## Manufacturing Science and Technology
## Room: 302 - Session MS+PS+TF-ThA

## Functionalization of Paper and Textiles & Their Applications
**Moderator:** Jack Rowe, North Carolina State University, Bridget R. Rogers, Vanderbilt University

2:20pm **MS+PS+TF-ThA1 Vapor-Phase Infiltration of Cellulose and Cotton**, ***Mato Knez***, *K. Gregorczyk, M. Garcia, I. Azpitarte*, CIC nanoGUNE, Spain, *D. Pickup, C. Rogero*, Centro de Física de Materiales (CSIC-UPV-EHU), Spain **INVITED**

There is a significant interest in using inexpensive biological materials as substrates and scaffolds for emerging applications due to their natural occurrence. Of particular importance is the use of paper based materials and substrates for potential applications in energy storage, catalysis, solar cells, etc. Atomic layer deposition (ALD) has been proven to be the technique of choice to modify paper and other cellulose based materials due to its low reaction temperatures, extreme thickness control, and conformality. Furthermore, vapor phase infiltration techniques, which are a recent modification to ALD, have allowed infiltration of metal-organic precursors into a variety of organic materials including spider silk, porphyrins, and polytetrafluoroethylene (PTFE), leading to a more detailed understanding of the reaction between these organic substrates and the metal-organic precursors, as-well-as surprising changes in bulk properties. Understanding the chemical interactions between precursors and substrates are crucial in order to approach applications. We modified cellulose and cotton with common ALD precursors and monitored the chemical changes after the reaction a semi-*in-situ* XPS experiments. Our findings show that the precursors induce small, but important changes to the biopolymer upon chemical interaction and that the precursors indeed react different to each other. The experiments also compare well to the final results of standard *ex-situ* XPS. Changes in the bulk mechanical properties of the substrates were studied through use of tensile testing. The ultimate tensile strength (UTS), Young's modulus (YM), and toughness are shown to be a non-linear function of both the precursor used and the number exposure cycles.

3:00pm **MS+PS+TF-ThA3 Patterned Photoreduction of Metal Atoms on Polymeric Substrates for Flexible Electronic Applications**, ***Halil Akyildiz***, *J.C. Halbur*, North Carolina State University, *A.T. Roberts*, Redstone Arsenal, *H.O. Everitt*, Duke University, *J.S. Jur*, North Carolina State University

Flexible electronics are of interest for displays, sensors, and health monitoring systems. Polymeric substrates, being flexible, easy to manufacture and inexpensive, are wanted for such applications. However, polymers, aside from good properties usually require alteration of electronic and optical properties. Sequential vapor infiltration (SVI) is a technique that modifies polymer properties by formation of hybrid materials via infiltration of organometallic precursors into bulk polymers. In this work we present how SVI tailors the optical properties of polyethylene terephthalate (PET) fibers by infiltration of trimethylaluminum (TMA) precursors to form PET-Alumina hybrid structures. Photoluminescence (PL) spectroscopy showed an order of magnitude increase in photoluminescence as compared to the pristine PET fibers which is attributed to the increased interactions between polymer chains by formation of alumina polymer coordination complexes. Furthermore metal ions out of a metal salt solution were reduced onto the modified substrates by photo catalytic effect. Patterned silver lines on PET fabric were successfully achieved by selective excitation of the fabric using a laser source showing promising results for integration of electronic devices.

3:20pm **MS+PS+TF-ThA4 Multifunctional Fabrics via Tungsten ALD on Kevlar**, ***Sarah Atanasov***, *B. Kalanyan, G.N. Parsons*, North Carolina State University

Multifunctional materials combine two or more distinct capabilities into a single article unit. Kevlar is a high strength fiber used for personal protection and other mechanically demanding applications. Adding conductivity to Kevlar creates a new multifunctional protective/electronic material for electromagnetic shielding, communications, and erosion resistant, anti-static fabrics and cables for space and automotive technologies. For this study, we coated Kevlar fibers and woven mats with ALD tungsten, using $WF_6$ and dilute silane ($SiH_4$, 2% Ar) at 220°C. Kevlar's thermal stability makes it a very amenable polymer for ALD coating at relatively high temperatures. Before W ALD, we deposited a $TiO_2/Al_2O_3$ bilayer by ALD onto the Kevlar, at various temperatures (50-220°C). The $Al_2O_3$ layer promotes W nucleation. The $TiO_2$ layer is important because previous mechanical analysis indicates that the TMA precursor degrades the Kevlar polymer backbone, whereas $TiO_2$ ALD using $TiCl_4$ and $H_2O$ was less damaging. XPS analysis confirms the presence of $TiO_2$, $Al_2O_3$ and W on the fibers after each coating step. After W ALD, the yarns and mats are highly conductive (~3000 S/cm) and remain flexible. Tensile testing shows that upon coating with 20 ALD cycles, the strength of the Kevlar decreases from 3.32 GPa to 3.02 GPa. The ability to create highly conductive Kevlar with mechanical strength within 90% of the original mechanical performance could open new areas of application for large area low temperature ALD processing.

4:00pm **MS+PS+TF-ThA6 Direct and Self-Assembly of Nanocellulose Cleaved from Fiber Cell Walls and Integration in Device Manufacture**, ***Orlando Rojas***, North Carolina State University **INVITED**

We introduce our work related to the application of surface and colloid science in the development of cellulose nanomaterials. These efforts take advantage of the process by which nature assembles fibers in a highly hierarchical structure encompassing a wide range of sizes, from the nano to the meter scales. A number of materials cleaved from the cell wall have been the subject of intensive research, including, nanofibrillar cellulose and cellulose nanocrystals, i.e., defect-free, rod-like crystalline residues after acid hydrolysis of cellulose fibers. Interest in nanocellulose originates from its appealing intrinsic properties: nanoscale dimensions, high surface area, unique morphology, low density, chirality and mechanical strength. Directing their assembly back to different hierarchical structures is a quest that can yield useful results in many revolutionary applications. As such, we will discuss the use of non-specific forces to create ultrathin films of nanocellulose at the air-solid interface for applications in nanocoatings, sensors, etc. Assemblies at other interfaces will be introduced as means to produce Pickering emulsions. Methods common in biophysics and employed to control the packing density of nanocellulose at the air-liquid and air-solid interfaces will be presented. A convective assembly setup assisted by shear and electric fields will be discussed as a suitable method to produce highly ordered structures. Concepts related to piezoelectric cellulose nanocrystal films, organic-inorganic hybrid materials with magnetic and other properties. Overall, the prospects of such novel materials will be explained in light of the unique properties of cellulose and its nanostructured assemblies.

5:20pm **MS+PS+TF-ThA10 Van der Waals Materials on Nanostructured Paper -- Aqueous Gating and Sensing Application**, ***Wenzong Bao***, *Z. Fang, J. Wan, L.B. Hu*, University of Maryland, College Park

We report the first aqueous transistors on a bilayer-structured paper with a nanoscale smoother surface. Such transistors have a planar structure with source, drain and gate electrodes on the same surface of paper, and the mesoporous paper is used as an electrolyte container. Such transistors are enabled by a bilayer-structured all-cellulose paper with nano-fibrillated cellulose on the top surface that leads to an excellent surface smoothness, while the rest of micro-sized cellulose fibers can absorb electrolyte effectively. Based on 2D Van der Waals materials such as graphene and MoS2, we demonstrate high-performance transistors with large on-off ratio. Our devices also show excellent bending flexibility. Such planar transistors with absorbed electrolyte gating can be used as sensors integrated with other components towards paper microfluidic systems.

5:40pm **MS+PS+TF-ThA11 Mechanistic Understanding of Anomalous Scaling Law of Mechanical Properties of Nano-Cellulose Paper**, *S. Zhu, Z. Jia, Y. Li, Z. Fang, S. Parvinian, N.J. Weadock, O. Vaaland, Y.C. Chen, L.B. Hu*, ***Teng Li***, University of Maryland, College Park

The quest of both strength and toughness is perpetual in advanced material design; unfortunately, these two mechanical properties are generally mutually exclusive. A general and feasible mechanism to address the conflict of strength vs. toughness still remains elusive. Here we demonstrate an anomalous but highly desirable scaling law of the mechanical properties of cellulose nanopaper: both its strength and toughness increase simultaneously (40 & 130 times, respectively) as the size of the constituent cellulose fibers decreases (from a diameter of 27 microns to 10 nm). Our theoretical mechanics modeling and molecular dynamics simulations reveal the underlying mechanistic understanding of such an anomalous scaling law. These stimulating results suggest a fundamental bottom-up strategy generally applicable for other material building blocks, and thus hold the promising potential toward a new scaling law: the smaller, the stronger AND the tougher. There are abundant opportunities to utilize the fundamental bottom-up strategy to design a novel class of functional materials that are both strong and tough.

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