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

Processes for Mesoscale Structure on Paper and Textiles
Moderator: Jesse Jur, North Carolina State University

8:00am **MS+PS+TF-ThM1 High-Performance Composites Based on Wood Cellulose Nanofibrils**, ***Qi Zhou***, KTH Royal Institute of Technology, Sweden **INVITED**

With increasing concerns for the climate and environment, it has been recognized globally that paradigm-shifting research is required to improve the performance of materials based on renewable resources. Attempts to develop very high performance natural cellulosic fibers based composite materials using intact cells from hemp, flax and cotton have failed mainly due to the inherent imperfections of the secondary cell walls of natural fiber cells. These issues have been recently addressed by replacing with cellulose nanofibrils (CNFs), which are three orders of magnitude smaller than the intact fiber cells. The extraction process of CNFs from renewable resource has been extensively investigated in the past decade. A critical challenge in the fabrication of high performance products based on CNFs is to tailor their surface structure and functionality in an efficient and environmentally friendly fashion, thus to accommodate a wider range of applications and sustainability requirements for the next generation of materials. In this talk, I will present our recent work on the fabrication of functional composite materials based on CNFs. In particular, several novel surface modification techniques of CNFs and their effects on nanostructure and material properties of CNFs based composites will be discussed.

8:40am **MS+PS+TF-ThM3 Manufacturing and Applications of Carbon Nanotube Textiles**, ***Philip Bradford***, North Carolina State University **INVITED**

Carbon nanotubes (CNTs) are short nanofibers that are usually produced in the form of a black powder. This powder is then incorporated into other materials to produce a wide array of multifunctional products. Processing raw CNTs into materials that look and behave like traditional textiles is a growing area of interest, however the CNTs are often processed in solution and the end products look more like papers than textiles. There are currently only a couple of options for creating fabrics out of CNTs which preserve the high surface area of the individual tubes and retain high porosity. This presentation covers the work of my research group to make this type of fabric from a special type of CNT structure called drawable CNT arrays. These arrays are synthesized in a low pressure chemical vapor deposition process and then utilized for CNT nonwoven fabric formation. My group is also exploring many novel applications for the use of these unique fabrics.

The nonwoven CNT fabrics produced in our lab contain millimeter long CNTs, have a preferential CNT alignment, low CNT bundling and high porosity. These features make them attractive for use in: composites reinforcement, battery electrodes, sensing, filtration and barrier fabrics. Of particular interest to the AVS community may be our recent work with collaborator Dr. Jesse Jur at NC State, to study the atomic layer deposition (ALD) of thin inorganic layers into CNT arrays and fabrics. Through optimization of CNT pretreatment, ALD parameters and sample orientation, we have been able, for the first time, to uniformly coat CNT structures whose characteristic aspect ratios are extremely large. Due to the un-bundled nature of the CNT fabrics we have the ability to uniformly coat CNTs along their entire millimeter length, making for some very unique hybrid CNT structures.

9:20am **MS+PS+TF-ThM5 Carbonized Cellulose Fibers for Low-Cost Energy Storage**, ***Fei Shen***, *L.B. Hu*, University of Maryland, College Park

A low-cost but scalable carbon film was successfully obtained via cellulose fiber carbonization. This cellulose derived film can be also applied as an alternative anode for lithium or sodium ion battery due to its natural mesoporous structure of the starting material which was excellent for ion storage. Furthermore, this new type of carbonized cellulose possesses electrically interconnected three-dimensional framework with advanced dual properties of anode material and current collector, afford to result in a higher energy density by eliminating the extra mass of inactive materials such as binder and carbon black in conventional designs. Electrochemical studies showed the film achieved a high capacity of 800mAh/g for lithium ion battery and a moderate capacity of 200mAh/g for sodium ion battery at C/10.

9:40am **MS+PS+TF-ThM6 Traditional, 20th, and 21st Century Strengthening Techniques for Cultural Heritage Papers Weakened by Cellulose Depolymerization**, *L. Pei, M. McGath,* ***John Baty***, Johns Hopkins University

Cellulose depolymerization leading to paper brittleness can occur throughout the sheet, or be localized to where a corrosive substance is present. Uniform brittleness is associated with mass-produced, inexpensive, and acidic papers. Rendering millions of books and unbound papers useless, paper brittleness impairs scholarly communication and destroys historic and artistic works. Localized brittleness is most commonly associated with corrosive pigments and inks, including iron gall ink. It visually alters and can also physically destroy paper-based works. In the absence of techniques to restore the cellulose polymer to its initial condition, diverse techniques have been developed to strengthen paper. Traditional conservation techniques vary from conceptually simple ones, such as backing the sheet with a reinforcing layer, to complex ones, such as splitting the sheet into two plies to adhere a reinforcing sheet in-between. 20th century techniques include the widespread lamination of documents with a cellulose acetate film, the present condition of which we have studied and discuss along with its successor, the encapsulation of papers within a polyester film envelope to which the sheet is only electrostatically attracted. Both of these techniques involve the addition of a visible film, altering the look and feel of the artifact. Therefore, we are studying chemical vapor deposition (CVD) using Parylene to deposit a thin, conformal, barely perceptible coating to add strength to brittle papers. We conclude that, here as elsewhere, scientific research can improve traditional conservation techniques by making additional tools available to the conservator; that both cellulose acetate lamination and polyester film encapsulation have achieved a greater preservation benefit than they are credited for; and that CVD is a useful tool for both single-item as well as batch treatments to preserve cultural heritage papers weakened by cellulose depolymerization.

11:00am **MS+PS+TF-ThM10 Visualizing the Interface in Strained Cellulosic Nanocomposites**, ***Chelsea Davis****, J. Woodcock, A.M. Forster, M. Zammarano, I. Sacui, N. Chen, SJ. Stranick, J.W. Gilman*, National Institute of Standards and Technology (NIST)

In fundamental composite theory, the nature of the interface is often the key parameter which determines the strength of the resulting composite structure. While it is possible to observe interfacial failure and characterize the areal coverage of the matrix on the surface of the reinforcement phase in conventional composite materials, directly quantifying interfacial strength and contact area in a nanocomposite becomes far more difficult. A novel solution developed at NIST has been to utilize Förster resonance energy transfer (FRET) imaging[1,2] by preferentially labeling the interface within a nanocomposite system, allowing direct imaging of the interface with an optical microscope.[3] Zammarano et al. have shown that the incorporation of a FRET dye pair onto the surface of a cellulosic nanoreinforcement phase (dye 1) and within a polymer matrix (dye 2) allows visualization of the nanoscopic interphase region as the two dyes transfer energy on the same scale as the interphase depth (1 nm-100 nm).[3,4]

Building upon this FRET-based interfacial characterization technique, our goal is to develop a globally nondestructive measurement system that allows the quantitative characterization of key interfacial properties; first, the wetting and surface contact formed between the nanocellulose and an epoxy matrix and second, the deformation of the interface on the nanoscale upon application of small mechanical strains. We are constructing a suite of mechanical strain tools to enable *in situ* mechanical interrogation with simultaneous FRET imaging. The development of the first of these tools, uniaxial tensile test will allow a preliminary observation of small strain effects on the interphase region regarding the fluorescent response of the FRET dye pair. As a first proof of concept, it has been shown that FRET can be used to observe nanoscopic interfacial fracture and to determine local (microscopic) stress concentration zones before macroscopic failure of the nanocomposite is observed.

This *in situ* FRET/mechanical deformation approach allows the use of an optical microscope to probe nanoscale features in a powerful way, enabling characterization of nanomaterials which will complement measurements made by electron microscopy and standard mechanical property testing methods.

Topic Area: Novel nanocomposites, Multi-technique characterization of nanostructured materials

[1] T. Förster, *Ann. Phys.***1948**, *248*.

[2] E. a Jares-Erijman, T. M. Jovin, *Nat. Biotechnol.***2003**, *21*, 1387.

[3] M. Zammarano, P. H. Maupin, L.-P. Sung, J. W. Gilman, E. D. McCarthy, Y. S. Kim, D. M. Fox, *ACS Nano***2011**, *5*, 3391.

[4] C. Berney, G. Danuser, *Biophys. J.***2003**, *84*, 3992.

11:20am **MS+PS+TF-ThM11 SERS-based Chemical and Biological Analytics on Inkjet-fabricated Paper Devices**, ***Ian White***, University of Maryland

SERS-based chemical and biological analytics on inkjet-fabricated paper devices

Abstract. As a bio/chemical sensing technique, surface enhanced Raman spectroscopy (SERS) offers sensitivity comparable to that of fluorescence detection while providing highly specific information about the analyte. The high sensitivity of SERS detection results from the localized plasmons generated at the surface of noble metal nanostructures upon excitation by resonant electric fields at optical frequencies. Although single molecule identification with SERS was demonstrated over a decade ago, today a need exists to develop practical solutions for point-of-sample and point-of-care SERS systems. Recently, we demonstrated the fabrication of SERS substrates by inkjet printing silver and gold nanostructures onto paper and other similar membranes. Using a low-cost commercial inkjet printer, we deposited silver nanoparticles with micro-scale precision to form SERS-active biosensors. Using these devices, we have been able to achieve detection limits comparable to conventional nanofabricated substrates. Furthermore, we have leveraged the fluidic properties of paper to enhance the performance of the SERS devices while also enabling unprecedented ease of use, which is critical for extending chemical and biological analytics from central labs out into the field.

In this presentation we will review the capabilities of inkjet-fabricated paper SERS devices as chemical and biological sensors. We will introduce the fabrication of paper-based fluidic SERS devices using inkjet printing, and we will review results for chemical detection with paper SERS devices, including the use of the paper substrates as swabs and dipsticks for pesticide detection, as well as chromatography SERS on PVDF membranes for the detection of melamine in infant formula. We will then present the results of the fluidic paper SERS devices for biomolecule detection, including paper SERS dipsticks that leverage the chromatographic separation properties of paper to distinguish the outcome of multiplexed TaqMan PCR from a single reaction. In particular, we have utilized this technique to detect the presence of two drug resistance biomarkers for methicillin-resistant *S. Aureus* (MRSA).

11:40am **MS+PS+TF-ThM12 NSF Scalable Nanomanufacturing (SNM) Program**, ***Khershed P. Cooper*** **INVITED**

Abstract: Nanomanufacturing involves the fabrication of nano-scale building-blocks (nanomaterials, nanostructures), their assembly into higher-order structures such as nanodevices and nanosystems, and the integration of these into larger scale structures and systems such that both heterogeneity and complexity are possible with manipulation and control at nano-scale. In 2010, following a review of the NNI, PCAST recommended greater emphasis be put on commercialization of nanotechnologies by doubling Federal Government investment in nanomanufacturing R&D. In 2011, the inter-Agency NNI Signature Initiative (NSI) in Sustainable Nanomanufacturing was announced. In response to the NSI, the NSF Scalable Nanomanufacturing (SNM) Program was launched. SNM's emphasis is on research to overcome the key scientific and technological barriers that prevent the production of useful nanomaterials, nanostructures, devices and systems at an industrially relevant scale, reliably, and at low cost and within environmental, health and safety guidelines. The SNM program's objective is to address challenges presented at the various stages of the nanomanufacturing value chain of nano-scale building-blocks to nano-enabled products. It sponsors fundamental scientific research in well-defined technical areas that are strongly justified as approaches to overcome critical barriers to scale-up and integration. It seeks discovery of scalable processes and methods for large-area or continuous manufacturing at the nano-scale. It encourages the study of design principles for production systems leading to nanomanufacturing platforms, identification of metrology, instrumentation, and standards, and development of methodologies needed for process control and assessing quality and yield. SNM encourages an inter-disciplinary approach, industry collaboration and integration of research and education. SNM projects are studying a variety of building-blocks—CNT, graphene, membranes, BCPs, DNA, nanowires, nanofibers, QDs, etc., a variety of top-down and bottom-up processes—thermal, vapor-based, solution-based, lithography, patterning, bio-inspired, etc., targeting applications across the board—energy, environmental, electronics, sensors, structural, etc. Many projects are investigating roll-to-roll processing systems, some are studying in-line metrology and quality control. Moving ahead, SNM seeks to explore new research opportunities in processing (hierarchical nanomanufacturing, cyber-enabled nanomanufacturing, etc.), in materials (graphene, MoS2, etc.), in devices (plasmonics, ultrafine vias, etc.), and in manufacturing platforms (3D printing, bio-enabled assembly, etc.). SNM encourages an inter-disciplinary approach involving the disciplines of engineering, physical sciences and mathematics. The ultimate goal is to create a knowledge base for the reliable production of nano-enabled systems and products.

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