Thin Films
Room 206 B W - Session TF1-WeM
VSHOP III - Initiated Chemical Vapor Deposition

Moderators: Kwang-Won Park, Cornell University, **Stefan Schröder**, Kiel University, Germany

8:00am **TF1-WeM-1 Enzyme Microenvironment Engineering via Initiated Chemical Vapor Deposition*, Yifan Cheng,*** Virginia Tech **INVITED**

Enzymes enable efficient bioprocessing but often lose activity and stability under process-relevant stressors (e.g., low pH, elevated temperature). Complementary to enzyme-centric strategies such as directed evolution, we engineer the microenvironment of immobilized enzymes to shield them from harsh bulk conditions. Using initiated chemical vapor deposition (iCVD)—an all-dry, low-temperature polymerization—we fabricate conformal polycationic films on supports and subsequently immobilize lactase (β-galactosidase). These iCVD films act as proton-buffering layers that modulate the local pH at the enzyme–solution interface, enabling lactose hydrolysis in acid whey. iCVD offers nanoscale control over film thickness and functionality, compatibility with porous substrates (e.g., membranes), and solvent-free processing advantageous for sensitive biomolecules. By tuning cationic composition, we achieve local pH increases of up to 2 units (100-fold reduction in $[H^+]$) and preserve lactase activity under acidic conditions. Immobilization strategy—random versus site-directed—significantly influences the enzyme's kinetic parameters, and we track the evolution of these parameters over multiple use cycles. This microenvironment-engineering approach provides a general route to stabilize diverse biocatalysts without enzyme-specific re-engineering, linking active-site performance to thin-film and interface control.

8:30am **TF1-WeM-3 Engineering Protonation Depth and Charge Density in Polymers for Ph-Responsive Immobilized Lactase Catalysis*, Huida Duan,*** *Junxing Chen, Wei Sun, Yifan Cheng,* Virginia Tech

Polycationic polymer coatings with tunable physicochemical properties have emerged as promising platforms for enzyme immobilization in challenging environments such as low pH. However, how polymer thickness and charge density affect local protonation behavior and enzyme activity remains poorly understood. Here, we investigate the effect of polymer thickness and polycationic monomer composition on the protonation behavior and catalytic performance of immobilized β-galactosidase (LacZ). Copolymer films of glycidyl methacrylate (GMA), providing enzyme immobilization sites, and 2-(dimethylamino)ethyl methacrylate (DMAEMA), imparting protonation-dependent positive charges, were synthesized via initiated chemical vapor deposition (iCVD). Their chemical structures were confirmed by Fourier transform infrared spectroscopy (FTIR). Protonation depth was assessed by analyzing the intensity ratios of N–H bending to C=O stretching vibrations after acid treatment, while enzyme activity was evaluated under both neutral (pH 7) and acidic (pH 4) conditions using both random and site-directed immobilization strategies. FTIR results revealed that protonation was limited to a finite depth of ~255nm, with thinner films (<200nm) achieving complete protonation. Enzyme activity at pH 4 was retained only when protonated polycationic layers were present, and plateaued once protonation depth was saturated. Polymers with higher DMAEMA content (65%) outperformed those with lower content (25%), with activity increases up to 83%. Site-directed immobilization consistently preserved higher activity than random conjugation. These findings highlight the critical role of interfacial proton buffering in enabling biocatalysis under acidic conditions and provide design principles for functional polymer-enzyme interfaces in harsh environments.

8:45am **TF1-WeM-4 Recent Advances in the Understanding of Spontaneous Orientation Polarization in Polymer Thin Films Deposited by Initiated Chemical Vapor Deposition (iCVD)*, Stefan Schröder,*** *Torge Hartig, Thomas Strunskus, Tayebeh Ameri, Franz Faupel,* Kiel University, Germany

A recent study demonstrated the formation of a spontaneous orientation polarization effect in polymer thin films deposited via initiated chemical vapor deposition (iCVD). It enables the integration of permanent, high-precision electric fields into electronic devices. However, the understanding of the exact mechanism and dependence on the reaction kinetics is still at an early stage. This work reports on new insights on the polarization process based on theoretical and experimental results. The enhanced understanding enables improved control over the resulting surface potential of the polymer films and discovery of new monomers based on electric dipole moment calculations. Furthermore, a few examples of potential applications will be given.

9:00am **TF1-WeM-5 Surface Roughness Control in Vapor-Deposited Nanocoatings for Bio-Adhesion Mitigation*, Jessie Yu Mao,*** *Chengqian Huang, Mengfan Zhu,* Oklahoma State University **INVITED**

Superhydrophobic surfaces offer effective resistance against the adhesion of biomolecules like bacteria and proteins. This property holds promise for their application in medical devices, aiming to mitigate complications such as infections and thrombosis. Hierarchical roughness plays a pivotal role in enhancing superhydrophobicity by providing multiple scales of surface features, which collectively contribute to increased water repellency and reduced adhesion of biomolecules. Traditional fabrication of topographical roughness requires specific substrates or solvent-based processing, which could raise concerns regarding biotoxicity. We constructed topographical roughness using an initiated chemical vapor deposition (iCVD) method that is applicable independent of substrate material and geometry. We studied how the processing parameters affect the formed surface topography and the bio-adhesion properties. In addition, surfaces with hierarchical roughness were created by varying the vapor deposition parameters *in situ*. The hierarchically roughened surface demonstrated superhydrophobicity, with more than 80% reduction in the adhered bacteria and a 98.8% decrease in the surface fibrin clotting, as compared with the homogeneously rough surface. This iCVD technique presents a novel avenue for attaining superhydrophobicity on medical devices to reduce device-related adverse events.

9:30am **TF1-WeM-7 Precision Synthesis of Polymeric Materials Using initiated Chemical Vapor Deposition (iCVD) for Cyber Manufacturing, *Rong Yang,*** Cornell University

initiated Chemical Vapor Deposition (iCVD) is emerging as a powerful technique for the precision synthesis of polymeric materials. New advances in iCVD-based precision polymerization span the synthesis of shaped particles, strategies to suppress side reactions, and achieving emergent properties, all of which are enabled by engineering non-covalent interactions. This talk highlights one example in which engineering monomer absorption into liquid templates enables the integration of artificial intelligence (AI) for the precision manufacturing of polymeric particles with programmable size, shape, and chemistry. We engineer non-covalent interactions between monomers and mesogens to control monomer partition into a liquid crystal (LC) film, thereby enabling LC-templated continuous polymerization. By tuning the relative strengths of non-covalent cohesive force versus elastic force afforded by the LC template, we guide the synthesis pathway along a variety of trajectories that lead to tailored polymer morphology. In addition, the LC templates are self-reporting, which both guide and optically report on the evolution of the morphology of polymeric particles during continuous polymerization. We perform real-time analysis of the optical outputs using AI, enabling on-the-fly feedback and selection of synthesis conditions to achieve targeted polymer morphology. This capability, combined with the automated and scalable CVD technology, points to a new paradigm of cyber manufacturing for polymeric materials.

9:45am **TF1-WeM-8 PFAS-free initiators for iCVD, *Torge Hartig,*** *Hannes Nehls, Tim Pogoda, Joschka Paulsen, Julia Piehl, Thomas Strunskus, Franz Faupel,* Kiel University, Germany*; Tayebeh Ameri,* Kiel University, Germany, Iran (Islamic Republic of)*; Stefan Schröder,* Kiel University, Germany

Initiated Chemical Vapor Deposition (iCVD) is an all-dry method for the solvent-free deposition of ultra-thin conformal polymer coatings. In recent years a large library of more than 100 monomers in iCVD has been established representing an extraordinary toolbox while research on initiators has played a smaller role. TBPO (di-tert butyl peroxide) as the standard initiator in iCVD works generally well in all processes. While the deposition rates of TBPO are no problem in academia, faster rates are often required in industrial application. Hence, a focus on new initiators could open the doors to new process kinetics. Previously fluorocarbon initiators have been used for increased deposition rates. With the recent development of possible PFAS bans and fluorocarbon impact on reactor usage, new high-rate initiators are required for the iCVD process. Within this study the impact of the chemical structure of peroxides, including hydroperoxides, is explored, leading to drastically faster deposition rates.

Author Index

Bold page numbers indicate presenter