Thin Films
Room 317 - Session TF1-WeM
VSHOP Hybrid CVD and MLD

Moderators: Prof. Dr. Sumit Agarwal, Colorado School of Mines, USA, **Prof. Matthias Young**, University of Missouri

8:00am **TF1-WeM-1 Thin-film and Redox-active Polyvinyl Metallocene via Chemical Vapor Deposition***, **Shadi Motamed**, Hamidreza Mohajeri Khorasani, Maria Aydt, Mona Bavarian, Siamak Nejati,* University of Nebraska-Lincoln

Metallocene containing polymers such as poly(vinyl ferrocene) (PVF), have gained attention for electrochemical and electronic applications due to the reversible Fe(II)/Fe(III) redox activity of the ferrocene groups in this redox-active polymer. Nonetheless, the current approach to prepare this polymer is mainly based on solution-phase synthesis, limiting the integration of PVF into high aspect ratio electrode architecture for sensing and separation purposes. Herein, to overcome the limitations associated with solution-phase processing of PVF, a solvent-free method was introduced. Thin films of PVF were synthesized by hot filament chemical vapor deposition. The vapor-phase polymerization process enables the direct deposition and synthesis of organometallic polymer coatings while maintaining the ferrocene functionality during film growth. The resulting thin films of PVF deposition on silicon substrate were characterized using scanning and transmission electron microscopy, nuclear magnetic resonance and X-ray photoelectron spectroscopy, along with gel permeation chromatography. The cyclic voltammetry data was used to evaluate the redox activity of the deposited coatings. The results showed Δ*Ep*=0.02V vs. reference electrode and Coulomb efficiency of 94.5% compared to vinyl ferrocene with Δ*Ep*=0.09V vs. reference electrode and Coulomb efficiency of 90%. This indicates a higher reversibility and faster electron-transfer kinetics of PVF when compared to its parent monomer. We report on conditions that led to the successful deposition of PVF thin films through vapor phase and highlight PVF potential as redox-active coatings and electrochemical sensors.

8:15am **TF1-WeM-2 Amine Functionalization of Polydioxanone at Low Temperature By oMLD of Poly(p-phenylenediamine)***, **Nazifa Z. Khan**, Nikhila C. Paranamana, Xiaohua Liu, Matthias J. Young,* University of Missouri-Columbia

Polydioxanone (PDO) is a biodegradable aliphatic polyester extensively utilized in biomedical applications due to its flexibility and biocompatibility, and is absorbed by the body within two months post-implantation. However, PDO inherently lacks chemically reactive amino functional groups, thereby preventing its surface modification with peptides or growth factors for tissue engineering applications. In this study, we investigate the application of low-temperature oxidative molecular layer deposition (oMLD) of amino-containing poly-p-phenylenediamine (PPDA) to functionalize PDO. PPDA was deposited using oMLD at a reduced temperature of 90°C to accommodate PDO, considering its melting point is 110°C. Subsequently, PDO was spin-coated with high uniformity, followed by the low-temperature deposition of PPDA on the spin-coated PDO. The linear growth and saturation behavior were assessed using Quartz Crystal Microbalance (QCM). Amine functionalization was characterized through Raman spectroscopy and Fourier Transform Infrared Spectroscopy (FTIR), while the uniformity of thickness was measured using Spectroscopic Ellipsometry (SE). The water stability of the bilayer was evaluated by immersing the samples in water and measuring the thickness vs time, in which the PPDA was found to be unstable in water. QCM results indicated that at lower temperatures, the oMLD growth mechanism produces short-chain polymers, explaining the rapid loss of the oMLD films in water. Raman spectroscopy data also revealed the presence of a polyaniline-type structures within the network at low deposition temperature, contributing to the polymer's dissolution. Following ultraviolet (UV) post-treatment, an amine-containing component of the film remained intact even after >1 week of immersion in water, as confirmed by XPS analysis. This study, illustrates that the oMLD of PPDA at low temperature with UV-posttreatment produces stable surface amine groups on PDO, allowing a potential pathway for subsequent chemical functionalization of PDO for applications such as tissue regeneration.

8:30am **TF1-WeM-3 oCVD Enabled Conjugated Polymer Alloying for Filler-Free High-Capacity Chloride Storage Cathodes***, **Aqeel Khan**, Trisha Andrew,* University of Massachusetts - Amherst

Rechargeable chloride ion batteries (CIBs), which utilize Cl^- ions as charge carriers, offer a compelling route to sustainable and biocompatible electrochemical energy storage by combining high theoretical energy density with the natural abundance of chloride resources. p-Doped conjugated polymer electrodes are particularly promising for CIBs, where their chemical tunability, facile processability and compatibility with aqueous operations create numerous pathways for cathode engineering and fabrication. However, a persistent gap remains between theoretically predicted and practically realized capacities of existing polymer-based electrodes, primarily due to the challenge of reconciling the orthogonal design principles for efficient ionic and electronic transport throughout the active electrode volume during cycling. Here, we report a generalizable strategy to fabricate conducting polymer electrodes for CIBs—oxidative chemical vapor deposition (oCVD) enabled controlled phase “alloying”—that allows uniform structural integration of amorphous, swellable, redox-active ionic phases with crystalline, capacitive, electron conducting phases. We describe a representative conducting polymer alloy (CPA) that integrates electron-conductive, crystalline PEDOT:Cl domains within a redox-rich, amorphous PANI:Cl matrix to electronically connect redox-active nitrogen sites in PANI while maintaining its swellable amorphous matrix for reversible Cl^- ion insertion and extraction. As a result, the as-prepared CPA film delivers a high specific capacity of 101.5mAh/g over a wide range of film thicknesses, without using conductive fillers or additives. This oCVD enabled polymer alloying strategy can be generalized to any appropriate combination of conjugated polymer structures for designing conducting polymer electrodes for anion batteries. Further, these oCVD-grown conducting polymer interphases can also function as transport mediating and protective layers for existing metal (oxy)chloride salt-based cathode materials, suppressing interfacial dissolution and buffering destructive phase-induced volumetric changes during charge-discharge cycling. Unlike conventional carbon additive-based approaches, vapor-deposited protective layers can be grown directly over the reactive particle surfaces, where dissolution, cracking, and transport bottlenecks originate. By correlating electrochemical behavior with nanoscale interfacial stabilization, this study aims to establish vapor-deposited conducting polymer interphases as a viable route to stabilizing high-capacity Cl^- storage electrodes and improving the durability of the chloride ion batteries under aqueous operating conditions.

8:45am **TF1-WeM-4 Rational Design of Fluoroalkyl-Free Liquid-Repellent Coatings Accessed via Photoinitiated Chemical Vapor Deposition (piCVD)***, **Camryn Payne**, Sejin Choi, Aruzhan Abdikadyrova, Trisha Andrew,* UMass Amherst

Liquid-repellent thin-film coatings are an integral part of multiple high-demand, high-volume products and industries, including food and cosmetics packaging, garments and technical textiles, membranes/separations and microelectronics encapsulation. Until recently, the pervasive molecular engineering paradigm for creating rugged and high-performing liquid-repellent thin-film coatings was to use oligomers and/or polymers formed from long fluoroalkyl chain-containing monomers. Growing knowledge about the destructive long-term health and environmental consequences of fluoroalkyl-containing compounds has motivated broad efforts in developing fluoroalkyl-free coatings for diverse applications. Polymer chemical vapor deposition (CVD) provides multiple compelling options for rugged thin-film coatings, particularly in situations where porous, textured, rough and/or nonplanar substrates need to be coated. Thermally-initiated polymer CVD (iCVD), where thermal decomposition of selected peroxides produces the species that initiates polymer/film growth, is the most common process used for polymer CVD, but it struggles to polymerize monomers containing silicon and/or silicone moieties, which are touted as the most likely contenders for fluoroalkyl-free liquid-repellent coatings. We will describe a photoinitiated chemical vapor deposition (piCVD) process that uses UV-blue light to effect a Norrish Type I/II decomposition of a carbonyl species to initiate polymerization and film growth. We will present our chemically informed framework for monomer, crosslinker, and photoinitiator selection and discuss correlations between reactant properties, polymer/film growth behavior and resulting coating performance. Through systematic variation of monomer structure, crosslinker length, and deposition parameters, the influence of chemical structure on film morphology and performance is evaluated. As expected, monomer identity strongly influences the liquid repellent properties of

coatings formed on diverse substrates, including cotton gauze, paper, and glass. A champion hydrophobic coating will be described, created via piCVD using a branched silicone-containing acrylate monomer, that affords a high water contact angle of 112.7o on paper and selected textiles.

9:00am **TF1-WeM-5 Designing Functional Polymer Thin Films via Initiated Chemical Vapor Deposition***, **Stefan Schröder,*** Kiel University, Germany **INVITED**

Functional polymer thin films play an increasingly important role in tailoring surface and interfacial properties for applications ranging from electronics to biomedical systems. Precise control over film thickness, surface chemistry, and coating conformality is essential for engineering functional interfaces at the nanoscale. Solvent-free initiated chemical vapor deposition (iCVD) provides a versatile platform for polymer thin film fabrication by avoiding dewetting and surface tension effects commonly associated with solution-based approaches. The process enables conformal deposition of polymer coatings with nanoscale thickness control on large-area substrates and complex surface geometries, while preserving delicate substrates through room-temperature processing. Particular emphasis will be placed on the relationship between surface chemistry, deposition conditions, and film growth mechanisms, including recent insights into interfacial reaction pathways. The talk further highlights the broad applicability of iCVD-derived thin films in surface functionalization, sensing, biomedical interfaces, and electronic devices.

9:30am **TF1-WeM-7 Kinetically Defined Radical Quenching Window for Area-Selective Photoinitiated Chemical Vapor Deposition (AS-PiCVD)***, **Junjie Zhao,*** Zhejiang University, China

Self-aligned polymer thin-film patterning is increasingly important for heterogeneous device integration, yet vapor-phase radical polymerization often produces nonselective coatings once active species are generated. Our recent efforts have addressed this challenge through confining radical generation on target surfaces. Photocatalytic surface-initiated CVD (PS-iCVD) enabled localized radical formation on photocatalytic TiO_2 surface for area-selective polymer growth[1], while visible-light-initiated CVD (VLiCVD) further demonstrated enhanced selectivity on FeOx surface by reducing monomer photolysis in the vapor phase under 420 nm irradiation[2].

Building on these advances, we report an area-selective photoinitiated CVD (AS-PiCVD) strategy governed by kinetic modulation rather than growth-surface activation alone. Using glycidyl methacrylate (GMA) as both monomer and photolytic radical source under 365 nm irradiation, we established a mathematical kinetic model showing that pGMA deposition follows an apparent second-order dependence on surface-adsorbed monomer concentration. This model links monomer adsorption, photolytic radical generation, chain propagation, and burial-mediated termination, providing a quantitative basis for controlling PiCVD growth. We indentified the kinetic conditions when pGMA growth is sustained on dielectric surfaces while Au suppresses deposition through radical quenching. The resulting AS-PiCVD process achieves self-aligned pGMA patterns on SiO_2/Au, Al_2O_3/Au, and TiO_2/Au substrates, with selectivity over 90% maintained at polymer thicknesses of tens of nanometers. This work advances light-mediated polymer CVD toward kinetically programmed, all-dry, and maskless fabrication of functional polymer patterns.

[1] Y. Shen, X. He, W. Meng, X. Huang, P. Cai, Z. Yang,W. Du, X. Zhang, Y. Luo, J. Zhao. Visible-Light-Driven Sustainable Chemical Vapor Deposition of Polymer Films and Patterns. *Small*, **2025**, *21* (23), 2502586.
[2] Y. Shen, M. Qiu, X. Huang, W. Du, X. He, Y. Luo, Z. Yang, J. Zhao. Photocatalytic Surface Initiation for Area-Selective Chemical Vapor Deposition of Polymer Thin Film. *ACS Materials Letters*, **2024**, *6*, 4058-4065.

9:45am **TF1-WeM-8 Development of Vapor-Imprinted Polymers for Food Spoilage Monitoring via Selective Acetoin Detection***, **HUIDA DUAN**, Ze Zong, Jacob Lahne, Rich Helm, Haibo Huang, Sean O'Keefe, Wei Zhou, Yifan Cheng,* Virginia Tech

Real-time monitoring of food spoilage is essential for improving supply-chain management and reducing food waste. Volatile organic compounds released during microbial metabolism and chemical degradation provide molecular signatures of spoilage. However, reliable detection remains challenging because many spoilage-associated volatiles occur at trace levels and coexist with structurally similar interferents. Molecularly imprinted polymers (MIPs) offer a route toward selective vapor recognition, but their solvent-based synthesis and complex post-processing limit their integration into miniature or packaging-compatible sensors. Here, we introduce vapor-imprinted polymers (VIPs) fabricated by initiated chemical vapor deposition (iCVD) as solvent-free, one-pot sensing layers for detection of acetoin, a representative spoilage-related volatile. Acetoin-imprinted poly(ethylene glycol dimethacrylate) films were directly integrated with surface-enhanced Raman scattering (SERS) substrates, enabling vapor-phase molecular recognition without solution processing or template extraction. The binding response of VIPs toward acetoin and the structurally related interferent butanedione was evaluated by SERS and analyzed using principal component analysis (PCA) and partial least squares discriminant analysis (PLS-DA). Compared with non-imprinted polymer controls, VIPs exhibited markedly enhanced recognition of acetoin at 10 ppb, increasing classification sensitivity from 74.4% to 92.4% and specificity from 76.4% to 94.4%. Preliminary interference studies further indicate that VIPs retain a stronger response toward acetoin than non-imprinted controls, including in the presence of butanedione, suggesting improved target recognition under chemically complex vapor environments. This work highlights the potential of VIP–based sensing layers for enabling real–time, selective monitoring of food spoilage in packaging systems.

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