Thin Films
Room 206 B W - Session TF2-WeM

VSHOP IV - Oxidative Chemical Vapor Deposition & Molecular Layer Deposition

Moderators: Sung Gap Im, KAIST, **Reeja Jayan**, Carnegie Mellon University, USA

11:00am **TF2-WeM-13 Ozone-Initiated Oxidative Chemical Vapor Deposition of PEDOT Coatings on 2D and 3D Substrates***, **Blake Nuwayhid**, Travis Novak, Jeffrey Long, Debra Rolison,* U.S. Naval Research Laboratory

Vapor-phase routes to organic conducting polymers offer many advantages over more commonly studied solution-phase methods. Conductive polymers often require functionalization to be soluble in an appropriate solvent, and techniques such as spin-coating or drop-casting are generally only suitable for relatively flat substrates. Oxidative chemical vapor deposition (oCVD) is an alternative that allows for control of coatings over complex 3D substrates. Poly(3,4-ethylene dioxythiophene) (PEDOT) is the most widely studied oCVD-fabricated polymer, in which all previous reports used undesirable oxidants such as iron chloride ($FeCl_3$), vanadium oxytrichloride ($VOCl_3$), or antimony pentachloride ($SbCl_5$). The $FeCl_3$ is a low-vapor-pressure solid, whereas, $VOCl_3$ and $SbCl_5$ are highly corrosive liquid precursors. These inorganic oxidative initiators necessitate post-deposition treatments to remove inorganic byproducts from the resulting polymer film. We demonstrate a new approach to oCVD PEDOT using O_3 as the oxidation source, resulting in a totally dry and cleaner deposition process than that obtained from the aforementioned oxidants. We deposit PEDOT in a custom-built oCVD reactor in a temperature range of 40–100 °C, in which the process shows monomer adsorption–limited behavior with growth rates decreasing from 1.2 nm/min at 40 °C to 0.24 nm/min at 100 °C for a process pressure of 400 mTorr. We further explore the deposition kinetics and chemical composition as a function of temperature, pressure, and O_3 concentration. We find that films deposited at <100 °C are not crosslinked, but a gentle thermal annealing at 100 °C in an Ar atmosphere induces polymer crosslinking as determined by spectroscopic ellipsometry. Compositional analysis using XPS and FTIR show that the as-deposited films are over-oxidized, possessing S=O bonds in the thiophene chain. We further characterize the thermoelectric and electrochemical properties of the O_3-deposited PEDOT and introduce additives to boost electronic conductivity.

11:15am **TF2-WeM-14 Oxidative Chemical Vapor Deposition of Nanometer-Scale Polyaniline on Si/Cobalt Phthalocyanine (CoPc) Photocathodes for Enhanced Stability and CO/H_2 Selectivity during Photoelectrochemical CO_2 Reduction***, **Hyuenwoo Yang**, Yuchen Liu, Seoyeon Kim, Hannah Margavio,* North Carolina State University*; Carrie Donley,* University of North Carolina at Chapel Hill*; Hwan Oh,* Brookhaven National Laboratory*; Renato Sampaio,* University of North Carolina at Chapel Hill*; Gregory Parsons,* North Carolina State University

Photoelectrochemical CO_2 reduction (CO_2RR) to value-added products offers a promising route for carbon utilization, yet photocathode stability and selectivity remain critical challenges. We present a Si/CoPc/Polyaniline (PANI) photocathode, integrating a p-type Si substrate with cobalt phthalocyanine – carbon nanotube (CoPc-CNT) and a ~10 nm oxidative chemical vapor deposition (oCVD) PANI overlayer, achieving exceptional durability and CO selectivity. The oCVD process enables precise PANI thickness control, optimizing stability without sacrificing catalytic access. At -0.4 V vs RHE in CO_2-saturated 0.1 M $KHCO_3$ under 1 sun illumination, Si/CoPc/PANI sustains current density for 24 hours, with faradaic efficiency for CO (FE_{CO}) exceeding 88%, far surpassing unprotected Si/CoPc's ~20-minute lifespan due to CoPc detachment. Across -0.4 to -0.8 V, Si/CoPc/PANI maintains stability for 3 hours, retaining FE_{CO} at 89% at -0.8 V. Comparative tests reveal thicker PANI layers (20 nm, 45 nm) reduce current density and fail within 24 hours, highlighting 10 nm as optimal.

UV-vis spectropscopty, x-ray photoelectron spectroscopy (XPS), Raman spectroscopy and Fourier transform infrared spectroscopy (FTIR)characterize oCVD PANI overlayer on Si/CoPc photoelectrode. This synergy of oCVD PANI and CoPc yields a robust photocathode, advancing CO_2RR toward practical applications by addressing stability bottlenecks, with implications for scalable, vacuum-deposited protective layers in energy conversion systems.

11:30am **TF2-WeM-15 Temperature Effects in Oxidative Molecular Layer Deposition (oMLD) of Polypyrrole***, **Mahya Mehregan**, Shima Mehregan, Andrew Reinhard, Matthew Maschmann,* University of Missouri-Columbia*; Matthias Young,* University of Missouri, Columbia

Polypyrrole (PPy) is a conjugated polymer with moderate electrical conductivity (~100 $S{\cdot}cm^{-1}$) and high theoretical charge storage capacity of 411 mAh/g, making it of interest for electrochemical applications including supercapacitors, batteries, and sensors. Using solution-phase synthesis, the maximum charge storage capacity observed for PPy has been limited to ~140 mAh/g. In recent work, the use of oxidative molecular layer deposition (oMLD) to form PPy was found to enhance the charge storage capacity to >300 mAh/g, but the origins of this effect are not fully understood. In this work, we examine how the deposition temperature used for oMLD over the range of 100–150°C influences the PPy growth chemistry, final polymer structure, and electrochemical properties. We employ in situ quartz crystal microbalance (QCM) during oMLD deposition to understand how growth temperature affects the growth mechanism. We also employ ex situ differential scanning calorimetry (DSC), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM) to validate the insights from QCM, and measure how the deposition temperature influences polymer structure and morphology. We identify that lower deposition temperatures produce higher amounts of surface sorbed $MoCl_5$ during growth, leading to faster film nucleation and higher $MoCl_x$ residue in the final films. We find that deposition below the glass transition temperature introduces microstructure differences, while deposition above the glass transition temperature produces uniform films. We also report high-energy synchrotron X-ray Diffraction (HE-XRD) of PPy formed at 150°C and compare against electrodeposited PPy. Together, these studies establish a deeper understanding of the process/structure/property relationships for PPy formed by oMLD, informing its use for electrochemical applications.

11:45am **TF2-WeM-16 Oxidative Molecular Layer Deposition of Polythiourea for Nitrate Sensing***, **Shima Mehregan**, Mahya Mehregan,* university of missouri*; Erick Gutierrez Monje, Matthias Young,* University of Missouri

Low-cost nitrate sensors are critical to enable efficient use of agricultural nutrients and reduce environmental impact from nutrient runoff. In previous work, we established a new strategy to fabricate low-cost nitrate sensors based on differences in ion transport kinetics through ion-selective membranes. However, to be successful, these membrane layers must be formed with highly reproducible thickness and composition, which is not straightforward with wet-chemical polymer synthesis. In this study, we examine the use of polythiourea (PTU) films formed by oxidative molecular layer deposition (oMLD) of thiourea (TU) and molybdenum pentachloride ($MoCl_5$) as nitrate-selective membrane layers. oMLD provides precise control over PTU membrane thickness, composition, and morphology through sequential surface reactions, providing more reproducible sensors and overcoming the limitations of wet chemical membrane synthesis. We employ *in situ* quartz crystal microbalance (QCM) studies during alternating exposures of TU and $MoCl_5$ to understand the oMLD growth mechanism. We characterize the chemical structure of oMLD PTU using Raman Spectroscopy and X-ray Photoelectron Spectroscopy (XPS) and the microstructure using Scanning Electron Microscopy (SEM). We then report the fabrication of PTU-based thin-film nitrate sensors and apply nonequilibrium anion detection to evaluate their sensitivity in the presence of different anions, including chloride, nitrate, and phosphate. We find that PTU membrane layers are highly selective toward nitrate, and improve nitrate selectivity over chloride relative to commercially available electrochemical nitrate sensors, with high reproducibility among devices. This work establishes oMLD PTU as a viable membrane material for low-cost nitrate sensors.

12:00pm **TF2-WeM-17 Polyurea Molecular Layer Deposition Using Low Melting Point Precursors for Use in Biosensor Design***, **Jay Werner**, Seancarlos Gonzalez, David S. Bergsman,* University of Washington

In biosensor design, biomolecules are often chemically bound to the sensor as part of the detection mechanism. As a result, surface functionalization is a critical part of biosensor design to mediate the connection between the analyte and the detector. Silane-based self-assembled monolayers (SAMs) are commonly used for this purpose, however, because of the sub-nanometer thickness of a true monolayer and the propensity of silanes to form unstable multilayer structures, it can be challenging to create and verify a SAM. Molecular layer deposition (MLD) is a promising tool which may be able to take the place of SAMs in some surface functionalization applications where a stable multilayered film would be acceptable. MLD is a vapor phase deposition process that uses a sequence of organic precursors that react via highly energetic reactions in a self-limiting way. These properties allow for the repeatable, stepwise, and conformal deposition of thin films, even in high aspect ratio features. In this work, we present a polyurea MLD chemistry based on low melting point 2,4-toluene diisocyanate (TDIC) and ethylene diamine (ED) to form a polyurea thin film at room temperature. Previous polyurea MLD processes have used high melting point 1,4-phenylene diisocyanate (PDIC) as an aromatic isocyanate precursor, often requiring heat to achieve sufficient vapor pressure. This heat can complicate the deposition process and reduce precursor lifespan. In contrast, TDIC is a liquid at room temperature and is cheaper and more widely available than PDIC. In addition to characterizing this process' growth behavior and composition, we assess the zeta potential, water contact angle, and primary amine availability for crosslinking chemistry. We also assess how these properties are affected by UV-ozone (UVO) etching treatments, which may be used to improve wettability in biosensor design.

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