate detection of physiological signals from the human body is essential for health monitoring, preventive care, and treatments.

Wearable bioelectronics developments applied directly on the epidermal surface provide a promising future biopotential sensing option. Wearable textile electrodes for biopotential sensing are a promising candidate for long-term health monitoring. Wearable health-monitoring devices should be simple to use, stigma-free, and capable of delivering high-quality data. Smart textiles, which incorporate electronic elements directly into the fabric, offer a seamless way to incorporate sensors into garments for a variety of purposes. This work describes different types of flexible and reusable textile-based dry electrodes for biopotential monitoring. This work also describes the direct writing of laser-induced graphene (LIG) on a Kevlar textile for the production of reusable dry electrodes for long-term ECG monitoring. The electrode as-prepared has a high electrical conductivity and skin contact impedance of 100 ± 1 kΩ to 7.9 ± 2.7 kΩ for frequencies ranging from 40 Hz to 1 kHz, which is comparable to conventional Ag/AgCl wet electrodes.

The outcomes demonstrate comparable performance with significantly reduced electrode-skin impedance for clinical-grade devices. Even after several hours of usage, these electrodes do not irritate the skin and are effective without any skin preparation. As a result of their flexibility and a better match to the modulus of the skin, it is anticipated that the suggested dry electrodes will provide comfort for long-term biopotential monitoring. A simple, cost-effective, and scalable fabrication approach enables the fabrication of flexible electrodes of arbitrary shape for long-term biopotential monitoring.

1. Y. Maithani, B. Choudhuri, B. R. Mehta, and J. P. Singh: Self-adhesive, Stretchable, and Dry Silver Nanorods Embedded Polydimethylsiloxane Biopotential Electrodes for Electrocardiography. *Sensors Actuators A Phys.***332**, 113068 (2021).
2. Y. Maithani, B. Choudhuri, B. R. Mehta, and J. P. Singh: Modelling and Analysis of Active Biopotential Signals in Healthcare , Volume 2 A comprehensive review of the fabrication and performance evaluation of dry electrodes for

long - term ECG monitoring. *IOP Publ. Ltd 2020***2**(chapter 8), 1 (2020).

9:20am **BI1+AS+EM+NS+SE+TF-TuM-5 Functional Plasma Polymers for Biosensing Applications***, **Melanie McGregor**,* University of South Australia **INVITED**

Materials with intricate nanostructures display wetting properties that modern technologies already use to lubricate engines or waterproof clothing. Yet, their full potential in applications for sustainable catalysis, air purification or biosensing cannot be realised until we understand how nano-objects adsorb to surfaces with features of comparable size. Indeed, controlling or even predicting how proteins, antibodies, exosomes, surfactant or nanoparticles stick to nano-engineered surfaces is a challenge because key aspects of the wetting phenomenon remain poorly understood at this scale. In this talk, I will briefly review what we currently know about “nanowetting”.[1] I will then introduce the concept of plasma polymerisation as a technique to control both surface chemistry and surface topography. I’ll use the example of plasma deposited polyoxazoline (POx) to highlight this technique’s attributes, drawbacks and recent progress made in understanding the unique chemistry and reactivity of POx films, using both plasma in-situ and post deposition spectroscopic analysis.[2]Plasma deposited Polyoxazoline thin films share many valuable properties with polyoxazoline prepared via conventional organic chemistry: they are biocompatible, non-cytotoxic and low fouling.[3] What is more, they bind biomolecules covalently, support cell adhesion, and are generated in a solvent free, single step process, which makes them particularly attractive for industrialization. For these reasons, plasma deposited polyoxazoline are used in applied biomedical research, from in vitro stem cell culture to controlling immune responses.[4]

I’ll conclude this presentation with tangible outcomes of the translational research projects I’ve conducted with various industries, where we used nanoengineered plasma polymers, to create materials for cancer diagnosis and growing organoids.[5]

[1]**M. MacGregor** and K. Vasilev. *Advanced Materials Interfaces,4*, 1700381.,2017**;M. MacGregor** et al., *Nanoscale*, 8(8),4635-4642, 2016

[2] **M. Macgregor***et al.*Chemistry of Materials, 29(19)8047-51,* 2017; **M. N. MacGregor**-Ramiasa et al., *J. Mat. Chem. B*, 3, 6327-6337, 2015

[3]**M. N. Ramiasa** et al. *Chem. Commun.*, 51, 4279-4282,2015**;**A. A. Cavallaro, **M. N. Macgregor**-Ramiasa, K. Vasilev, *ACS Appl. Mater. Interfaces8*, 6354, 2016.

[4] R. M. Visalakshan, A. A. Cavallaro, **M. N. MacGregor**, et al. *Adv. Funct. Mat.*, 29, 1807453, 2019**;**

[5]**M. MacGregor***et al. *Biosensors and Bioelectronics,* 171: 112699,2020; K.M. Chan […]**M. MacGregor****Cancers* 13(21), 5544 2021

Biomaterial Interfaces Division
Room 318 - Session BI2+AS-TuM

Characterization of Biological and Biomaterials Surfaces

Moderators: Kenan Fears, U.S. Naval Research Laboratory, **Graham Leggett**, University of Sheffield, UK

11:00am **BI2+AS-TuM-10 Getting to the Surface of Biology***, **Lara Gamble**,* University of Washington **INVITED**

A variety of different surfaces (or interfaces) exist in biology. The surface of a biomaterial is the interface between that biomaterial and the biological environment. State-of-the-art instrumentation, experimental protocols, and data analysis methods are needed to obtain detailed information about these surface and interface structures and their compositions. Surface analysis tools such as time-of-flight secondary ion mass spectrometry (ToF-SIMS) can provide images of polymer biomaterials, cells, and tissues with chemical and molecular specificity. These chemically specific images could revolutionize our understanding of biological processes such as the role of changes in tumor metabolism that affect responses to chemotherapy. Since many biomaterials (e.g. porous polymer scaffolds), cells, and tissues are three-dimensional constructs, it is of interest to be able to characterize their chemical composition in 3D. However, it is challenging to characterize these topographically complex materials with surface-sensitive techniques. With the use of gas cluster ion beams (GCIBs) surface analysis tools such as x-ray photoelectron spectroscopy (XPS) and ToF-SIMS can attain very fine z-resolution (<10 nm) in-depth profiles. In this presentation, ToF-SIMS analysis of biologically relevant samples in 2D and 3D will be presented.

11:40am **BI2+AS-TuM-12 3D Investigation of Sr^{2+} Mobility in Bone Marrow by ToF- and Orbi-SIMS***, C. Kern, A. Pauli, R. Jamous, T. El Khassawna, **Marcus Rohnke**,* Justus Liebig University Giessen, Germany

Next generation biomaterials will be functionalised with drug release systems. In osteoporosis research strontium ions (Sr^{2+}) have emerged as promising therapeutic agent in modified bone cements for better fracture healing. In previous work we focused on the Sr^{2+} release off a functionalised bone cement and its dispersion in the mineralised areas of rat bone. [1, 2] Here, we go one step further and investigate Sr^{2+} transport within the much more complex system bone marrow in a passive dispersion experiment. First, we present an experimental cryo-workflow for transport studies within bovine bone marrow. As analytical tools for tracking the Sr^{2+} diffusion in 3D and spatially resolved characterisation of the bone marrow we apply time-of-flight secondary ion mass spectrometry (ToF-SIMS) and orbitrap secondary ion mass spectrometry (Orbi-SIMS). Within a time-dependent experimental series, the validity of our experimental approach is shown. Average diffusion coefficients of Sr^{2+} in bovine bone marrow in fast diffusion areas ($D_{\mathrm{bovine,FD}}=(2.09\pm2.39)\cdot10^{-9}$ cm^{2}s^{-1}), slow diffusion areas ($D_{\mathrm{bovine,SD}}=(1.52\pm1.80)\cdot10^{-10}$ cm^{2}s^{-1}), and total area diffusion ($D_{\mathrm{bovine,TA}}= (1.94\pm2.40)\cdot10^{-9}$ cm^{2}s^{-1}) were obtained. In a subsequent proof-of-concept study, we successfully applied the developed protocol to the determination of Sr^{2+} diffusion in bone marrow of osteoporotic rats [fast diffusion: $D_{\mathrm{rat,FD}}=(9.02\pm5.63)\cdot10^{-10}$ cm^{2}s^{-1}); slow diffusion: ($D_{\mathrm{rat,SD}}=(6.48\pm3.88)\cdot10^{-10}$ cm^{2}s^{-1}); total area diffusion ($D_{\mathrm{rat,TA}}= (8.89\pm5.37)\cdot10^{-10}$ cm^{2}s^{-1}]. Detailed 2D and 3D mass spectrometric imaging analysis as well as Orbi-SIMS spectral analysis revealed that Sr^{2+} diffusion is slower in bone marrow areas with high intensity of lipid and fatty acid signals than in areas with less intensity of lipid signals. Overall, our results provide important insights about Sr^{2+} diffusion in bone marrow and we are able to show that both cryo-ToF-SIMS and Orbi-SIMS are useful tools for the investigation of rapid diffusion in water-containing highly viscous media.

[1] M. Rohnke, S. Pfitzenreuter, B. Mogwitz, A. Henß, J. Thomas, D. Bieberstein, T. Gemming, S.K. Otto, S. Ray, M. Schumacher, M. Gelinsky, V. Alt, Strontium release from Sr^{2+}-loaded bone cements and dispersion in healthy and osteoporotic rat bone, J. Controlled Release **262** (2017) 159

[2] C. Kern, M. Quade, S. Ray, J. Thomas, M. Schumacher, T. Gemming, M. Gelinsky, V. Alt, M. Rohnke, Investigation of strontium transport and strontium quantification in cortical rat bone by time-of-flight secondary ion mass spectrometry, J. R. Soc. Interface **16** (2019) 20180638

12:00pm **BI2+AS-TuM-13 Comparison of NAP-XPS and Cryo-XPS for Studies of the Surface Chemistry of the Bacterial Cell-Envelope***, **Paul Dietrich**,* SPECS Surface Nano Analysis GmbH, Germany*; M. Kjærvik,* BAM Berlin, Germany, Norway*; M. Ramstedt,* Umeå University, Sweden*; W. Unger,* BAM, Germany

Bacterial interactions with the environment are based on processes involving their cell-envelope. Thus, techniques that can analyze their surface chemistry are attractive tools for providing an improved understanding of bacterial interactions. One of these tools is x-ray photoelectron spectroscopy (XPS) with an estimated information depth of <10 nm for Al Kα-excitation. XPS-analyses of bacteria have been performed for several decades on freeze-dried specimens to be compatible with the classical ultra-high vacuum conditions needed. A limitation of these studies has been that the freeze-drying method may collapse cell structure. However, recent developments in XPS allow for analysis of biological samples at near ambient pressure (NAP-XPS) or as frozen hydrated specimens (cryo-XPS) in vacuum. In this talk, we present the analysis of bacterial samples from a reference strain of the Gram-negative bacterium *Pseudomonas fluorescens* using both techniques. We will present the results obtained and, in general, observed good agreement between the two techniques. Furthermore, we will discuss advantages and disadvantages of these two analysis approaches and the output data they provide. XPS reference data from the bacterial strain are provided, and we propose that planktonic cells of this strain (DSM 50090) to be used as a reference material for surface chemical analysis of such bacterial systems.

Chemical Analysis and Imaging Interfaces Focus Topic
Room 302 - Session CA+2D+AS+BI+HC+LS+NS-TuA

In Situ Microscopy, Spectroscopy and Processing at Liquid-Solid-Gas Interfaces

Moderators: Andrei Kolmakov, National Institute of Standards and Technology (NIST), **Xiao-Ying Yu**, Oak Ridge National Laboratory, USA

2:20pm **CA+2D+AS+BI+HC+LS+NS-TuA-1 Understanding Charge Carrier Variations on the Nanoscale Using Microwave Near-Field Microscopy***, **T. Mitch Wallis**, S. Berweger, P. Kabos,* National Institute of Standards and Technology **INVITED**

Understanding the spatial distributions of charge carriers and their polarity in nanoscale semiconductors and their devices remains a long-standing challenge. Scanning probe-based microwave impedance microscopy (MIM, also called scanning microwave microscopy, SMM) can directly probe charge-carriers on the nanoscale via the high-frequency capacitive interaction between the sharp tip and sample of interest.

Here we will first provide an overview of MIM, including applications to model systems. We will then focus on studies of active devices of semiconducting materials, including GaN nanowires and 2D crystals of elemental tellurium. We will conclude with an overview of recent efforts on photoconductivity mapping in 2D materials and hybrid organic-inorganic lead-halide perovskite thin films. In particular, for the latter we leverage the high bandwidth inherent in the microwave signal to obtain temporal resolution as high as 5 ns.

3:00pm **CA+2D+AS+BI+HC+LS+NS-TuA-3 Oxidation/Reduction of Cu Nanoparticles at a Single-Layer Graphene/Electrolyte Interface Monitored by Scanning Kelvin Probe Microscopy***, **Sidney Cohen**, S. Khatun, M. Andres, I. Pinkas, I. Kaplan-ashiri, O. Brontvein,* Weizmann Institute of Science, Israel*; I. Rosenhek-Goldian,* weizmann Institute of Science, Israel*; R. Weatherup,* Oxford University, UK*; B. Eren,* Weizmann Institute of Science, Israel

The need to probe chemical and physical processes occurring in at liquid/solid interfaces at small scales is being addressed by several cutting-edge techniques. Scanning probe microscopy (SPM) is now a well-established tool for simultaneous morphological, electrical, and mechanical characterization at the nanoscale. Scanning Kelvin Probe microscopy (SKPM) is an SPM method which can measure the work function at nm distance scales. This technique is not conveniently applied within a solution environment. In this work, micro-electrochemical cells were capped by a single layer graphene upper membrane which is transparent to the electrostatic field, enabling high resolution surface measurements of electrical processes occurring at the interfacial liquid region below the membrane. This talk will present this set-up, and show how it can be used to examine stability, and surface interactions in the oxidation/reduction processes of copper nanoparticles (NPs) attached to the graphene under operating (operando) conditions. Complementary techniques including cyclic voltammetry, and ex-situ electron microscopy and x-ray photoelectron spectroscopy gave a complete description of the processes. As an established catalyst for CO_2 reduction, the behavior of Cu in electrochemical conditions is of great interest in both science and technology. The measurements described here provided a nm-scale view of differences in Cu NP oxidation in ambient air and electrochemical conditions, detecting both a galvanic corrosion in air, and reversible reduction of the NPs at cathodic potentials in alkaline solution. Detachment of the NPs after long measurements of redox cycling is documented and rationalized.

3:20pm **CA+2D+AS+BI+HC+LS+NS-TuA-4 Investigation Tritium and Lithium transport along the Tritium-Producing Burnable Absorber Rod***, **Jiyoung Son**,* Pacific Northwest National Lab*; J. Gao,* PNNL*; G. Sevigny, S. Tripathi, B. Matthews,* Pacific Northwest National Lab*; X. Yu,* Oak Ridge National Laboratory

The compositional and microstructural changes in functional materials are critical for nuclear materials in fusion and fission applications. We investigated tritium (^{3}H) and lithium isotope (^{6}Li, ^{7}Li) transport within a neutron-irradiated target rod, aka, Tritium-Producing Burnable Absorber Rod (TPBAR), used in a light water reactor. TPBARs employ the iron aluminide-coated austenitic stainless-steel cladding and associated cruciform as key components. We used multimodal imaging tools and studied the specimens from irradiated TPBAR components. Specifically, a scanning electron microscope with focused ion beam (SEM-FIB) was used to prepare lift-out samples of the irradiated coating and cruciform samples for follow-up microanalysis. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was utilized to detect light isotopes in relation to tritium and lithium diffusion and transport. The observed distributions in the irradiated cladding specimens suggest light isotope mobility between internal target components as a result of neutron irradiation. We compared irradiated claddings of two different configurations in SIMS, and the chemical mapping and depth profiles of aluminide coatings show distinct light isotopic distributions. The cruciform specimens extracted from corresponding locations to the claddings also give interesting results. Overall, advanced correlative imaging results confirm tritium diffusion and lithium transport during the tritium production process. Such results give new insights into the fundamental transport mechanism within the target during irradiation and under non-equilibrium, extreme conditions.

4:20pm **CA+2D+AS+BI+HC+LS+NS-TuA-7 Development of a Workflow for Multiscale Elemental Analysis with X-ray Fluorescence Microscopy and Tomography***, **Si Chen**,* Argonne National Lab*; Y. Luo,* Argonne National Laboratory*; T. Paunesku,* Northwestern University*; O. Antipova, Y. Liu, N. Zaluzec, Z. Di,* Argonne National Laboratory*; G. Woloschak,* Northwestern University **INVITED**

Scanning X-ray fluorescence (XRF) microscopy and tomography provides powerful capabilities to assess the elemental distribution in a three-dimensional (3D) space and differentiate their inter- and intra-cellular interactions in complex biological cells and tissues. Like other microscopy techniques, there is often a tradeoff between spatial resolution and field-of-view that each XRF instrument can provide. For example, XRF nanoprobes are specialized for analysis with <50 nm resolution, but the region can be analyzed within a reasonable time frame is limited to only a few tens of microns. Therefore, the capability to combine the use of multiple instruments becomes important for hierarchical analysis.

In this presentation, we will discuss the Bionanoprobe (BNP) instrument and applications. The BNP is an XRF nanoprobe located at the Advanced Photon Source of Argonne National Laboratory. It is dedicated to the studies of biological tissues and cells with a subcellular spatial resolution. In conjunction with a microscale-resolution XRF instrument, we have demonstrated a workflow to perform multiscale elemental mapping and tomography on HeLa cells treated with non-targeted nanoparticles. While nanoscale tomography revealed the nanoparticle distribution in individual cells, statistical information on cell-nanoparticle interaction was obtained with the microprobe from a large population of cells.

It is important to note the challenges in sample preparation for such multiscale analysis across platforms. Different instruments often require different specimen dimensions in order to achieve their optimal performance. To enable analysis on the same specimen, we have introduced an intermediate specimen manipulation step between micro- and nano-scale measurements utilizing focused ion beam (FIB). Local regions of interest identified with the microprobe were isolated with a FIB instrument and further analyzed at the BNP. Angular enlargement for tomography data collection enabled by the FIB operation significantly improved the tomography reconstruction quality.

5:00pm **CA+2D+AS+BI+HC+LS+NS-TuA-9 in Situ Molecular Imaging of Green Solvents for CO_2 Capture***, **Xiao-Ying Yu**,* Oak Ridge National Laboratory, USA

Switchable ionic liquids are emerging green solvents in for carbon dioxide (CO_2) capture, cleaner separation, and efficient biomass production.However, the liquid structure and composition of SWILs are not fully understood.Besides off-line analyses using NMR and IR, our knowledge of the sustainable green solvents is limited.We used in situ liquid time-of-flight secondary ion mass spectrometry (ToF-SIMS) to study such solvents in this work.This is a unique in situ molecular imaging technique enabled by the invention of a vacuum compatible microfluidic reactor termed system for analysis at the liquid vacuum interface (SALVI).Green solvents of interest were synthesized and reported previously. They were introduced into the microfluidic channel for in situ analysis using liquid ToF-SIMS.Two model systems are illustrated in this talk.The first consists of 1, 8-diazabicycloundec-7-ene (DBU) and 1-hexanol with different CO_2 loadings.The second has koechanol with various CO_2 loadings.Koechanol acts as both acid and base in the latter.Our results show two coexisting liquid phases in these green solvents.This phenomenon was only hypothesized in previous theory prediction.We provide the first physical evidence of the complex liquid – liquid (l – l) interface using three-dimensional chemical mapping with submicrometer resolution.In addition, more complex stoichiometry is discovered due to CO_2 uptake.More importantly, we have provided the first chemical spatial visualization elucidating the evolving l – l interface.The more detailed molecular level understanding of the liquid structure and composition are instrumental to build the foundation for predicative material synthesis, CO_2 capture, and other versatile applications.

5:20pm **CA+2D+AS+BI+HC+LS+NS-TuA-10 Depth Dependence of Salt Ions at the Liquid/Vapor Interface Studied by Ambient Pressure X-Ray Photoelectron Spectroscopy***, A. Siebert, K. Goodman,* ***Monika Blum,*** LBNL

Liquid/vapor interfaces play an important role in chemical, biological, technological, and environmental processes. Perhaps one of the most important interfaces for the environment is the interface between atmospheric aqueous aerosols and the surrounding air, which affects reactions like the scattering and absorption of sunlight as well as the probability of aerosols to serve as cloud condensation nuclei. [1,2] However, the experimental investigation of this active region is complicated by the necessary pressures far away from the ultra-high-vacuum (UHV) region, which is usually required in most surface science studies.[3]

In the recent past, ambient pressure X-ray photoelectron spectroscopy (APXPS) has proven to be a very powerful tool to study the chemical and electronic structure of liquids, solutions, and their interfaces with different media, not requiring the UHV conditions of standard XPS measurements. In this contribution we will utilize a colliding micro flat jet system with synchrotron-based APXPS to gain full insight into the depth dependency of different aqueous salt solutions, e.g. $CaCl_2$,at low salt concentrations. We will present a comparison of bulk ion concentrations in aqueous salt solutions and the surface ion concentration obtained from the ratio between the probed core level area and the peak area of the liquid water phase. This allows us to model the depth profile of salt ions in aqueous solutions and to correlate the data with existing theoretical models.

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Biomaterial Interfaces Division
Room Ballroom A - Session BI-TuP
Biomaterial Interfaces Poster Session

BI-TuP-2 Direct Detection of COVID-19 Oligonucleotides Through Formation of Nanoparticle Satellite Conjugates*, **Hannah Umoeka,** A. Martinez, C. Afzulpurkar, M. Sharma, S. Talasila, T. Nguyen, D. Singh, I. Shortt, E. La Plante, S. Koh,* The University of Texas at Arlington

Polymerase chain reaction (PCR) and reverse transcription polymerase chain reaction (RT-PCR) have been the gold standards for accurately detecting specific oligonucleotide sequences of various pathogens such as COVID-19. However, considering the hour-long thermal cycling of PCR and RT-PCR, as well as the requirement of lab space and trained personnel, it would be beneficial to have a method that enables a rapid and point-of-care detection of a specific sequence of oligonucleotides. Here we present an approach in which a specific COVID-19 sequence is directly and rapidly detected on a small Si substrate (<1 cm^2) without any amplification. As a target oligonucleotide, we used the 67-mer DNA having the same sequence as the complementary DNA that the current CDC approved COVID-19 RT-PCR test is targeting. The target oligonucleotide is sandwiched between a capture Au nanoparticle (*C*-AuNP) and a detection Au nanoparticle (*D*-AuNP), to produce a nanoparticle satellite conjugate, where a *C*-AuNP is a 50 nm Au nanoparticle on which 20-mer capture DNA (*C*-DNA) is immobilized and a *D*-AuNP is a 30 nm Au nanoparticle on which 18-mer detection DNA (*D*-DNA) is immobilized. *C*-DNA is complementary to a portion of the target oligonucleotide while *D*-DNA is complementary to the other portion of the target oligonucleotide. The nanoparticle satellite conjugates are detected by electrically contacting the *C*-AuNP to one electrode and the *D*-AuNP to the other electrode, where an electrical current is produced when a voltage is applied between the two electrodes. The nanoparticle satellite conjugates were controllably placed on exact substrate positions using the electrostatic funneling (*Nano Lett*., Vol.7, 439-445, 2007) and self-limiting single-nanoparticle placement (*Langmuir*, Vol.37, 11961-11977, 2021; *Appl. Phys. Lett.*, Vol.93, 073110, 2008), with self-assembled monolayers (SAMs) of 16-mercaptohexadecanoicacid and 3-aminopropyltriethoxysilane providing the electrostatic guiding structure. The total hybridization time for the assay was 10 minutes for 5 nM target COVID-19 oligonucleotides and optimization for higher sensitivity is currently underway. Our approach can be used for detection of any oligonucleotide sequence. For example, this method enabled detection of anthrax oligonucleotides by adequately changing the *C*-DNA and *D*-DNA sequences. This work was supported by the National Science Foundation (ECCS-2031770, DMR-2122128, CMMI-1463451, and CMMI-2143159).

BI-TuP-3 Study of Catechol Reaction Mechanisms*, J. Appenroth,* ***Laura L. E. Mears****, A. Celebi, M. Valtiner,* Vienna University of Technology, Austria

Redox-active catechols, in particular *L*-DOPA and dopamine, are found in many adhesive biological systems. For exmple, in marine mussels *L*-DOPA containing byssus threads are shown to adhere to different substrates in harsh saline environments. Their oxidation and reduction can be driven both by pH changes and electrochemistry. While various models have been proposed, the exact reaction paths of these catechols remain a topic of discussion.

First, we will present new insights gained on the dynamics and redox activity of catechols in aqueous solution. Their reaction paths and products were studied using electrochemistry, UV-vis and NMR spectroscopy and the results are compared to DFT based ab initio thermodynamics. To characterize the energy change during binding/unbinding events of catechols, we then show bond rupture experiments of single catechol molecules against gold surfaces using AFM and Optical Tweezers.

By combining these methods we are able to shed new light on the redox active behaviour of catechols.

BI-TuP-6 Direct Observation of Focal Adhesion by Nanoendoscopy-AFM in Live Cells*, **Alam Mohammad Shahidul**, T. Shirokawa, T. Ichikawa, K. Miyazawa, k. Miyata, T. Fukuma,* Kanazawa University, Japan

Cells are the basic building units of all living organisms. It is essential to visualize the cell structures and their dynamics at the subcellular level to understand the mechanisms of basic cellular functions. Despite the enormous efforts, there are still many things that remain underexplored about this basic unit of life. Direct imaging of such nanostructures and their dynamics inside living cells has been a great challenge. Traditional approaches including tear down the cell into various components, which may distort its natural behavior. Moreover, many nanoscale dynamics are not yet visible because of the limited resolution. Therefore, we have developed nanoendoscopy-AFM (Atomic Force Microscopy), a label-free, non-harmful imaging technique that allows us to see the intracellular structures of a living cell without breaking it apart. A long ultrathin nanoprobe is inserted into living cells to perform 2D and 3D imaging by AFM. We can visualize intra-cellular structures ranging from whole-cell to unsupported actin fibers. Further, we proved that such an imaging method based on ultrathin nanoprobes does not significantly affect cell viability. Our next aim is to investigate focal adhesions (FA) in living cells that play a crucial role in cell motility. Multiple proteins (paxillin, integrin, vinculin, etc.) form this dynamic nanostructure, which mechanically connects intracellular actin bundles to the extracellular substrate. However, it remains elusive due to the difficulties of its direct observation. We are succeeded in the direct imaging of focal adhesion in a living cell with an originally developed nanoprobe. In the future, we want to study the dynamic behavior of FAs along with TIRF microscopy which will have a significant influence on cell biology and medical sciences.

BI-TuP-8 pH Responsive Functionally Graded Nano-Composites Coatings for Studying Hepatocellular Carcinoma Cellular Behaviour*, **Juhi Jaiswal**, M. Dhayal,* Indian Institute of Technology (Banaras Hindu University), India

In the present study, a process has been developed for metal-polymer coatings on tissue culture plastic surfaces through an in-situ reduction process by chitosan. The reduction of the metal compound by chitosan was performed, thereby exploring the role of different functional moieties of chitosan in the reduction process at acidic and basic pH. Time-dependent reduction kinetics for different chitosan concentrations by monitoring the in-situ reduction of nanometal assemblies (< 10 nm) at the polymeric surface has been demonstrated to understand the role of chitosan amine and hydroxyl functional moieties in the reduction process. The FTIR spectra were used to quantify the relative change in nitrogen and oxygen atom-containing functionalities in nano-composites. ^{1}H NMR spectra of the nanocomposite were further used to identify a relative change in the corresponding peak during the interaction of different molecules in functionally graded composites. A uniform distribution of less than 10 nm nanoparticles was confirmed by TEM image analysis of composite metal-polymer coatings on a copper grid. The UV-Visible spectroscopic analysis confirmed the obtainability of tunable size, density, and functionality in composite films. XRD analysis of nanocomposite coatings confirmed the presence of nanoparticles having two (111) and (200) crystal plans. In-vitro cell viability and proliferation analysis for the HepG2 cell line was performed. These coatings can be used to develop active biomaterial for cancer therapeutics because of the existence of composite in two forms, gel and sol directed by environmental pH.

BI-TuP-9 'Plasmoresistor' Device – Electronic Transduction of Plasmon Signals for Highly Sensitive Detection of Biomolecules*, **Corbin Feit**,* University of Central Florida*; P. Rathi, S. Singamaneni,* Washington University, St. Louis*; P. Banerjee,* University of Central Florida

Sensing of biomolecules with plasmonic nanoparticles has become the "gold standard" for lab-on-a-chip devices. Observing changes to localized surface plasmon resonance (LSPR) frequency of nanoparticles provides label-free, real-time measurements without the need for chromophores or fluorophores. When a molecular binding event occurs on a plasmonic nanoparticle, the change of the local dielectric environment leads to a shift in the LSPR frequency. This optical shift in LSPR is measured via optical spectroscopy techniques such as UV-Vis or Raman spectroscopy. However, challenges to miniaturization and hardware portability remain, making point-of-care diagnostics harder to achieve.

Therefore, in this work, we present detailed results of a "plasmoresistor" sensor that monitors the photocurrent generated by hot electrons emitted from plasmonic gold nanorods. This device overcomes the limitations that arise from the above described, state-of-the-art optical readout technologies. Upon excitation of the LSPR, hot electrons are generated, transferred, and conducted through a vicinal ZnO film. Thus, the change in photocurrent (i.e., resistance) performs the sensing action. Nanoscale engineering involving area-selective atomic layer deposition is required to deposit a conductive and optically transparent ZnO, while keeping viable plasmonic nanostructured surfaces exposed for conjugation with the biomarkers.

This transformative plasmoresistor device is expected to pave the way for highly sensitive plasmonic sensors that operate through electrical detection. The use of expensive, bulky and labor-intensive instrumentation will become obsolete.

BI-TuP-10 Hemoglobin-Bound Iron Fraction In Thin Films Rapidly Solidified From 100µL Drops Measured By Extended X-ray Absorption Fine Structure (EXAFS)*, **Arjun Sekar**, A. Suresh, R. Rane, A. Thinakaran,* Arizona State University*; J. Bischoff,* Simon Fraser University, Canada*; N. Herbots,* Arizona State University*; K. Kavanagh,* Simon Fraser University, Canada

Iron (Fe) bound to Hemoglobin in blood is key to detection of anemia. Blood diagnostics(BD) via High Performance Liquid Chromatography(HPLC) require significant volumes of blood per test (8-10 mL). Such volumes lead to Hospital Acquired Anemia in a large fraction of patients(74%) [1]. Conducting BD on smaller volumes is a pressing need for modern medicine.

Recent ongoing developments of X-ray synchrotron sources and detectors with higher X-ray intensities are now making possible investigating direct EXAFS analysis on smaller blood volumes.

In this work, we use hyper-hydrophilic coatings to rapidly solidify blood drops(10-250 µL) [2], making solid state analysis feasible. Our process yields flat, Homogeneous Thin Solid Films (HTSF) in minutes without coagulation. HTSFs are sufficiently uniform, over analyzed areas (~ 5 mm^2) such that the Fe composition can be measured with an accuracy of ± 10% using conventional solid-state techniques such as X-ray Fluorescence (XRF) and Ion Beam Analysis. This is unlike conventional Dried Blood Spots(DBS). DBS are non-uniform and exhibit high fracture rates followed by detachment. In addition, Fe-rich Red Blood Cells(RBC) migrate to the periphery of DBS, while no such phase separation occurs in HTSFs [2]

We have confirmed that our process to solidify blood drops into HTSF does not modify the bonding of Fe in hemoglobin by carrying out Extended X-ray Absorption Fine Structure (EXAFS) directly on such HTSFs.

Hemoglobin is a *globular* protein, which means it folds into a spherical shape, defining bonding lengths and species surrounding Fe. Hemoglobin consists of four *heme* groups, each with an Fe bound to a *histidine* residue via N. In each *heme*, Fe is bound directly to four N nearest neighbors within a plane, with a 5th nearest neighbor and a 6th N atom. EXAFS has been reported for measurements on concentrated hemoglobin separated from whole blood and has detected oxidized Fe in hemoglobin, matching results from HPLC [3]. We carried out EXAFS at the Canadian Light Source (CLS) using fluorescence detection near the Fe absorption edge (7.126 to 7.8 keV). Our EXAFS spectra on small volume HTSF blood share similarities to previous reports on hemoglobin and consistently measure the expected Fe-N bond length of 1.97±0.02 Å [3].

Acknowledgements: CLS, NSERC, MatthewNewville

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BI-TuP-12 Detecting Shared Touch Surface Contamination with a Deep Learning-Enhanced Smartphone and Nanopatterned Material System*, **Ainslie Allen**, J. Andle, O. Biswas,* University of Maine*; R. Perry,* VEMI Lab*; S. Yasaei Sekeh, C. Howell,* University of Maine

Shared-touch surfaces can transmit diseases when not cleaned properly. Some methods of surface contamination detection exist, but nearly none are immediately accessible, hands-free, and do not require specialized equipment. This work is focused on building a deep-learning driven, smartphone-based system that interacts with nanopatterned surface appliques and identifies contamination on a surface. We used a nanopatterned material that acts as a diffraction grating and measured the difference in the refracted light pattern when the material was clean and when it was contaminated. Unlike nearly all other applications of nanopatterned diffraction gratings, our applique material is mass-produced by a Maine paper company, making it both able to be applied over large areas and affordable. The light diffracting off our nanopatterned material resulted in bright rainbows which changed significantly in intensity, length, and color composition, as measured with a standard smartphone camera, when the surface was contaminated with oil. Using this system, we were able to detect oil contamination down to a volume of 0.1µL over a surface area of 64cm2 when the data were processed manually. We then trained a convolutional neural network (CNN), ResNet 50, to detect these differences. The network was able to detect contamination at an even lower volume of 0.0001 µL over a surface area of 64cm2. Training the CNN on the collected data improved the detection performance by over 100%. Additionally, by changing the angle of the smartphone and the light source, we were able to effectively scan the surface to search for areas of contamination and under ambient light conditions, making it more applicable to use in everyday life. Adding the angle and light features into the CNN method provides extra information to the neural network and leads to a robust learning process. Together, the results demonstrate that a deep-learning-enhanced nanopatterned material system can detect general surface contamination, which may help identify potentially infectious contamination on shared touch surfaces.

BI-TuP-13 Smartphone Enabled Micro/ Nano Microscopy for Biomedical Sensing*, M. Sami,* Rutgers University*; **Umer Hassan**,* Rutgers, The State University of New Jersey

Biomarker quantification finds many applications in disease diagnostics. Detecting biomarkers require developing technologies with micro-nano sensing resolutions to enable their specific identification. Here, we report a 3D printed, portable, fluorescent microscopy system to image micro/ nano particles for biomedical applications. The 3D printed microscopy system houses an excitation source (laser diode/ LED), optical filters and lenses to achieve desired optical resolutions. The images can be taken by using a regular smartphone camera. A sample slot is housed within the platform to place the desired biological samples e.g., microparticles, or fluorescently tagged blood cells. We tested the setup using blood samples from patients at Robert Wood Johnson Hospital. We imaged leukocytes stained with nuclear stain using the platform and tested them with control microscopy instrument. We found a strong correlation between the two platforms with $R^2$of 0.99. Further, we developed a machine learning model based on artificial neural networks (ANN) to count the microparticles and blood cells in the captured images.

Lens of smaller focal lengths allow the improvement in achieving higher resolution. Further, excitation methods can also be varied for improved particles imaging performance. For sub-micron and nanoparticles imaging, we explored multiple microscopy imaging modalities including perpendicular, parallel, and slanted. We found that slanted imaging methodology where laser diode exposes the samples at various angles allows higher imaging quality and improves the nanoparticles sensing resolution and accuracy. Our system is versatile and interoperable between multiple smartphones. We tested its imaging capability using iPhone XR, Samsung Galaxy S9, Samsung Ultra S21, and Nokia Lumia. This setup can be translated for different biomarkers (e.g., cells, proteins, etc.) quantification and developing associated diagnostic products.

Applied Surface Science Division
Room 320 - Session AS+BI+CA+HC+LS+PS+SE+SS-WeM

Analysis of Surfaces and Interfaces Related to Energy and the Environment

Moderators: Kateryna Artyushkova, Physical Electronics, **Tony Ohlhausen**, Sandia National Laboratory

8:00am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-1 Adhesion Properties of Industrial Steel Samples***, **Lukas Kalchgruber**, M. Hahn, L. Mears, M. Valtiner,* TU Wien, Austria

Solving industrial questions is of utmost importance to improve material properties, developing industrial applications and understanding fundamental processes. One of these questions is how different pre-treatments alter the adhesion process between steel and polymers.

To study the effect of the pre-treatment on the subsequent adhesion process, steel was treated either thermally or via plasma.

To characterize adhesion, the surface force apparatus (= SFA) was utilized in reflection mode. In the SFA experiment, the steel is brought into contact with another surface which is prepared on a fused silica optical disc. Before the optical discs can be used in SFA, a semitransparent, reflective layer needs to be deposited on the curved surface. Additionally, they were spin coated with few µm thin, homogeneous, smooth layers of SEBS polymer. Afterwards, a suitable particle free contact was established between the polymer and the steel sample in the SFA, which generated the following data types:

1. Newton rings à Provide information about the contact area
2. Force data à Adhesive pressure (referenced to contact area)
3. Fringes of chromatic order (= FECO) à Time-Distance-Curves

The main selling points of this technique are as follows: firstly, the model system is very close to the actual problem, as the steel sample in question can be used directly. Secondly, direct information about the adhesive pressure can be obtained. Thirdly, considerably more information about the adhesive behavior of the system is available beyond just one number.

The SFA results achieved are promising. We have a method that allows us to quantify the adhesive pressure in a model system and differentiate between differently treated steel samples. We have further put our adhesion results into context with the support of XPS characterization of the surface. Thermally treated samples have a hydroxide/oxide ratio of roughly 50/50 while samples treated with plasma show a ratio of 90/10. The hydroxide to oxide ratio correlates with the adhesion measured by SFA, which emphasizes the role of hydroxide in preventing adhesion.

8:20am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-2 An Electrochemically Polymerized Protective Layer for Magnesium Metal Anode***, Y. Wang,* University of Maryland College Park*; **Alexander Kozen**,* University of Maryland

Rechargeable magnesium (Mg) batteries are promising beyond Li-ion technologies due to their high volumetric capacity (3832 mAh cm^{-3}) and high natural abundance. Nonetheless, Mg metal anode is incompatible with most conventional electrolytes which leads to the formation of an ionically passivating layer. Mg also suffers from growth of dendrites similar to Li, which causes failure of the cells. In this study, we electrochemically polymerized 1,3-dioxolane (DOL) to form a thin Mg^{2+}-conducting elastomeric artificial solid electrolyte interphase (ASEI) layer by electrochemically pretreating Mg metal anodes. We found that this protective ASEI layer enables excellent cyclability of Mg-Mg symmetric cells at high current density (0.5 mAcm^{-2}) over 400 hours at a stable low overpotential (0.50 V vs. Mg^{2+}/Mg) without cell short-circuiting, while untreated pristine Mg symmetric cells quickly failed. The formation of this ASEI also significantly lowered the impedance of the cells, which proved its capability of conducting Mg^{2+} ions. Comprehensive surface chemistry analysis was done by X-ray photoelectron spectroscopy (XPS) which showed that an ASEI mainly consists of poly-DOL was formed, along with various Mg salts which are instrumental to the conductance of Mg^{2+} ions. More importantly, poly-DOL component in the elastomer was well preserved post-cycling, which contributed to the long-term cyclability and low voltage hysteresis of pretreated Mg-Mg cells, as compared to the pristine ones. Focused ion beam (FIB) – scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) mapping showed that a generally uniform layer was formed on the surface and this ASEI is roughly 200 µm thick and was able to suppress the growth of Mg dendrites after cycling for 400 hours at 0.03 mA cm^{-2} current density, as compared to the rampant sphere-shaped dendrites on the surface of pristine Mg anodes after cycling. This is the first ever report on the successful formation of poly-DOL ASEI on Mg metal anodes as a protective layer and by electrochemical polymerization method that effectively enhanced the electrochemical cycling performance of the Mg metal anodes.

8:40am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-3 Analysis of Surfaces and Interfaces in Polymer Electrolyte Membrane Fuel Cell and Electrolyzer Devices***, **Svitlana Pylypenko**,* Colorado School of Mines **INVITED**

Implementing a hydrogen-based infrastructure depends on developing electrochemical energy conversion devices such as fuel cells and electrolyzers. Polymer electrolyte membrane fuel cells (PEMFCs) have been the focus of research for lightweight renewable transportation applications such as motor vehicles for years, but they also offer the potential to fuel stationary applications, including residential power, due to their potential to produce industrial amounts of energy via a renewable route. Polymer electrolyte membrane water electrolysis (PEMWE) is a promising strategy to produce and store renewable energy in the form of hydrogen for subsequent use in either manufacturing processes, or to run a fuel cell, which can generate electricity on demand.

Great improvements have been made in the development of catalysts and electrodes for PEM systems, improving their activity and stability while reducing the amount of precious metals used. The properties of the electrodes used in these devices are influenced by multiple parameters: the chemical identity of the catalyst and the ionomer; the morphological properties of the catalyst (e.g. shape and surface area); ink formulations; and the various processing parameters used to prepare the electrode. Due to the breadth of possible variable combinations and the inherent complexity of electrode materials, it is unsurprising that PEM electrodes are both morphologically and chemically heterogeneous. Characterization of relevant surfaces and interfaces in these devices, therefore, represents a challenge that requires a multi-technique approach that evaluates all relevant scales and properties and brings a better understanding of the evolution of surfaces and interfaces under more realistic conditions. This talk will discuss the progress towards the comprehensive characterization of the most critical surfaces and interfaces in PEM devices using a combination of X-ray and electron spectroscopy and microscopy methods. Several challenges related to the characterization of catalyst-gas and catalyst-ionomer interactions in these systems will be covered along with results obtained with near-ambient pressure x-ray photoelectron spectroscopy (nAP-XPS). The development of characterization strategies to enable the exploration of a large processing parameter space will be presented, which can then be used to fabricate optimized electrodes with state-of-the-art catalysts as well as electrodes that integrate novel catalysts, all made with scalable routes. And finally, the development of novel approaches toward the characterization of other components of PEM devices such as porous transport layers will also be briefly discussed.

9:20am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-5 XPS Analysis of Battery Materials***, **Sarah Zaccarine**, B. Schmidt, K. Artyushkova,* Physical Electronics USA*; A. Baniya, Q. Qiao,* Syracuse University

Lithium-ion batteries (LIBs) have experienced success including rechargeability and long lifetimes but their limited energy density restricts applications moving forward. Lithium metal batteries (LMBs) offer similar benefits but with much higher achievable energy densities, making them a promising future battery technology. Both LIBs and LMBs are multi-layered, complex systems with many materials and interfaces that each play a critical role in performance and stability. Tuning the composition and morphology of these materials is necessary to create stable, high-performing devices, but the multi-component interfaces, interactions, and dynamic nature of these systems makes characterization challenging. In order to optimize materials properties and improve battery lifetimes, there is a pressing need for physicochemical characterization approaches with high spatial resolution, chemical and morphological analysis, and correlation of synergistic properties.

X-ray photoelectron spectroscopy (XPS) is commonly used to characterize the chemical composition of battery materials, and the depth resolution (~10nm) is ideal for analyzing thin layers and interfaces. However, modern XPS instruments have a variety of operating modes and analytical accessories that enable characterization across a variety of lateral and vertical size regimes. Small and large spot comparisons can track overall composition and local features and changes, with scanning microprobe analysis allowing for spatial resolution down to a few microns. X-ray induced secondary electron imaging (SXI), including high-resolution mosaic imaging over a wide sample area, can be used for easy identification of important features and morphological imaging of various battery component materials to complement chemical information. Chemical mapping can visualize distribution of individual elements or chemical species to understand how materials are distributed and change with testing. Additional options address stability concerns associated with Li materials, including a cooling stage to preserve battery chemistry during extended experiment times, where time-resolved profiles are used to compare chemical degradation under controlled temperatures, and incorporating Al Kα and Cr Kα X-rays for non-destructive XPS and hard X-ray photoelectron spectroscopy (HAXPES) analysis of surface (up to ~10nm, Al) and subsurface (up to ~30nm, Cr) composition. Combined, these powerful capabilities enable thorough characterization of battery materials properties for micro- and large-area spectroscopic analysis of surfaces and interfaces and how these properties change under various analytical and operating conditions.

9:40am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-6 Novel Battery Material Analysis with High-Resolution and High-Throughput XPS***, J. Counsell, S. Coultas,* Kratos Analytical Inc., UK*; C. Moffitt,* Kratos Analytical Inc.*; C. Blomfield,* Kratos Analytical Inc., UK*; **Adam Roberts**,* Kratos Analytical Limited, UK

Several material systems will be discussed to give an overview on how XPS can yield information regarding the distribution and chemical speciation of battery materials.

Na-ion batteries are considered to be environmentally favourable alternatives to Li-ion batteries, particularly in the extremely large-scale application of grid storage, given the abundance of Na. However, to date, the battery performance has not been competitive, and promising ternary materials have been plagued by poor stability in air and unsatisfactory long-term cycling. Herein, air/moisture stability is effectively and systematically investigated with XPS, paving the way for material stability to be modified through rational design. Chemical assignments were correlated with performance and oxidation degradation [1]

The significance of sensitivity and detection limit, comparisons of surface and bulk and an approach for pragmatic peak fitting of difficult elemental lines will be discussed along with considerations such as etch artefacts and degradation.

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11:00am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-10 Multimodal Analysis and Imaging of the Boehmite Layer on AA6061***, **Lyndi Strange**,* Pacific Northwest National Lab*; X. Yu,* Oak Ridge National Laboratory*; V. Shutthahandan, M. Song, Q. Miller, M. Bowden, J. Gao, Y. Zhang, J. Son, R. Shimskey, R. Prabhakaran,* Pacific Northwest National Lab*; V. Joshi,* Pacific Northwest National Laboratory

Low-enriched uranium (LEU) alloyed with 10% Mo (U-10Mo) is being considered as a promising alternative to oxide-based dispersion fuel with high-enriched uranium for use in research reactors. The configuration of this proposed LEU monolithic fuel plate consists of the U-10Mo plate-type fuel foil with a 25 µm Zr interlayer barrier clad with an aluminum alloy (AA6061). The clad AA6061 is coated with a boehmite layer to prevent corrosion. The boehmite layer has a high pH passivation range, which makes it resistant to oxidation and preferable to protect the Al cladding. Boehmite is usually formed on the AA6061 surface by autoclave processing. Various surface cleaning techniques have been employed such as polishing and etching to clean the surface of the AA6061 prior to boehmite formation. In this study, we examine how pre-treatment of AA6061 using polishing followed by both acid and alkaline etching affects the chemical composition of the boehmite layer using multimodal analysis. Time-of-flight secondary ion mass spectrometry (ToF-SIMS), x-ray photoelectron microscopy (XPS), transmission electron microscopy (TEM), and grazing incidence x-ray diffraction (GI-XRD) were used to understand the changes in the boehmite layer as a result pre-treatment. ToF-SIMS provides a surface sensitive technique to understand the surface composition and characteristics. Spectral similarities were verified using principal comment analysis (PCA). XPS is a complimentary technique that provides quantitative information about the oxidation states present on the surface. Both the SIMS and XPS results suggested oxidation at the surface, which was further investigated using TEM-SAED and GI-XRD. While the GI-XRD results suggested the dominant phase present on the coupon surface is boehmite, TEM-SAED found small amounts of α- and γ-Al_2O_3 present as a result of alkaline etching.

11:20am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-11 Study of $Cs_x(CH_3NH_3)_{1-x}PbBr_3$ Perovskite with XPS Imaging and Small Area Spectra***, **Tatyana Bendikov**,* Weizmann Institute of Science, Israel*; Y. Rakita,* Columbia University*; H. Kaslasi, G. Hodes, D. Cahen,* Weizmann Institute of Science, Israel

Interest in halide perovskite (HaPs) is motivated by the combination of superior optoelectronic properties and ease in synthesizing these materials with a surprisingly low density of electrically active defects.[1] HaPs possess high chemical sensitivity, especially those having an organic cation at their *A* position (AMX_3). Although a direct role of the *A* cation in this sensitivity is unclear, and the structural and optoelectronic backbone lie within the *M-X* bond, the type of the *A* cation was shown to impact the chemical stability and, usually indirectly, affect optoelectronic properties of HaPs.[2-3]

X-ray Photoelectron Spectroscopy (XPS), is a surface sensitive technique with a sensitivity that goes down to a single atomic layer, and can provide unique information that relates the elemental composition with the chemical and electronic states of the different elements in the material. Our study focuses on the XPS imaging in combination with selected small area XPS spectra and uses solution-grown, single crystals of mixed *A*-cation $Cs_xMA_{1-x}PbBr_3$(MA = $CH_3NH_3^+$) HaPs as a candidate for investigating heterogeneity within the crystals. With XPS we followed the variations in chemical composition of these crystals. By observing the surface, we found significant changes in the N/Cs ratio, which increases towards the interior of the crystal. Similar variations in N/Cs, but also in Pb/(N+Cs) ratios were found when we studied cross-sections of cleaved crystals. This compositional heterogeneity within the HaPs crystal was not previously reported and was discovered and monitored due to exclusive capabilities of the XPS technique.

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11:40am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-12 Surface Characterization of Mineral Associated Organic Matters in Environmental Samples by Using X-Ray Photoelectron Spectroscopy (XPS)***, **Qian Zhao**, M. Engelhard, O. Qafoku, K. Hofmockel,* Pacific Northwest National Laboratory

Surface characterization is an important analytical approach to understanding the most dynamic interface of a material. The understanding of soil organic matter (SOM) persistence is critical to global carbon (C) cycling. Minerals play an important role in persisting SOM by associating with organic matters (OM) through different interactions. Yet mechanisms of the accumulation of OM in soil are still unclear. Chemical characterization of OM that is associated with minerals provides a mechanistic understanding of mineral-OM interactions. X-ray photoelectron spectroscopy (XPS) analysis allows us to probe the chemical states and speciation of OM on the surface of mineral grains or soil particles. This work used both synthetic mineral-OM complexes and natural soil samples to investigate the chemistry of organics that associate with minerals. In the synthetic system, we adsorbed four organic compounds on a calcite crystal. XPS analysis found the relative concentration of C was higher in OM adsorbed calcite than that in pristine calcite. Further, the deconvolution of C 1s spectra reveals that the calcite surface had a relatively lower abundance of carbonate but a higher abundance of alkanes in the OM adsorbed calcite than pristine calcite, indicating the adsorption of OM on the calcite surface. In the soil system, we incubated agricultural soils with ^{13}C-glucose for 12 months to trace the fate of microbial residues. Size and density fractionation was used to separate mineral-associated organic matter (MAOM) from whole soil. XPS analysis determined C chemistry of necromass on soil particle surfaces by scanning C 1s region of MAOM and non-MAOM fractions. We found that the MAOM fraction had a relatively higher abundance of carbonyl and carboxylic C functional groups and a relatively lower abundance of C-C/C=C group than non-MAOM fraction. It suggests that MAOM fraction is enriched in microbial-derived molecules (i.e., proteins) but has fewer plant detritus (i.e., carbohydrates or lignin) on mineral surfaces. XPS technique allows us to understand the surface chemistry of microbial necromass that is associated with minerals in soil. The chemical speciation information provides us with the potential bonding environment at the interface of minerals and OM.

Nanoscale Science and Technology Division
Room 304 - Session NS+AP+BI+SS-WeM

Frontiers in Scanning Probe Microscopy Including Machine Learning

Moderators: Wonhee Ko, University of Tennessee, Knoxville, **Adina Luican-Mayer**, University of Ottawa, Canada

8:40am **NS+AP+BI+SS-WeM-3 Decay Rate Spectroscopy for a Direct Probe of Josephson and Andreev Currents on the Atomic Scale*, Wonhee Ko,*** University of Tennessee, Knoxville*; J. Lado,* Aalto University, Finland*; E. Dumitrescu, P. Maksymovych,* Oak Ridge National Laboratory

The tunneling current in superconducting tunnel junctions involves several mechanisms in addition to the normal-electron tunneling, such as Josephson tunneling and Andreev reflection. Identification of the tunneling mechanisms as a function of external parameters, such as barrier height, bias voltage, temperature, and so on, is the key to elucidating the characteristics of the superconductors, such as paring symmetry and topology. Here, we present a method to identify distinct tunneling modes based on the decay rate of tunneling current measured by scanning tunneling microscopy (STM) [1,2]. Precise control of the tip-sample distance in picometer resolution allows us to quantify the decay rate as a function of bias V and tip height z, with which we identified the crossover of tunneling modes between single-charge quasiparticle tunneling, (multiple) Andreev reflection, and Josephson tunneling. The method was both applied to S-I-S [1] and S-I-N [2] junctions, to unambiguously identify Josephson and Andreev currents. Moreover, mapping decay rates in the atomic resolution with STM revealed the intrinsic modulation of Andreev reflection and Josephson current. The result shows that the decay rate spectroscopy will be crucial for addressing the superconducting characteristics of the materials and their applicability for Josephson-junction devices.

This research was performed at the Center for Nanophase Materials Sciences which is a DOE Office of Science User Facility.

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9:00am **NS+AP+BI+SS-WeM-4 Machine Learning-Driven Automated Scanning Probe Microscopy: Application to Ferroelectric Materials*, Yongtao Liu,*** *K. Kelley, R. Vasudevan,* Oak Ridge National Laboratory, USA*; H. Funakubo,* Tokyo Institute of Technology, Japan*; S. Kalinin,* University of Tennessee Knoxville*; M. Ziatdinov,* Oak Ridge National Laboratory, USA

Scanning probe microscopy (SPM) has become a mainstay of many scientific fields including materials science, condensed matter physics, and so on. Machine learning (ML) and artificial intelligence (AI) have been applied to determine the physical mechanisms involved in phenomena encoded within microscopy data, enabling ML/AI to rapidly become an indispensable part of physics research. However, the real-time connection between ML and microscopy—which enables automated and autonomous experiments for microscopy imaging and spectroscopy measurements—still lags. Until now, the search for interesting functionalities in microscopy experiments has been guided by auxiliary information from microscopy to identify potential objects of interest based on human intuition; the exploration and verification of physical mechanisms depend on human-based decision making, i.e., operators determine the parameters for subsequent experiments according to the previous experiment. Here, we developed ML-driven automated experiment (AE) scanning probe microscopy (SPM) workflow to learn the functionality and mechanism in materials in an automatic manner. We demonstrate the application of deep kernel learning and hypothesis learning based workflows by investigating ferroelectric materials, including studies of domain wall dynamics, domain switching mechanism, the conductivity of topological defects, and relationship between domain structure and local properties. Using these approaches, we observe larger hysteresis opening near 180° domain walls due to the larger polarization mobility in the vicinity of the 180° walls in a $PbTiO_3$ sample and find that the domain switching in a $BaTiO_3$ thin film is determined by the kinetics of the domain wall motion, etc. We implemented these approaches in SPM for ferroelectric materials investigation, however, the workflows are universal and can apply to a broad range of imaging and spectroscopy methods, e.g., electron microscopy, optical microscopy, and chemical imaging.

Acknowledgements: This work (implementation, measurement, and data analysis) was primarily supported by the center for 3D Ferroelectric Microelectronics (3DFeM), an Energy Frontier Research Center funded by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences under Award Number DE-SC0021118. This work (ML development) was supported by the Center for Nanophase Materials Sciences, a US Department of Energy Office of Science User Facility.

9:20am **NS+AP+BI+SS-WeM-5 AVS Dorothy M. and Earl S. Hoffman Scholarship Talk: Direct Imaging of Light-Matter Interaction of 0-dimensional Excitonic Emitters using Tip-enhanced Scanning Probe Technique*, Kiyoung Jo*[1]***, *E. Marino, J. Lynch, Z. Jiang, N. Gogotsi,* University of Pennsylvania*; P. Schuck,* Columbia University*; N. Borys,* Montana State University*; C. Murray, D. Jariwala,* University of Pennsylvania

Strong light-matter interactions of 0-dimensional emitters on plasmonic Au substrate were explored using both contact and tapping mode tip-enhanced scanning probe micro-spectroscopy. The plasmonic tip engaged with contact mode couples with the excitonic dipole in CdSe-CdS nanoplatelets, leading to strong exciton-plasmon coupling. Unlike the contact mode, the directional propagation of surface plasmon polariton from the excitonic emission of the nanoplatelets on Au as wave-like fringe patterns was probed by taking advantage of the tapping mode. Since tapping mode operates a few nanometers away from the surface, the near-field photoluminescence with in-plane wavevectors can be collected, leading to form fringe patterns propagating from the quantum plate. Extensive optical simulations proved that the fringes are the result of standing wave formed between the tip and the nanoplatelets. The effect of excitonic dipole orientation and dielectric layers on the fringe patterns were investigated by the simulation which matched with experimental results. The fringe patterns were also observed in WSe2 nano-bubbles, and the CdSe/CdS nanoplatelet in SiO2/Si substrate which means the phenomenon is universal in 0-dimensional emitters and various substrates. We envision that the discovery excels in understanding in-plane near-field light signal transduction from 0-dimensional emitters toward nano and quantum photonics.

9:40am **NS+AP+BI+SS-WeM-6 Nanoscale Subsurface Depth Sensitivity of Contact Resonance Atomic Force Microscopy on Layered Films*, Gheorghe Stan,*** National Institute for Science and Technology (NIST)*; C. Ciobanu,* Colorado School of Mines*; S. King,* Intel Corporation

Probing the mechanical properties is one of the basic inquiries that can reveal the structure and integrity of an isolated material or multicomponent system. At the nanoscale, due to size constrains and defects, mechanical tests become even more relevant as the properties of a part may differ by those of the whole. Over years, contact resonance AFM (CR-AFM) has proved to be a reliable AFM-based technique for nanoscale mechanical property measurements. Mostly operated into the elastic modulus range from few GPa to hundreds of GPa, CR-AFM was used to test different materials and structures at the nanoscale and considered for discerning the mechanical response of subsurface inhomogeneities and buried domains. It remains, however, to directly prove the extent of its quantitative capabilities both in terms of elastic modulus and depth sensitivity. In this work, we develop a quantitative methodology to test the elastic modulus and depth sensitivity of CR-AFM against a set of low-k dielectric bilayer films with the top layer of various thicknesses. We have analyzed the measured contact stiffness as a function of load and film thickness with both a semi-analytical model and three-dimensional finite element analysis. Both analyses confirmed the expected elastic moduli of the layered structures and provided a robust quantitative estimation of the subsurface depth and material sensitivities of CR-AFM. We also developed a correlative measurement-model analysis to assess the convoluted contributions of the structural morphology and mechanical properties to the contact stiffness used by AFM-based subsurface imaging. The results explain the inherent difficulties associated with solving concurrently the material contrast and location of subsurface heterogeneities in nanomechanical subsurface imaging.

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[1] **AVS Dorothy M. and Earl S. Hoffman Scholarship Recipient**

11:00am **NS+AP+BI+SS-WeM-10 The Impact of Temperature on Viscoelastic Properties of Nanoscale Domains Within Polymer Composites***, **Bede Pittenger**, S. Osechinskiy, J. Thornton, S. Loire, T. Mueller,* Bruker Nano Surfaces

The behavior of polymer composites is controlled by the properties of the components as well as the microstructure of the material. Because confinement effects and interphase formation can alter properties of the microphases, only measurements performed directly on the composite can provide the needed local property distribution. Mechanical properties of polymers are generally temperature (and time) dependent, so a full understanding requires measurements over a range of temperatures and frequencies. Ideally, one would like to observe the mechanical behavior of these microscopic domains while they pass through their glass transitions to appreciate the influence of size effects and confinement on time dependent mechanical properties.

Recently, Atomic Force Microscopy based nano-Dynamic Mechanical Analysis (AFM-nDMA) was introduced. Like bulk DMA, this mode provides spectra of storage and loss modulus across frequency and temperature, allowing construction of master curves through Time Temperature Superposition (TTS). In addition, it allows high resolution measurements localized to the microscopic structures within heterogeneous samples. This presentation will examine the capabilities of this new mode with examples in a wide range of polymers and composites.

11:20am **NS+AP+BI+SS-WeM-11 AFM Force Spectroscopy Combined with Machine-Learning Methods for Identifying Malaria Derived- EV Subpopulations***, **Irit Rosenhek-Goldian**, P. Abou Karam,* Weizmann Institute of Science, Israel*; T. Ziv,* Technion - Israel Institute of Technology, Israel*; H. Ben Ami Pilo, I. Azuri, A. Rivkin, E. Kiper, R. Rotkopf, S. Cohen,* Weizmann Institute of Science, Israel*; A. Torrecilhas,* Federal University of São Paulo, Brazil*; O. Avinoam,* Weizmann Institute of Science, Israel*; A. Rojas,* University of Costa Rica*; M. Morandi, N. Regev-Rudzki,* Weizmann Institute of Science, Israel

The Malaria (*Plasmodium falciparum*) parasite releases extracellular vesicles (EVs) which modulate the mechanical properties of the host red blood celland thus facilitate parasite action. It is understood that EVs are composed of sub-populations with different functions, but little is known of their nature and specialized function. Here, we report the use of Atomic Force Microscopy (AFM) imaging and puncture analysis, combined with state-of-the-art size separation techniques and several biochemical, microscopic and spectroscopic characterization techniques in an attempt to differentiate and characterize the different populations. Specifically, we subjected malaria-derived EVs to size-separation analysis, using Asymmetric Flow Field-Flow Fractionation (AF4). The fractions obtained were characterized by Cryo-transmission electron microscopy (cryo-TEM), and AFM which revealed the presence of two distinct EV subpopulations - small (10-70 nm) and large (30-500 nm). Proteomic analysis revealed that the small EVs were enriched in complement-system proteins and the large EVs with proteasome subunits. In addition, Förster resonance energy transfer (FRET)-based fusion assay showed that small EVs fused to early-endosome liposomes at significantly greater levels than large EVs. Finally, AFM puncture analysis characterized by unsupervised machine-learning verified the presence of two distinct fractions with respect to mechanical behavior which correlate with the EV size groupings. These results shed light on the sophisticated mechanism by which malaria parasites utilize EV subpopulations as a communication tool to target different cellular destinations or host systems.

Nanoscale Science and Technology Division
Room 304 - Session NS1+BI-WeA

Nanopore Sensing and Fabrication, Operation and Metrology of Biodevices

Moderators: David Czaplewski, Argonne National Laboratory, **Georg Fantner**, EPFL, Switzerland

2:20pm **NS1+BI-WeA-1 Single Cell and Single Molecule Biophysics with Glass Nanopores***, **Georg Fantner**, A. Radenovic, S. Leitao, V. Navikas, B. Drake,* EPFL, Switzerland **INVITED**

Scanning ion conductance microscopy (SICM) has been around for decades, yet it has not received as much attention as other forms of scanning probe microscopy. Recently, this true non-contact techniquehas kindled renewed interest among biophysicists and biologists because it is ideally suited for label-free imaging of fragile cell surfaces where it achieves exquisite resolution down to the nanometer regime without distorting the cell membrane. SICM uses a glass nanopipette as a scanning probe and measures the current through the glass nanopore as a proximity detection of the sample surface. The challenge to harness this technique for time resolved 3D nanocharacterization of living cells lies in the relatively slow imaging speed of SICM. In this presentation I will show how we apply what we have learned from high-speed AFM to the field of SICM. By reengineering the SICM microscope from the ground up, we were able to reduce the image acquisition time for SICM images from tens of minutes down to 0.5s while extending the imaging duration to days.

SICM, however, is much more versatile than just an imaging tool. I will also discuss our recent results using SICM as a single molecule characterization tool. We term this method scanning ion conductance spectroscopy (SICS). Using capillaries with exceptionally small nanopores, we are able to detect and manipulate single molecules in a repeatable and high throughout manner.

3:00pm **NS1+BI-WeA-3 Ultrasensitive Nanoporous Gold Substrates for SERS Detection in Liquids or Gases***, **Issraa Shahine**, B. Humbert, J. Mevellec, M. Richard-Plouet, P. Tessier,* Nantes Université, CNRS, Institut des Matériaux de Nantes Jean Rouxel (IMN), France

The design of three-dimensionally structured, gold nanoporous membranes is described. Our aim is to design surface enhanced Raman scattering (SERS) substrates to detect very low concentrations of molecules in liquid or gaseous phases. The SERS substrates are constituted of stacked ultrathin nanoporous gold thin layers. They are obtained in a two-step process: first deposition of alternative copper and gold stacked nanolayers by magnetron sputtering, and second, chemical etching to dissolve copper, resulting in the nanoporous morphology. The obtained thin layers of gold give rise to superior surface enhanced Raman scattering (SERS) capability using 2,2-bipyridine (BP) as probe molecules for detection. The SERS intensity mapping confirm the presence of hot spots with a low detection limit down to 10^{-18} mol.L^{-1} of BP concentration. The ultrasensitivity at low concentration molecules is assigned to the effects of the localized enhanced electromagnetic fields around the nano ligaments. An additional Raman mechanism is also highlighted by µ-Surface Enhancement Spatially Offset Raman spectroscopy (µ-SESORS): gold ligaments inside nanoporous layers act as waveguides for the incident light, leading to a significant increase in the size of the active SERS area. These SERS substrates have the ability to detect low BP vapor pressure in air.

This process is a reliable method for fabricating uniform, highly reproducible and efficient SERS substrates, with a robust SERS response at extremely low detection limits.

Applied Surface Science Division
Room 320 - Session AS+AC+BI+CA+HI-ThM

Unraveling the Composition of Complex Systems with SIMS

Moderators: Steve Consiglio, Tokyo Electron, **Gregory L. Fisher**, Physical Electronics

8:20am **AS+AC+BI+CA+HI-ThM-2 Ex-Situ, Surface and Bulk Investigations of Defluxing Chemistry Effects on Solder Mask**, ***J. Elliott Fowler,*** Sandia National Laboratories*; R. Gerhardt,* Georgia Institute of Technology*; J. Ohlhausen, R. Callaway,* Sandia National Laboratories*; M. Watt,* Georgia Institute of Technology*; S. Grosso, S. Rosenberg,* Sandia National Laboratories

Solder masking is an integral process in the manufacture of printed circuit board assemblies (PCBAs) – it serves to protect the unfinished copper traces from environmental effects, define the soldering pads and provide an adherable surface for conformal coating. Liquid photo-imageable (LPI) solder mask is one of the most popular choices for PCBAs due to ideal electrical and physical properties as well as chemical. LPI solder mask is a heterogeneous epoxy acrylate-based matrix, thus its surface chemistry can be very distinct from its overall bulk chemistry. The surface chemistry is of particular interest as it must be compatible with and resistant to a wide range of chemistries and environments which the PCBA will experience during its production and fielding lifetime. For instance, sensitivity to moisture is a well-known issue. Several studies of solder mask moisture absorption reveal that it reaches a saturation of ~1 weight percent in high-humidity environments, and corresponding changes in insulative properties occur. Risks to mask performance have arisen as a result of the use of new flux formulations which require increasingly aggressive aqueous defluxing chemistries for removal. We hypothesize that alkaline defluxing chemistries will significantly modify the surface chemistry of solder mask, making it more vulnerable to moisture and thus deteriorating their insulative properties.

A commercially available LPI solder mask material was prepared on squares of FR4 board and exposed to increasingly alklaine cleaning chemistries: including DI water, a pH neutral and a pH >10 defluxing chemistry. Samples were tested with three complementary surface-sensitive analytical techniques, x-ray photoelectron spectroscopy (XPS), time of flight secondary ion mass spectrometry (TOF-SIMS) and contact angle goniometry. TOF-SIMS results show that both pH neutral and alkaline chemistries alter the surface, removing PDMS and leaving organic residues. Contact angle goniometry shows that the alkaline chemistry makes the board's surface significantly more hydrophilic. XPS results show a decrease in Si at the surface correlating to a decrease in PDMS versus the control, with the largest decrease occurring due to the alkaline chemistry. In all cases, the surface is somewhat recoverable; however, recovery is less pronounced with increasing pH. AC impedance spectroscopy and DC Surface Insulation Resistance (SIR) testing of exposed samples in elevated humidity environments was performed to resolve changes in insulative performance due to observed changes in mask surface chemistry.

SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525

8:40am **AS+AC+BI+CA+HI-ThM-3 Unraveling the Composition of Complex Systems with SIMS**, ***Birgit Hagenhoff,*** Tascon GmbH, Germany **INVITED**

For more than four decades SIMS has proven to be a valuable tool in academic research as well as for industrial applications. Whereas the first years focussed on understanding the underlying physical processes using mono-elemental samples, the advent of ToF-SIMS (Time-of-Fligt Secondary Ion Mass Spectrometry) instrumentation in the 80s of the last century opened the path to using SIMS as a screening tool for characterising "the unknown", i.e. samples about which hardly anything is known before the analysis, where sample preparation should be as scarce as possible and where the analysis is performed without any chromatographic pre-step to separate out sample compounds.

Over the years, intensive discussions between those developing instruments and those applying them on a daily basis lead to a fruitful and steep learning curve in the SIMS communities. Meanwhile SIMS instruments offer a multitude of operational modes and are capable of analysing as 3D volume pixel by pixel. The lateral resolution has almost reached the physical limit of the collision cascade with values well below 100 nm and a depth resolution in the nm-range can be achieved. The development of cluster ion sources leads to the possibility to also probe organic materials in depth. At the same time data evaluation routines have become more powerful to address the large amount of data (several GByte for a 3D data set).

Generally, users would like to address three main questions: what (identification) is sitting where (localization) and how much is it (quantification)? Whereas the localization problem, as mentioned above, meanwhile is comparatively straightforward, identification and quantification still are challenging. In identification, the parallel presence of many elements and organic compounds in the SIMS spectra still asks for an expert to solve the analytical puzzle. Here, the application of multivariate statistical techniques and, more recently, machine learning approaching offer promising paths into the future. For a reliable quantification, the influence of the SIMS matrix effect on the results has to be taken into account. Here, the availability of suited reference samples plays a key role for closing the gap to quantitative techniques, like e.g. XPS (X-ray Photoelectron Spectroscopy).

The talk will therefore focus on identification and quantification issues including the use of multivariate statistics, MS/MS approaches and the use of reference sample comparing SIMS with the quantitative techniques XPS and LEIS (Low Energy Ion Scattering).

9:20am **AS+AC+BI+CA+HI-ThM-5 Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) as a Novel Approach to the Characterization of Coatings and Interfaces of Porous Transport Layers**, ***Genevieve Stelmacovich,*** *M. Walker, J. Foster,* Colorado School of Mines*; D. Cullen ,* Oak Ridge National Laboratory*; A. Paxson ,* Plug Power*; G. Bender, T. Schuler, S. Ware,* National Renewable Energy Laboratory*; S. Pylypenko,* Colorado School of Mines

The United States energy infrastructure aims to move towards the integration of hydrogen energy. As such, the production of reliable hydrogen generation through the optimization of water electrolyzers is imperative. In proton exchange membrane water electrolyzes (PEMWE's), the porous transport layer (PTL) plays an important role. Due to the harsh conditions of the cell, titanium is the current state-of-the-art anode PTL material. However, titanium quickly forms a layer of titanium oxide which significantly decreases conductivity of the PTL and respectively decreases the overall efficiency of the PEMWE system. To mitigate oxide effects, coatings are commonly applied to the PTL.

Focused Ion Beam Scanning Electron Microscopy (FIB-SEM) in conjunction with Scanning Transmission Electron MicroscopyEnergy-dispersive X-ray Spectroscopy (STEM-EDS) analysis is a commonly used technique to characterize PTL materials and PTL coatings, specifically to look at coating homogeneity and unfavorable oxide layer formation. Unfortunately, this approach is both time-consuming and labor intensive. Additionally, STEM-EDS analysis only provides elemental information, so if several oxide layers preside, it can be difficult to differentiate them, and thus lead to a lack of understanding fundamental degradation mechanisms. These technique deficiencies have motivated the development of an alternative approach that allow more efficient characterization of these materials. Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is a valuable technique that is commonly used to characterize thin films and buried interfaces. ToF-SIMS can be performed relatively quickly, provides chemical information, and is sensitive to trace elements. This technique also enables visualization of elemental distribution, which provides more detailed surface and interface information. This presentation will demonstrate capabilities of ToF-SIMS for characterization of PTLs comparing results to TEM analysis of cross-sections obtained with FIB-SEM. This study will highlight similarities and differences between the techniques, expand on technique optimization for these morphologically challenging samples, and suggest paths for future investigation moving forward.

9:40am **AS+AC+BI+CA+HI-ThM-6 Construction of Accurate 3D NanoSIMS Depth Profiling Images of Cells in the Presence of Lateral Variations in Sputter Rate**, *M. Brunet, B. Gorman,* ***Mary Kraft,*** University of Illinois Urbana-Champaign

We have developed a strategy for constructing accurate 3D NanoSIMSdepth profiling images of cells in the presence of lateral variations in sputter rate. In this strategy, we use the secondary electrons acquired in parallel with the negative ions during depth profiling to reconstruct the 3D morphology of the cell every time a depth profiling image is acquired. The morphologies created for each raster plane in the depth profile are adjusted to ensure that the height at every pixel decreases with increasing image plane. The resulting reconstructions of the cell's morphology are used to define the z-positions of the voxels in the component-specific 3D NanoSIMS images. We validated this strategy by comparing morphology reconstructions for secondary electron depth profiling images acquired with focused ion beam - secondary electron microscopyand AFMdata acquired from the cell before depth profiling. The shape, curvature, and relative height of the reconstructed morphology agreed well with the AFM data. Depth correction of 3D NanoSIMSdepth profiling data of a metabolically labeled mammalian cell using this strategy improved visualization of the^{18}O-cholesterol and ^{15}N-sphingolipids distributions intransport vesicles and organelle membranes. Accurate 3D NanoSIMS images that show the intracellular distributions of molecules of interest may now be constructed in the presence of variations in sputter rate and the absence of correlated topography data.

11:00am **AS+AC+BI+CA+HI-ThM-10 Innovations in Nuclear Materials Analysis with SIMS*, Christopher Szakal,*** National Institute of Standards and Technology (NIST) **INVITED**

Global nuclear safeguards efforts, coordinated by the International Atomic Energy Agency (IAEA), require precision measurements to answer questions related to nuclear treaty compliance. Despite those questions seeming relatively simple, and the elemental composition of the target analytes often consisting of just uranium and oxygen, the complex processes employed to answer those questions reveal the importance of subtle nuances to meet analytical objectives. This presentation will explore the complexity of this type of analyte system and how innovations in secondary ion mass spectrometry (SIMS) resulted in a routinely utilized tool to address nuclear safeguards requirements for environmental sampling analysis. The complexity is largely driven by the small amounts of nuclear particle material available for analysis, including challenges for 1) representative sampling of analyte material to represent actual nuclear processes, 2) accuracy and precision of uranium isotopic analyses across a wide dynamic range, and 3) determining when a nuclear process created the analyte material. Precision SIMS measurements provide the opportunity to address these analytical complexities to answer key nuclear safeguards questions, but the presentation will also highlight when limitations are inevitable for which questions can be answered.

11:40am **AS+AC+BI+CA+HI-ThM-12 Understanding Surface Bonding and Molecular Structure with MS/MS Imaging: From Click-Chemistry to Biogenesis*, Gregory L. Fisher,*** Physical Electronics

A TOF-TOF imaging mass spectrometer allows TOF-SIMS (MS^1) imaging and tandem MS (MS^2) imaging to be achieved in a lossless fashion [1,2]. Secondary ions for MS^1 and MS^2 analysis are produced from the same surface area by a primary ion nanoprobe. Monolayer film samples may be characterized without undesired erosion or degradation; even sub-monolayer 2D films are readily characterized. Kilo-electron volt collision-induced dissociation (keV-CID) enables compositional identification and structural elucidation of precursor ion moieties. This analytical capability has been brought to bear for straightforward molecular identification as well as multifaceted studies involving surface modification, polymers, composites, catalysis, forensic and failure analysis, biology and pharmaceuticals. TOF-SIMS tandem MS imaging was employed to unravel the click-chemistry of sub-monolayer films [3] and shed new light to unlock the mystery of molecular biogenesis [4,5].

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12:00pm **AS+AC+BI+CA+HI-ThM-13 Probing Grain Boundary Segregation in 304L Stainless Steel using Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS)*, James Ohlhausen,*** *E. Barrick, D. Susan, C. Robino, K. Hattar, J. Herrmann, P. Duran, J. Rodelas,* Sandia National Laboratories

Boron-rich phases in austenitic stainless steels can promote liquation cracking in the heat affected zone during welding. Stainless steels with boron concentrations even as low as 20 wt. ppm are susceptible to grain boundary cracking after heat treatments. The kinetics of phase transformations during heat treatment that generate the crack susceptible microstructure are currently unknown. Time-of-flight Secondary Ion Mass Spectrometry (ToF-SIMS) was used to map Boron at grain boundaries and in the bulk at trace levels for a series of 304L stainless steel coupons that were heat treated across a range of temperatures and cooling rates to investigate these phase transformations.ToF-SIMS and Scanning electron microscopy (SEM) were used to observe the distribution of chromium borides before and after heat treatment. These results will be used to enable quantitative prediction of thermal processing conditions to avoid weld cracking.Sample preparation methods, ToF-SIMS acquisition conditions and data analysis will be discussed.

SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525

Advanced Surface Engineering Division
Room 317 - Session SE+AS+BI+SS+TF-ThM

Nanostructured and Multifunctional Thin Films and Coatings I

Moderators: Suneel Kodambaka, University of California Los Angeles, **Jianliang Lin**, Southwest Research Institute

8:00am **SE+AS+BI+SS+TF-ThM-1 Nanostructured Optical Thin Films for Energy Applications and More*, Bill Baloukas,*** Polytechnique Montréal, Canada **INVITED**

The range of applications of optical coatings is ever expanding, and the list of requirements they must fulfil, be it in terms of performance and in terms of functionality, is also increasing. This has stimulated the need for thin film materials with novel nanostructures often based on unconventional materials. The present talk will focus on various coating systems for applications ranging from antireflective (AR) coatings to plasmonic nanocomposites to passive and active materials for anticounterfeiting, smart windows and micro/nanosatellites.

AR coatings are the most widely implemented optical coating solution as they can be found on ophthalmic and camera lenses, displays, solar cells, etc. Most often based on dielectric materials, their mechanical performance can often be problematic when implemented onto polymer substrates, the latter possessing much higher thermal expansion coefficients. As a means of improving their elastoplastic properties, hybrid films consisting of a combination of organic and inorganic materials were explored. We will also show how this concept was pushed further by producing ultralow refractive index hybrid films by glancing angle deposition (GLAD).

GLAD films have also found application in angular selective coatings, which display anisotropic optical properties. Typically based on metals, we show how the angular selectivity (AS) can be tuned independently from the thickness of the film by conformally overcoating dielectric GLAD films with an absorbing film (e.g.: TiN) deposited by atomic layer deposition (ALD).

While the previous examples are based on passive materials, we have also extensively studied active materials, mainly electrochromic (EC) WO_3 and thermochromic (TC) VO_2. We will discuss how by tuning the deposition conditions, one can deposit, for instance, electrochromic interference filters and highly durable EC films when in the presence of significant ion bombardment. In the case of TC VO_2 films, we will show how, by incorporating them into judiciously designed optical filters, one can enhance their overall optical performance (e.g.: luminous transmittance, solar transmission variation, emissivity change, etc.).

Finally, we will conclude this talk by discussing our most recent implementation of a gas aggregation cluster source to produce various nanoparticles of interest for the above-mentioned optical applications.

8:40am **SE+AS+BI+SS+TF-ThM-3 Constitution, Microstructure and Mechanical Properties of Magnetron Sputtered RuAl Thin Films*, Vincent Ott,*** Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany*; T. Wojcik,* TU Wien, Austria*; S. Ulrich,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany*; S. Kolozsvári,* Plansee Composite Materials GmbH , Germany*; P. Polcik,* Plansee Composite Materials GmbH, Germany*; P. Mayrhofer, H. Riedl,* TU Wien, Austria*; M. Stueber,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany

Considering high temperature applications, aluminide intermetallics arrived increasing importance over the last decades. They are well known for their mechanical properties, such as high melting point, strength and good oxidation resistance. In Ni-superalloys, for example, aluminide precipitations are widely used as toughening phase, increasing the high temperature strength and durability of the construction material. Although they are commonly used as an additive in composite materials, their usage as a bulk material is hindered by their poor manufacturing due to its brittle behavior at room temperature.

A relatively new candidate material of B2 structured aluminides is the RuAl intermetallic phase. Compared to other candidates of its class, such as NiAl or TiAl, RuAl exhibits a ductile-brittle-transition below room temperature, which may considerably expand the range of its potential applications.

Thin film synthesis can enable the exploitation of their full potential for example as a protective coating in aircraft and aerospace applications. To elucidate this potential, RuAl single layer thin films were synthesized by magnetron sputtering, utilizing a powder manufactured sputtering target with a composition of 50 at. % Ru and 50 at. % Al. Thin film deposition was done for a variation of the process parameters such as the mode of the power supply, gas pressure and substrate bias voltage to investigate their impact on the thin films constitution and microstructure. Major structural thin film characterization was done by X-ray diffraction and transmission electron microscopy methods. These data are subsequently used to discuss the mechanical properties of the thin films, determined by microindentation.

9:00am **SE+AS+BI+SS+TF-ThM-4 Microstructure, Thermal Stability and Oxidation Resistance of an arc-evaporated $Cr_{0.74}Ta_{0.26}N$ Coating*,* *Christina Kainz*,** Christian Doppler Laboratory for Advanced Coated Cutting Tools at the Department of Materials Science, Montanuniversität Leoben, Austria*; M. Tkadletz, M. Burtscher,* Department of Materials Science, Montanuniversität Leoben, Austria*; C. Saringer,* Christian Doppler Laboratory for Advanced Coated Cutting Tools at the Department of Materials Science, Montanuniversität Leoben, Austria*; A. Stark, N. Schell,* Institute of Materials Physics, Helmholtz-Zentrum Hereon, Germany*; C. Czettl, M. Pohler,* CERATIZIT Austria GmbH, Austria*; D. Kiener,* Department of Materials Science, Montanuniversität Leoben, Austria*; N. Schalk,* Christian Doppler Laboratory for Advanced Coated Cutting Tools at the Department of Materials Science, Montanuniversität Leoben, Austria

CrTaN coatings have recently received increasing industrial interest due to their combination of high hardness, beneficial fracture toughness and promising performance in cutting tests. However, up to now, no thorough investigation on the thermal stability and oxidation resistance of this coating system is available. Thus, this work aims to elucidate the evolution of the microstructure and phase composition of an arc evaporated $Cr_{0.74}Ta_{0.26}N$ coating in protective atmosphere and air up to 1400 °C. The as–deposited coating crystallizes in an fcc–$Cr_{0.74}Ta_{0.26}N$ solid solution with a preferred <311> orientation. Alternating Cr–enriched and Ta–enriched nano–layers are identified in the cross–section, which arise from the three–fold rotation during deposition. $Cr_{0.74}Ta_{0.26}N$ powder is stable in protective atmosphere up to temperatures of ~1200 °C, where a transformation into fcc-$Cr_{0.74}Ta_{0.26}N$ to t–$Cr_{1.2}Ta_{0.8}N$ sets in. Vacuum annealing of $Cr_{0.74}Ta_{0.26}N$ on sapphire substrate results in the loss of the nano-layers at 1000 °C, a texture change to <200> at 1270 °C and the transformation to t-$Cr_{1.2}Ta_{0.8}N$ at 1300 °C. When exposed to ambient atmosphere, powdered CrTaN starts to oxidize to t–$CrTaO_4$ and r–Cr_2O_3 at 1050 °C. A partly oxidized CrTaN coating on sapphire was found to consist of intact fcc-$Cr_{0.74}Ta_{0.26}N$ grains close to the substrate interface, a porous transition layer of r-Cr_2O_3 and t-$CrTaO_4$ and a dense r-Cr_2O_3 layer at the surface. The present study confirms the exceptional thermal stability and oxidation resistance of CrTaN coatings, making them promising candidates for use in demanding machining applications.

9:20am **SE+AS+BI+SS+TF-ThM-5 Microstructural Characterization and Tribological Evaluation of TiN, CrN, TiSiCN, and CrSiCN Coatings for Applications in Cold Regions*, Nicholas D'Attilio,*** *F. Thompson, G. Crawford,* South Dakota School of Mines and Technology*; E. Asenath-Smith,* US Army Corps of Engineers Cold Regions Research and Engineering Laboratory

Transition metal nitride and nanocomposite coatings have the potential to improve the efficiency, service lifetime, and durability of equipment operating in the extremely cold and dry environments found in Earth's polar regions. Ceramic coatings are sensitive to their operating conditions, and development efforts have been focused on ambient and high temperature environments. Thus, there is a need to understand the influence of arctic conditions on the performance of these materials. To investigate the influence of coating phase content on cold environment performance, TiN, CrN, TiSiCN, and CrSiCN coatings were deposited by plasma enhanced reactive magnetron sputtering. The structure and composition of the coatings was characterized by scanning electron microscopy, energy dispersive X-ray spectroscopy, atomic force microscopy, and X-ray diffraction. Tilting base contact angle goniometry was used to determine the surface energy using the Owens-Wendt-Rabel-Kaelble method. Coating hardness and apparent elastic modulus were measured by nanoindentation. Sliding wear tests were conducted under simulated arctic conditions with a ball-on-flat tribometer equipped with an active cooling stage. Coating microstructure, surface properties, and their relationships to the wear mechanisms identified at low temperatures are discussed.

9:40am **SE+AS+BI+SS+TF-ThM-6 Development and Evaluation of TiAlNb/YSZ Protective Coatings for Titanium Alloys*, Jianliang Lin,*** Southwest Research Institute, San Antonio Texas*; T. Stinnett,* Lockheed Martin Missiles and Fire Control

There are increasing demands in the development of advanced thermal protection coatings for aerospace components made by titanium alloys for hypersonic applications. A conventional thermal barrier coating based on MCrAlY/YSZ produced by thermal spray or EB-PVD (Electron Beam Physical Vapor Deposition) provided thermal protection, but was found insufficient in thermal stain tolerance and mechanical strength match for titanium alloys. In this study, TiAlNb alloy with specific chemistry was selected as the bond coat for Ti-6Al-4V alloys. The TiAlNb bond coats were prepared by different magnetron sputtering techniques, including plasma enhanced magnetron sputtering (PEMS), high power impulse magnetron sputtering (HiPIMS), and a combination of PEMS and HiPIMS. The structure, adhesion, oxidation resistance, and thermal fatigue resistance of the TiAlNb coatings was studied by different means. Then an yttrium stabilized zirconium oxide (YSZ) top coat was applied on the top of the optimized TiAlNb by thermal spray. The thermal strain resistance and phase stability of the overall coating system were evaluated using high energy laser irradiation and compared to a thermal spray MCrAlY/YSZ coating in ambient air. It is found that TiAlNb/YSZ outperform MCrAlY/YSZ in high energy laser irradiation, and exhibited no structure and integrity degradation.

11:00am **SE+AS+BI+SS+TF-ThM-10 Imperfections in Metal Diborides – from Ab-Inito Calculations to Transmission Electron Microscopy*, Martin Dahlqvist,*** IFM, Linköping University, Sweden*; M. Dahlqvist,* Linköping University, Sweden **INVITED**

Transition metal diborides (MB_2) are considered as an extremely hard ceramics owing to their outstanding chemical, mechanical, corrosion, thermal and electrical properties. This makes MB_2 coatings attractive for applications in erosive, abrasive, corrosive, and high-temperature environments [1]. Typical coatings are overstoichiometric in boron ($B/M>2$) [2] but the recent addition of understoichometic MB_2 coatings ($B/M<2$) have widened their compositional range [3-8]. However, when comparing calculated and measured lattice parameters of MB_2, perfect match is found for *M* from Group 3 (Sc, Y) and 4 (Ti, Zr, Hf) while deviations are found for *M* from Group 5 (V, Nb, Ta) and 6 (Cr, Mo, W). Reason for this have been discussed to be attributed to non-stoichiometric MB_2. In our quest for improving the properties of MB_2 we must thus not only master their composition but also related defects. Reliable theoretical studies thus require detailed information about type of defects and their distribution in MB_2. It will be shown how theory can be used to identify possible defects in MB_2 and explain the discrepancy between theory and experiment. It will be demonstrated that vacancies in MB_2 have a significant impact for *M* from Group 5 (Nb, Ta) and 6 (Mo, W) with improved thermodynamical and dynamical stability as well as mechanical properties. Moreover, extended planar defects have also been identified for multiple MB_2 where atomically resolved aberration-corrected scanning transmission electron microscopy imaging, electron energy loss spectroscopy elemental mapping and first principles calculations have been applied to decode the atomic arrangements of the observed planar defects in non-stoichiometric MB_2 coatings.

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11:40am **SE+AS+BI+SS+TF-ThM-12 Mechanical Property and Corrosion Resistance Evaluation of $Ti_xZrNbTaFeB_y$ High Entropy Alloy Thin Films***, B. Lou,* Chang Gung University, Taiwan*; F. Kan,* Ming Chi University of Technology, Taiwan*; **Jyh-Wei Lee**,* Ming Chi University of Technology, Taiwan

High entropy alloy (HEA) thin films have been widely explored due to their unique properties as compared with conventional alloy coatings. In this work, an equimolar TiZrNbTaFe HEA target and a TiB2 target were used to fabricate five TixZrNbTaFeBy HEA thin films with different Ti and B contents using a hybrid high power impulse magnetron sputtering and radio frequency power deposition system. The Ti and B contents were increased by decreasing the input power of TiZrNbTaFe HEA target. The (Ti+B)/(Zr+Ta+Nb+Fe) ratio of the thin films increased from 2.70 to 19.44 as the ZrTiNbTaFe HEA target input power decreased from 200 to 50 W. The TixZrNbTaFeBy thin film kept its amorphous structure while the (Ti+B)/(Zr+Ta+Nb+Fe) ratio was less than 19.44. A nanocomposite microstructure consisting of TiB_2 nanocrystallites embedded in an amorphous TiZrNbTaFe matrix was obtained for the $Ti_{26.4}Zr_{1.1}Nb_{1.0}Ta_{1.3}Fe_{1.1}B_{61.1}$ thin film. The hardness of TixZrNbTaFeBy thin films increased with increasing Ti and B contents. Good adhesion properties were found for five thin films. Each amorphous TixZrNbTaFeBy thin film enhanced the corrosion resistance of bare 304 stainless steel substrate because of the dense microstructures to block the attack of corrosive electrolytes. The amorphous structured $Ti_{26.9}Zr_{3.5}Nb_{3.4}Ta_{3.8}Fe_{3.7}B_{54.6}$ thin film coating exhibited a potential application as a protective coating in harsh environments due to its high hardness of 18.8 GPa, excellent adhesion, good wear resistance, and adequate anticorrosion property.

12:00pm **SE+AS+BI+SS+TF-ThM-13 Tuning the Properties of Thin Films via Disorder***, **Alessandro Troglia**, M. van de Poll,* Advanced Research Center for Nanolithography (ARCNL), Netherlands*; J. van de Groep, A. de Visser,* Van der Waals-Zeeman Institute, University of Amsterdam, Netherlands*; R. Bliem,* Advanced Research Center for Nanolithography (ARCNL), Netherlands

Structural disorder in thin films is often considered detrimental compared to the well-defined nature of epitaxial layers. However, some examples of amorphous thin films show superior properties such as better corrosion resistance, mechanical strength and catalytic performance. Structural disorder can thus serve as an ideal parameter to tune the properties of thin films to specific applications. In this work, we investigate how structural disorder affects the properties of metallic thin films for two selected alloys: CuZr and HfMoNbTiZr. Due to its excellent glass-forming ability, CuZr is an ideal model system for metallic glasses, while the refractory high-entropy alloy (HEA) HfMoNbTiZr has shown a strong preference towards crystallinity. For both materials, amorphous and crystalline alloy thin films of identical composition were achieved by varying the substrate temperature during deposition onto sapphire substrates via pulsed laser deposition (PLD). Grazing-incidence x-ray diffraction (GI-XRD) demonstrate that CuZr thin films grown at room temperature are fully amorphous, while signs of polycrystallinity are observed at 500°C. The effect of disorder is clearly visible in the optical, transport and corrosion properties. The amorphous films are optically transparent in the visible, while polycrystalline films are dark and reflective. The temperature-dependent electronic transport changes its mode from a bad metal to a charge-hopping conductor with an increase in structural disorder. Moreover, the surface chemical properties measured with x-ray photoelectron spectroscopy (XPS) show a clear preference in the surface oxidation of the Cu species. Cu is fully metallic in the disordered film after air-exposure, whereas both oxide and hydroxide species are detected in the polycrystalline film. On the other hand, HfMoNbTiZr thin films grown with PLD are amorphous according to GI-XRD and display a remarkable thermal stability. In contrast with literature, no sign of crystallinity is detected with GI-XRD from room temperature up to 700°C. A further increase of the growth temperature reveals the onset of directed crystallization at 900°C. These results pave the way to the synthesis of metallic thin films with superior and tunable properties via disorder for a wide variety of technological applications.

2D Materials Technical Group
Room 303 - Session 2D+AS+BI+HC+SS-FrM

2D Materials: Biological, Electronic, Energy, and Other Applications

Moderators: Robert Hovden, University of Michigan, **Jyoti Katoch**, Carnegie Mellon University

8:20am **2D+AS+BI+HC+SS-FrM-1 Printable Electrochemical Biosensors based on 2D and 3D Graphene***, A. Ebrahimi, **Derrick Butler**, V. Kammarchedu, K. Zhou,* Penn State University **INVITED**

The increasing demand for low-cost and field-deployable biosensors has driven researchers to explore robust and scalable biochemical sensor materials and fabrication strategies. Compared to more complicated and expensive photolithography methods, printing techniques – including inkjet and direct laser writing – can enable tailorable and easily-prototypable sensors that are conducive to testing at the point of need. Electrochemical sensors have the potential to meet these criteria and integrate well with printing methods.[1] In recent years, graphene has emerged as a key material in the area of electrochemical biosensors due to high conductivity, wide electrochemical window, biocompatibility, tunability, and excellent surface sensitivity.[2] In particular, advances in preparation of solution-phase graphene suspensions (such as inks containing 2D graphene sheets) have brought about breakthroughs in printed electronics, while the advent of laser-induced graphene (LIG) has enabled the direct writing and integration of 3D porous graphene patterns in various low-cost substrates.Over the past few years, our group has developed different facile functionalization methods to enhance the sensitivity and specificity of printed devices based on graphene ink and LIG, with special attention to sensor performance in complex biological fluids (such as serum, saliva, sweat).[3,4] We have investigated application of the sensors for *in vitro* detection of small molecules involved in neurological functions, kidney disease, and wound infection as well as real-time monitoring of drug-induced response of cancer cells and biofilm biomarkers. Interfacing of the printed sensors with low-cost readout electronics and smartphone has been also demonstrated to showcase the sensor applicability for remote sensing at the point of need. Convergence of machine learning with electrochemical sensing has been also investigated, demonstrating a significant enhancement of sensitivity, while enabling reliable multiplexing of example biochemical markers in saliva and sweat. This talk will highlight our recent progress and ongoing work on advancing printable graphene biosensors in more detail.

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9:00am **2D+AS+BI+HC+SS-FrM-3 A Large Area Selective Emitter for Thermophotovoltaic Applications***, **Minsu Oh**, K. Grossklaus, D. DeMeo, Z. Kranefeld, T. Vandervelde,* Tufts University

Thermophotovoltaic (TPV) devices enable energy harvesting from waste heat. In a TPV system, photons radiated by a selective emitter are converted into electricity by a photodiode due to the photovoltaic effect. The total photon flux available for power conversion is determined by the temperature, emission spectrum, and size of the emitter. Due to the engineerability of metamaterial's optical properties, they have been widely used to create TPV emitters with a desired emission spectrum for varying heat source temperatures. However, the difficulties in fabricating nano- or micrometer-sized metamaterial features that are two-dimensional over large areas pose challenges to realizing a large emitter. This fundamentally limits the output power of a TPV system due to power density restrictions. Therefore, achieving large area emitters with engineerable optical properties are critical for utility of TPV devices at scale with a reasonable power output. In this work, we experimentally demonstrate a 4-inch diameter selective emitter fabricated from one-dimensionally patterned Si and Cr. The selective emission of the emitter peaks at 3.75 µm, which targets 773K blackbody temperature, with a bandwidth of less than 1.5µm. The emission bands of this structure can also be engineered for varying source temperatures owing to the interference effects. Moreover, due to the fabrication ease, our emitter can easily be scaled up to any size of the substrate. We also present the impact of temperature and oxidation on the emission band when heated up to 1000K.

9:20am **2D+AS+BI+HC+SS-FrM-4 Advanced Two-Dimensional Nanohybrids for Efficient Electrocatalytic Hydrogen Evolution***, **Fei Yao**,* University at Buffalo-SUNY

Hydrogen (H_2) shows great potential in reducing greenhouse gas emissions due to its environmentally friendly nature and high gravimetric energy density. It can be generated via electrochemical water splitting based on the hydrogen evolution reaction (HER). It is well known that Pt-group metals (PGMs) are excellent catalysts for HER, but their broad adoption is limited by high cost and scarcity. Recently, two-dimensional (2D) molybdenum disulfide (MoS_2) is regarded as a promising alternative to PGMs due to its large surface area, rich active sites, and ideal hydrogen adsorption energy. However, its practical application is hindered by the intrinsically low electrical conductivity arising from the semiconducting nature of 2H phase MoS_2. On the other hand, 2D Ti_3C_2 MXene with high electrical conductivity, excellent hydrophilicity, and large interlayer distance has been intensively investigated in energy storage devices lately. Compared with charge-neutral graphene, MXene exhibits a negatively charged surface due to the existence of numerous surface functional groups (-OH, -O, -F, *etc.*), which not only enhances the dispersion of MoS_2 precursors but also promotes MoS_2 nucleation, making it a superior template for MoS_2 synthesis. Nevertheless, undesired oxidation of MXene occurs in aqueous solutions, reducing the overall catalyst stability.

To address the above issues, we employed a one-step solvothermal method using DI water/DMF as bisolvent and constructed a metallic 1T phase-enriched MoS_2/MXene/CNT composite as HER catalyst. A low overpotential (169 mV) and Tafel slope (51 mV/dec) along with the highest turnover frequency (7 s^{-1} at - 0.23V vs. RHE) and an ultralong lifetime (72 hours) was successfully achieved. The origin of the outstanding HER performance of the ternary composite can be ascribed to: (i) the prevention of 2D layer restacking as well as the enlarged surface area due to the 2D/2D MoS_2/MXene integration and ion intercalation; (ii) the vertical growth of MoS_2 flakes on the MXene template which increases the exposure of MoS_2 edge planes, maximizing the total number of active sites; (iii) the synergistically enhanced conductivity because of the formation of hybrid 1D/2D conductive network via the integration of 1T-phase metallic MoS_2, conductive MXene backbone with suppressed oxidation along with the CNT crosslinks, minimizing the charge transfer resistance at the electrode/electrolyte interface. This work demonstrated an effective strategy for two-dimensional material structure-property engineering with the aim of optimizing the HER performance which will shed light on the development of the next-generation PGM-free HER electrocatalysts.

9:40am **2D+AS+BI+HC+SS-FrM-5 Bandstructure Engineering in Two-Dimensional Semiconductors***, **Keun Su Kim**,* Yonsei University, Republic of Korea **INVITED**

The tunable band structure of two-dimensional quantum mater is not only interesting in itself, but also useful for the fundamental study of condensed matter physics. As example, surface chemical doping can be used to reduce the band gap of black phosphorus over the energy range greater than its intrinsic band gap [1]. This could be used to deliberately induce a topological phase transition to a Dirac semimetal phase protected by spacetime inversion symmetry [2]. It could also be used to trace the evolution of quantum phases (pseudospin) order across the topological phase transition [3]. In this talk, I will introduce our recent study on the band renormalizations and pseudogap of black phosphorus doped by alkali metals [4]. Using angle-resolved photoemission spectroscopy (ARPES), we found that the simple quadratic band dispersion of doped black phosphorus anomalously bends back towards zero wavenumber, which can be explained by Anderson-McMillan's framework developed for the band structure of liquid (or disordered) metals in the 1960s. This is a natural consequence of resonance scattering by the potential of dopant ions with short-range order. The depth of scattering potential tuned by different kinds of alkali metal (Na, K, Rb, and Cs) allows us to classify the pseudogap of p-wave and d-wave resonance.

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10:20am **2D+AS+BI+HC+SS-FrM-7 Graphene – Ferritin Interface Unpins Fermi-Level and Induces Temperature Dependent Coherent Tunneling Across Biomolecular Junctions***,* ***Ayelet Vilan,*** Weizmann Institute of Science, Israel*; N. Kumar Gupta,* National University of Singapore*; S. Kumar Karuppannan,* National Quantum Fabless Foundry, Singapore*; R. Reddy Pasula,* Nanyang Technological University Singapore*; J. Martin, W. Xu,* National University of Singapore*; E. May,* Nanyang Technological University, Singapore*; A. Pike,* Newcastle University, UK*; H. Astier, T. Salim,* National University of Singapore*; S. Lim,* Nanyang Technological University, Singapore*; C. Nijhuis,* University of Twente, Netherlands

Molecular electronics is one road to ultimate miniaturization: can we reduce the size of an electronic element to a size of a single molecule? However, as the size reduces to few-atoms level, it becomes harder to distinguish the role of the molecular core from that of the contacts. Here we show the prominent role of graphene interfaces with Fe storing proteins in the net charge transport across their tunnel junctions. Here, ferritin (AfFtn-AA) is adsorbed on graphene by non-covalent amine-graphene interactions. In contrast to junctions with metal electrodes, graphene has a vanishing density of states toward its intrinsic Fermi-level ("Dirac point"), which increase away from the Fermi-level. Therefore, the amount of charge carriers is highly sensitive to temperature and electrostatic charging (induced doping), as deduced from a detailed analysis of charge transport as a function of temperature. Moreover, increasing the iron loading of ferritin, changes the graphene from n- to p-doping. Remarkably, the temperature dependence can be fully explained within the coherent tunneling regime due to excitation of hot carriers. The sensitivity of graphene (and 2D materials in general) to electrostatic charging opens rich possibilities in employing interface electrostatics in tuning the electronic properties of molecular junctions and is important for 2D / biomolecules hybrids in general.

10:40am **2D+AS+BI+HC+SS-FrM-8 The Influence of Selenium Incorporation on the HER Catalytic Activity of Electrodeposited Se-MoS_x Electrocatalysts***,* ***Lee Kendall,*** *G. Zangari , S. Mc,* University of Virginia

With the increase in the global consumption of energy, the need to meet the growing energy demands has put significant pressure on the current means of energy production and storage.To meet this demand, water splitting has seen substantial efforts in developing catalytically active materials that replace costly materials, such as Pt, to allow for economically viable implementations.MoS_2 has attracted significant attention over the past decade due to its low cost and availability. Additionally, MoS_2 is one of the most promising materials for electrocatalytic hydrogen evolution as its Gibbs free energy of hydrogen adsorption, $\Delta G^{H}_{0,ads-}$, is the closest to Pt, a state-of-the-art catalyst, when compared to other metallic materials. However, due to the limited number of accessible edge sites, as well as high kinetic barriers for H_2 evolution, the catalytic performance of MoS_2 is still far from the needed requirements. To address this, researchers have investigated amorphous MoS_x due to its increased structural heterogeneity that increases catalytic site density. Combined with short-range atomic arrangements that enable adequate electronic conductivity, amorphous MoS_x is an attractive candidate for electrochemical processes.This can be further improved, however, as the bridging bonds are the most catalytically active while the terminal and apical are significantly less active.To increase their activity, we investigated incorporating selenium into MoS_x due to the success in crystalline, selenium alloyed MoS_2. This success centered on obtaining a more thermoneutral ΔG^{H}_{ads} for the sulfur edges and basal plane, similar motif to terminal and apical bonds in the amorphous system, respectively.To accomplish this, we used an electrodeposition technique that allows for the incorporation of selenium into the MoS_x polymeric chains. We will report on this investigation of the electrodeposition of Se-MoS_x and its effect on the physical, electronic, and catalytic properties towards the hydrogen evolution reaction. Through electrodepositing catalytically active Se-MoS_x thin films, this effort demonstrates improved HER efficiency over current, low-cost materials.

11:00am **2D+AS+BI+HC+SS-FrM-9 Two-Dimensional Skintronics***,* ***Dmitry Kireev,*** *D. Akinwande,* The University of Texas at Austin **INVITED**

Modern healthcare displays a significant shift from hospital-based medicine towards a personalized, ambulatory, and wearable approach. In this regard, the development of skin-wearable electronics (*skintronics*) is an essential step toward mobile health monitoring, the healthcare Internet of Things, and eventually preventive medicine. Continuous long-term monitoring of brain activity, heart activity, body hydration, or temperature, is vital for better comprehension of human physiology, understanding systematic disease risk factors, and building preventative care solutions. In this work, we utilize *graphene* and other *2D materials* such as platinum diselenide ($PtSe_2$) and platinum ditelluride ($PtTe_2$) to construct the thinnest elements of skintronics - electronic tattoos. The $PtSe_2$ and $PtTe_2$ e-tattoos that can be grown at comparably low temperatures (400ºC) were found to have superior sheet resistance and electrode-skin impedance compared to monolayer graphene e-tattoos. On the other hand, we also report on the significant advancement of the classic graphene electronic tattoos by introducing graphene nanoscrolls and stacking multiple graphene monolayers. Moreover, we show that graphene tattoos can be made insusceptible to sweat by introducing microholes into their structure. Significantly, we show that graphene electronics tattoos can be used for deep tissue monitoring, detecting complex analytes such as blood pressure and respiration rate in a continuous and entirely non-invasive manner. Beyond the simple use of graphene tattoos as passive electronic elements, we have discovered that the semimetallic 2D material can be used as transistors, biased electrostatically through the body itself, creating transistor tattoos. The body-gated graphene tattoo transistors can function as biosensors or small-signal amplifiers, contributing to the development of higher-fidelity electrophysiology measurements and decreased susceptibility to movement-related artifacts.

11:40am **2D+AS+BI+HC+SS-FrM-11 Ultrasonic-Assisted Assembly of Metal Nanoparticles within Graphene Oxide for Tailoring Stem Cell Response***, J. Jaiswal ,* Indian Institute of Technology (Banaras Hindu University) , India*;* ***Marshal Dhayal,*** Indian Institute of Technology (Banaras Hindu University) , India

Recently 2D material-assisted stimulation for cellular functions has gained significant attention. In this paper, we will be presenting the methodology used for preparing tunable properties of 2D surfaces incorporating metal nanoparticles (NP) within graphene oxide sheets. The study will report the use of mechanical forces generated through an ultrasonication-assisted method for increased diffusion of metal ions in graphene oxide (GO). The transmission electron microscopy (TEM) analysis has been used to confirm the distribution of metal particles in GO sheets whereas Raman spectra were used to identify the relative changes in the Raman bands. The study presents a correlation of these observations with corresponding confirmation in the distortion of multilayer assembly of thin layers of GO by the nucleation of metal nanoparticles. The X-ray diffraction (XRD) spectra of GO-NP also demonstrated similar outcomes in Raman spectra. UV-visible spectra and X-ray photoelectron spectroscopy (XPS) analysis were used to determine optical activity and relatively % proportions of their atomic concentrations. These unique combinations of functionally graded GO-NP were used to study the response of human mesenchymal stem cells. This method may be helpful to address the challenges associated with developing metallic assembly within graphene oxide without chemical functionalization of their inert surface for their application in the biomedical field.

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