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Undergraduate Poster Session Room On Demand - Session OD-UP On Demand Undergraduate Poster Session On Demand

OD-UP On Demand-1 Evaluating Hydrophobic Recovery of Nitrogen Plasma Treated Silk Fibroin Films, *Chase Lenert-Mondou, M. Hawker*, California State University, Fresno

Silk fibroin (referred to as silk) is a natural polymer derived from the cocoon of a silkworm. It has increased in popularity due to its potential uses in biomedical applications (i.e., tissue engineering, drug delivery, sutures, implants). However, the native silk polymer is hydrophobic, requiring modification to become more hydrophilic to promote cell adhesion and biocompatibility for in vivo applications. One of the techniques used to increase the hydrophilicity of polymers such as silk is low temperature plasma (LTP) modification. Nitrogen LTP has been well-documented as a strategy to enhance nitrogen-containing polar functional groups on a polymer's surface. LTP is a useful technique as it is a solvent-free, amenable process for polymer modification. However, LTP-modified polymers have been known to experience hydrophobic recovery, in which the surface reverts to a more hydrophobic state upon aging, making the hydrophilic modification short-lived. The hydrophobic recovery process has not previously been evaluated for silk using nitrogen LTP.

The goals of the present study were to 1) systematically explore the impact of varying key nitrogen LTP parameters (applied power and time) on silk film wettability, 2) study how the silk film secondary structure impacts the efficacy of nitrogen LTP modification, and 3) evaluate the hydrophobic recovery of silk films following nitrogen LTP treatment. Our initial water contact angle goniometry results demonstrated that varying plasma parameters had little effect on film wettability. To evaluate the potential impact of silk secondary structure on hydrophobic recovery, silk films were submerged in methanol for 30 minutes to induce beta sheet formation. This process drives water out of the matrix, causing the silk to adopt a more crystalline beta-sheet rich conformation. Methanol-treated silk films, along with unmodified controls, were then subjected to nitrogen LTP modification. Samples were aged under ambient conditions for up to 6 weeks, and film wettability was measured as a function of aging time using water contact angle goniometry to evaluate the hydrophobic recovery behavior. Methanol-treated and control silk films had initial water contact angles of $\sim 60^\circ$ and 70° , respectively. After nitrogen LTP treatment, silk films exhibited contact angles of $\sim 23^\circ$ and 35° , respectively, demonstrating a substantial increase in hydrophilicity. We will corroborate wettability data with FTIR, which was used to measure silk film secondary structure as a function of aging. We have observed minimal hydrophobic recovery after aging for 6 weeks, suggesting that nitrogen LTP can be used for long-lasting silk film modification.

OD-UP On Demand-4 Examining the Impact of BHT Inhibitor on the Microstructure of Spun-Cast Nanoporous Films of PMMA, *Sadie Flagg, T. Knippenberg, B. Augustine*, High Point University

Tetrahydrofuran (THF), a common organic solvent for polymers, is often stabilized with butylated hydroxytoluene (BHT) due to THF forming peroxide compounds. In prior work we have shown that solutions of 996 kg/mol poly(methyl methacrylate) (PMMA) dissolved at a concentration of 15.0 mg/mL in THF and spun-cast onto Si substrates produces thin nanoporous films unlike smooth films prepared from other solvents such as toluene and chloroform. In this study, we examined the effect of the interaction between BHT and THF on the PMMA films by varying the concentration of BHT present in the THF solutions from 0 - 5000 ppm. The influence of BHT's molecular structure was then examined by replacing the BHT with analogous compounds phenol and p-cresol in THF. Solutions also prepared with toluene and BHT were tested to determine if the films produced using BHT alone caused microstructural changes. Optical microscopy of the films exhibits color variation which may be due to opalescence caused by porosity variations in the films. All films were examined using tapping mode atomic force microscope (AFM) imaging. While the toluene/BHT and the THF/phenol solutions produced smooth non-porous films the p-cresol solution exhibited some areas of porous structure similar to the THF/BHT solutions. This suggests the importance of both the butyl and methyl groups in BHT in order to produce the nanoporous structure formation of PMMA. Varying concentrations of BHT appears to have a direct effect on the porosity of the films, although this may be dependent on the presence of water in the THF, as new anhydrous

THF reproduced these results with less consistency. We are in the process of performing molecular dynamic (MD) simulations on the solvent and inhibitor solutions to better determine the origin of the nanoporous film structure and thus understand the molecular interactions resulting in the film morphology.

OD-UP On Demand-7 Polymer Directed Synthesis of NiO/C for Supercapacitor Electrode, *Manzili Kokayi, B. Bastakoti*, North Carolina A&T State University

Supercapacitors are growing in popularity due to their cycling stability, quick charge-discharge rates, and high power density. These devices rely heavily upon the types of materials used within them. The capacitance of metal oxides can be higher than carbon based electrodes; however, they suffer from drawbacks such as low power density and poor conductivity. The present study explored the excellent design strategy for the synthesis of nanocomposites in which the pseudocapacitive NiO is intimately associated with a porous nanostructured carbon substrate. NiO was chosen because it has been shown to produce a synergistic effect when combined with carbon, creating a more stable electrode with higher conductivity. The use of polymeric templates in synthesis allows tuning the structure in nanoscale. The finding is very encouraging given easy synthetic routes and our material would be a very promising electrode material for future pseudocapacitors.

OD-UP On Demand-10 Insight Into the Formation, Desorption, and Structural Effects of Subsurface Oxygen on Ag(111) Using a Lattice-Gas Model and Monte Carlo Simulations, *Elizabeth Lander, C. Mize, L. Crosby, S. Roy*, University of Tennessee Knoxville

Theoretical gas-surface models are commonly utilized to compute elementary steps of surface chemistry. Adsorption, for example, is crucial in processes such as heterogeneous catalysis, chemical separations, protein denaturation, and nanoelectronics. To this end, we have developed a fully parametrizable lattice-gas model using electronic structure theory, which includes both surface and subsurface adsorption. Utilizing density functional theory (DFT), we have applied this model to investigate atomic oxygen adsorption on Ag(111). Our previous results on an unreconstructed surface show a high population of oxygen adsorbed in the second subsurface, the region between the second and third silver layers, at coverages in excess of 1/2 ML. Canonical Monte Carlo simulations indicate a similar distribution at temperatures of 600K, however, simulations of grand canonical Monte Carlo at 497 K and high oxygen pressure of 1020 Torr present little to no subsurface oxygen adsorption. In order to extend this model, we have introduced silver-silver and silver-oxygen pairwise interactions on and within the surface to allow for lattice distortion and reconstruction due to accumulation of atomic oxygen on the surface and in the subsurface. Through the addition of these interactions, our goal is to study the role of surface and subsurface oxygen in inducing well-known surface reconstructions of Ag(111), such as p(4x4) and c(4x8), as a function of surface temperature and oxygen pressure using Monte Carlo simulations.

OD-UP On Demand-13 Vapor Phase Synthesis and Characterization of Single and Few Layers of MoS₂, *Sabrina Jackson, NCA&T; O. Ayanbajo, S. Shendokar, S. Aravamudhan, NCA&T*

Two-dimensional (2D) materials are excellent platforms to realize tunable quantum states. Among the many 2D materials, Transition Metal Dichalcogenides (TMDs) such as MoS₂, MoSe₂, WS₂, and WSe₂ are 2D Van der Waals materials with weakly bound atomic planes. For example, MoS₂ (a TMD) is a lubricant and indirect bandgap semiconductor in its bulk form. However, when thinned down to a single layer form, it becomes a direct bandgap (1.9 eV) semiconductor with strongly bound excitonic and trionic states. Quantum computing could take advantage of this ability to control electronic and excitonic phase transitions in these atomically layered materials. In this work, we present a low temperature synthesis process to produce high quality single and few layers of MoS₂ using direct vapor phase sulfurization of MoO₃. Characterization were performed by Raman Spectroscopy, Atomic Force Microscope, and Electron Microscopy techniques.

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OD-UP On Demand-16 Characterization of Ru-ZrO₂ Water Splitting Catalyst, Paul Bean, P. Godbold, S. Zhang, University of Virginia

Much research into nanoparticle synthesis is motivated by the desire to control catalysis. Nanoparticle size, composition, and architecture are major contributors to catalytic activity and stability. Thus, it is of interest to develop well-defined nanostructures in order to precisely control activity and increase stability. In the Zhang lab at UVA, we are developing methods to form active single atomic sites in metal oxides. A variety of characterization methods – namely Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), and Energy Dispersive x-ray Spectroscopy (EDS) – allow us to characterize the synthesized nanomaterials. Use of these two microscopy techniques in tandem reveal the morphology of our material on a scale from multi-microns to several nanometers, while EDS can analyze the elemental composition of our metal. Following our lab's recent development of well-defined single site Co doped TiO₂ nanorods, which are highly active and stable in alkaline oxygen evolution reaction (OER), we are investigating the synthesis of single site Ru doped ZrO₂ for use in acidic OER. Initial electrochemical testing has shown Ru-ZrO₂ to be both active and stable in acidic conditions, making this an ideal candidate for optimization. TEM imaging show that most methods yield similar nanoparticles, but co-inspection with SEM and EDS reveals an uneven Ru distribution in some synthesis, suggesting that certain precursors and amounts of Ru encourage the formation of separate Ru-dominated oxides as opposed to forming evenly doped Ru-ZrO₂ particles.

OD-UP On Demand-19 Extreme Atomic-Scale Surface Roughening: Amino Acids on Ag on Au(111), Emily Cook, K. Boyd, J. Phillips, M. Paszkowiak, E. Iski, University of Tulsa

Electrochemical scanning tunneling microscopy (EC-STM) has unique benefits over the more commonly used ultrahigh vacuum STM (UHV-STM). EC-STM has the ability to perform electrochemical techniques such as cyclic voltammetry (CV) and imaging while applying a potential to the surface in ambient conditions and under a liquid layer. This allows for surface studies to be extended to biologically relevant conditions to further understand biomolecule-surface interactions. As technology continues to decrease in size, altering metal surfaces on the nanoscale using biological molecules is advantageous because biomolecules are ubiquitous and non-toxic. Furthermore, metal surfaces can act as a substrate on which amino acid self-assembly can be studied to better understand the origins of homochirality.

Thin films are a form of surface modification where a small amount of material is deposited on a surface and due to its thinness, the film can have different properties than its corresponding bulk material. An example of this is a Ag monolayer deposited via underpotential deposition (UPD) on Au(111) which was found to be thermally stable up to 1,000 K. However, this property only held when the Ag was deposited in one of two UPD potential regions. Moreover, studies of amino acids on Au(111) demonstrated that the amino acids can trap Au adatoms into single atom high islands on the surface, with the island areas increasing as a function of amino acid molecular weight. As the surface temperature was increased, the island areas grew in area and height, demonstrating a Volmer-Weber (VW) growth mode.

To further understand the chemical properties of Ag thin films, L-isoleucine was added on a Ag monolayer on Au(111). This resulted in a markedly different surface morphology than a Ag monolayer on Au(111) or amino acids on bare Au(111) because there was the observation of extreme surface roughening that encompassed many layers of the surface, with each layer having the height of one Au or Ag atom. It is hypothesized that the carboxyl and amino groups of the molecule chelate the metal atoms and remove them into solution or move them across the surface to promote roughening. The Ag thin film changes the surface energy to result in an alternative and unexpected growth mode that involves growth out of and into the surface and provides a mild, electrochemical method by which surface roughening can occur.

OD-UP On Demand-22 Examining Internal Temperatures of Nitrogen-Containing Plasmas to Understand the Gas-Catalyst Interface, Melanie Fouts, J. Blechle, Wilkes University

In an effort to address growing environmental concerns, selective reduction of nitrogen oxide pollutant gases (N_xO_y) generated from vehicular and industrial exhaust is of increasing importance. Currently, the three-way catalytic converter serves as the primary method of pollution control, however such systems suffer from reduced efficacy at lower temperatures and are hindered by an inability to chemically reduce all relevant nitrogen oxides. One promising alternative is plasma-assisted

catalysis (PAC) which can improve energy-efficiency and reaction selectivity at preferred operating conditions. Despite these advantages, such systems have yet to see commercial use due to the complexity of the plasma's extensive parameter space. Thus, there is a need to understand the influence of plasma conditions on the chemistry at the gas-surface interface.

To this end, a model PAC system was designed by interfacing inductively coupled plasmas with catalytic substrates. Specifically, plasmas formed from N₂ and O₂ feed gases were studied in the presence of ceramic, precious metal, and composite catalysts. Optical emission spectroscopy (OES) was used to determine internal temperatures and densities of N₂ and NO molecules based upon changes in applied power (25–200 W), system pressure (50–200 mTorr), and the method of substrate implementation. In 100 mTorr N₂ plasmas, calculated vibrational temperatures (T_v) for N₂^{*} (C³Π→B³Π) increase proportionally with a linear dependence on applied power (4400–6000 K). By contrast, the addition of a ceramic material both individually and as a composite ceramic-Ag surface results in a ~12% drop in T_v across all powers (3500–5000 K). However, the Ag substrate alone does not influence T_v , except at 200 W when values decrease by ~10% relative to the pure N₂ plasma (5400 K). Diagnostic OES data collected across all system conditions will also be correlated with SEM analysis to examine changes in surface morphology. This comparison allows for improved understanding of the interconnected relationship between reactive species and catalytic surfaces. Such measurements provide insight into the complex energetic environment of the plasma and are crucial to unraveling the mechanisms that will lead to future PAC success.

OD-UP On Demand-25 Oxygen-Induced Surface Reconstructions on curved-Ag(111), Faith Lewis, D. Killelea, Loyola University Chicago

Curved crystals allow for systematic investigation of the roles of terrace widths and geometries in surface reactions. We seek to understand how the (111) terrace width affects the growth and morphology of oxygen-induced surface reconstructions on Ag(111). Scanning tunneling microscopy (STM) was used to obtain atomic scale images of oxidized c-Ag(111) surfaces to determine what phases were present after various exposures to gas-phase atomic oxygen (AO). My project specifically looked at absorption patterns, in particular the low-temperature striped phase and the p(4x5√3)-O adlayer, and under what conditions and step widths they were favored.

OD-UP On Demand-28 Water Adsorption on Curved Ag Surfaces, Christina Grytsyshyn, D. Killelea, Loyola University Chicago

Studies of water adsorption on metal surfaces provides insight to the nature of water-water and water-metal interactions. Observing the adsorption of D₂O on a curved Ag(111) crystal will allow for the investigation of how water interacts with the different facets of the surface, where the molecules will be arranged differently, thus allowing data to be gathered on water's interactions with multiple surfaces all in the same experiment. The surface interactions and adsorption locations will be studied using a combination of temperature programmed desorption (TPD) and scanning tunneling microscopy (STM) experiments. The water structures formed display the balance of attractive and repulsive forces, and how water molecules arrange themselves on the surface of a metal can give insight on the catalytic properties of that metal, providing necessary fundamental information for further research.

OD-UP On Demand-31 Crystal Growth and Magnetic Properties of MgCr₂O₄, Ajeya Dixon, S. Karna, D. Temple, Norfolk State University

Spinel containing transition metals or rare earth elements have been extensively studied as prime candidates to exhibit geometric magnetic frustration. Chromium-rich spinels, such as ZnCr₂O₄ and MgCr₂O₄, have attracted particular attention due to antiferromagnetic ordering transitions at low temperature that are coupled to lattice distortions. Recently, we have grown MgCr₂O₄ single crystal using floating zone crystal growth technique and will perform structural and magnetic characterizations in near future. X-ray powder diffraction refinement indicates that the crystal structure is cubic having Fd-3m symmetry.

OD-UP On Demand-34 Single Crystal Growth of Bi₂CuO₄ Using the Optical Floating Zone Technique, Tekiyah Robinson, S. Karna, D. Temple, Norfolk State University

Topological materials having 8-fold electronic degeneracy protection by nonsymmorphic symmetries of a crystal exhibit double Dirac fermions which have been predicted in CuBi₂O₄. In addition, more recent and accurate density functional theory calculations demonstrate that it should

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be an antiferromagnetic Mott insulator. Here, we have grown CuBi_2O_4 single crystal using floating zone crystal growth technique. First, polycrystalline CuBi_2O_4 was synthesized by the direct solid-state reaction of Bi_2O_3 and CuO in a 1:1 molar ratio, mixed thoroughly using a mortar and pestle. X-ray diffraction was employed to check phase purity of the polycrystalline samples and confirmed that CuBi_2O_4 crystallizes in the space group $P4/ncc$ which consists of planar $[\text{CuO}_4]^{6-}$ units with Bi^{3+} ions occupying the spaces between units. The resistivity and magnetoresistance measurements are planned to do in near future on CuBi_2O_4 single crystal.

OD-UP On Demand-37 Characterization of Triple Cation, Mixed Halide Perovskites in Deposited in Near-Ambient Conditions, *Samuel Candelario Torres*, North Carolina Central University; *N. Edwards*, North Carolina Central University; *M. Wu*, North Carolina Central University

Lead halide perovskites combining Cs, formamidinium and methylammonium cations with iodine and bromine anions demonstrate increased stability compared to single cation perovskites and photovoltaic conversion efficiencies exceeding 20%. These perovskites are sensitive to moisture during thin film deposition, with most reported films fabricated in nitrogen filled gloveboxes, and rapidly degrade under exposure to high relative humidities. The addition of lead thiocyanate has recently been shown to increase film quality and improve moisture tolerance. We report here on the fabrication of triple cation mixed halide perovskites in a 10% relative humidity environment, investigating the impact of the addition of lead thiocyanate on film morphology and the lifetimes and diffusion coefficients of photogenerated charge carriers. From confocal photoluminescence (PL) microscopy, we conclude that the addition of lead thiocyanate at concentrations of 2 - 8 wt% increases grain sizes and reduces compositional heterogeneity over micron length scales. Time resolved photoluminescence mapping measurements confirm this increased film quality, with increased carrier lifetimes and reduced lifetime dispersion observed in samples with lead thiocyanate. Diffusion coefficients determined through time resolved photoluminescence microscopy with spatially fixed excitation and spatially scanned collection showed reduced diffusion coefficients, but increased diffusion lengths after the addition of lead thiocyanate. These findings provide guidance for potential low-cost fabrication of perovskite solar cells.

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