Nanomaterials
Room Hau - Session NM-WeE
Nanocomposites

Moderator: Richard Tilley, University of New South Wales, Australia

5:40pm **NM-WeE1 Nanocrystal-in-Glass Composite Thin Films for Electrochromic Smart Windows***, **Delia Milliron,*** University of Texas at Austin, USA **INVITED**

Degenerately doped metal oxide semiconductors, like ITO, exhibit plasmonic resonance at near and mid-infrared wavelengths tunable by varying their composition. Nanocrystals of many such materials have now been synthesized and applications are emerging that leverage the responsiveness of their localized surface plasmon resonance (LSPR) to electronic charging and discharging. In this talk, I'll focus on how we are applying this concept to develop electrochromic glass that can dynamically control heat loads and daylighting in buildings. We demonstrated that dual-band electrochromism (voltage control over near infrared and visible light transmittance independently) is achievable by embedding plasmonic ITO nanocrystals in a redox-active niobium oxide glass matrix. To develop a practical technology on the basis of this concept, the component materials and their mesoscale architecture can both be optimized so that we now can modulate a large fraction of incident solar radiation on demand. To enable low-cost manufacturing, we have recently developed low-temperature processing strategies and have now fabricated complete dynamic glass prototypes. The materials innovations needed to enable this progress will be emphasized.

6:20pm **NM-WeE3 Functionally Graded Nanocarbon-reinforced Metal Matrix Composite Materials***, **Hansang Kwon**, G.J. Park,* Pukyong National University, Republic of Korea*; S. Lim, J.H. Park,* Next Generation Materials Co., Ltd, Republic of Korea

Functionally graded nanocarbon particles reinforced aluminium (Al) matrix composites have been successfully fabricated by solid-state spark plasma sintering process [1]. The multiwalled-carbon-nanotubes (MWCNT) were used as a main reinforcement and the MWCNT were well dispersed in the Al particles using high energy ball milling process. Several different types of MWCNT were used in the same volume. The ball milled Al-MWCNT powder mixtures were fully densified and demonstrated good adhesion with no serious micro-cracks and pores within a multilayer composite. Each multilayer contained different amounts of the MWCNT, showed different microstructures and mechanical properties. It is possible to control the mechanical, thermal and electrical properties of the functionally graded multilayer composite through the efficient design of an MWCNT reinforced gradient layer.

[Reference]

[1] KWON, H., LEPAROUX, M. & KAWASAKI, A. 2014. Functionally Graded Dual-nanoparticulate-Reinforced Aluminum Matrix Bulk Materials Fabricated by Spark Plasma

6:40pm **NM-WeE4 Boron Nitride Nanotube-Titanium Alloy Nanocomposites***, **John-Andrew Hocker,*** NASA Langley Research Center, USA*; S-H. Chu, V. Yamakov,* National Institute of Aerospace, USA*; J. Newman, S. Messina, E. Judd,* NASA Langley Research Center, USA*; C. Rohmann, D. Bernhardt,* The University of Queensland, Australia*; C. Park, C. Fay,* NASA Langley Research Center, USA

Titanium alloys, such as Ti-6Al-4V, are used in aerospace applications that require light weight, high strength and corrosion resistance. Boron nitride nanotubes (BNNT) are a unique high strength, high aspect ratio, neutron absorbing nanomaterial with good thermal and chemical stability. Adding low density BNNT enables structural mass savings and may impart multifunctional capabilities such as the piezoelectric effect, and increased thermal conductivity. Recent theoretical studies indicate that BNNTs should exhibit a stronger interfacial binding with titanium than they do with aluminum or copper. Guided by those results, a series of nanocomposites was fabricated to experimentally investigate the reinforcing effect of BNNTs on the Ti-6Al-4V alloy. BNNT-Ti-6Al-4V nanocomposites were prepared by first consolidating the powder/BNNT blends at several loadings, 0.01 to 10 weight percent BNNT, in a circular die at elevated temperature and pressure. These consolidated specimens were then placed in a furnace and sintered under vacuum at ~1300°C. The resulting physical and mechanical properties of the metal matrix nanocomposites will be discussed, and compared with morphological results from X-ray diffraction, and optical, scanning electron, and scanning probe microscopies.

7:00pm **NM-WeE5 Fabrication and Applications of Nanocomposites Based on Anodic Aluminium Oxide***, **Jinghua Fang**,* University of Technology Sydney, Australia

Engineering a new class of nanocomposite-metamaterials can achieve ultra-sensitive sensors for bio-imaging, gas detection, air and food contamination control. This is critical to meet the global challenges of environmental conservation and efficient use of energy and mineral resources, especially for point-of-use applications. Using anodic aluminium oxide (AAO), here we report the fabrication of metamaterials with different metal nanostructures, we also investigate the applications of these fabricated metamaterials based on AAO templates.

7:40pm **NM-WeE7 Graphene-based Nanocomposite Hydrogels for Contaminant Removal***, **Nathalie Tufenkji**, N. Yousefi, K. Wong, A. Angulo,* McGill University, Canada

Due to its exceptionally high specific surface area and abundance of surface functional groups, graphene oxide (GO) is of great interest as a high performance sorbent for dyes, heavy metal ions, oils, toxins and organic solvents from contaminated waters. However, recovery of GO after the water treatment process is difficult due to its high stability in water. Thus, self-assembly of GO sheets into porous 3D macrostructures such as hydrogels has been explored as a technique to exploit their high surface area while facilitating easy recovery from treated water. Nonetheless, creating mechanically robust hydrogels with acceptable adsorption capacities is not straightforward. We report a simple method for preparation of ultra-strong nanocomposite GO hydrogels at low pressure using vitamin C as a natural cross-linker. The structure and chemical compositions of the hydrogels are examined using microscopy and spectroscopy techniques. We demonstrate that hydrogels with high storage moduli can be used to effectively remove model dyes such as methylene blue, heavy metal ions and emerging contaminants such as the pharmaceutical products diclofenac and sulfamethoxazole from aqueous solutions. We will describe the novel aspects of the hydrogel synthesis that give rise to its exceptional mechanical strength and adsorption capacity.

8:00pm **NM-WeE8 Towards Producing Bulk Monolithic Core/Shell Nanocomposites***, B.N. Feigelson, **James Wollmershauser**, K. Manandhar,* U.S. Naval Research Laboratory, USA

With designed bulk nanostructured solids, one could potentially combine properties that are mutually exclusive in a single bulk material, and, as a result, dramatically improve the desired performance. However, a major research challenge and roadblock is how to produce 3D nanostructured materials consistently with the required phases arranged in designated spatial order that are at the same time fully dense without porosity and detrimental phases. Known state-of-the-art techniques for producing bulk nanostructures cannot simultaneously meet all these requirements. As a result, the inherent properties of such bulk monolithic nanostructured materials are greatly unknown and unexplored.

We developed an Enhanced High Pressure Sintering (EHPS) process to consolidate oxide, metal, and semiconductor nanoparticles into 3-dimensional monolithic nanostructured materials. EHPS incorporates stringent environmental control and utilizes high pressures to break agglomerates while simultaneously exploiting the increased pristine surface potential of nanoparticles for surface-energy-driven densification without microstructural changes. Using this approach, monolithic nanocrystalline transparent ceramics with grain size bellow 30 nm are demonstrated. Such ceramics exhibit a 30% increase in hardness over a corresponding order of magnitude reduction in grain size and suggest that Hall-Petch type (strengthening via grain size reduction) relations exist in ceramics at least down to 30nm [1].

Core/shell nanoparticles offer fundamentally new means for nanostructured solids design and tailoring basic properties of these artificial materials. To provide flexibility in core/shell nanoparticles design, a particle atomic layer deposition (pALD) reactor was incorporated in the EHPS facility. The new setup allows to controlling environment during all stages of the nanoparticles processing, atomic layer deposition and sintering. Spinel/alumina core/shell nanoparticles were the first material system tested for producing the first core/shell ceramic nanocomposite. Alumina shell was grown on spinel nanoparticles, and then core/shell nanoparticles sintered under pressure without exposing to atmospheric air. The developed nanocomposite

ceramics demonstrated better hardness and fracture toughness than pure nanocrystalline spinel.

[1] Wollmershauser, J. A.; Feigelson, B. N.; Gorzkowski, E. P.; Ellis, C. T.; Goswami, R.; Qadri, S. B.; Tischler, J. G.; Kub, F. J.; Everett, R. K., *Acta Materialia*, 69 , 9-16 (2014).

8:20pm **NM-WeE9 Nanoscale Bioinspired Interfaces in Carbon Fibre Reinforced Polymer Composites*, Bronwyn Fox,*** Swinburne University, Australia

Carbon fibre composites, where bundles of carbon fibres are embedded in a polymer matrix, offer enormous design flexibility due to the ability to tailor properties such as strength and modulus. They are used to lightweight aerospace and automotive structures and are seeing an exponential increase in demand with the global market predicted to grow to $36 billion by the year 2020. The Achilles heel of these materials lies in their ability to withstand damage from impact loads. Once damaged, the ultimate strength of the material is reduced via the formation of microcracks that lead to delamination failure. The microcracks are often found to originate at the interface between the fibre and the matrix, yet interfacial adhesion in composite materials is poorly understood and still hotly debated in the literature. The relative influence of fibre grade (standard, intermediate or high modulus), fibre surface roughness and chemistry in interfacial adhesion and therefore microcracking is required. This new knowledge will lead to the development of engineered interfaces in composites for improved performance. There are many examples of tailored interfaces in nature from which we can draw inspiration. Nacre (mother of pearl) is a natural high-performance composite comprising nanocrystals of CaCO3, aragonite, embedded in a multi-layered, multi-component soft organic matrix. The CaCO3 crystals do not bind directly to the organic chitin layer, but are separated by an intermediate protein layer. This intermediate phase creates a soft/soft/hard interface that can be likened to an engineered interphase in carbon fibre composites. Commercial carbon fibres are usually electrolytically oxidised and then coated with either an epoxy or a polyurethane sizing to protect the fibre during processing and to facilitate handling. The nature and presence of this sizing may influence the chemistry of the surrounding polymer matrix to create an interphase region. We have explored a range of strategies to tailor the fibre surface roughness and chemistry to ensure compatibility with the polymer matrix. The electrolytic treatment was systematically varied to ensure that the fibre surface was free of amorphous carbon debris, a range of chemical treatments were used including the attachment of small molecules to the fibre surfaces. Novel sizing systems and plasma polymer coatings have also been applied to the fibres. This paper will describe our recent results on the effect of a range of fibre treatments to improve interfacial performance in carbon fibre composites.

8:40pm **NM-WeE10 Photo-stability Enhancement of Colloidal CdSe/ZnS QDs Passivated in Al_2O_3 using Atomic Layer Deposition*, Chih-Yi Cheng,*** *C.-H. Chen, M.-H. Mao,* National Taiwan University, Taiwan, Republic of China

Colloidal quantum dots (QDs) have many advantages, such as the tunability of emission wavelength during synthesis and easy integration.[1] However, they are very sensitive to environment conditions because of high surface to volume ratio. Photo-oxidation of QDs is one of the critical problems. It creates defect states and decreases the quantum yield.[2] Strong photo-degradation was observed even in the core/shell structure under laser excitation.[3] Recently we reported the method of passivating QDs in Al_2O_3 using atomic layer deposition (ALD) and systematically studied the time-resolved photoluminescence (PL) of QDs.[4] In this work, we took a further step to investigate the impact of laser excitation on QD PL intensity by applying the ON/OFF cycles (5 min each). One unpassivated and one passivated QDs samples were prepared with details described elsewhere.[4] The STEM image shows a clear single QDs layer uniformly passivated by an Al_2O_3 layer. Both samples were studied under a 532 nm continuous wave laser excitation with a power density of 407 kW/cm^2. The unpassivated QDs showed rapid PL degradation due to strong photo-oxidation. Moreover, the PL intensity did not recovery after OFF periods indicating an irreversible process. In contrast to the sever photo-degradation of the unpassivated QDs, the passivated QDs were found to remain stable. It is interesting that both samples show small PL recovery at the beginning of each ON period. This can be explained by photo-ionization of QDs. During the ON period, the electrons are ejected from QDs and form an electrostatic barrier which leads to PL intensity reduction due to Coulomb blockade.[5] The ionized QDs can be neutralized during the OFF period and then the PL intensity can be recovered to some extent. However, the PL recovery of unpassivated QDs is gradually reduced after several cycles because more and more QDs photo-oxidized. Since the passivated QDs didn't suffer from photo-oxidation, it shows similar amount of PL recovery in every ON period. In conclusion, we demonstrated the photo-stability enhancement of QDs by Al_2O_3 passivation using ALD technique. This method can provide good encapsulation of QDs and the application of this technique for other types of QDs, such as PbS, will be also presented in this study.

Reference:

[1]J. Y. Kim, et al., Adv. Mater. **25**, 4986 (2013).

[2] W. G. J. H. M. van Sark, et al., J. Phys. Chem. B **105**, 8281 (2001).

[3]H. Zhang, Y. Liu, X. Ye, and Y. Chen, J. Appl. Phys. **114**, 244308 (2013).

[4]C.-Y. Cheng and M.-H. Mao, J. Appl. Phys. **120**, 083103 (2016).

[5]K. Patty, et al., J. Appl. Phys. **116**, 114301 (2014).

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