

SYMPOSIUM NM04/BI01/ET14

TUTORIAL: Life Cycle Analysis from an Industrial Perspective
November 25 - November 25, 2018

* Invited Paper

TUTORIAL Life Cycle Analysis from an Industrial Perspective

Sunday Afternoon, November 25, 2018
Hynes, Level 2, Room 200

Environmental issues keep steadily increasing, thus there is a strong urge to discuss how materials scientists could more rapidly respond to the worldwide concerns. This joint tutorial effort would be organized by the three symposia together. To ensure the success of such synergistic efforts it is also urged a close dialogue with society so to establish guidelines for policymakers, thus this tutorial will incorporate both the societal and the engineering aspects of life cycle analysis (LCA) would be covered. The main objective of this tutorial is to explore communications pathways between companies and materials researchers that further elevate the profile and challenges of sustainability that represents a societal necessity and a viable and critical topic for research.

1:30 PM

Societal Aspect of LCA Jean-Pierre Birat; ArcelorMittal

Materials are not simply the product of an engineering discipline, Materials Science, but also "social constructs" that have entertained a close relationship with society all through the historical timeline and remain a core element of our modern world, what is called a Key Enabling Technology. How this can be analyzed by parallel approaches of hard and soft sciences will be explained in the class as well as the tryptic of economic, environmental and social values of materials. Examples reported in the 13 past SAM conferences will be used as examples.

2:45 PM BREAK

3:15 PM

Engineering Aspect of LCA Alan Rae; IncubatorWorks, USA

The instructor will provide an overview on all the aspects considered in a life cycle analysis aimed to the engineering design of an industrial process. A part of the tutorial will involve the interaction with the audience in order to apply some of the concepts described in the first part of the tutorials to common objects.

4:15 PM Sustainability Challenge Alan Rae, IncubatorWorks

The symposia organizers will divide the participants into groups and a sustainability challenge will integrate the concepts presented by the instructors so to review and facilitate networking among participants and instructors

4:45 PM

Final Remarks

SYMPOSIUM NM04

Nanomaterials and Nanomanufacturing for Sustainability
November 26 - November 29, 2018

Symposium Organizers

Babak Anasori, Drexel University
Monica Jung de Andrade, The University of Texas at Dallas

Maria Perez Barthaburu, University de la Republica
Yin Ting Teng, Republic Polytechnic

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The University of Texas at Dallas, School of Natural Sciences and Mathematics

* Invited Paper

SESSION NM04.01: Synthesis and Nanomanufacturing I

Session Chairs: Eric Detsi and Monica Jung de Andrade

Monday Morning, November 26, 2018

Sheraton, 2nd Floor, Back Bay C

8:30 AM NM04.01.01

Molten-Salt Synthesis of Iridium Oxide Nanorods for Oxygen and Hydrogen Evolution Reactions Yuanbing Mao, Jahangeer Ahmed and Swati Mohan; The University of Texas at Rio Grande Valley, Edinburg, Texas, United States.

Electrocatalytic water splitting has been considered as a viable strategy to convert and store energy renewably, but has been hampered by the slow kinetics of the oxygen evolution reaction (OER). Hence there is an urgent need to improve the performance of currently used materials and/or develop new materials. Iridium oxide is an effective stable electrocatalyst with low over-potential and high current for efficient fuel generation technologies. To further improve its activity, we developed a facile one-step molten salt synthesis process to generate ultrafine iridium oxide nanorods (IrO₂ NRs). The electrocatalytic performance of these IrO₂ NCs for OER in acidic media was compared with that of commercial IrO₂ nanoparticles (NPs) in terms of specific capacitance, total charge, most accessible charge, electrochemically active surface area, and roughness factor. Our IrO₂ NRs demonstrated enhanced electrocatalytic OER activity in 0.5 M H₂SO₄ compared to the commercial IrO₂ NPs. Moreover, compared to commercial IrO₂ NPs and previous reports, our IrO₂ NRs showed enhanced electrocatalytic activity for both OER and HER after passing either N₂ or O₂ gas in a 0.5 M KOH electrolyte, as confirmed by cyclic voltammetry, chronoamperometry and electrochemical impedance spectroscopy. Our results are comparable with, and in most cases, higher than reported data in the literature. Therefore, the current study reported a type of highly electrocatalytic efficient IrO₂ nanostructures, but also a simplistic, reliable and scalable synthetic process for them. It is expected that these IrO₂ NRs can serve as a benchmark in the development of active OER and HER (photo)electrocatalysts for various applications in the near future.

8:45 AM *NM04.01.02

Nanomanufacturing Scale Up—Exploring the Benefits and Concerns Jacqueline A. Isaacs¹, Dhimiter Bello³, Christopher J. Bosso¹, Ahmed A. Busnaina¹, Matthew J. Eckelman² and Joey Mead³; ¹Northeastern University, Boston, Massachusetts, United States; ³University of Massachusetts Lowell, Lowell, Massachusetts, United States.

Given the potential benefits and concerns over the use of nano-enabled products (NEPs), *and* because many businesses are currently working to commercialize NEPs, it is critical to assess the technological, environmental, and economic tradeoffs. This work explores the use of life cycle assessment, risk assessment, life cycle costing, material flow analyses, decision analysis optimization tools, and net benefit analyses for carbon nanotube (CNT) and nano-silver applications throughout the product life cycle, and in particular, how to responsibly manufacture and potentially recycle nano-enabled products in light of the uncertain and often ambiguous environmental and health effects associated with CNT and nano-silver exposures. In general, the application of green engineering principles steered our efforts in investigating NEPs using a myriad of tools. Several applications were investigated using these techniques with respect to their lifecycle impacts with varying amounts of CNT (bio- and chemical sensors, electronic switches, batteries, EMI-shielding, and polymer-based composites) or with varying amounts of nano-silver (clothing, medical bandages and protective gear, packaging, as well as children's goods). With insights from the assessment tools and a holistic, systems approach to the issues of uncertainty and risk, product redesign can be pursued to reduce the environmental and health impacts of nano-enabled products and to understand the environmental and health risks of nanomaterials relative to one other. Opportunities to mitigate exposures during manufacture and disposal processing were explored, with best practices recommended. Product stewardship initiatives were explored in light of existing U.S. practices. As an interdisciplinary project, the research included expertise across the various fields of nano-engineering, policy, nano environmental health and safety, exposure sciences and nanotoxicology, and led to greater understanding of the challenges of sustainable development and governance of emerging nanotechnologies. Ultimately, results contribute new data, approaches, and methods to the future responsible *and* sustainable development of nanotechnology.

9:15 AM NM04.01.03

Gamma-Radiation-Induced Synthesis of Metal and Metal Oxide Nanoparticles I.L. Soroka; Applied Physical Chemistry, The Royal Institute of Technology, Stockholm, Sweden.

Gamma-radiation-induced synthesis of metal and metal oxide nanoparticles involves reactions of dissolved precursor metal salts with products of water radiolysis. When exposed to ionizing radiation water decomposes to form chemically reactive radicals and molecular species. The products of water radiolysis range from highly oxidizing, e.g. hydroxyl radicals to highly reducing, e.g. hydrogen radicals and solvated electrons. The oxidants and reductants produced upon radiolysis react then with solutes and change their oxidation state. These chemical changes lead to the formation and subsequent precipitation of insoluble species, since the solubility and reactivity of metal ions depend on their oxidation states. Synthesis of nanomaterials can be done by using either reductive or oxidative routes. To reach the controlled redox conditions and avoid the unwanted reactions one can add other organic or inorganic compounds which act as scavengers of the radicals. The amount of material obtained by gamma-radiation-induced synthesis can be controlled by the yield of reductive/oxidative radiolysis products formed in solution. Radiation induced synthesis is a powerful tool to produce the materials of complex shape and compositions. It has the following advantages as compared to the other methods: The nanoparticles with very narrow size distribution and

uniform shape can be synthesized; there are possibilities to synthesize the nanostructure in confined media, such as porous materials, nanotubes etc. The formation of radicals stops immediately when the solution is removed from the radioactive source. Therefore the amount of reacting radicals and thus the amount of obtained precipitate is controlled by the total radiation dose with a high accuracy. Moreover, the radiation induced method is cost-effective processing, since it implies direct energy transfer without intervening media. It has low energy consumptions, since the radiation source does not require external energy supply. It requires minimal use of potentially harmful chemicals (initiators, crosslinking agents, acids etc.). Thus, radiation-induced synthesis can be considered as a green method.

In the current work we demonstrate how gamma radiation induced synthesis can be implemented to produce metal (Ag, Cu, Ni) and metal oxide (Cu_2O , Co_3O_4 , CeO_2) nanoparticles having narrow size distribution for different applications. The nanomaterials are produced both free standing and on solid supports. Metal nanoparticles are synthesized using the reductive route while metal oxide particles are produced using both oxidative and reductive routes [1, 2].

References

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2. I. L. Soroka, N. V. Tarakina, A. Hermansson, L. Bigum, R. Widerberg, M. S. Andersson, R. Mathieu, A. R. Paulraj, Y. Kiros. *Dalton Trans.* 2017, **46**, 9995-10002.

9:30 AM NM04.01.04

Photoelectron Spectroscopy Investigation of GaN/Si Heterostructures for Photoelectrochemical Water Splitting Srinivas Vanka^{1,2}, Elisabetta Arca³, Glenn Teeter³ and Zetian Mi²; ¹McGill University, Montreal, Quebec, Canada; ²University of Michigan, Ann Arbor, Michigan, United States; ³National Renewable Energy Laboratory, Golden, Colorado, United States.

Surface, interface, and bandgap engineering play a pivotal role for designing tandem photoelectrodes for photoelectrochemical water splitting to potentially realize solar-to-hydrogen efficiencies >20%. III-nitride semiconductors, e.g. GaInN, have emerged as one of the most promising materials to realize high efficiency photoelectrodes: their fundamental bandgap can be varied across nearly the entire solar spectrum by changing the alloy compositions and the band edge positions straddle water oxidation and reduction potentials under visible light irradiation. In this context, we have performed, both theoretically and experimentally, a detailed investigation of the structural, electronic, and photoelectrochemical properties of Ga(In)N/Si heterostructures. Detailed X-ray photoelectron spectroscopy (XPS) measurements reveal that the conduction band edge of GaN and Si are near-perfectly aligned, which enables efficient extraction of photo-generated electrons from the underlying Si wafer to GaN nanowires. Band diagrams were constructed from the measured valence band minimum (VBM) and the observed core-level shifts between different thickness GaN/Si samples. Deposition of 2-3 nm of GaN evidently passivates the Si surface and induces a small amount of upward band bending (BB). The interfacial valence-band offset calculated from measured VBMs and core-level shifts was 2.52 ± 0.1 eV. This value, in combination with the individual band gaps of Si and GaN, leads to a conduction band offset of -0.22 ± 0.1 eV, where the negative sign indicates that the CBM of GaN is lower than that of Si. It is to be noted that n^+ -(In)GaN acts like a hole blocking layer which helps in charge carrier separation and thereby reduce the surface recombination of the photo-generated carriers. With the incorporation of Pt co-catalyst nanoparticles on Ga(In)N surface, we have demonstrated solar water splitting on Ga(In)N/Si photocathode with a maximum current density of >35 mA/cm² and an applied bias photon-to-current efficiency >10% in 0.5 M H₂SO₄ under AM1.5G one-sun illumination. This work shows the use of GaN nanowires as a multi-functional protection layer as well as excellent charge extraction of the photogenerated electrons from the underlying Si wafer.

9:45 AM NM04.01.05

Structure and Reactivity of Zinc Oxide Nanoparticles—A DFT Study Takat B. Rawal^{1,2} and Loukas Petridis^{1,2}; ¹Department of Biochemistry and Cellular and Molecular Biology, University of Tennessee, Knoxville, Tennessee, United States; ²UT/ORNL Center for Molecular Biophysics, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Zinc oxide (ZnO) nanoparticle, an active ingredient of bactericides, has potential applications in treating citrus greening disease owing to its unique properties. Here, employing density functional theory we study the structures and reactivity of sub-nanometer-sized ZnO nanoparticles. Examination on the propensity of binding of water, urea, salicylic acid and citric acid molecules to the surface of ZnO nanoparticle (diameter ~14Å), indicates that the molecules bind strongly at Zn atoms at the nanoparticle edges. Strikingly, the binding of urea, salicylic acid and citric acid through their O (O=C) atoms at the Zn sites can be traced to the electronic structures. We also investigate the solvation effects on the binding characteristics of these molecules. Finally, we compare the structures and energetics of molecules adsorbed on the nanoparticle with those on extended ZnO(10-10) surface, and find that the edge Zn sites of the nanoparticles are more active than the surface Zn sites of the extended surface. Overall, our results provide insights into the reactivity of ZnO nanoparticle in different local environments, and may offer guidelines to design the ZnO-nanoparticle-based material as an antibacterial agent for agricultural applications.

*This work is supported by USDA NIFA under grant FLAW-2014-10120.

10:00 AM BREAK

10:30 AM NM04.01.06

Hybrid Nanomaterials and Their Applications in Energy and Water Areas Pei Dong¹, Yongjie Zhan³ and Jun Lou²; ¹George Mason University, Fairfax, Virginia, United States; ²Rice University, Houston, Texas, United States; ³Northwest University, Xi'an, China.

Water and energy are two of the world's most valuable resources. In the near future, as the industrial sector expands, demand for water and energy will be even greater than it is today. Recently, advanced materials have been widely implemented in energy and water areas. Here, hybrid nanostructures composing of graphene-like film and bamboo-like carbon nanotubes have been synthesized in a simple, one-pot, catalyst-free chemical vapor deposition process. Pre-sputtered carbon coating on a copper substrate is considered as the key factor contributing to the final morphology. Furthermore, this hybrid nanostructure product has been shown to be a potential alternative material in solar cell and water desalination applications for sustainability.

10:45 AM *NM04.01.07

Smart Gel-Based Materials from Design to Application via Organic-Inorganic Hybrid Technology Meifang Zhu, Kai Hou, Peiling Wei, Tao Chen, Mengge Xia and Zhouqi Meng; State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai, China.

Smart gels-based materials can response external stimulus, such as temperature, pH value, light, electric, magnetic etc., via significant volume phase transition, have attracted a great amount of attentions.¹ Recently, organic/inorganic hybrids have been developed as a novel platform for design of gels-based materials with diverse scales and dimensions, showing multi-functions to broad their applications in smart sensing and biomedical fields. Here, combing our long-term research, series of organic-inorganic hybrid gels-based materials with diverse dimensions to meet practical applications requirements have been designed and prepared. In details, we prepared zero-dimensional (0D) nanogels, functionalizing with photothermal agents and anti-

cancer drugs to deal with cancer.²⁻⁴ As for 1D fiber, we obtained hydrogel fibers continuously with high efficiency based on a novel dynamic-crosslinking-spinning technology, the hydrogel fiber could be functionalized with conductive agents using a subtle coaxial spinneret, provide promising candidate for artificial nerves.⁵ Furthermore, several 3D smart bulk hydrogels were synthesized by in-situ introduction of functional nanoparticles into hydrogels, which could be used in fields of sensors including micro-channel valves and temperature switches.⁶⁻⁹

Acknowledgement: This work is financially supported by National Key Research and Development Program of China (2016YFA0201700/2016YFA0201702), Project of Shanghai International Science and Technology Cooperation Fund (14520710200) and Program for Changjiang Scholars and Innovative Research Team in University (T2011079, IRT_16R13), and the Program of Talents of Discipline to University (111-2-04), and Innovation Program of Shanghai Municipal Education Commission (2017-01-07-00-03-E00055).

References

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11:15 AM NM04.01.08

Nanostructured Devices and Catalysts for the Solar-Driven Reduction of CO₂ to Fuels [Marcel Schreier](#)¹, Michael Graetzel² and Yogesh Surendranath¹; ¹Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; ²Chemistry and Chemical Engineering, Ecole Polytechnique Federale de Lausanne, Lausanne, Switzerland.

CO₂-derived fuels present an attractive way towards a sustainable energy system. Mimicking natural photosynthesis by synthesizing carbon-based energy carriers using renewable energy allows for closing the anthropogenic carbon cycle and therefore represents an attractive way to store intermittent power, a challenge that has not yet found a satisfying solution.

Using solar power as the energy source for fuel synthesis will require large surfaces of absorbers and efficient catalysts, which should be fabricated from abundant materials. In this context, we show the application of cheap and scalable Cu₂O photocathodes in combination with molecular rhenium catalysts, both in solution and covalently bound to the nanostructured photoelectrode surface. Both systems feature substantial photocurrents and photovoltages, demonstrating protected Cu₂O photocathodes as viable candidates for solar-driven CO₂ reduction processes.

Moving from organic solvents into aqueous systems, we demonstrate the unassisted and sustainable splitting of CO₂ into CO and O₂ using perovskite photovoltaics as light absorbers and nanostructured gold and IrO₂ as catalysts, reaching an efficiency of 6.5 %. Building up on this work, we show how ALD modification of CuO nanowires can lead to a bifunctional and low-cost catalyst both for CO evolution from CO₂ and for the oxygen evolution reaction. By ALD modification, the wide product distribution of Cu-based catalysts could be narrowed to yield predominantly CO. Investigations into the microkinetics on these electrodes indicate that the selectivity change is due to the suppression of H₂ evolution, while the rate of CO production remains similar. Together with the use of a bipolar membrane, allowing for separating product gases while maintaining a sustained pH gradient, we used these electrodes demonstrate long-term solar CO production at an efficiency of 13.4 %, driven by a single 3-junction photovoltaic.

Going beyond the production of CO, a novel approach was used to gain insight into the mechanism of hydrocarbon formation at copper electrocatalysts. Studying this process in nonaqueous electrolytes at low temperatures allows for fine-tuned control of the proton donor and the CO binding strength, enabling activation-controlled kinetic studies over an extended parameter range. From these measurements, we are able to show that the rate of methane and hydrogen formation is governed by the competition of CO and H for surface sites while ethylene formation remains weakly impacted by this effect. The presentation illustrates the pathway to ever more insight and to efficient catalysts and devices for the reduction of CO₂, first to CO and subsequently to hydrocarbon fuels such as methane and ethylene.

11:30 AM RAPID FIRE PRESENTATION

SESSION NM04.02: Synthesis and Nanomanufacturing II

Session Chair: Meifang Zhu

Monday Afternoon, November 26, 2018

Sheraton, 2nd Floor, Back Bay C

1:45 PM NM04.02.02

Etched Metal Superhydrophobic Surfaces for Enhanced Condensation [Soumyadip Sett](#), Kalyan Boyina, Kazi Fazle Rabbi, Bassel Abu Jabal, Justin Olson, Longnan Li and Nenad Miljkovic; University of Illinois, Urbana, Illinois, United States.

Inspired from natural surfaces such as lotus leaves, water strider legs, the Namib desert beetle, and geckos' feet, the past few decades have seen significant research and development in the design and manufacturing of water repellent or superhydrophobic surfaces. For superhydrophobicity, surfaces need to be fabricated in two steps, initially creating micro/nanostructures, thereby providing roughness to the primary substrate, followed by the deposition of a low surface energy coating. The low surface energy leads to higher advancing and receding contact angles with water droplets, lower contact angle hysteresis, and hence easy droplet removal, promoting dropwise condensation and enhancing heat transfer. Recent studies have focused on chemical oxidation of metallic surfaces to form conformal micro/nanoscale structured metal oxide layers at the solid-air interface. The process is usually self-limiting, with both the oxide layer thickness and structure length scale ranging from 10 nm to 100 μm. Despite enabling efficient dropwise condensation, the metal oxide layers create a significant conduction parasitic thermal resistance due to their lower thermal conductivities (around 10 W/m.K) when compared to their pure metal counterparts (around 100 W/m.K). Furthermore, the application of metal oxide structures for industrial applications remains a challenge due to their poor durability. Here, we develop micro/nanostructured surfaces via direct electrolytic etching of metals. Different length scale surface structures and roughness are obtained by controlling the etching time and supply voltage of the electrolytic process. The etched metallic structures are made of the base metal, enabling higher thermal conductivity and lower parasitic resistance. Furthermore, the uniform metallic composition of the base metal and etched structures enables greater durability from thermo-mechanical stresses. Linear abrasion tests revealed greater durability of our etched metal structures when

compared to metal oxides. After coating the developed surfaces with a low energy self-assembled monolayer using vapor deposition, these surfaces show water droplet contact angles greater than 160°. Our work not only develops metal etched structured surfaces for durable condensation of steam and enhancement of condensation heat transfer coefficient, it enables a scalable manufacturing technique for durable superhydrophobicity.

2:00 PM NM04.02.03

Periodic Step Nanostructure Evolution at the Thin Film Gold/Substrate Interface Linfeng Chen¹, Maria Koifman Khristosov¹, Cecile Saguy³, Alex Katsman¹ and Boaz Pokroy^{1,2}; ¹Materials Science and Engineering, Technion–Israel Institute of Technology, Haifa, Israel; ²The Russell Berrie Nanotechnology Institute, Technion–Israel Institute of Technology, Haifa, Israel; ³Solid State Institute, Technion–Israel Institute of Technology, Haifa, Israel.

Nanoscale step structures have attracted recent interest owing to their importance in both fundamental and applied research, for example in adsorption, in catalysis, and in directing nanowire growth. In this in situ study, self-ordered vicinal-like surface structures were obtained by annealing of thin films of gold deposited on ultraflat Si/SiO₂ substrate. Annealing at temperatures ≥ 200 °C efficiently promoted the formation of vicinal-like structures on the inner gold/substrate interface. Gold grains near the inner surface exhibited an orientation with the [111] direction very close to the substrate normal. Furthermore, the step periodicity depended on the grain/substrate orientation angle. Smaller misorientation resulted in a larger average step periodicity, similar to that seen in regular vicinal surfaces of gold single crystals. Formation of low-index terraces and atomic steps at the inner gold interface (while the silica surface remains ultraflat) can be considered as a kind of solid–solid dewetting. We suggest that the formation of vicinal-like structures could be attributed to the thermally activated surface reconstruction driven by minimization of the total surface energy, which includes the gold/substrate cohesion energy and the GB energies. The process is controlled by diffusion of gold from the inner gold/substrate interface, most probably to the grain boundaries and then to the outer surface of the film. Substantial bulk diffusion across the film during annealing at 400 °C for 4 h can also provide a required mass transport from the inner to the outer surface. This work contributes to the understanding of the atomic step structure formation at the gold/substrate interface, which will be helpful in the use of vicinal-like surfaces as templates for growing of regularly spaced nanostructures. It also offers a method for the in situ investigation of both the grain orientation and the grain interface step periodicity in a given grain, and then can be utilized for further explorations of vicinal-like surfaces.

2:15 PM *NM04.02.04

Sustainable Hydrogen Solution Enabled Through Hydrolysis with Water-Reactive Nanoporous Metals Eric Detsi, John S. Corsi and Jintao Fu; University of Pennsylvania, Philadelphia, Pennsylvania, United States.

Water-reactive nanostructured metals and metalloids such as nano-Mg, nano-Al, nano-Zn and nano-Si with minimum surface oxide coverage have a broad range of potential applications. They can serve as catalysts for combustion, as active materials in hydro-powered spaceship engines, and as materials for onboard hydrogen production to power portable devices and hydrogen fuel-cell vehicles. The degree of reactivity of this class of materials with water is linked directly to their nanoscale size and to the extent in which the surface of these nanomaterials is covered with oxide. For example, smaller nanostructures exhibit faster kinetics in their reaction with water to produce hydrogen. Nearly oxide-free, ultrafine nanoscale structures with characteristic sizes in the range of 10-20 nm are commonly required for effective reactivity with water. Nanofabrication of these highly-reactive materials with such ultrafine structure sizes and minimum surface oxide coverage is still a fundamental challenge due to their high chemical reactivity. In this talk, I will present a novel, cost-effective, and scalable route to sustainable hydrogen for on-board application. Our new route involves: (i) the hydrolysis of neutral water with nanoporous aluminum to produce hydrogen and aluminum hydroxide without the typical use of catalysts, and (ii) the recycling of aluminum hydroxide back to aluminum metal without any CO₂ footprint. While over 95% of hydrogen used worldwide is produced by steam reforming of natural gas, this method is not sustainable because CO₂ is co-produced during the process. Sustainable hydrogen can be generated by electrolysis of water into hydrogen and oxygen, but this method is relatively expensive (~40-53 kWh of energy is needed to produce 1 kg of H₂) and not very efficient (40-60% yield). The new method presented in this talk requires only 24-47 kWh of energy to produce enough nanoporous aluminum to generate 1 kg of hydrogen with 50-85% yield by hydrolysis in neutral water. [1,2]

References:

- [1] Eric Detsi and John S. Corsi: “*Bulk Nanoporous Aluminum for On-board Hydrogen Generation by Hydrolysis*”. Patent Application, #18-8558-104377.000203
- [2] John S. Corsi, Jintao Fu, Zeyu Wang, and Eric Detsi: “*Sustainable Hydrogen Solution Enabled through Hydrolysis of Nanoporous Aluminum in Neutral Water*” (Under review)

2:45 PM NM04.02.05

High Temperature Nanomanufacturing for Emerging Technologies Yonggang Yao; University of Maryland, College Park, Maryland, United States.

High temperature processing can provide sufficient activation energy for materials’ compositional, structural, and morphological evolutions, and is essential for various kinds of reactions, synthesis, and post-treatment. However, the current high temperature heating sources, mostly furnaces, are far from satisfying for nanomaterials processing owing to their bulky size and limited temperature and ramp range (~1300 K, ~10 K/min). Here we have focused on the study of electrical triggered Joule heating as a new route for high temperature engineering of nanomaterials toward nanomanufacturing. We developed facile, highly stable and controllable heating strategies for micro/nanoscale high temperature engineering. Ultrahigh temperature annealing (>2500 K) is applied to carbon nanomaterials to address the defects and poor interfacial problems. Ultrafast thermal shock (~2000 K in 55 ms) is applied to metal salt loaded carbon substrates for *in-situ* synthesis of ultrasmall, well-dispersed nanoparticles. The high temperature engineering on nanomaterials is highly facile, energy-efficient, and reliable toward scalable nanomanufacturing. More exciting results and products are expected for various nanomaterials during/after the unique high temperature engineering.

3:00 PM BREAK

3:30 PM OPEN DISCUSSION

3:45 PM NM04.02.07

Additive Manufacturing of Gold Nano-Dimers Under Ambient Conditions Chenglong Zhao; University of Dayton, Dayton, Ohio, United States.

The terms “nonmanufacturing” and “nanofabrication” are often used interchangeably. Recently, Liddle *et al.* have distinguished between nanomanufacturing and nanofabrication by using the criterion of economic viability. Nanomanufacturing, which utilizes efficient and cost-effective nanofabrication methods to manufacture nanostructures and functional devices, has the characteristic of being a source of money, while nanofabrication is often a sink. Nanomanufacturing is indispensable in today’s “nano-world” as the devices keep shrinking in size. The functional devices with internal building blocks at the nanoscales have intriguing and extraordinary properties for many applications. For example, the color of gold nanoparticles

distributed in a material does not appear yellow its familiar color for bulk gold; instead, the color of nano-gold changed to ruby red. The melting point of gold at the nanoscale is also significantly lower than its bulk counterparts.

There are a large number of nanofabrication approaches available, but only a few are suitable for large-scale nanomanufacturing. Therefore, the exploration of new technology is desperately needed to expand the nanomanufacturing toolbox. Here, we demonstrate a method that can be used for affordable nanomanufacturing at the ambient conditions. A low-cost continuous-wave (cw) laser is used to directly kick and transfer nanostructures from one substrate to another in ambient conditions. Unlike the direct laser ablation method, where expensive pulsed lasers are typically used to ablate the materials disruptively, the method demonstrated here has no damage on the nanostructures, therefore, this method can maintain the geometry of nanostructures and transfer them selectively in an additive manner.

4:00 PM *NM04.02.08

Sustainable Nanomanufacturing Research at NSF Khershed Cooper; Advanced Manufacturing, National Science Foundation, Alexandria, Virginia, United States.

Nanomanufacturing is the fabrication of nano-scale building-blocks (nanomaterials, nanostructures), their assembly into higher-order structures, and the integration of these into larger scale systems with manipulation and control at nano-scale. Typically, the scale ranges from 1-100 nm. Processes can be top-down (additive/subtractive) or bottom-up (self- and directed-assembly) or an integration of the two. Manufacturing processes need to be scalable, controllable, reproducible, efficient and low cost. The combination of large-scale production and nano-scale products raises environmental and sustainability issues. Questions needing answers are: 1) How can industry develop new nanotechnologies in a responsible and sustainable manner; 2) How can it be ensured that nanomanufacturing processes are safe for producers and products are safe for consumers and the environment. This talk discusses NSF-supported projects in sustainable nanomanufacturing that address life-cycle analysis, recycling, environmentally-benign nanomaterials and processing, green nanomanufacturing, clean energy, wastewater treatment, among others. It will conclude with a discussion on future directions and their implications.

4:30 PM RAPID FIRE PRESENTATION

SESSION NM04.03: Poster Session I: Synthesis and Nanomanufacturing
Session Chairs: Babak Anasori, Monica Jung de Andrade and Maria Perez Barthaburu
Monday Afternoon, November 26, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

NM04.03.01

Heterojunctions TiO₂/SrTiO₃ Prepared by Core-Shell Route Maria A. Zaghete, Rafael Amoresi, Isabela Iani and Natalia Jacomaci; DBQT, UNESP, Araraquara, Brazil.

During the last decades new methods or materials have been developed looking for better photocatalytic activity to TiO₂ such as addition of dopant, construction of heterojunctions like TiO₂/SrTiO₃. These modifications are based on charge transfer, heterojunctions shown a good alternative that present synergy of intrinsic conduction potential bands. In this way the composites TiO₂/SrTiO₃ present as good alternative in that one, SrTiO₃ shows band gap of 3.4 eV. In this work, the composite was obtained recovering SrTiO₃ nanoparticles with titanium sol gel. This procedure showed up easy and fast compared to current methods used to obtain composites with both ceramics phases. To obtainment the TiO₂/SrTiO₃ heterojunction the SrTiO₃ particles (1% and 5% m/m) was insert into titanium sol-gel solution resulting a suspension, which remained on soft stirring at room temperature 24 hours. Then the gel was dried at 100 °C for 24 hours, after that was thermally treated at 400 °C for 2 hours. The interface showed interesting characteristics those results in defects at medium range. The appearance of the intermediate phases observed in the interface region is due to the cubic structure of SrTiO₃ which offer lower free energy of crystallization, and thus the growth of the monoclinic and rhombohedral TiO₂ phases. The heterojunctions TiO₂/SrTiO₃ presents unusual photoluminescent as a result of these intermediate phases that promote structural defect. The new route to the formation of heterojunction allowed a solid-solid interface between TiO₂ and SrTiO₃ particles which is responsible for promote electronic, optical and photocatalytic properties due to improvement in charge carrier transfer in this region. Acknowledgments (FAPES- 2013/07296-2) and CNPq-PIBIC

NM04.03.02

Synthesis and Conjugation of Selenium-Based Nanoparticles and its Capacity for Generation of Cytotoxic Reactive Oxygen Species Nadja M. Maldonado Luna¹, Myrna Reyes-Blas², Sonia J. Bailon Ruiz³ and Oscar J. Perales Perez⁴; ¹Mechanical Engineering, University of Puerto Rico at Mayagüez, Mayaguez, Puerto Rico, United States; ²Chemistry, University of Puerto Rico at Mayagüez, Mayaguez, Puerto Rico, United States; ³Chemistry, University of Puerto Rico at Ponce, Ponce, Puerto Rico, United States; ⁴Material Sciences and Engineering, University of Puerto Rico at Mayagüez, Mayaguez, Puerto Rico, United States.

The use of nanoparticles in nanomedicine is dependent of their bio-compatibility, size, physicochemical stability, absence of aggregation in aqueous phase and capacity to generate toxic species at controlled doses. It is expected that nanoparticles with intrinsic optical properties and stability in water can be ingested by cells and generate toxic species like reactive oxygen species (ROS). Selenium is commonly used as an anti-fungal agent, and as a nutritional supplement in its inorganic and organic form. The use of selenium-based nanoparticles in the biomedical field builds the basis of a new type of treatment based on bio-essential elements that will be inherently less toxic to normal cells. Based on these considerations, this research is focused on the size-controlled synthesis of selenium based-nanoparticles, its conjugation with proteins in order to improve its stability in water and the evaluation of their capacity to generate ROS in aqueous phase. The synthesis of selenium nanoparticles was achieved in a single step through microwave-assisted synthesis by reduction of sodium selenite (Na₂SeO₄) to elemental selenium in presence of ethylene glycol, sodium chloride and polyvinylpyrrolidone (PVP) at basic pH conditions. UV-vis spectra of the suspension of Se nanoparticles produced at different times of reaction (i.e. 3, 5 and 8 minutes) and constant temperature (180°C) exhibited strong absorption peaks centered on 260nm. These peaks are attributed to the excitation of the localized surface plasmons that causes strong light scattering by the electric field at a wavelength (260 nm), where resonance occurs. These nanostructures are then conjugated with albumin via a ligand exchange approach to improve its stability in water and protect the integrity of the core.

The capacity of generation of ROS by these size-controlled selenium nanoparticles will be determined and compared to well-known CdSe/S photosensitizer, also conjugated with albumin.

NM04.03.03

Graphene-Based 'Hybrid' Mesoporous Capacitive Deionization Electrodes for Use in Water Desalination [Sanju Gupta](#), Alex Henson and Brendan Evans; Western Kentucky University, Bowling Green, Kentucky, United States.

In this work, we developed interconnected network of mesoporous graphene-based electrodes to achieve optimal desalination during capacitive deionization (CDI) of brackish water, attributed to higher specific surface area, electrical conductivity, good wettability of water, environmentally safe, efficient pathways for ion and electron transportation, as potential successor of current filtration membranes. While the pressure driven transport data on highly ordered, continuous, thin films of multi-layered graphene oxide and holey graphene is expected to demonstrate faster transport for salt water, higher retention for charged and uncharged organic probe molecules with hydrated radii above 5 Å as well as modest retention of mono- and di-valent salts for ~150 nm thick membranes. The highly ordered graphene nanosheets and nanoscaled porous graphene in the plane of the membrane make organized, molecule-hugging cylindrical and spherical channels, respectively, thus enhance the permeability and hydrodynamic conductivity. The results illustrate that both the mesoscale and nanoscale pores are favorable for enhancing CDI performance by buffering ions to reduce the diffusion distance from external electrolyte to the interior surfaces and enlarging surface area analogous to electrochemical double-layer supercapacitors where in electrical energy storage is through concurrent surface ion adsorption and electron transfer. We determined the salt ion species rejection by composite CDI electrodes by > 65% for actual seawater in one cycle which can be further increased through use of nanoparticles for ion selectivity. This work is supported in parts by KY NSF EPSCoR and WKU Research Foundation internal grant.

NM04.03.04

3D Hierarchical Structure for Water Splitting with Extraordinarily Enhanced Photoactivity [Junho Jun](#), Suchoel Ju, Seungho Baek, Minseop Byun and Heon Lee; Korea University, Seoul, Korea (the Republic of).

As the need for renewable energy continues to increase, hydrogen, the most promising clean energy source, is receiving a great deal of attention. Solar water splitting, which is the most efficient way to produce hydrogen without any pollutants, has been actively studied since the discovery of the TiO₂ photocatalyst by Fujishima in 1972. Nevertheless, the production efficiency of this method is still very low, making it impractical for commercial use, and many studies are underway to improve the efficiency of solar water splitting. The mechanism of the reaction at the photoelectrode can be roughly divided into three sub-categories: absorption (E_{abs}), electron separation (E_{sep}), and surface reaction (E_{trans}), each with its own efficiency. In order to produce an efficient optical electrode, the material used for solar water splitting must be efficient for all three reactions. Especially, it is challenging to decouple the efficiency between light absorption and charge separation ($E_{\text{sep}} \times E_{\text{trans}}$).

Nanostructuring is one of the most efficient method to overcome this coupling issue. By nanostructuring with one or more materials, nanostructured layer can have increased light absorption with even a thin layer, which is good condition for short carrier diffusion length of oxide materials such as BiVO₄, Fe₂O₃.

Herein, We fabricate Au/BiVO₄ 3D nanostructured photoelectrode via nanoimprint lithography(NIL) and various deposition method. NIL has advantages on fabrication of nanostructure in large area. Using NIL, we can fabricate uniform nanostructure such as nanocone or high-aspect ratio pillar. After that, we deposit various materials on nanostructured template by Atomic layer deposition(ALD) or photo assisted electrodeposition (PED). This 3D hierarchical structure has an optical effects that can enhance light-matter interaction including anti-reflection and light-scattering, and also help generated electron-hole pair to separate owing to enlarged interface and etc. Compared with flat sample, we confirmed that This 3D hierarchical photoanode can greatly increase $E_{\text{sep}} \times E_{\text{trans}}$.

NM04.03.05

One -step Flame Synthesis of W/Mo/N-Doped Titanium Dioxide Nanoparticles for Enhanced Photocatalytic Activity [Yujuan Zhang](#), Zhizhong Dong, Bernard Kear and Husnu E. Unalan; Rutgers, The State University of New Jersey, Piscataway, New Jersey, United States.

W/Mo/N-doped titanium dioxide (W/TiO₂) nanoparticles are synthesized using a multiple diffusion flames setup, where tungsten mesh, molybdenum wire, and CN₂H₂ is utilized as doping source and titanium isopropoxide (TTIP) serves as precursor for TiO₂. At relatively lower tungsten loading rates, nanoparticles are produced in W-TiO₂ form with an obvious shift angle (0.15°) in the XRD pattern. However, at high tungsten loading rates, homogeneous nucleation of WO₃ occurs concurrently with homogeneous nucleation of TiO₂, thereby leaving less tungsten ions to be doped into the TiO₂ matrix. Molybdenum wire is placed on top of the tungsten mesh to achieve W-Mo co-doping of TiO₂. Cyanamide solution is injected into the central flame to produce N-doped TiO₂. UV-Vis spectroscopy shows that the as-synthesized doped nanoparticles possess enhanced absorbing ability in the visible light wavelength range compared with that for non-doped TiO₂ nanoparticles. Photocatalytic activity of the doped nanoparticles are tested via batch phase water reduction with methanol as a sacrificial agent. As-synthesized samples having a higher H₂ evolution meanwhile are more active under dark and UV illumination comparing to that for Pt25.

NM04.03.06

Ultra-Fast Additive Nano-Patterning Process and Its Applications with Large Area and Flexible Form-Factors [Hanul Moon](#)¹, Hyeonho Jeong¹, Han-Jung Kim¹, Min Yoon¹, Chang-Goo Park², Yong Suk Oh¹, Hyung Jin Sung¹, Dae-Geun Choi² and Seunghyup Yoo¹; ¹Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of); ²Korea Institute of Machinery and Materials, Daejeon, Korea (the Republic of).

Nano-scale patterns have been intensively studied in wide range of fields because they provide enhanced performance or new functions that cannot be observed in macro- or micro-scale patterns. However, conventional nano-patterning process based on lithographic methods have limited wide-spread of nano-patterns due to complex process steps requiring expensive equipment. To fully open the possibility of nano-patterns in various fields, an alternative method is required to fabricate nano-patterns in a facile way that secures significantly improved cost-effectiveness, and versatility allowing large-area fabrication or various form-factors such as flexibility. Here, we proposed an additive nano-patterning process from solution route using selective-wetting phenomenon in response to such requirements.

The proposed process proceeds to 1) nano-imprinting on to hydrophobic/hydrophilic bilayers and 2) solution dragging. Appropriate post-processes such as annealing can be followed. The former step results in 3D structures consisting of nano-scale engraved hydrophilic parts and embossed hydrophobic parts. Then, by dragging a solution on top of the surface, the solution is automatically confined in the engraved hydrophilic parts without residue on the embossed hydrophobic top surface by selective-wetting phenomenon. The 3D engraved structure is also essential to cause nano-patterns with sufficient amount of target materials. The results verified that the yield of the nano-patterning process is almost perfect once the imprinting onto the bilayer is successful. 150 nm-diameter dot arrays of Ag over the area of 10 cm × 10 cm were successfully fabricated with high yield, and was served as a plasmonic color filter of uniform magenta color. The mechanism of the proposed nano-patterning process was analyzed using fluid-dynamics simulation, and verified control parameters aiming at higher process speed and smaller pattern size.

Virtually, any kind of solutions can be applied to the process, and nano-patterns of Ag, metal-oxide, and organic materials could be fabricated by using a metal-nano-particle ink, a sol-gel solution, and organic solvent. In terms of throughput, the dragging speed of solution could be over 4.5 m/min. The selective-wetting phenomenon also enables self-aligned multiple deposition of nano-patterns, thus allows thickness controllability and multi-layer nano-patterns consisting of different materials. Thanks to the simple and facile process, the proposed method could efficiently make nano-patterns on various

substrates including plastics and papers. According to the aforementioned advantages, we believe the proposed process significantly improves the usefulness of nano-patterns in wide range of fields, especially if they require nano-patterns over large-area with various form-factors fabricated by a cost-effective way.

NM04.03.07

Investigation of Magnetic Properties of Electrodeposited Cobalt Ferrite Films with Control of Grain Size and Surface Morphology Brent Williams and Carlos Castano; Mechanical and Nuclear Engineering, Virginia Commonwealth University, Richmond, Virginia, United States.

Cobalt ferrite is a material which has been researched for its applications in spintronics, magnetic sensing, and catalysis. Though synthesis methods have been established for formulating films including pulsed laser deposition, chemical vapor deposition, and rf sputtering most of these methods need high vacuum and power sources to formulate a film. Within this work a facile method for synthesizing films through electron deposition without the need of high energy appliances. The main component for the process includes an aqueous solution which can be reused with reproducible results. Through varying Co/Fe content, time, potential, and ramp rates, control over grain size and morphology of the surface was established. X-ray diffraction (XRD), energy dispersive spectroscopy (EDS), and scanning electron microscopy (SEM) were used to confirm phase, composition and surface morphology. Variations in magnetic properties such as transition temperatures, magnetic saturation, coercivity, were observed from grain size and surface morphology. The current research seeks to improve facile thin film methods which may be facilitated in a variety of magnetic applications.

NM04.03.08

On-Demand Band-Gap Tuning of Colloidal Perovskite Nanocrystals Enabled by Fast Anion-Exchange Reactions Kameel K. Abdel-Latif, Robert W. Epps, Michael Bowen, Corwin Kerr and Milad Abolhasani; Chemical Engineering, North Carolina State University, Raleigh, North Carolina, United States.

Since the discovery of the colloidal perovskite nanocrystals three years ago, they have rapidly grown to become one of the most promising classes of nanomaterials for large-scale applications in optoelectronic devices. Anion exchange reactions of the highly luminescent cesium lead halide perovskites (CLHPs) provide a facile post-synthetic route for the tuning of the absorption/emission band-gap of CLHPs. These post-synthetic reactions allow the utilization of CLHPs in various optoelectronic applications including third-generation photovoltaic cells and light emitting diodes. Studies of anion-exchange reactions are typically conducted using the time- and material-intensive flask-based synthesis approach. Batch scale synthesis strategies are notorious due to (a) batch-to-batch variation, (b) inefficient and irreproducible mixing timescales, (c) manual sampling and characterization at room temperature, and (d) poor size distribution of the resulting nanocrystals after scale-up. Here, we present a modular multiphase microfluidic strategy with an *in situ* spectral monitoring capability that enables the systematic kinetic study of anion-exchange reactions of CLHP nanocrystals. Utilizing the microfluidic nanocrystal synthesis platform, we monitor absorption and emission spectra of CLHPs, in real-time, over residence times ranging between 100 ms and 17 min. In-situ monitoring of the optoelectronic properties of CLHPs over different synthesis conditions enables fundamental and applied studies of structural tuning of CLHPs via anion-exchange reactions. The enhanced mixing feature of the multiphase flow along with the novel anion-exchange framework using ZnX_2 ($X=I$ or Cl) facilitates on-demand bandgap tuning of high-quality CLHPs (*i.e.*, narrow size distribution with high quantum yield) via a positive feedback loop in which synthesis parameters are varied until the target optoelectronic characteristics are achieved.

NM04.03.09

Corporate Responsibility—A Green Initiative to Reduce Chlorobenzene Based Chemistries in Semiconductor Processing Monique Farrell, Kevin Frey and John Mason; Northrop Grumman, Linthicum, Maryland, United States.

Climate change and an increase in endangered species, are examples of technological advances negatively impacting the environment. As technology demands increase, an earnest effort to reduce the environmental impact of processing and manufacturing related activities is critical. From a business perspective, minimizing or removing toxic chemicals from processes, is a high impact area that can increase work environment safety and decrease waste management costs. This work presents processing considerations when transitioning to greener alternative polymer resist solvents, for applications in nanomanufacturing with sustainability considerations. Within government contracting, process modifications that change product form, fit, or function require qualification and at minimum justification. This work presents the conversion from a chlorobenzene to anisole based solvent using a 495 kMW polymethyl methacrylate polymer resin, without impacting form, fit, or function of the intended device. Resist conversion is of interest as the difference in the substituents of the two solvents, impact the effective toxicity of the materials. Specifically, the oral median lethal dose (LD_{50}) for chlorobenzene is 1110 mg/mL, while anisole is 3700 mg/mL. Developing a process that utilizes anisole as opposed to chlorobenzene, addresses this safety concern and contributes to green initiatives worldwide. Within this work, an electron beam lithography fabricated transistor consisting of a source, drain and gate were converted from a chlorobenzene based resist to a process utilizing an anisole solvent; while maintaining process of record specifications. The purpose of this work is to provide a starting platform for individuals seeking to convert from a chlorobenzene solvent to an anisole based resist, for sub-micron lithography steps.

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NM04.03.10

The Role of the Counterion on the Crystal-Shape and Photocatalytic Properties of ZnO Nanostructures Grown via Hydrothermal Route Ariadne C. Catto¹, Luis F. da Silva¹, Mateus Ferrer², Osmando F. Lopes³, Valmor R. Mastelaro³ and Elson Longo¹; ¹Federal University of São Carlos, São Carlos, Brazil; ²University of São Paulo State—UNESP, Bauru, Brazil; ³University of São Paulo, São Carlos, Brazil.

Nowadays, a concern over environmental problems has enhanced our awareness of the need to develop alternative and environmentally friendly process aiming at increase environmental protection. For the treatment of waste water and pollutant degradation, photocatalysis is considered one of the most promising and sustainable way due to its high-efficient, eco-friendly, low toxicity and low cost.

Zinc oxide (ZnO) exhibiting different morphologies and high surface/volume ratio exhibit many favorable optical, electronic and surface properties leading it a promising candidate in field of photocatalysis as a sustainable and eco-friendly technology. Motivated by these considerations, the goal of this study consisted to investigate the influence of zinc precursor on the structural, microstructure, surface and photocatalytic properties of nanostructured ZnO films grown under hydrothermal conditions.

The nanostructured ZnO films were grown via hydrothermal method using different zinc salts, including acetate ($Zn(CH_3COO)_2 \cdot 2H_2O$), nitrate ($Zn(NO_3)_2 \cdot 6H_2O$), and sulfate ($ZnSO_4 \cdot 7H_2O$) under identical conditions. The crystalline structure and morphological features were investigated by X-ray diffraction (XRD) and field-emission scanning electron microscopy (FE-SEM) measurements, while the surface properties were probed by using X-ray photoelectron spectroscopy (XPS).

XRD patterns of the ZnO films were indexed to the wurtzite ZnO structure, however the sample synthesized from zinc sulfate also presented additional peaks assigned to the zinc hydroxy-sulfate-hydrate phase. FE-SEM analyses reveal that the morphology of the ZnO structures is strongly dependent on the zinc salt. The zinc nitrate provides the formation of the same morphology of the acetate, with an anisotropic growth preferentially along the (0001)

direction resulting in hierarchical nanorod-like structures with an average diameter of ca. 90 nm. The average rod diameter was larger for ZnO samples synthesized using zinc acetate (ca. 2 times). Regarding the zinc sulfate, the change in microstructure was more significant, where SEM images revealed the formation of hexagonal microplate-like structures. In this case, the growth along (0001) was dramatically suppressed, producing a micrometric 2D morphology.

With respect to photocatalytic activity, the ZnO samples were studied for the degradation of methylene blue (MB), and rhodamine B (RhB) dyes under ultraviolet light. The ZnO film prepared from zinc nitrate exhibited the best photocatalytic activity compared to other samples, followed in turn by the sample prepared with acetate, and sulfate. The enhancement of photocatalytic activity was attributed to structures size, surface morphology including the higher fraction of exposed (0001) ZnO polar facets, as well as the presence of oxygen defects.

NM04.03.11

High Volume Manufacturing of Boron Nitride NanoBarbs [Steve Wilcenski](#); BNNano, Inc., Cary, North Carolina, United States.

Boron nitride nanotubes have become a material of significant interest due to their unique combination of physical and chemical properties. Among the desirable properties are the high thermal stability, high thermal conductivity, electrical resistivity, very high strength and stiffness, and super hydrophobicity. This combination of properties makes boron nitride nanotubes an attractive material for use in wide-ranging markets from aerospace to automotive and defense to biomedical.

The most significant limitation to these potential applications has been the lack of supply of high purity boron nitride nanotubes in the marketplace. Recent advances in the manufacture of this material are now enabling additional research and product development. The high-volume NanoBarb process is uniquely positioned to manufacture and supply commercial volumes of high purity boron nitride nanotubes to fulfill this need.

NM04.03.12

Rational Design of Novel Dielectric and Photocatalytic Core-Shell Nanomaterials by a Sacrificial Template Method [Prabodha M. Balapuwaduge](#)¹, Swati Naik¹, Liang Hong², Robert Klie² and Gabriel Caruntu¹; ¹Central Michigan University, Mount Pleasant, Michigan, United States; ²Physics, University of Illinois at Chicago, Chicago, Illinois, United States.

SrTiO₃ has a well-known perovskite crystalline structure and exhibits excellent dielectric, electro-optic and catalytic properties, being the leading candidate in many cutting-edge technological applications. We report here on the rational synthesis of SrTiO₃/TiO₂ nanodimensional heterostructures by using TiO₂ colloidal nanocrystals as sacrificial templates under different reaction conditions, with the main goal of achieving control over the morphology (size, shape), internal structure and surface composition of the resulting nanoparticles. Both the synthesis of TiO₂ nanocrystals and their subsequent conversion into SrTiO₃ were performed using a hydrothermal method. These nanostructures were characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), vibrational spectroscopy (Fourier transform infrared spectroscopy (FT-IR) and Raman spectroscopy) and optical absorption measurements. Various reaction parameters have been finely tuned in order to optimize the reaction conditions. A detailed characterization of the dielectric properties of these nanopowders was carried, revealing that dielectric permittivity has a value around 120 at room temperature with a low loss, which make these nanomaterials desirable for applications in energy storage and as dielectrics. Moreover, the photocatalytic properties of SrTiO₃-TiO₂ heterostructures were analyzed by using dye degradation method under ultraviolet light. An enhanced photocatalytic activity was observed, which can be ascribed to the improved charge separation between photogenerated electrons and holes in conduction and valence bands of SrTiO₃ and TiO₂. Thus, this synthesis strategy of nanoscale heterostructures is useful to develop functional materials with superior efficiency for implementation into functional electrical devices, as well as photocatalysts.

NM04.03.13

Hierarchical Porous Solvogel Monoliths—Synthesis and Application [Marie-Christin Röpert](#), Christoph Weidmann and Rainer Ostermann; Westphalian University of Applied Science, Recklinghausen, Germany.

Bimodal pore systems are of utmost importance for many high-tech applications, for example in chromatography or as carrier material for catalysts. A hierarchical structure with both micro/mesopores and macropores allows to obtain both high surface areas and good transport properties (accessibility of and low pressure drop in the porous structure). The inorganic sol-gel-chemistry offers reliable routes to synthesize materials with tunable pore sizes, most prominently via phase separation during condensation and solidification of silica precursors [1]. This concept was successfully transferred from inorganic to organic polymers, based on the radical polymerization of divinylbenzene [2]. In contrast to these studies, we extend this strategy to novel bicontinuous porous polymers, which form readily under mild conditions. Therefore, we use the cyclotrimerization of inexpensive diisocyanates to obtain materials with continuous macropores and very high adsorption capacities. The ratio of solvent, polymer and diisocyanate in the studied system can be varied over a wide range, allowing to independently control both pore size and volume. In addition, the isocyanate chemistry allows using tailored prepolymers to optimize the properties (e.g. shrinkage) or functionalizing the resulting solvogels for adjusting polarity and incorporating catalysts. Furthermore, the crosslinked polyisocyanurate network is thermally and mechanically stable and therefore suitable for applications involving high pressure or temperature.

We will present the considerations leading to systems of suitable solvents and polymers for controlled phase separation, focus on the parameters for synthesis and functionalization, as well as giving a first outlook on applications.

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NM04.03.14

Effect of Surface Modification and Confinement Effect of Crystalline and Amorphous SiC for Sustainable Renewable Energy and Environmental Remediation [Aakash Mathur](#)¹, Dipayan Pal¹, Ajaib Singh¹, Rinki Singh³ and Sudeshna Chattopdhyay^{1,2,3}; ¹MEMS, Indian Institute of Technology Indore, Indore, India; ²Physics, Indian Institute of Technology Indore, Indore, India; ³BSBE, Indian Institute of Technology Indore, Indore, India.

Silicon carbide (SiC) became an important material whose popularity has been constantly increasing due to its excellent mechanical, electrical, optical and chemical properties, which recommend it for cleaner, smaller, stronger and more efficient technologies for solar cell applications as well as for environmental monitoring and depollution^[1]. The occurrence of different polytypes of SiC makes it suitable for photocatalytic material for hydrogen generation and environmental remediation^[2] in crystalline SiC forms and for solar cell applications as diffusion barriers, antireflection coatings in amorphous SiC form^[3]. Herein, the confinement effects of the different polytypes of crystalline SiC particles and amorphous SiC thin films are being addressed. Here, we report the significant enhancement of photocatalytic activity and substantial bandgap narrowing of EG/SiC composites. Graphitization of SiC by high temperature thermal decomposition method^[4] has been employed to grow epitaxial graphene (EG) on silicon carbide (EG/SiC hybrid system) to modify the surface and interface structure in controlled manner. The systems have been characterized by Raman and UV-vis spectroscopies along with the XRD, SEM and HRTEM analysis. Significant enhancement of the photocatalytic activity (~1000%) and bandgap narrowing (~30%) of

EG/SiC systems were observed, relative to the bare SiC, depending on the quality and quantity of the EG and heterojunction interface structures. Furthermore, we report on a dual ion beam sputtering assisted deposition (DIBSD) of confined SiC thin films (about 450 nm to 20 nm thickness range) with low surface roughness. The thin films have been characterized by Spectroscopic Ellipsometry technique along with AFM, XPS, XRD and XRR. Clear indication of systematic band gap variation was observed along with the changes in surface roughness as an effect of confinement of DIBSD grown SiC films. The effect of different types of SiC (polytypes/amorphous) at their different confinement levels (thin films, nanoparticles) have been studied further to explore the potential application in photocatalysis for renewable energy and environmental remediation (e.g., waste water treatment) and for different optoelectronics and solar cell applications

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NM04.03.16

Core-Shell Nanoparticle Synthesis—A Novel Strategy to Achieve Heterostructures at the Nanoscale using a Molten Salt Solvent Benjamin Levitas¹, Yuexing Zhu¹, Katsuyoshi Kakinuma² and Srikanth Gopalan¹; ¹Boston University, Boston, Massachusetts, United States; ²Fuel Cell and Nanomaterials Center, University of Yamanashi, Yamanashi, Japan.

In the last three decades, solid oxide fuel cells (SOFCs) have garnered significant interest for viable alternative energy systems owing to their high electrical efficiency and fuel flexibility. In this work, we introduce a novel synthesis of cathodes in SOFCs, wherein oxygen reduction occurs in two steps—adsorption and electronation, and surface/bulk diffusion to incorporation sites. Transition metal oxides such as strontium-doped lanthanum manganite (LSM) and strontium-doped cobalt iron oxide (LSCF) have been used as cathode materials, however both individually lack the key characteristics to successfully complete oxygen reduction. Furthermore, the accumulation of chromium (chromium poisoning) on SOFC cathodes is known to significantly hinder the performance of the cells. Incorporating core-shell composites as the cathode material could alleviate this problem: effectively combining the functionalities of both materials and providing a nanoscale protection from Cr poisoning with a shell such as Cr-doped LSM (LSCM). Core-shell oxide composites have broad applications in fuel cells, catalysis, magnetic devices, spintronics, nanophotonics, and many more fields. However, synthesizing core-shell composites previously has proved difficult requiring multiple steps, resulting in non-uniform core-shell structures. In this work we propose utilizing a molten salt synthesis process to create core-shell composites with precise composition with relative ease. The core is synthesized using high-temperature calcination and ball milled with the precursors of the target shell material. The milled powder mixtures are added to a LiCl-KCl eutectic melt to form core-shell hetero-structures via heterogeneous nucleation. Prior results have shown the successful formation of LSM and LSCF using the molten salt synthesis, along with the formation of core-shell LSCF-LSM hetero-structures. Synthesis temperatures dropped from the conventional 1000 °C to 500 °C, with dwell times as low as 10 minutes. Furthermore, SOFC cathodes consisting of LSCM were found to have stable polarization resistances, whereas the polarization resistance in LSM cathodes steadily increased. This result provides a strong motivation to further explore LSCM as a shell for core-shell cathodes to ensure protection from chromium poisoning. In essence, this work demonstrates an inexpensive, sustainable method to synthesize core-shell cathodes that can simultaneously provide high power densities and low rates of degradation arising from Cr-poisoning.

NM04.03.17

All-Solution-Processed Transistors on Paper for Cheap Flexible Electronic Applications Do Hoon Lee, Taewan Kim, Hyun Soo Kim, Ye Rim Lee and Byung Yang Lee; Korea University, Seoul, Korea (the Republic of).

Paper electronics is receiving great interest because it is one of the best candidates for next generation devices with many useful features such as low cost, disposability, and flexibility. In this work, we demonstrate the fabrication of zinc oxide nanowire (ZnO NW) field-effect transistors (FETs) on paper with facile, low-cost and large area manufacturing. This was achieved using the high absorption property of paper. By absorbing silver nanowire (AgNW) solution into the paper, AgNW network formed on the paper surface that acts as a gate electrode with low sheet resistance ($9 \pm 5 \Omega/\text{sq}$) and low RMS roughness of $120 \pm 20 \text{ nm}$. Then, a dielectric layer was deposited by injecting poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) solution on top of the gate. This enabled precise control of the dielectric layer thickness by controlling the concentration of the solution according to pore size of the paper. As a result, a uniform thin dielectric layer of less than 10 nm was formed. The ZnO NWs were self-assembled on a dielectric layer by a simple dipping and pulling method. Afterwards, electrodes were formed via inkjet printer. The all solution-processed flexible FETs on paper exhibit electrical performance with charge carrier mobility of $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and current on/off ratio of 2×10^3 . Furthermore, even after 100 bending cycles, only a 10% decrease in mobility was observed. By utilizing simple equipments such as a vacuum chamber and a syringe pump alone, we could produce outstanding FETs that are desirable for cheap flexible electronic applications.

NM04.03.18

Magnetic Separation and High Reusability of Chloroperoxidase Entrapped in Multi Polysaccharide Micro-Supports Sonia García-Embid^{1,2}, Francesca Di Renzo³, Laura De Matteis^{4,2}, Nicoletta Spreti³ and Jesús M. de la Fuente^{1,2}; ¹Instituto de Ciencia de Materiales de Aragón (ICMA), CSIC/University of Zaragoza, Zaragoza, Spain; ²CIBER-BBN, Instituto de Salud Carlos III, Madrid, Spain; ³Department of Physical and Chemical Sciences, University of L'Aquila, L'Aquila, Italy; ⁴Instituto de Nanociencia de Aragón, University of Zaragoza, Zaragoza, Spain.

The World Commission on Environment and Development introduced the term sustainable development, indicating the present need of modern industrial processes to optimize the use of raw materials, reduce waste and avoid the use of toxic molecules. Amongst the approaches used over the years to achieve this sustainability, biocatalysts, especially enzymes, have been in the spotlight due to their great properties. Sustainability of enzymatic catalysis is maintained through the whole cycle: from their production (living organisms) to the waste treatment.[1] However, their present application at industrial scale is hampered by the high costs in their production that decrease cost-effectiveness of their application. Reutilization of the enzyme is therefore the tool to obtain more cost-effective and sustainable industrial processes. Immobilization of these biocatalysts allows an easy recovery of the material and protection from the reaction conditions in the different production steps.[2] Nowadays, nanotechnology offers one of the most forefront approaches for enzyme immobilization. Magnetic nanoparticles allow an easy recovery of an immobilized enzyme using a simple magnet to separate the catalyst from the reaction product. To improve colloidal stability of the support, reduce interactions between the magnetic cores and prevent interactions with the environment that can affect both support and enzyme stability, a polymer coating is an easy and cheap approach.[3] Using this approach, in this work we developed a hybrid, modular micro-support based on organic and inorganic nanocomponents. The easiness of tuning the composition of the support makes this system a potentially universal support for the immobilization of very different catalytic systems. Here we present the application of the developed micro-support for the immobilization of chloroperoxidase (CPO), an enzyme able to catalyze many reactions of large-scale interest. A multipolysaccharidic shell containing the immobilized enzyme and obtained through a combination of chitosan and alginate, biodegradable polymers from natural sources, was used to stabilize a nanoemulsion core in which magnetic nanoparticles were embedded. Microsupports obtained through different combinations of nanocomponents were characterized and tested in terms of their chemical stability under reaction conditions.

An excellent reusability of the entrapped enzyme was observed opening the way to the immobilization of different catalytic systems and to the scale-up study in view of future industrial application.[4]

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NM04.03.19

Synthesis and Characterization of Ferroic Materials, Introducing Perovskite and Pyrochlore Europium Titanate Nanocrystals Synthesized by Gel-Collection Nasim Farahmand; Chemistry, The City University of New York, New York, New York, United States.

Europium Titanate is one of the most interesting materials used in various applications such as sensors, memory devices and energy storage. Its unique features are due to its rich properties, mostly in the area of magnetic properties, which is a result of its seven unpaired spins in its 4f orbital. There are several methods in order to synthesis Europium Titanate compounds, most of which are among solid state reactions. In this work we have synthesized Europium Titanate compounds both in Perovskite and Pyrochlore crystal structure using gel-collection method. This method is based on the sol-gel transition of metal alkoxide in alcohol, controlled by water. Followed by hydrolysis, the crystallization process initiates to give a fully crystalline material. Despite the solid state reactions, the gel-collection is a simple, green and high yield process producing uniform and aggregate free nanocrystals. The synthesized material was heat treated both in air and in Argon. XRD of the samples heated in different temperatures indicated interesting results. A dramatic change observed in X-ray diffraction at 750°C indicates a dramatic transfer from amorphous to crystal. While the heated samples in air proved to be pyrochlore structure with interesting electrical properties which make them good candidates as dielectric materials, the sample heated in tube furnace indicates a perovskite structure.

In conclusion we could make europium titanate both in perovskite and pyrochlore structure using the gel-collection method. PDF analysis was done and proved that our perovskite structure is likely to be cubic pm3m, while our pyrochlore structure is in good agreement with the refinement for cubic Fd3m.

NM04.03.20

Facile Solution Synthesis of V-VI-VII Inorganic Semiconductors and Their Potential for Applications in Electronic Devices Prashant Kumar, Hendrik Faber, Kalaivanan Loganathan, Yuliar Firdaus, Emre Yengel and Thomas Anthopoulos; KAUST Solar Center, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia.

V-VI-VII compounds are semiconductor materials consisting of elements from group V, VI and VII of the periodic table. These materials usually consist of at least one metal, one chalcogen and one halogen. The recent discovery of BiSI and SbSI as efficient solar cell materials has stimulated research interest from different disciplines to explore various interesting (opto-)electronic properties and applications for V-VI-VII materials.

Traditionally, V-VI-VII compounds are synthesized at high temperature following an elemental reaction/flux method using specifically designed and dedicated experimental apparatuses. Unfortunately, both the solid state as well as solution phase synthesis suffers from the formation of V-VI and V-VII phase binary products and phase pure material can only be synthesized under specific experimental conditions. Simultaneously, specific precautionary/safety conditions are required, making the synthesis of these systems only accessible to experts.

In order to further study of these materials in terms of applied, as well as fundamental research, the development of a robust synthetic methodology is therefore highly desirable. Specifically, a low temperature solution based synthesis route with easy-to-handle precursors will open up lots of research possibilities and will facilitate potentially more widespread practical uses in the future.

Herein we report a low cost, energy efficient and less time-consuming solution-based synthesis of nanoparticles of various compositions in V-VI-VII materials using Bismuth-Sulfur-Iodine as the model system. In addition to separate precursors for all the required constituent elemental precursors, we have also employed a molecular precursor approach and summarized results will be presented. Synthesized nanoparticles can be dispersed well in organic/aqueous solvents and deposited in the form of homogeneous thin films. Electronic devices such as diodes, transistors and solar cells are used for a comparative study of the electronic transport properties of the synthesized materials.

NM04.03.21

UV-Enhanced Gas Sensors Based on SnO₂ Nanoparticles Obtained via Microwave-Assisted Nonaqueous Method Luis F. da Silva^{1,2}, Mattia A. Lucchini², Ariadne C. Catto³, Waldir Avansi Jr¹, Sandrine Bernardini⁴, Caue Ribeiro de Oliveira⁵, Markus Niederberger² and Khalifa Aguir⁴; ¹Department of Physics, Federal University of São Carlos, São Carlos, Brazil; ²Department of Materials, ETH Zürich, Zürich, Switzerland; ³Institute of Physics of São Carlos, University of São Paulo, São Carlos, Brazil; ⁴Laboratory of Microsensors, Aix Marseille University, Marseille, France; ⁵Embrapa Instrumentation, São Carlos, Brazil.

Gas sensors based on semiconducting metal oxide (MOS) nanostructures have drawn the attention of researchers mainly due to their sensitivity and stability. Nowadays, these sensor devices are necessary for the detection of harmful gases arising from industrial processes, vehicle emissions, and environmental control. In last decades, several MOS have been used as sensitive layer, due to its excellent performance. Among them, tin oxide (SnO₂) has been widely investigated as resistive gas sensors. Despite its remarkable properties, gas sensors based on SnO₂ require thermal activation (< 150 °C) for an enhancement of their gas sensing performance. Recently, the use of UV-light irradiation to activate the gas sensors has been an efficient and inexpensive way for room-temperature stimulation and improvement of the gas sensing properties. In this work, we present an investigation on the influence of the experimental parameters (time and temperature) in the preparation of the SnO₂ nanoparticles via microwave-assisted nonaqueous route. The SnO₂ samples were evaluated as ozone gas sensors operating at room-temperature under continuous UV illumination. The structural (long- and short-range order), surface, and morphological properties were characterized by X-ray diffraction (XRD), X-ray absorption and, X-ray photoelectron spectroscopies, and high-resolution scanning transmission electron (HR-STEM) analyses. The XRD and Sn LIII-edge XANES measurements indicated an increase of crystallization degree with time and temperature treatment, where Sn⁴⁺ ions are in an octahedral coordination. Regarding the surface properties, XPS spectroscopy indicated a significant reduction of carbon species (from precursors) and oxygen vacancies on the samples surface. HR-TEM analyses showed an increase of particle size from 3 to 15 nm, as well as, the formation of necks between the particles, as function of time and temperature treatment. DC electrical measurements revealed that SnO₂ nanoparticles were sensitive to sub-ppm ozone levels (80 to 1400 ppb) at room temperature under UV-light illumination, presenting a fast response, good reproducibility, and total reversibility. These findings demonstrate that this chemical method provides a fast and efficient route to manufacturing ozone gas sensor devices for practical applications.

NM04.03.22

All Gas-Phase Synthesis and Functionalization of Silicon Nanocrystals Zhaohan Li and Uwe R. Kortshagen; Mechanical Engineering, University of Minnesota, Minneapolis, Minnesota, United States.

Silicon nanocrystals have attracted increasing attention as light emitting materials, luminescent downshifters, and imaging sensors. Among various quantum dot materials, silicon is earth abundant, biocompatible, and has low toxicity compared with group II-VI and III-V materials. Nonthermal plasma synthesis has been successfully applied for production of quantum confined, luminescence silicon nanocrystals with narrow size distribution. However, the relatively low luminescence efficiency of silicon nanocrystals will limit their use as light emitting materials. Engineering of silicon nanocrystal surfaces is usually necessary for enhanced luminescence performances, and this is typically done by functionalization of silicon surfaces with organic ligands. In this work, we develop an all gas-phase synthesis route that integrates nonthermal plasma synthesis, plasma-assisted functionalization and in-flight heating within one flow stream. In this approach, ligands are attached to nanoparticle surfaces in the plasma afterglow, after which the gas stream carrying nanocrystals enters a tube furnace. With the appropriate furnace temperature, the as-produced silicon nanocrystals have photoluminescence quantum yield exceeding 20%. This is a five-fold increase relative to the case when no in-flight heating is applied. We attribute the enhanced photoluminescence to a reduction of dangling bond densities and a change of surface silyl species composition associated with heating. Compared with colloidal synthesis methods, the all gas-phase approach eliminates the use of solvents, produces no by-products, and has higher process yields. With gas-phase deposition methods, silicon nanocrystals can be directly deposited as nanocrystal thin films with densities approaching the theoretical limit of random close packing. We further demonstrate that it is feasible to control the average interparticle distance in nanocrystal films by using ligands with different lengths for functionalization.

This work was supported by the DOE Energy Frontier Research Center for Advanced Solar Photophysics.

NM04.03.23

New Green Chemical Method for the Preparation of the Semiconducting FeCrO₃ and NiO Nanoparticles [Rajesh Kumar Rajagopal](#) and Venimadhav Adyam; IIT Kharagpur, West Bengal, India.

In the recent years, focus on the nanoparticle synthesis has shifted towards the clean and eco-friendly methods, for: simple, cheap, nontoxic, reusability and ecofriendly green chemical synthesis. Here, a novel, environmentally benign method for the FeCrO₃ and NiO nanoparticles is reported by using the gelling property of biopolymer pectin. The prepared powders are calcinated at different temperatures, from Transmission electron Microscope (TEM) analysis revealed the 300°C calcinated has the particle size of ~ 6 nm and uniformly distribution spherical shape nanoparticles. For the 500°C particle size was ~ 36 nm, UV-Vis spectroscopy confirmed the narrowing of the band gap for the nanoparticle. The proposing method is highly reproducible and simple for the preparation of the nanoparticles.

NM04.03.24

Variable Kinetic-Control Effect Towards Porous Nanoamaterials via Solvents Selection [Amrita Sarkar](#) and Morgan Stefik; Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina, United States.

Controlled fabrications of porous nanostructured materials are pivotal for studying structure-property and performance relationships in energy storage and conversion devices. Regardless of great success, fully tunable nanostructures are remains elusive based upon block copolymer self-assembly. Fundamental studies of structure-performance relationship in energy devices require tunable materials with architecture control where one can tailor pore size and wall-thickness independently. A unique kinetic-controlled self-assembly based approach, termed as persistent micelle templating (PMT), recently reported establishing a custom-made block copolymer structure-directing agent, poly(ethyleneoxide-*block*-hexyl acrylate) and a solution processing guideline where the kinetic rates are regulated by adjusting cosolvent amount. It directs to formation of nanostructured materials with tunable 6-9 nm wall-thickness with ~2Å precision and constant pore diameters of 13 nm with a wide range of inorganic material addition. Also, interestingly, the nanoscale morphology remains constant throughout the addition of various amounts of inorganics. This approach launches a new era to fine-tune small architectural feature limiting micelle chain exchange. However, the excessive amount of cosolvent may cause the formation of secondary pores into the material wall. This is addressed by improving the PMT approach via adding major solvents of higher Hildebrand solubility parameters (δ) and minimizing the cosolvent amount. This new approach not only avoids the formation of secondary pores, it also expands the PMT window tunability. PMT control with a range of solvents will be presented here.

NM04.03.25

Low Temperature Sintering Copper Fine Particle System [Tetsu Yonezawa](#) and Hiroki Tsukamoto; Hokkaido University, Sapporo, Japan.

We are now proposing low temperature sintering copper fine particle systems. Usually, in order to sinter metal components at very lower temperature than melting temperature, nano-sized objects are frequently used. Nanoparticles or other nano-sized objects show melting point depression, which are often used for low temperature sintering. Gold and silver nanoparticles have been proposed for low temperature sintering printed electronics materials. However, they are noble metals and these materials are very expensive. Therefore, low temperature sintering system of copper is eagerly desired. However, since copper is easily oxidized even under air, its surface is necessary to be coated with organic materials and inorganic materials to prevent oxidation, so even if stable copper nanoparticles are prepared, their sintering temperature cannot be lowered according to the passivate layer. Therefore, in order to perform low temperature sintering of submicron copper fine particles, we attempted to prepare the surface stable state of specially designed copper fine particles. Detailed discussion will be done at the site.

NM04.03.26

Controlling Morphology of Noble Metal Replica Nanostructures Using Silver Halide Templates for Sustainability and Environmental Applications [Jang Ho Joo](#) and Jae-Seung Lee; Materials Science and Engineering, Korea University, Seoul, Korea (the Republic of).

Noble metal nanostructures have been extensively investigated owing to their morphology-dependent physical and chemical properties. In particular, a number of synthetic methods have been developed to prepare the nanostructures with various shapes and sizes. Generally, template-assisted growth methods have been widely used to synthesize the noble metal nanostructures because the morphology of the template can easily determine the shapes and sizes of the replicated nanostructures. Therefore, controlling structural properties of templates is essential to synthesize the replica metallic nanostructures having desired physical and chemical properties. Especially, nanometer-sized silver halide templates have been conventionally replicated into gold and silver nanostructures, and demonstrated excellent photocatalytic properties under visible light irradiation. In fact, the silver halide nanomaterials hardly generate hot electrons under visible light because of their wide band gap, which is a crucial disadvantage as visible light photocatalysts. On the other hand, the gold or silver metal nanoparticles on the surface of the silver halide templates can absorb light using localized surface plasmon resonance (LSPR), which consequently results in the generation of hot electrons in the silver halide templates. In spite of the aforementioned advantages of silver halides over conventional TiO₂ catalysts, limited morphologies of the silver halide templates are hurdles for many applications. In this work, we present our systematic investigation of key factors to control shapes and sizes of AgCl templates, and demonstrate their replicated noble metal nanostructures. Not only the mole ratio of silver ion and chloride ion, but also the concentration and molecular weight of polyvinylpyrrolidone (PVP) dominantly affect the shape and size of the AgCl nanotemplates. To precisely figure out the components, we analyzed several metallic replica nanostructures with different shapes and sizes using energy dispersive x-ray spectrometer. In addition, the surface-enhanced Raman scattering (SERS) properties of the replicated metallic structures were

observed, which was additionally supported by theoretical simulation. Importantly, the synergistic effect of gold and silver was determined to be crucial for the SERS activity. Finally, we demonstrated the shape-dependent photocatalytic properties of the noble metal replica nanostructures under visible light for the removal of Cr(VI), which would be highly important for the environmental applications.

NM04.03.27

Excellent Acetone Sensor Based on Ordered Mesoporous In-SnO₂ Loaded g-CN Ritu Malik¹, Vijay Kumar² and S.P. Nehra³; ¹University of Kiel, Kiel, Germany; ²University of California, Berkeley, Berkeley, California, United States; ³University of California, Santa Barbara, Santa Barbara, California, United States.

Need for fabrication of low temperature gas sensors has fostered extensive research in realizing 2D materials with high surface area for fast response and low ppm detection of volatile organic compounds (VOCs). In this work, a fast response and low ppm acetone gas sensor operating at near room temperature has been fabricated successfully by utilizing cubic mesoporous g-CN (commonly known as g-C₃N₄), synthesized through template inversion of mesoporous silica, KIT-6. Upon exposure to 20 ppm acetone at 200 °C, the optimized In-SnO₂/g-CN showed significant higher response ($R = R_a/R_g = 18.2$), fast response (14 s), and full recovery within 4 s in air. The sensor was also able to detect 20 ppm ($R=1.7$) and 50 ppm ($R=3.9$) acetone gas at 80 °C. Compared to mesoporous In-SnO₂, the g-CN supported In-SnO₂ nanocomposite shows ~2.8 fold increase in response to acetone gas while reducing the operating temperature by 50 °C. This outstanding response is due to easily accessible 3D mesoporous structure with higher surface area and their unique planar morphology of In-SnO₂/g-CN. The findings reported in this study shows promising glimpse for designing a novel strategy to the development of ultrasensitive VOCs sensors working at low operating temperature.

NM04.03.28

Controlled Synthesis of Transition Metal Doped Lead Sulfide Semiconductors Emmanuel Onche and David J. Lewis; Materials, University of Manchester, Manchester, United Kingdom.

Semiconductors are important materials for a wide range of scientific and industrial applications.¹⁻⁴ Continuous effort are made to improve limitations in their electronic, optical and magnetic properties.⁵⁻⁷ These properties are dependant on chemical composition, the type and method of synthesis. Doping – an intentional introduction of impurities (dopant) into the semiconductor (host) is often used to improve properties. The optical properties can also be tuned by introducing different impurity atoms, the concentration of these dopants determine the degree to which the band gaps are tuned. In this work, imidodithiodiphosphinates complexes of Mn(II), Zn(II) and Pb(II) were synthesised and used deposit metal sulfide materials using melt reactions. Controlled doping of Zn²⁺ and Mn²⁺ into host PbS was carried out between 2 to 12 percent. Peak shifts in XRD and Raman indicated successful doping. The P-XRD peaks of the Mn²⁺ doped PbS shifted towards lower 2θ angles while that of the Zn²⁺ doped PbS shifted towards higher 2θ angles. The cubic structure of the PbS phase was not altered even at high dopant concentration.

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NM04.03.29

Liquid-Crystalline Dendrons Modified Self-Assembling Fe₃O₄ Nanoparticles Takehiro Yachi¹, Masaki Matsubara², Atsushi Muramatsu¹ and Kiyoshi Kanie¹; ¹Institute of Multidisciplinary Research for Advanced Material, Tohoku University, Sendai, Japan; ²National Institute of Technology, Sendai College, Natori, Japan.

Two- and three dimensional arrangement of magnetic nanoparticles (NPs) enables us to control the magnetic properties and novel functions since the magnetic properties of the NPs are affected by the interparticle interactions. Liquid crystalline dendritic molecules are representative organic materials with self-assembling property by the change in the temperature. In our previous studies,^{1,2} precise modification of liquid crystalline dendrons on the surface of the functional NPs enables us to introduce self-assembling and dynamic structure-changeable abilities into the NPs.

In the present study, we focused on Fe₃O₄ NPs to introduce the dynamic functions into the NPs by the surface dense modification by the liquid crystalline dendron.

The Fe₃O₄ NP-cores were synthesized by the thermal decomposition method in the presence of oleic acid and oleylamine as ligands. Then, oleic acid and oleylamine on the particle surface were changed to phosphonic acids by the ligand exchange reaction, followed by the introduction of the carboxyl group onto the NPs surface. In this case, dodecylphosphonic acid (DPA) and carboxyl group-terminated 16-phosphonohexadecanoic acid (PHDA) were used as a ligand. From the TEM observations, particle mean diameter of the phosphonic acid modified Fe₃O₄ NPs was assigned as 7.1 ± 0.4 nm. It is to be noted that the interparticle distance was controlled to 9.0 ± 0.8 nm and that the phosphonic acids were bound to the surface of Fe₃O₄ NPs, confirmed by the absorption at 1070 cm⁻¹ due to Fe-O-P bond. In addition, the ligand exchange was successfully performed with high efficiency because any peaks of oleic acid were not detected.

After modification by DPA and PHDA, amidation between carboxy group of NPs and amide group-containing dendron was carried out to obtain Fe₃O₄ NPs with double layers structure in which the inner was phosphonic acids and the outer dendron. The amount of COOH groups on the particle surface was controlled by change in the molar ratio of DPA and PHDA in feed. At the same time, the modified density of the dendrons layer was brought to form an ordered NPs array. FT-IR profile of the dendron-modified NPs showed the absorption at 1645 cm⁻¹ derived from the amidation bond between surface of Fe₃O₄ NPs and dendron. Further, TEM images exhibited interparticle distance increased to 11.6 ± 1.5 nm under well-ordered two dimensional array at the ratio of DPA and PHDA as 4 : 1. It indicated that self-assembling property was added to Fe₃O₄ NPs by modification with liquid-crystalline dendrons. In conclusion, the modification by liquid crystalline dendron have successfully enabled Fe₃O₄ NPs to control to give the ordered array.

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NM04.03.30

Subtractive Laser Patterning of Silver Nanoparticle Ink by Marangoni Effect Saewoong Park¹, Wooseop Shin¹, Younggeun Lee¹, Seongje Park¹, Jaemook Lim¹, Junyeob Yeo² and Sukjoon Hong¹; ¹Optical Nanoprocessing Lab, Department of Mechanical Engineering, Hanyang University, Ansan, Korea (the Republic of); ²Novel Applied Nano Optics Lab, Department of Physics, Kyungpook National University, Daegu, Korea (the Republic of).

Patterned metal film is an inevitable component for wide range of electronic devices, and it is fabricated by standard photolithography and vacuum deposition methods in general. These conventional fabrication methods have achieved tremendous success to date, but also possess a number of limitations such as requirement of high vacuum environment, high processing temperature and the use of toxic chemicals. As a consequence, the need for alternative method is growing continuously in the area of low cost, large area electronics in particular.

Regarding this matter, selective laser sintering (SLS) of silver (Ag) nanoparticle (NP) ink has been reported recently to create metal pattern through all-solution process in low temperature and non-vacuum environment. In the previous studies, Ag NP ink is firstly coated on the target substrate and selectively sintered to create continuous metal patterns at micron scale by utilizing the focused laser as a localized heater, while the other NPs are removed by a simple cleaning procedure with the solvent. The entire process can be conducted in a relatively low-temperature owing to the melting temperature depression of the Ag NP from its size effect. However, despite these advantages, SLS process is often not compatible to highly dense patterns due to its direct writing nature: the processing time increases proportionally to the pattern density.

In this study, instead of the previous additive SLS process which turns Ag NP ink into conductive layer upon the scanning, we introduce subtractive laser patterning of Ag NP ink that removes the Ag NP ink selectively based on the thermocapillary effect for high density metal patterns. The laser-induced thermocapillary effect was already examined in the previous studies on the SLS process of metal nanoparticles, but it has been considered as unwanted phenomenon since the thermocapillary flow either displaces the NP ink to the sides or create secondary microstructures such as elevated rims. In contrast, we utilize more drastic laser-induced thermocapillary effect in order to thrust Ag NP out of the laser scanning path entirely.

According to our experimental results, the most significant parameter in the subtractive laser patterning of Ag NP ink is its coating condition. Coating condition changes the thickness, the viscosity, which are highly related to the physical events that happen during the laser irradiation including sintering, evaporation and thermocapillary flow. At the optimum spin coating condition of 500 rpm for 300 seconds, we found that the Ag NP ink is selectively removed from the scanning path of the focused laser beam at 0.3W power and 1mm/s speed with the smallest amount of heat affected zone. Through the proposed method, two types of negative photomask – single slit and alphabetic letters – which are difficult and time-consuming to achieve with the conventional SLS process are created successfully and tested through optical means.

NM04.03.31

Unique p-n Heterostructured Water-Borne Organic Semiconductor Colloids via PC60 Micelle Surfactants—Toward Extremely Efficient Photo-Induced Particle Activity Yu Jin Kim, Xiaobing Zuo, Richard D. Schaller and H. Christopher Fry; Argonne National Laboratory, Lemont, Illinois, United States.

In the last a few years, research using water-borne organic semiconductor nanoparticles (NPs) has intensified as an eco-friendly route to electronic materials without toxic chlorinated-solvents. The water-processable NPs are so far the most environmentally friendly outcome. In syntheses of the NPs, typically sodium dodecyl sulfate (SDS) is used as a surfactant. However, they suffer limited charge carrier behavior particularly for the charge separation owing to their confined structure, a randomly blended core of p- and n-type materials surrounded by a surfactant shell. To overcome this phenomenon, we introduced a new surfactant, PC60, which comprises an n-type semiconducting fullerene molecule grafted with a polyethylene glycol (PEG) chain. We found that the PC60 has a spherical micelle structure with double-layer formation, which allows specific shell structure in the heterojunction NPs. Consequently, unique p-n heterostructured NPs with precisely phase-separated core (p-type)-shell (n-type) morphology were obtained when combined with p-type semiconducting polymer, and they showed superior photo-induced charge separation characteristics. Furthermore, we could control the shell morphology of the NPs through one- or two-phase methodology, and the resulting water-borne NPs showed not only shell-morphology-dependent carrier quenching effect but also ultra-stable colloidal property under thermal- and long-term conditions. Our NPs, thus, can open up and provide a new paradigm in the current fields of water-based organic semiconductor colloids.

NM04.03.32

Versatile Nanomanufacturing of Ternary III-V Nanostructure Arrays via Inverse Metal-Assisted Chemical Etching Thomas S. Wilhelm^{1,2}, Zihao Wang¹, Cody W. Soule³, Mohadeseh A. Baboli^{1,2}, Jian Yan⁴, Stefan F. Preble¹ and Parsian Mohseni^{1,2}; ¹Microsystems Engineering, Rochester Institute of Technology, Rochester, New York, United States; ²NanoPower Research Laboratory, Rochester Institute of Technology, Rochester, New York, United States; ³Microelectronic Engineering, Rochester Institute of Technology, Rochester, New York, United States; ⁴Matrix Opto Co., Ltd., Suzhou, China.

Ternary III-V semiconductor alloys, such as InGaP and AlGaAs, play vital roles in many nanoelectronic, optoelectronic, and photovoltaic devices. However, these materials are often plagued by a variety of nanomanufacturing difficulties that stem from either detrimental or incompatible top-down etching, or expensive bottom-up growth techniques. Here, low-cost, high-throughput, and lean nanofabrication processes are demonstrated via metal-assisted chemical etching (MacEtch), with the potential to revolutionize wafer-scale III-V nanomanufacturing. Specifically, novel Au-catalyzed etching approaches are defined for fabrication of suspended InGaP nanofolios and ordered arrays of AlGaAs nanopillars. MacEtch methods show promise as robust, solution-based alternatives for fabrication of high aspect-ratio nanostructures with smooth surfaces. These methods rely on catalytic oxidation of a semiconductor directly beneath a metal catalyst layer, followed by site-specific dissolution of the selectively oxidized material. MacEtch techniques combine many of the advantages of other top-down etching approaches, such as the anisotropic nature of reactive ion etching (RIE), and the fabrication simplicity and cost-efficiency of conventional wet chemical etching. Additionally, many of the corresponding disadvantages are not present, including surface damage from high-energy ion bombardment and use of hazardous gases associated with RIE, and the crystallographic dependences or isotropic nature of traditional wet etching. While MacEtch research has been predominantly focused on silicon processing, these techniques have been recently adapted to overcome fabrication challenges associated with III-V nanomaterials synthesis. In this work, Au-enhanced inverse-MacEtch (I-MacEtch) of heteroepitaxial InGaP/GaAs systems is presented, and differential etch rates between epilayer and substrate are exploited as a viable method to produce suspended III-V nanofolios. A comparison of vertical etch rates (VER) between nominally undoped, p-type, and n-type InGaP is detailed, showing VER in the I-MacEtch regime is independent of doping type. Au-enhanced I-MacEtch of AlGaAs is also demonstrated, and the VER and lateral etch rates (LER) are shown to be tunable with Al fraction and etching temperature. Control over the VER/LER ratio allows for etch conditions to be tailored to provide ordered AlGaAs nanopillar arrays with predefined aspect ratios. The work detailed here provides efficient means to customize nanomanufacturing processes for specific needs, such as tuning MacEtch process parameters to achieve a desired ternary III-V nanostructure geometry. It is anticipated that these processes can be utilized for adaptable and versatile manufacturing of nanomaterials for LEDs, lasers, HEMTs, and multijunction solar cells applications.

NM04.03.34

Detecting Entrapped Humans with Nanostructured Gas Sensors Nicolay J. Pineau, Andreas T. Güntner and Sotiris E. Pratsinis; ETH Zurich, Zurich, Switzerland.

Earthquakes are lethal natural disasters frequently burying people alive under collapsed buildings. Tracking entrapped humans from their unique volatile *chemical signature* with hand-held devices would accelerate urban search and rescue (USaR) efforts.¹ Here, a compact and orthogonal sensor array has been designed to detect the breath- and skin-emitted metabolic tracers acetone, ammonia, isoprene, CO² and RH, all together serving as sign of life. It consists of three nanostructured metal-oxide sensors (Si-doped WO₃², Si-doped MoO₃³ and Ti-doped ZnO⁴), each *specifically tailored* at the *nanoscale* for highly sensitive and selective tracer detection along with commercial CO₂ and humidity sensors. When tested on humans enclosed in plethysmography

chambers to simulate entrapment, this sensor array rapidly detects tracers of human presence with low parts-per-billion (ppb) level accuracy and precision, unprecedented by portable detectors but required for USAR.⁵ These results were validated by bench-top selective reagent ionization time-of-flight mass spectrometry (SRI-TOF-MS). As a result, an inexpensive nanostructured sensor array is presented that can be integrated readily into hand-held or even drone-carried detectors for first responders to rapidly screen affected terrain.

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NM04.03.35

Chlorine-Free and Low-Temperature TiO₂ ALD Process by Using Tetrakis(dimethylamino)titanium as Titanium Precursor Chi-Chung Kei, Wen-Hao Cho, Yu-Hsuan Yu, Narmatha Koothan, Bo-Heng Liu, Cheng-Ye Yang, Chien-Lin Chen and Po-Han Huang; Instrument Technology Research Center, National Applied Research Laboratories, Hsinchu, Taiwan.

TiO₂ has attracted much attention because of potential applications in photocatalytic degradation of pollutants and hydrogen generation. TiO₂ deposition on organic templates has been regarded as a feasible route to fabricate TiO₂ nanostructure catalyst. Compared with conventional deposition methods, atomic layer deposition (ALD) can improve the catalytic properties of TiO₂ nanostructures because of the conformal coating behavior and precise thickness control. Therefore, it is worthwhile to develop low-temperature ALD for growing TiO₂ nanostructures by using organic templates. Previously, we found that the TiO₂ nanotubes prepared at low temperature contained residual chloride from the ALD reaction using TiCl₄ and H₂O precursors. The existence of residual chloride would lead to a lower efficiency of catalytic reaction. In this study, a chlorine-free and low-temperature ALD process was developed to grow TiO₂ films. H₂O and tetrakis(dimethylamino)titanium (TDMAT) were used as the co-reactant and titanium precursor of TiO₂ ALD, respectively. Each cycle consisted of a precursor pulse for 0.1 s and a purge with N₂ for 10 s. The growth rate of TiO₂ prepared by ALD at 110 °C is 0.06 nm/cycle. The growth rate of TiO₂ would decrease to 0.053 and 0.043 nm/cycle at a growth temperature of 150 and 200 °C, respectively. The appearance of hydrocarbon residue in the X-ray photoelectron spectroscopy (XPS) reveals that the low process temperature of ALD would result in incomplete reaction of TDMAT.

NM04.03.36

Photocatalytic Degradation Mechanism of Indigo Carmine Using ZnO, and Ag-Doped, Ni-Doped, and (Ag,Ni) co-Doped ZnO Thin Films Vinoth Kumar Jayaraman, Agileo Hernandez-Gordillo and Monserrat Bizarro; Instituto Investigaciones en Materiales, Mexico City, Mexico.

Zinc oxide (ZnO) films, as well as Ag-doped, Ni-doped, and (Ag,Ni) co-doped ZnO thin films were grown on glass substrates using pneumatic spray pyrolysis. Zinc acetate, silver nitrate, and nickel acetate were used as precursors. Ni doping was performed for the atomic concentrations 1, 3, 5, 7%. Silver doping was carried for the atomic concentrations 1, 3, 5, 7 and 9% (until the solubility limit). Ag-Ni co-doping was executed by various combinations of Ag and Ni concentrations (5:5, 5:9, 7:9 at.%). The fabricated films were further characterized to understand the structural and morphological properties. The structural and morphological studies showed that films were of polycrystalline and grown with nanostructures like nanospikes, nanocombs, hexagons and trigonal flakes, respectively. Photocatalytic activities of these films were tested using a solar simulator lamp on indigo carmine dye (which is being used widely in textile and cosmetic industries). The photocatalytic results were analyzed using UV-Vis spectra. The degradation of peaks of indigo carmine behaved differently with respect to the films with different dopants conditions. The 100% discoloration of indigo carmine occurred for Ag-Ni co-doped ZnO thin films in less than one hour, whereas the Ag-doped ZnO, Ni-doped ZnO, and undoped ZnO achieved only 30-50% of discoloration in one hour. In this work, we propose the possible degradation mechanism of indigo carmine dye with respect to dopants type and their concentration.

NM04.03.37

One-Step Aqueous Synthesis of Zn-Based Quantum Dots as Direct Generators of Reactive Oxygen Species Julio A. Rivera de Jesus¹, Sonia J. Bailon Ruiz² and Oscar J. Perales Perez³; ¹Department of Chemical Engineering, University of Puerto Rico, Mayagüez, Puerto Rico; ²Department of Chemistry and Physics, University of Puerto Rico, Ponce, Puerto Rico; ³Department of General Engineering, University of Puerto Rico, Mayaguez, Puerto Rico.

Semiconductors quantum dot (QDs) are fluorescent nanocrystals with a ranging diameter of 2 nm - 10 nm. Due to their intrinsic optical properties, which are dependent of their size, these nanoparticles have many industrial and bio-medical applications e.g. bio-imaging, diagnostic, LED's (light emitting diode) production, and photocatalyst of organic compounds. More recent applications are based on their potential use as photosensitizer to generate cytotoxic reactive oxygen species (ROS) when activated by light. The factors that govern the cytotoxicity associated to the generation of ROS include the particle size, shape, surface chemistry, the presence of lattice defects, degree of aggregation, among others. Based on these considerations, the present work was focused on: (i) the development of a synthesis protocol of water dispersible pure and doped ZnS-based QDs, (ii) modify their surface chemistry with biocompatible molecules and, (iii) evaluate their potential capacity to generate ROS under light irradiation. QDs were synthesized in water using a microwave reactor system under controlled temperature and reaction time in presence of 3-mercaptopropionic acid (MPA) as sulfide supplier. ZnS QDs were also doped with Mn²⁺ or Cu²⁺. As-synthesized ZnS QDs, as evidenced by XRD, were optically characterized by X-ray Diffraction (XRD), HRTEM, UV-Vis and Photo-luminescence spectroscopy techniques. UV-Vis analyzes evidenced the presence of excitonic peaks around 310 nm, 314 nm and 315 nm for ZnS, Cu-ZnS and Mn-ZnS, respectively. The band gap energy of the pure ZnS QDs was estimated at 3.70 eV that indicates a strong quantum confinement effect, as evidenced by this high value compared to the bulk (3.54 eV). In addition, the photoluminescence analyses of the QDs showed a strong emission peak (438nm for pure ZnS) that was red-shifted when Mn²⁺(487nm) or Cu²⁺ (521nm) were used as dopant species. The incorporation of these transition metals into the ZnS lattice should have created new intermediate energetic levels between the valence and conduction bands of the ZnS particle. The effect of doping on the crystal size and the corresponding capacity of ZnS-based QDs to generate ROS, via the photo-degradation of specific organic dyes, will also be presented and discussed.

NM04.03.38

Sodium Titanate Nanomaterials as Active Catalysts for Biodiesel Production from Renewable Sources Mark Eugenii Martinez-Klimov, Pedro Roquero and Tatiana Klimova; Facultad de Química, Universidad Nacional Autónoma de México, Coyoacán, México.

Sodium titanate nanomaterials (nanotubes, nanorods and nanobelts) synthesized by the Kasuga method have already been tested as catalysts for biodiesel production from vegetable oil and methanol giving good results. In the present work, we modified sodium titanate nanotubes (STN) by the addition of different amounts of sodium carbonate in order to increase their basicity and, consequently, improve their performance in the transesterification reaction. Catalysts with sodium carbonate loadings between 1 and 10 wt. % were prepared. Hereinafter, these catalysts will be denoted as STN-x, where x represents nominal Na₂CO₃ weight loadings in the samples. Synthesized catalysts were characterized by N₂ physisorption, X-ray powder diffraction (XRD), FT-IR, scanning electron microscopy (SEM-EDX), transmission electron microscopy (TEM), and CO₂ temperature-programmed desorption (CO₂-TPD). The STN reference had high sodium content (10.3 wt. %) and attractive textural characteristics (surface area of 222 m²/g and pore volume of 0.46 cm³/g). Addition

of sodium carbonate to STN resulted in a slight decrease in the specific textural characteristics of the STN materials. However, all of them maintained a characteristic nanotubular structure and showed the presence of only the sodium trititanate crystalline phase ($\text{Na}_2\text{Ti}_3\text{O}_7$). No agglomeration of sodium carbonate was detected by XRD. Addition of sodium carbonate to the STN allowed us to obtain 1D nanostructured materials with a higher amount of sodium, which resulted in an increase in the total amount of basic sites and especially in the proportion of strong basic sites. Thus, STN-3 and STN-5 materials had about 18 – 19 % of strong basic sites, which represents a noticeable increase in comparison with the starting STN reference (13 % of strong basic sites). Catalytic activity tests were performed in transesterification of soybean oil with methanol. Reactions were performed in a batch reactor, at 80 °C, 1 h reaction time, 1 wt. % of the catalyst, using methanol:oil molar ratio of 20:1. The best results were obtained with the catalysts containing 3 and 5 wt. % of sodium carbonate, which gave methyl esters (ME) yields of 90-91 %. In the same conditions, the reference STN catalyst resulted only in a 53 % of ME yield. Such a strong increase in the catalytic activity of Na_2CO_3 -containing sodium titanate nanotubes was attributed to a synergistic effect between the impregnated sodium salt and 1D nanostructured STN material.

NM04.03.39

Sustainable and Green Manufacturing of Diagnostic Iron Oxide Nanoparticles using Natural Products Isabel Gessner¹, Lisong Xiao² and Sanjay Mathur¹; ¹University of Cologne, Cologne, Germany; ²University of Duisburg-Essen, Duisburg, Germany.

During the last years, an enormous variety of nanomaterials with different shapes and compositions have been developed for a broad range of applications including optics and electronics but also for their employment in health care and foods. However, many of these fabrication processes still rely on the employment of toxic and environmentally hazardous substances, offering potential risks to manufacturers and customers. Therefore, alternative synthetic procedures are focus of current research to allow for the synthesis of nanomaterials under the important aspects of biosafety and environmental compatibility.

Herein we report a green and facile one-pot synthesis for the preparation and in situ functionalization of water-dispersible and biocompatible iron oxide nanoparticles (IONPs) for their employment as contrast agents for magnetic resonance imaging (MRI). Two classes of naturally available nutrients namely ascorbic acid (vitamin C) and green tea were employed. In the first approach, easily water-dispersible crystalline IONPs were produced in a hydrothermal synthesis using ascorbic acid as reducing agent whereby the oxidation product instantly formed a protecting and stabilizing layer around the particles. As-obtained particles were not only highly biocompatible, but demonstrated enhanced r2/r1 ratios compared to the clinically approved contrast agent Sinerem. In this context we further developed the synthesis of iron oxide nanoparticles using green tea catechins. Green tea is a promising material which additionally exhibits beneficial antioxidative, anticancer and anti-inflammatory effects. Similar to vitamin C, green tea functionalized IONPs were long-term stable in water and highly biocompatible. Moreover, *in vivo* studies revealed accumulations of the particles in tumor tissues similar to clinically approved contrast agents. Indeed, a strong contrast enhancement was visible based on high relaxivity values, which further support their employment as novel MRI contrast agents in clinics.

NM04.03.40

Nanostructured TiO₂ Support Effect on Hydrothermal Stability of Platinum-Based Catalysts Xingxu Lu^{1,2}, Wenxiang Tang¹ and Puxian Gao^{1,2}; ¹Institute of Materials Science, Storrs, Connecticut, United States; ²Department of Materials Science and Engineering, University of Connecticut, Storrs, Connecticut, United States.

Platinum (Pt) based catalysts are widely used in petrochemical refinery, automotive emission control, and fuel cell applications (1). However, the catalytic activity of Pt nanoparticles (NPs) catalysts tends to decrease drastically as a result of the loss of active surface area *via* sintering at high temperature (2). TiO₂ is an earth-abundant and chemically stable material and has been extensively studied as support for Pt-based catalysts (3). However, for the precursors of TiO₂, such as layered protonated titanates (LPTs), the sintering resistance effects on noble metal NPs are not well studied. The high surface area and cation exchange capacity of LPT make it the ideal supports for catalytically active materials (4). In this work, the promotional effects of the support structures on the hydrothermal stability of the TiO₂ nano-array supported Pt catalysts were studied. Two types of TiO₂ nano-array supported Pt catalysts were prepared with different initial support structures, namely the anatase TiO₂ and LPT nanowires. Pt NPs were loaded onto both types of supports and went through the same hydrothermal aging at 800 °C for 50h. The evolution of the Pt NPs before and after the hydrothermal aging was studied by scanning transmission electron microscope and CO oxidation was employed as a probe reaction to compare the catalytic performance of these catalysts. According to the microstructural evolution of the Pt NPs and the catalytic activity of the sample before and after hydrothermal aging, the LPT nano-arrays based Pt catalysts showed better hydrothermal stability than the crystalline anatase nano-arrays based ones. The better hydrothermal stability of the LPT nano-array supported Pt NPs might be due to the greater interaction between the Pt NPs and the LPT surfaces formed during the dip-coating process through ion-exchange. The sintering resistance of the Pt NPs is therefore enhanced by the potentially better anchoring effect from the LPT nano-array supports. Considering the wide application of TiO₂ supported Pt catalysts, this new finding may provide a new pathway to design highly stable Pt-based catalysts for different gas phase reactions.

Keywords: Pt-based catalysts; Hydrothermal stability; Layered protonated titanates; Sintering resistance; CO oxidation.

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NM04.03.41

Enhanced Performance of Inverted Indium Phosphide Quantum-Dot Light-Emitting Diodes via Thermal Annealing Jiwon Lee and Changhee Lee; Electrical and Computer Engineering, Seoul National University, Seoul, Korea (the Democratic People's Republic of).

Indium phosphide (InP) quantum-dots (QDs) have attracted as most promising luminescent material for developing cadmium-free QD light-emitting diodes (QLEDs). However, the performance such as efficiency, maximum luminance and operational lifetime of InP QLEDs is still far behind that of CdSe QLEDs [1, 2]. This is mainly attributed to unoptimized synthesis of InP QDs and device structure. InP QDs have relatively low electron affinity (EA), so the electron injection barrier is quite large with conventionally available electron transporting materials, thereby resulting in low electron injection [2]. In this work, we will demonstrate that thermal annealing of zinc oxide nanoparticle (ZnO NPs) electron transport layer and the QD emissive layer can lead to enhanced QLED performance. The current density of electron-only devices with ZnO NPs increases and exhibits trap-free space-charge-limited-current (SCLC) characteristics after thermal annealing. Furthermore, the photoluminescence (PL) quantum yield of the QD layer increases with thermal annealing due to increased packing density of QDs, as previously reported [3]. Optimizing annealing temperature of inverted green InP QLEDs results in increased external quantum efficiency from 2.32% to 3.61% and maximum brightness over 10,000 cd/m². The half-lifetime (LT₅₀) at an initial luminance of 1000 cd/m² increases up to nearly 2 hours. Therefore, thermal annealing process can be effectively utilized to optimize the device performance of InP QLEDs.

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NM04.03.42

Efficient Photocatalysis with Biomimetic Hedgehog Supraparticles Luiz F. Gorup², Gleiciani d. Silveira³, Naomi S. Ramesar³, Douglas G. Montjoy³, Siuon Tung³, Emerson R. Camargo¹ and Nicholas A. Kotov³; ¹Federal University of Sao Carlos, Sao Carlos, Brazil; ²Chemistry, Federal University of Grande Dourados, Dourados, Brazil; ³Chemistry, University of Michigan, Ann Arbor, Michigan, United States.

Nanostructured hedgehog supraparticles (SPs) were formed by the self-assembly of erdite nanoparticles (NaFeS₂·2H₂O) into a remarkable functional geometry. The nanoscale corrugation with the particles allows for enhanced dispersion stability and leads to greater effectiveness for photocatalytic degradation. The self-assembly of nanoparticles is a promising strategy to fabricate hybrid biomimetic nanostructures that can be used as an innovative alternative to obtain superior properties from conventional material. In the present study, erdite hedgehog supraparticles were successfully synthesized using a cost-effective self-assembly method and employed as a photocatalyst for degradation of organic dyes. The nanostructures were formed by altering the ionic strength of the synthesis solution, resulting in SPs (6.62 μm ± 1.4) with spikes that provided a surface area greater than 8.2 m²/g. The structural morphology and optical features of the synthesized erdite SPs were confirmed by X-ray diffraction, electron microscopy and UV-visible spectrophotometry. The pollen morphology prevents aggregation of the particles and promotes high surface area. The supraparticles exhibit excellent photocatalytic properties by utilizing H₂O₂ (SP+ H₂O₂) in a fenton reaction, resulting in degradation of methylene blue (MB) (25 ug/mL) in 5 minutes under 302 nm light. Additionally, The SP+ H₂O₂ are very effective in the catalytic degradation of phenol red (PhR), nitrophenol (NPh), and rhodamine B (RhB) under UV light, visible light, and dark condition. Finally the erdite SP catalyst has excellent activity and recyclability for more than 55 cycles, with the addition of H₂O₂ on average every 13.8 ± 2.2 cycle. The excellent photocatalytic activity is owing to the synergistic interaction between the SPs and H₂O₂. The SPs exhibit high adsorption capacity and low recombination of the photo-generated electrons and holes due to the shape and erdite composition. This work showed how particles with singular morphology, such as, hedgehog supraparticles are highly attractive because of their enhanced properties.

NM04.03.43

Defect Engineering of Low-Dimensional Heterostructures Toward an Efficient Electrocatalysts Sehms Ozden; Los Alamos National Laboratory, Los Alamos, New Mexico, United States.

Designing novel efficient and robust catalysts with enough active sites and excellent conductivity is one of the key parameters for water splitting devices to produce hydrogen as a clean energy source. Existing Pt-based noble catalysts have some issues with their relatively high-cost and limited abundance. In this regard, the development of novel catalysts that exhibit higher catalytic activity, longer durability and lower cost can significantly facilitate the realization of clean energy. Recently, low-dimensional materials such as nanotube, graphene, MoS₂ and h-BN, have gain attention for hydrogen evolution reactions (HER), oxygen reduction reactions (ORR) and oxygen evolution reactions (OER) etc.. Although these nanostructures have been used for HER, ORR and OER, they need to be engineered to improve their catalytic activity for large scale industrial applications. Novel catalysts with unique properties can be fabricated by creating heterostructures of low dimensional nanomaterials with rich defect density. Here, we will discuss outstanding catalytic activity of metal-free low-dimensional carbon-based hybrid heterostructures with rich defect density as an efficient electrocatalyst. In addition, the role of increased defect density on the free-energy of hydrogen adsorption from density functional theory (DFT) calculations will be discussed.

NM04.03.44

Characteristics of Biogenic Sulfide Semiconductor Nanomaterials Yoriko Tominaga, Ryo Shimizu, Shachiko Maki, Makoto Maeda and Yoshiko Okamura; Hiroshima University, Higashihiroshima, Japan.

We report here the characteristics of PbS formed by bacteria. X-ray diffraction (XRD) measurements and transmission electron microscope (TEM) revealed clear diffraction peaks and lattice fringes, respectively, revealing that the bacteria synthesized polycrystalline PbS. Current-voltage (I-V) measurements showed that the electric current along the PbS increased linearly with increasing applied voltage, and the amount of the current increased with increasing the area of crystalline PbS.

Biomineralization have been actively studied for more than 20 years. It can be performed to form such as magnetite, silica, calcium carbonate, hydroxyapatite, metal particles and so on under ordinary temperature and normal pressure. This can develop material synthesis techniques with low power consumption at low cost. Under this kind of circumstances, microbial synthesis for sulfide semiconductors such as CdS and PbS has been explored in some previous studies. The studies have already demonstrated the formation of nanocrystallite of these sulfide semiconductors by some yeasts. However, it has not been clarified whether they can have crystalline quality that may be applied to the semiconductor devices or not. In this study, we aim to reveal their crystalline qualities and semiconductor characteristics by focusing on PbS towards the future fabrication of the biogenic semiconductor devices.

We established bacterial strains involved in PbS formations and confirmed micro structures and crystalline quality of PbS formed by the bacteria using a X-ray diffractometer and a JEOL JEM-2010 TEM equipped with an energy dispersive X-ray spectroscopy (EDS) system, operated at 200 kV. XRD spectra of the PbS samples exhibited clear diffraction peaks, and there were good agreements with experimental data and theoretical ones of polycrystalline PbS on peak diffraction angles on each crystal plane of PbS. TEM images and EDS analysis for the samples also showed that the materials consisted of Pb and S, and lattice fringes and electron diffraction patterns corresponding to crystalline PbS. I-V characteristics were measured using probe after Indium electrodes were formed on the surface of the PbS samples mounted on semi-insulated InP substrate. When the shape of PbS was formed to be spherical nanocrystallites, the amounts of the current were in the range between 0 and 17.5 pA with applied voltage was in the range between -1 and 1 V. On the other hand, the shape of crystalline PbS was changed to be thin film, the amounts of the current were changed to be in the range between 0 and 18.5 μA. The former amounts of the current increased to be 0 - 25.0 pA under light irradiation. These results suggested that the biogenic PbS have bandgaps and it exhibited general fundamental characteristics of the semiconductors.

NM04.03.45

3D Cubic Ordered Mesoporous SnO₂@SBA-16—A Highly Sensitive Humidity Sensor Vijay K. Tomer¹, Ekta Poonia² and Krishan Kumar²; ¹Berkeley Sensor and Actuator center, University of California, Berkeley, Berkeley, California, United States; ²Department of Chemistry, Deenbandhu Chhotu Ram University of Science and Technology, Sonapat, India.

The need for the development of highly sensitive humidity sensors for monitoring of indoor climatic conditions has always remained a challenging task. Myriads of study have been performed to formulate an ideal humidity sensor, wherein, the mesoporous materials are leading among the others in the quest for designing highly sensitive humidity sensor. Due to high surface to volume ratio, easy charge transportation, tunable geometry of pore structure and excellent capability in the role of a host matrix for a variety of dopants (metals and metal oxides), the mesoporous materials have emerged as the new hot-spot for designing humidity sensors. In the present study, we propose a simple and low-cost strategy to prepare of 3-D cubic ordered mesoporous silica

nanohybrid impregnated with SnO₂ nanoparticles. The relative humidity (%RH) sensing results in the 11–98%RH range reveal that the SnO₂@SBA-16 nanohybrid sensor possesses fast response/recovery (4.2/3.5s), negligible hysteresis (0.8%), high sensitivity, wide range of applicability and high stability. The high resolution transmission electron microscopy (HR-TEM) confirms the porous nature of the nanohybrid. Field emission scanning electron microscopy (FE-SEM) revealed the long range network of these pores even after impregnation of SnO₂ which is an essential facet for high performance %RH sensor. The N₂ adsorption-desorption isotherm studies confirmed the high surface area (746m²/g) for the nanohybrid which suggests that the mesoporous nature remained intact even after impregnation of SnO₂ in the SBA-16 matrix. The XRD and IR analysis further indicated that the inclusion of SnO₂ does not disintegrate the 3D cubic channels of SBA-16. The present work not only highlights an efficient scheme for designing the high performance %RH sensors and but also advocates the promising applicability of mesoporous materials for gas sensing application.

SESSION NM04.04: Energy Harvesting and Storage I
Session Chairs: Raquel Ovalle-Robles and Maria Perez Barthaburu
Tuesday Morning, November 27, 2018
Sheraton, 2nd Floor, Back Bay C

8:15 AM NM04.04.01

Defect Enriched Fe Incorporated β -Ni(OH)₂ Nanosheets with Both High Total Electrode and Intrinsic Activity for Oxygen Evolution Reaction Tianyi Kou; University of California, Santa Cruz, Santa Cruz, California, United States.

Accompanied by the fast world population growth, the depletion of energy resources and environmental pollutions have become two major issues that pose serious threats to the survival of human beings. As a clean and renewable alternative, hydrogen has been given special attentions in the past decades and is believed to be a high gravimetric energy density carrier for fuel cells. Nonetheless, most of the hydrogen in earth is still generated through energy intensive industries such as steam reforming which unavoidably makes the energy resource shortage and environmental problems even worsen. In contrast, generating hydrogen in the cathode through water electrolysis is a green chemical route in which pollutant free and zero carbon emissions can be realized. Additionally, the energy sources driving water electrolysis can also be renewable, further making water electrolysis a promising strategy to produce hydrogen. However, the sluggish kinetics and high energy barriers of oxygen evolution reaction (OER) in the anode have largely restricted the overall efficiency of water electrolysis, and thus limited the hydrogen production. Different catalysts have been investigated so far to address the limitations of OER. Iridium oxides, for example, are found to exhibit a great OER activity but the high costs of iridium become the barrier of their large-scale application. Developing inexpensive catalysts is critical but to boost their activity is still challenging, as most of the OER catalysts still require an overpotential around 250 to 300 mV to achieve the geometric current density of 10 mA/cm². In this work, we synthesized Fe incorporated β -Ni(OH)₂ nanosheets on macroporous nickel foam through a facile one-pot hydrothermal method. The as-synthesized Fe incorporated β -Ni(OH)₂ nanosheets are found to be composed of mixed crystal and amorphous structures. Along the boundary of crystal and amorphous structures are enriched defect sites. By virtue of these structural merits and electronic structure modification of Fe dopants, the as-prepared Fe incorporated β -Ni(OH)₂ nanosheets exhibit a low and competing overpotential of 219 mV at a geometric current density of 10 mA/cm², demonstrating a high total electrode activity. In addition, at the overpotential of 300 mV, a electrochemical surface area current density of 6.25 mA/cm² has also been obtained, which represents the highest value among the reported NiFe based OER catalysts at the same or higher overpotentials, indicating its high intrinsic activity.

8:30 AM *NM04.04.02

Moving from Environmental Remediation to Energy—What We Learned about Nb₂O₅ Photocatalysts Caue Ribeiro de Oliveira; Brazilian Agricultural Res Corp, Sao Carlos, Brazil.

Literature has many examples of semiconducting materials as photocatalysts for degradation of water contaminants. Despite a large concentration in TiO₂ and TiO₂-based materials, other semiconductors have gained attention due specific aspects that promote higher photoactivity (e.g., in visible light, reduced electron-hole recombination) but few was done to understand the role of surface acidity in these process. A study-of-case is Nb₂O₅, which is a wide-band semiconductor, with similar electronic properties to TiO₂ but with very acidic surface. This feature indicates that the way that Nb₂O₅ plays its photooxidative role is different from other semiconductors, depending of the equilibrium of charges in degradation medium. We developed a method to produce this semiconductor through a peroxocomplex formation, which is further de-stabilized in hydrothermal conditions to promote oxide precipitation in a controllable manner. This synthesis, despite very simple, was easily controlled to produce different surface features, as well as heterostructures based on T/T Nb₂O₅ phases. This material has showed a considerable photoactivity in UV light for degradation of different pollutants, but also a good versatility: the mixture with g-C₃N₄ (a polymeric semiconductor) in adequate pH conditions has lead to a self-organized heterostructure, with also remarkable photoactivity. However, these materials did not present only photooxidative activity: measuring their potential for photoreduction, we have observed that modifications with other semiconductors (e.g. CuO) allows this system to promote Cr(VI) reduction and, more interesting, promote the CO₂ reduction to CO in significant yields, despite the acidic surface suggest that this reaction would not be favored. Therefore, the knowledge about this material for environmental remediation is now opening other application for this material in renewable energy production, which needs be deeper investigated.

Acknowledgements: FAPESP; CAPES; CNPq; FINEP; National System of Nanotechnology Laboratories – SISNANO/MCTI; Rede Agronano/Embrapa

9:00 AM NM04.04.03

Single-Source Precursors for Controlled Gas Phase Deposition of Iridium-Based Catalytic Coatings for Water Splitting Applications Lasse Jürgensen, Michael Frank, Jennifer Leduc and Sanjay Mathur; Inorganic Chemistry, University of Cologne, Cologne, Germany.

Investigation of the interplay of metal-organic chemistry will enrich the state-of-the-art of chemical vapor deposition (CVD) and atomic layer deposition (ALD) technology and open new possibilities for the applications of new Ir-based materials. Therefore new heteroleptic *Janus*-typed compounds exhibiting high volatility and defined thermal decomposition under CVD and ALD conditions are reported to elaborate the precursor chemistry – materials synthesis – functional property chain. The new precursors unify both reactivity and sufficient stability through its heteroleptic constitution to provide a precise control over compositional purity in CVD and ALD deposits. CVD- and ALD-grown materials were tested towards their (electro)catalytic applications, particular in the oxygen evolution reactions. In this work functional characterization of deposited materials will be reported and their catalytic behavior is examined. The deposition on various substrate materials without the need of additional reactant gases underlines the potential of this heteroleptic precursor class for CVD and ALD of metallic thin films. The presented CVD data opens new possibilities in the vapor phase synthesis of materials facilitating the application of such films, for example, as electro- or photocatalyst in oxygen evolution reaction (OER) and oxygen reduction reaction (ORR).

9:15 AM NM04.04.04

Nanostructured Co-Precipitated $Ce_xZn_{1-x}O_2$ Catalytic Nanoparticles for Solar Driven Thermochemical H_2O/CO_2 Valorization [Rahul R. Bhosale](#) and Gorakshnath Takalkar; Department of Chemical Engineering, Qatar University, Doha, Qatar.

Thermochemical splitting of H_2O and CO_2 generates a mixture of CO and H_2 i.e. syngas which can be used for the production of storable and transportable liquid hydrocarbon fuels via Fischer-Tropsch (FT) process and specialty chemicals. This offers a renewable, environment friendly and long-term solution for future energy demand with CO_2 mitigation. The MO-based two-step solar thermochemical fuel production process involves successive reduction and re-oxidation of the metal oxides resulting into production of O_2 and H_2 /syngas in separate steps. Among the various metal oxides investigated until now, ceria based redox materials are considered as a very good option due to their high thermal stability and faster kinetics. Recently we have explored transition metal doped ceria materials ($Ce_{0.9}M_{0.1}O_2$, where, M = transition metal dopants) towards thermochemical splitting of CO_2 . The obtained results indicate that the doping of Zn in the ceria fluorite crystal structure is very beneficial towards achieving higher levels of O_2 release and CO production. In this study, we have synthesized $Ce_xZn_{1-x}O_2$ (by varying x in the range of 0 to 0.5) using co-precipitation of hydroxide method. The physical properties of the $Ce_xZn_{1-x}O_2$ materials are analyzed using powder X-ray diffraction, BET surface area analyzer, scanning and transmission electron microscope, and energy dispersive spectroscopy. The synthesized $Ce_xZn_{1-x}O_2$ materials are further examined in multiple thermochemical CO_2 splitting cycles using a high temperature TGA. The gases evolved are analyzed using an online GC-MS set-up. Based on the variations in the mass loss/gain profiles and the GC-MS results, the amounts of O_2 released and CO produced by all $Ce_xZn_{1-x}O_2$ materials investigated in this study are calculated. The detailed analysis of the synthesis, characterization, and CO_2 splitting reactions will be discussed in detail.

9:30 AM NM04.04.05

Synthesis and Application of Metal Oxide Nanoparticles Towards Solar-Driven Reverse Osmosis Desalination [Rahul R. Bhosale](#) and Gorakshnath Takalkar; Department of Chemical Engineering, Qatar University, Doha, Qatar.

Reverse osmosis (RO) is one of the most widely employed technologies for water desalination. A drawback of this technology is high consumption of electricity by electric motors used for high-pressure water pumping. Energy consumption can account for up to 70% of the desalination costs. Due to the high-energy intensity, the carbon footprint of desalination processes is substantial. Most of pumps and compressors including those used in RO desalination plants are driven by electric motors or internal combustion engines. Pumping systems account for nearly 20% of the world's electrical energy demand and range from 25-50% of the energy usage in certain industrial plant operations. To improve economics of water desalination plants we propose innovative energy efficient, inexpensive, robust water pump powered by heat. The basic principle of the pump is the same as that of regenerative type external combustion engines. Regeneration of heat makes pumps of this type very energy efficient. The novelty of the pump comprises a new working cycle in combination with the use of a dense working fluid which is liquid in the cold space of the pump and gas or supercritical fluid in the hot space of the pump. Carbon dioxide, water-alcohols mixtures or mixtures hydrocarbons can be used as the working fluids. This pump does not have any high precision parts and even does not require super alloys and any other expensive materials. The pump can generate very high pressures (hundreds bars) and therefore can be used instead of modern plunger pumps driven by electric motors, thus eliminating completely the consumption of electricity for pumping in RO processes. Another important feature of the pumps is that no high temperature heat sources are needed. Heat sources with temperature of 200 – 300°C could be sufficient to create pressure drops typical of RO processes. Therefore, renewable energy sources such as solar radiation can be used to power the pump. Replacement of fossil fuels with renewable energy sources in desalination processes will minimize greenhouse gas emissions. In addition, a substantial improvement of the economics of the RO processes is expected due to the use of solar power. In this study, we have attempted to improve the solar energy absorption capacity of the solar unit by adding metal oxide nanoparticles. These metal oxide nanoparticles are synthesized in our laboratory using sol-gel method. Due to the improvement in the solar energy absorption capacity, the overall efficiency of the desalination process is observed to be enhanced significantly. The detailed results will be presented.

9:45 AM BREAK

10:15 AM *NM04.04.06

Overcoming the Gap of PCE in Non Fullerene OPV Device to Module [Phoebe Tan](#), Yi-ming Chang, Chuang-yi Liao, Yi-you Lai, Yu-Kuang Chen and Nai-Wei Teng; Raynergy Tek Incorporation, Hsinchu, Taiwan.

Organic Photovoltaics (OPV) has in recent years emerged as a low cost alternative to silicon photovoltaics. The solution processability of polymer based photovoltaics is particularly interesting owing to her potential scalability at mass printing production compared to her vacuum processed counterpart. Albeit the continuous breakthrough in non fullerene OPV system, which the latest research reported an excellent PCE of > 14% single junction devices, yet the main hurdles of OPV to commercialization has been linked to its lower performance PCE <7% when fabricating the large area OPV module. Clearly, the OPV device cell to module's loss in PCE is linked to the integration of a suitable solution processable interface layers. The optimization of hole transporting layer is imperative in the inverted device architecture. Here, we report on a newly designed non fullerene OPV system, using low bandgap small molecule Acceptor and a wide bandgap polymer donor and achieved PCE >13% using green solvent and a matching proprietary solution processed hole transporting layer (HTL) to minimize the gap from cell to modules. The proprietary HTL formulations consist of Pedot which is widely used in large area coating for large area OPV module. and a specific additives which serve as the energy bridge between the donor polymer and the Pedot. We achieved PCE >9%, and it is the first time of a complete total solution processed Non fullerene OPV with PCE exceeding 9%. Also, we have completed the environmental reliability tests of such OPV devices stack. i.e. the light soaking, damp heat and humidity freeze tests were made according to IEC61646 which show positive outcomes and strongly echoed that our total solution stack of OPV device could now meet the industry's expectation when coating for large area OPV modules.

10:45 AM NM04.04.07

Preparation and Characterization of Hematite Nanoparticles Decorated Zinc Oxide Particles ($ZnO/\alpha-Fe_2O_3$)—Photoelectrode Material for Solar Cells Application [Tatiana M. Mazza](#)¹, Gabriel H. Hata¹, Leticia G. da Trindade², Josiane C. Souza³, Mario R. Soares³, Edson R. Leite³, Ernesto Pereira³ and Elson Longo³; ¹Federal University of Sao Paulo, Santos, Brazil; ²Universidade Federal do Rio Grande do Sul, Porto Alegre, Brazil; ³Universidade Federal de Sao Carlos, Sao Carlos, Brazil.

There is a constant requirement to diversify the energy matrix due to the socio-environmental and economic impacts caused by the use of fossil fuels. In this context, renewable energies, such as solar cells, stand out as a possible solution to this problem and a good path towards sustainability. In order to make real this possibility, it is necessary to develop or optimized the properties of the structured materials used in this task. In this context, zinc oxide (ZnO) is a promising candidate for solar cells photoelectrode. ZnO is a broadband semiconductor with a band gap of 3.3 eV at 300 K and large exciton binding energy (60 meV). The zinc element (Zn) is extremely abundant on the planet and has high electronic mobility. On the other hand, hematite ($\alpha-Fe_2O_3$) has been widely used as photoelectrode materials due to its exceptional properties such band gap energy (2.1 eV), maximum theoretical efficiency

(12.9%), good electrochemical stability, abundance and non-toxicity. Considering all these aspects, in this work, we present the preparation and characterization of the optical and electrochemical properties of Fe₂O₃ nanoparticles decorated ZnO particles for future application of photoelectrode in dye-sensitized solar cell (DSSC). A hydrothermal assisted microwave method was used to produce the ZnO and the Fe₂O₃ nanoparticles. After that the ZnO and ZnO/Fe₂O₃ film was produced. A viscous paste of pure ZnO and ZnO/Fe₂O₃ (0.20g/20 μ mol) was prepared and 80 μ L of the paste mixture was placed on FTO (Fluorine doped oxide) substrate and the films were calcined at 400°C for 1h. A typical electrochemical cell system was assembled with 3 electrodes, work (FTO/ZnO; FTO/ZnO/Fe₂O₃ films), reference (Ag/AgCl) and counter electrode (Pt) immersed in an electrolytic solution. The films were characterized by X Ray Diffraction, nitrogen adsorption-desorption isotherms, Linear Sweep Voltammetry (LSV), Chronoamperometry, Scanning Electron Microscopy, Micro Raman and FTIR spectroscopy techniques. The microscopy images reveal that the Fe₂O₃ nanospheres decorated with extreme efficiency the flower structure of ZnO. A significant increase in the surface area is observed with the addition of the α -Fe₂O₃ in the ZnO flowers and also significantly alters the pore volume of this material. The LSV showed a high current density of the FTO/ZnO/Fe₂O₃ (0.58mA.cm⁻²) film being superior to the FTO/ZnO (0.16mA.cm⁻²) film in light condition. The analysis showed that these materials are promising photoelectrode for DSSC applications, characterizing them Fe₂O₃ nanoparticles improving the ZnO photoelectrochemical properties. Simultaneously with this the method that was used to produce the nanoparticles adds to the production process of the same, a methodology that does not require the need for high technology equipment, not have a high energy demand or time to run it and does not generate waste, that is, a highly practical, economically viable and environmentally friendly method.

11:00 AM NM04.04.08

Solar-Transparent Thermally-Insulating Silica Aerogels for Concentrating Solar Power Bikram Bhatia, Sungwoo Yang, Lin Zhao, Elise M. Strobach, Lee A. Weinstein, Thomas Cooper, Gang Chen and Evelyn N. Wang; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

The performance of concentrating solar power (CSP) receivers is limited by thermal losses, particularly at concentrations <100 suns. Existing CSP receivers rely on spectrally selective surfaces placed within vacuum glass enclosures to minimize heat loss due to radiation and convection. However, using spectrally selective coatings and maintaining a high-quality vacuum at high temperatures (400 °C) increases cost and significantly limits longevity. We have developed a high-temperature solar-transparent thermal insulation that enables high-efficiency heat collection and obviates the need for selective coatings and vacuum in CSP receivers. We use silica aerogels, a class of highly porous (porosity >90%) materials known for their thermally super-insulating properties, which we have engineered to achieve extremely high solar transparency. The optimized aerogel nanostructure has reduced pore sizes of 2-50 nm that minimizes scattering losses at low wavelengths, increasing the solar-weighted transmittance to >95% for an 8 mm thick sample compared to <85% typically reported in literature. The low near-UV scattering, high infrared absorption, and high porosity of our aerogels maximizes solar transmittance and minimizes heat loss due to conduction, convection and radiation, enabling CSP receiver efficiencies >80% even at concentrations <50 suns. In this work, we report the results of optical and high-temperature thermal characterization of the fabricated solar-transparent silica aerogel. We compare experimental results with a numerical model based on the spectral equation of radiative transfer that predicts the optical and thermal properties of silica aerogel. Finally, we model the performance of a linear CSP receiver comprising of our solar-transparent aerogel and optimize its thickness, density and pore-size to maximize receiver efficiency.

11:15 AM *NM04.04.09

Rational Design of Nanostructured Electrodes for Capacitive Energy Storage Husam N. Alshareef, Chuan Xia, Qiu Jiang and Narendra Kurra; Materials Science and Engineering, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia.

Electrochemical supercapacitors are important energy storage devices that bridge the gap between electrostatic capacitors and batteries. A critical component of supercapacitor design is the electrode material. We have been developing electrode materials and fabrication strategies for conventional electrochemical capacitors as well as micro-supercapacitors (in-plane devices fabricated on-chip). Pseudocapacitive materials in particular hold promise of significantly higher capacitance than carbon-based materials and hence have recently become a subject of intense investigations. These materials can store charge through both surface redox reactions and fast intercalation process leading to intercalation pseudocapacitance. We will discuss strategies that we have developed to rationally design pseudocapacitive materials, including oxide and chalcogenides. Material structure, conductivity, electrochemical activity, defect concentration, and dimensionality are critical parameters to maximize both ion and electron transport within the electrode material, and hence improve capacitor performance. Selected examples from our work will be presented to show how dramatic improvements in electrode performance can be achieved through rational approaches. For micro-supercapacitors, we also show that collector material type, geometry (e.g., 3D and macroporous structures), and microfabrication techniques can be used to improve the kinetics and capacitance of devices. Recent integration of microsupercapacitors in energy harvesting and sensing devices will also be discussed.

11:45 AM RAPID FIRE PRESENTATION

SESSION NM04.05: Energy Harvesting and Storage II
Session Chairs: Husam Alshareef and Phoebe Tan
Tuesday Afternoon, November 27, 2018
Sheraton, 2nd Floor, Back Bay C

1:30 PM *NM04.05.01

cSilk® Carbon Nanotube Sheet Based Origami Triboelectric Nanogenerators and Its Yarn Applications Jaeh Lee and Raquel Ovalle-Robles; LINTEC Nano-Science % Technology Center, LINTEC of America, Inc., Richardson, Texas, United States.

Due to an increase in demand, low-carbon and environmentally-friendly energy, as well as thin and light portable electronic devices and wearables that can generate power has attracted great attention. We have here demonstrated origami triboelectric nanogenerator (origami-TENGs) using cSilk® sheets as the starting material, having a high degree of alignment, being lightweight, and having a high electric conductivity. Sandwich structure combined with cSilk® Sheets and PEDOT:PSS as a current collector were prepared via layer-by-layer coating and acid treatment. Two individual strips (cSilk® Sheets/PEDOT:PSS) were prepared and infiltrated with two different polymers having the positive and negative triboelectric affinity. The cSilk® Sheet-TENG can be fabricated from these two separate strips that are folded together to form a resilient structure that reversibly compresses in response to an applied compressive force and spontaneously returns to its uncompressed state, spring-like, when the applied compressive force is removed. The output short-circuit current (I_{sc}) and open-circuit voltage (V_{oc}) of this cSilk®- Sheet TENG can reach 20 μ A and 1500 V, respectively. This generated electricity could directly light up 500 commercial light-emitting diodes (LEDs) connected in series without any energy storage devices. In addition, the as-fabricated cSilk® Sheet-TENGs are capable of harvesting mechanical energy from various kinds of human motions such as stretching, pressing, and bending. Furthermore, we have been developing TENGs using highly flexible, electrically conductive, and mechanically robust cYarn® fibers by providing twist-

insertion to cSilk® sheets. cYarn®-TENG can be woven to make a textile and harvest energy from human motions such as rubbing, bending, and stretching. Also, cYarn®-TENG can harvest energy by hand-powered torsional actuation.

2:00 PM NM04.05.02

Computational Modeling of 2D Materials and Their Heterostructures for Sustainable Energy Storage—Opportunities and Challenges Kamalika Ghatak, [Vidushi Sharma](#) and Dibakar Datta; New Jersey Institute of Technology (NJIT), Newark, New Jersey, United States.

Because of the low gravimetric capacity of conventional graphite anode (theoretical value ~ 372 mAh/g), and massive structural changes and volume expansion of silicon anode (on the order of 300%); extensive research has been carried out during last few decades to develop stable and high-capacity anode materials. Moreover, large-volume expansion leads to stress built-up at the interface between the Si film and the current collector, leading to delamination at the interface. We, therefore, examined the possibility of 2D materials for application of high-capacity anode materials. By first-principle calculations based on density functional theory (DFT), we investigated the adsorption of lithium (Li), sodium (Na), and calcium (Ca) on graphene with divacancy and Stone-Wales defects. We find that with controlled defect topology, we can achieve a maximum storage capacity of approximately 1675, 1450 and 2900 mAh/g for Li-, Na-, and Ca-ion batteries respectively. However, despite enormous opportunities, we need to concern about several challenges such as adatom trapping at the defect sites, the effect of defects on adatoms diffusivity, microstructural changes, e.g., mechanical degradation at defect sites, etc. In addition, our recent work shows that for the Si-based anode, we can achieve far better electrochemical stability by simply coating the current collector surface with graphene sheets. The combined DFT-MD work shows that graphene can be utilized as slippery interfaces to enhance the electrochemical stability of Si film anode in Lithium-Ion Batteries because of the less stress build-up and less stress cycling of the slippery substrate as opposed to a fixed surface. Our results indicate a new paradigm of 2D materials based energy storage. Besides graphene, several other 2D materials such as graphene allotropes, Transition Metal Dichalcogenides (TMD), etc. have tremendous potential in energy applications. Moreover, by building heterostructures (stacking of different 2D materials), it is possible to combine the advantage and eliminate the disadvantages of the individual sheet. However, we need a computational genome to identify the optimal heterostructures for the energy storage. In this presentation, we will provide a detailed overview of opportunities and challenges of modeling of 2D materials and its heterostructures for the next-generation sustainable energy storage applications.

2:15 PM NM04.05.03

One-Dimensional Nanomaterials for Emerging Energy Storage [Liqiang Mai](#); Wuhan University of Technology, Wuhan, China.

One-dimensional nanomaterials can offer large surface area, facile strain relaxation upon cycling and efficient electron transport pathway to achieve high electrochemical performance. Hence, nanowires have attracted increasing interest in energy related fields. We designed the single nanowire electrochemical device for in situ probing the direct relationship between electrical transport, structure, and electrochemical properties of the single nanowire electrode to understand intrinsic reason of capacity fading. The results show that during the electrochemical reaction, conductivity of the nanowire electrode decreased, which limits the cycle life of the devices. We have developed a facile and high-yield strategy for the oriented formation of CNTs from metal-organic frameworks (MOFs). The appropriate graphitic N doping and the confined metal nanoparticles in CNTs both increase the densities of states near the Fermi level and reduce the work function, hence efficiently enhancing its oxygen reduction activity. Then, we fabricated a field-tuned hydrogen evolution reaction (HER) device with an individual MoS₂ nanosheet to explore the impact of field effect on catalysis. We also identified the exciting electrochemical properties (including high electric conductivity, small volume change and self-preserving effect) and superior sodium storage performance of alkaline earth metal vanadates through preparing CaV₄O₉ nanowires. Our work presented here can inspire new thought in constructing novel one-dimensional structures and accelerate the development of energy storage applications.

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2:30 PM NM04.05.04

Correlating Nanoporous-Carbon Anode Materials Properties with Li-Ion Intercalation [Matthaeus Wolak](#), Katharine L. Harrison, Michael Siegal, Kyle Fenton and Dorina Sava-Gallis; Sandia National Laboratories, Albuquerque, New Mexico, United States.

Graphite is the state-of-the-art anode material for Li-ion energy storage due to its low cost and high coulombic efficiency, enabling long term cycling. Alternative carbons can store more lithium than graphite (specific capacity ~ 370 mAh/g), likely due to increased interplanar spacing, defects, pores, and grain boundaries; however, they suffer from low coulombic efficiency, capacity fade with repeated cycling, and often do not allow precise control of the relevant structural properties. Nanoporous-carbon (NPC) films can grow directly onto anode current collectors without the complication of binder materials, allowing direct correlations between nanostructures and the electrochemical properties governing Li-ion intercalation. Graphite is fully dense and alternative carbons are disorganized with pores and varied interplanar spacings. NPC can bridge the gap between alternative carbon materials through exquisite control of the mass density and surface area and help provide greater mechanistic understandings.

Using pulsed-laser deposition of pyrolytic graphite at room temperature, NPC self-assembles into randomly oriented nm-sized graphene fragments only a few layers thick. NPC density is controlled via the deposition energetics from below 0.1 g/cm³ to 2.25 g/cm³ (near graphite). The density is homogeneous throughout a sample, i.e. NPC does NOT consist of dense graphitic particles separated by voids. Such densities are due to expanded interplanar spacings between the graphene sheet fragments resulting from the deposition kinetics. NPC surface area increases with decreasing mass density, e.g. ~ 1300 m²/g for 1 g/cm³ NPC, so far only reported for foams with densities << 0.1 g/cm³.

NPC specific capacity increases above that for graphite with decreasing density, attributed to the plethora of grain boundaries, pores, and the greater interplanar spacings. NPC with densities < 1 g/cm³ have initial specific capacities 4 – 5X > graphite, higher than many alternative carbon materials. Coulombic efficiencies rise quickly after the first two cycles to a range between 98 and > 99%, indicating minimal initial SEI formation. Both specific capacities and coulombic efficiencies remain high beyond 100 cycles.

This work may lead to determining the optimal interplanar spacing between graphene sheets to maximize Li-ion accessibility while minimizing SEI formation for high cyclability, and may eventually lead to the development of appropriate bulk material fabrication processes.

We thank Lyle Brunke for assistance growing NPC films, Kyle Klavetter for discussions, and Carlos Gutierrez for programmatic guidance. This work is supported by the Laboratory Directed R&D program at Sandia National Labs, a multi-mission laboratory managed and operated by National Technology &

2:45 PM BREAK

3:15 PM NM04.05.05

Bio-Inspired Supercapacitors [Francesca Soavi](#)¹, Federico Poli¹, Antonio Terella¹, Jacopo Seri¹, Alessandro Brilloni¹, Ruben Aldrin Albis Vasquez¹, Francesca De Giorgio¹, Catia Arbizzani¹, Maria Letizia Focarete¹, Davide Fabiani¹, Clara Santato⁴, Carlo Santoro² and Ncholu Manyala³; ¹University of Bologna, Bologna, Italy; ²University of West of England, Bristol, United Kingdom; ³University of Pretoria, Pretoria, South Africa; ⁴Polytechnique Montréal, Montreal, Quebec, Canada.

Water and energy underpin the economic and social development of Countries. Water is needed for each stage of energy production, and energy is crucial for the provision and treatment of water. Within the so-called Water-Energy Nexus, smart and sustainable energy harvesters and storage technologies are required for an efficient managing of water and renewable energy sources. Within this context, microbial fuel cells (MFC) and supercapacitors (SC) are playing a key role. MFCs are bio-electrochemical devices that convert the chemical energy of wastewater organic compounds directly into electrical energy. SCs can store the energy harvested by the MFC and deliver it back at desired power.

Strategies that lower the environmental and economic impact of disassembly and recycling of waste devices are mandatory. The use of water-processable electrode binders and new membrane production techniques like electrospinning are viable approaches to decrease cost and environmental footprint.

A study on the development of bio-inspired supercapacitors, including natural binders, electrospun separators and eumelanine-based electrodes, as well their integration with MFCs is reported and discussed.

Acknowledgments

The research has been carried out under the Italy-South Africa joint Research Programme 2018-2020 and the Executive Bilateral Program Italy-Quebec 2017-2019, Italian Ministers of Foreign Affairs and of the Environment.

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3:30 PM NM04.05.06

Simulated Nanoparticle-Functionalization Interface Towards High Energy Density Dielectric Capacitors [Joshua Shipman](#), Brian Riggs, Binod Subedi, Jianwei Sun and Douglas Chrisey; Tulane University, New Orleans, Louisiana, United States.

Increasing the energy density of high power density dielectric capacitors using nanoparticles (NPs) has often been attempted, but interfacial breakdown has often resulted in lower storage density, cancelling the effect of a higher dielectric constant, especially at higher loadings. We present work in optimizing the interface using *a priori* simulations combined with experimental verification and feedback. We began by simulating a system used previously that has mitigated some of the interfacial effects using covalent bonding. We modelled the interface of nanoparticle and surface functionalization using a vacuum slab containing a barium titanate NP surface and a surface functionalization molecule. Several different possible metrics for the efficacy of the surface functionalization in mitigating the concentrated electric field at the NP interface were calculated and compared, including the binding energy of the molecule, the HOMO-LUMO gap, and the local dielectric constant. Ultimately, combing the local dielectric constant with a Monte Carlo simulation of the location of NP-functionalization dielectric traps in the material proved to be the most accurate predictor of a NP- functionalization's effect on the breakdown of the overall composite. 6 different functionalizations were examined both *in silico* and in spin coated and PulseForge (high energy pulsed Xe light illumination) cured samples. The overall energy density is presented and our model's efficacy at predicting the highest energy density of our experimentally produced films. We also discuss how our modelling technique could be applied elsewhere where interface control is paramount, such as supercapacitor electrodes, surface functionalization for organometallic perovskite solar cells, and quantum dot solar cells.

3:45 PM *NM04.05.08

2D Materials as Binders for Electrodes of Electrochemical Capacitors Bin Xu² and [Yury Gogotsi](#)¹; ¹Department of MSE and A.J. Drexel Nanomaterials Institute, Drexel University, Philadelphia, Pennsylvania, United States; ²State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing, China.

Carbon-based materials have attracted much attention as electrodes for electrochemical capacitors. However, they are usually made into free-standing films with the aid of polymeric binders which add electrochemically inactive weight. Fluorinated polymers used as binders produce toxic gases when incinerated. Here, we discuss manufacturing of freestanding supercapacitor electrodes made of highly porous carbide-derived carbon (CDC), highly accessible hierarchical porous carbon, and activated carbon fibers (ACF) using electrochemically active materials, such as reduced graphene oxide (rGO)¹ and Ti₃C₂ MXene², as the binders. In these hybrid electrodes, the 2D layers hold carbon particles together, producing freestanding films. The sandwiched carbon particles prevent layer stacking and increase accessibility of the active material to the electrolyte ions, which improves electrochemical performance. As a result, electrodes with excellent capacitance, high-rate performance and good lifetime can be manufactured and operated in aqueous and organic electrolytes. These hybrid electrodes material design is greatly viable in high-power and high energy applications.

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4:15 PM RAPID FIRE PRESENTATION

NM04.06.02

Ultra-Thin, Embedded High-Volumetric Density Capacitors with High Operating Frequency and Low Leakage Properties Parthasarathi Chakraborti; Intel Corporation, Hillsboro, Oregon, United States.

Smart systems have continuously evolved with the integration of computing, communication, power, and sensing functions that utilize heterogeneous technologies such as digital, RF, analog, MEMS, sensors and optics in ultra-miniaturized form-factors with escalating component densities. This entails the use of multiple power converters for specific voltage and current applications. These power converters invariably utilize components such as capacitors and inductors to store and release the energy in specific intervals determined by the switch frequency. Today's components with low volumetric density and thick form-factors are a major roadblock to miniaturization of the power modules. Moreover, such components are placed far away from the chips leading to large interconnect parasitics and lower operating frequencies. On the other hand, thin-film passive technologies are limited to low densities and would require a large area to meet the required capacitance or inductance values. Hence, novel thin-film technologies with high densities and small form-factors are required to enable miniaturization and performance at high frequencies. However, processing high surface area electrodes as thin-films with substrate-compatible processes, and achieving low leakage currents and low ESR (equivalent series resistance) for high frequency stability are major challenges to accomplish these goals. Furthermore, novel packaging technologies are required to integrate these high-density passives as thin-films in substrates. This research work addresses these challenges with tantalum-based ultrathin high-density capacitors at higher operating frequencies with lower leakage properties and their integration in silicon substrates. The work focusses on the processing of high-density capacitors as thin-films based on tantalum with low leakage properties ($< 0.01 \mu\text{A}/\mu\text{F}$) and for high-frequency applications in low power modules. The anodization kinetics and the underlying leakage current mechanisms are investigated to provide optimal process guidelines. The capacitors demonstrated high capacitance density of $0.1 \mu\text{F}/\text{mm}^2$ at 1-10 MHz in form-factors of $50 \mu\text{m}$, which corresponds to 6X higher volumetric density relative to the commercial capacitors. The aforementioned tantalum-based high-density capacitors are laminated as thin-films on silicon substrates followed by planarization, via-drilling, lithography and metallization to complete the integration process.

NM04.06.04

Reduced Graphene Oxide - Molybdenum Disulfide Aerogel Nanocomposite Electrodes for Supercapacitors Alptekin Aydinli^{1,2}, Ozgur Dogan³, Serkan Koylan¹, Erhan Bat³ and Husnu E. Unalan^{1,2}; ¹Department of Metallurgical and Materials Engineering, Middle East Technical University, Ankara, Turkey; ²Energy Storage Materials and Devices Research Center (ENDAM), Middle East Technical University, Ankara, Turkey; ³Department of Chemical Engineering, Middle East Technical University, Ankara, Turkey.

Supercapacitors have attracted extensive attention for their high specific power and moderate energy densities. Nanoscale structure and high surface area are the two main requirements for a supercapacitor electrode with high performance. We report on the fabrication and electrochemical characterization of hybrid aerogel nanocomposite supercapacitor electrodes composed of reduced graphene oxide and molybdenum disulfide nanosheets on nickel foams. Graphene oxide was produced using Tour Method. Reduced graphene oxide (rGO) aerogel was produced from graphene oxide dispersion via solvothermal technique followed by freeze-drying and thermal reduction. For the fabrication of hybrid electrodes, produced rGO aerogels were simply pressed onto nickel foams, which was followed by drop-casting of exfoliated molybdenum disulfide (MoS_2) nanosheets onto the rGO aerogel. Electrochemical properties such as specific capacity and capacity retention of the fabricated nanocomposite electrodes were examined through cyclic voltammetry, chronopotentiometry and electrochemical impedance spectroscopy in two electrode configuration. Results of the measurements were compared to that of control samples fabricated simply by pressing bare rGO aerogel and bare MoS_2 nanosheets directly onto nickel foams. In order to determine the effect of electrolyte type on the electrochemical properties of the hybrid nanocomposite electrodes, various environmentally friendly and neutral aqueous solutions, such as lithium sulfate (Li_2SO_4), sodium sulfate (Na_2SO_4), sodium chloride (NaCl) and potassium chloride (KCl) were investigated as the electrolytes. Fabricated hybrid supercapacitor electrodes showed encouraging results with a specific capacitance of $38.69 \text{ mF}/\text{cm}^2$ and a Coulombic efficiency of 83%. Following 1000 charge/discharge cycles, specific capacitance of the fabricated electrodes degraded to 94% of its initial capacitance value. A comprehensive analysis on the electrochemical properties of the fabricated supercapacitor will be presented.

NM04.06.05

Aqueous Phase Synthesis Method of Cu-In-S₂ Compound Solar Cell Nanoparticles by Controlling the Metal Complexes in Original Solutions Hideyuki Takahashi, Kohei Sato, Shun Yokoyama and Kazuyuki Tohji; Graduate School of Environmental Studies, Tohoku University, Sendai, Japan.

CIS (CuInS_2) type solar cell is one of the most suitable photovoltaic devices with high stability and efficiency, since the bandgap of CIS is 1.5eV while ideal band gap for solar cell is 1.4eV. Moreover, it does not contain toxic materials, such as Se. In usual case, these CIS type solar cell is synthesized by gas phase method. However, since vaporizing temperature of four elements (Cu, In, Ga, Se) is extremely different, productivity under the gas phase is relatively low, which read the large amount of waste of resources. Thus, to decreasing the cost of CIS type solar cell, synthesis method with high recovery rate should be developed.

On the other hand, it is also well known that liquid phase reduction methods can be easily produced the nano materials with high recovery rate. However, in many cases, crystallinity of the products was relatively low, consequently undesirable reaction was proceed at around of defects. Here, we reported the synthesis method for well crystallized and uniform alloy nanoparticles by restrict controlling the homogenization of metallic complexes in the aqueous solution which reading the control of reduction rate. For example, we have already developed a synthesizing method of single phase and homogeneous CI alloy nanoparticles in an aqueous solution. Synthesized CI nanoparticles were spin coated onto substrate and selenized, consequently it shows the photo voltaic effect. However, CIS_2 nanoparticles were not synthesized until now, because of ligand exchange reaction between the complexing agents and Cu and In.

Therefore, in this study, to prevent these undesirable reaction, we tried to control the condition of Cu-In-complexing reagent(s) system precisely by using the calculation. By using these calculation results, CIS_2 particles were tried to synthesized in an aqueous solution. Results of calculation indicated that iminodiacetic acid (IDA) was appropriate complexing reagent. In the ternary system of Cu-In-IDA, it was calculated that the Copper complexes and Indium complexes can be restricted to homogenized species, $[(\text{Cu}^{2+})(\text{IDA})]$ (pH3) and $[(\text{In}^{3+})(\text{IDA})_2]$ (pH3). Based on this calculation, a solution under the above condition was prepared, and both metal complexes were tried to co-sulfurize. As a results, particles with amorphous like morphology were obtained. Therefore, in order to improve the crystallinity, the particles were heated for 30 min at 500°C under N_2 atmosphere. XRD results of heat treated samples indicated that several peaks with a dominant CIS_2 peak were observed. Thus, it can be said that CIS_2 nanoparticles were successfully synthesized in an aqueous solution, without undesirable ligand exchange reaction during reaction.

These results indicated that homogenize metal complexes system of Cu-In-IDA are essential for the synthesis of CIS₂ particles. In our presentation, detailed and another results will be introduced.

This work has been supported by the Grant-in-Aid for Scientific Research (B) (18H03416).

NM04.06.06

Selective Solar Absorber Based on Nickel-Pigmented Anodic Aluminum Oxide Xuanjie Wang and Shankar Narayanan; Mechanical, Aerospace, and Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, New York, United States.

Fossil fuels-coal, petroleum and natural gas-have provided more than 80% of total U.S. energy consumption for more than 100 years. To alleviate our dependence on fossil fuels, renewable energy sources such as solar, wind, and geothermal play an important role in the future. Among them, solar harvesting takes advantage of clean and abundant energy from sun by converting the solar energy to electrical or thermal energy. Considering the clean source and product, solar harvesting is a promising tool to utilize endless energy and reduce greenhouse gases in the environment.

In a typical solar thermal conversion system, sunlight is absorbed in the form of heat at the absorber surface. To enhance the conversion, this absorber needs to strongly absorb the sunlight, while losing less heat to the environment by convection and radiation. Spectrally selective solar absorbers, having a strong solar absorptance and low infrared emittance, are now widely investigated for solar radiation capture in the form of heat. More specifically, Al₂O₃-based selective solar absorbers have been extensively investigated for their excellent optical properties and thermal stability. Several techniques, such as co-evaporation, reactive sputtering and solution-based methods, have been employed to fabricate Ni- Al₂O₃ based selective solar absorbers. The solution-chemical method is desirable due to its low cost and readiness. This method includes two steps: the generation of ordered anodic aluminum oxide pores and the impregnation of nickel. The anodic aluminum oxide with ordered pore geometry is typically fabricated by a two-step anodization in acid solution. The nickel impregnation can be performed under direct or alternating voltage. Salmi et al. carried out the impregnation in a nickel sulphate solution under alternating voltage, which resulted in a coating with a low emissivity (0.14 at 70°C) and high solar absorptivity (> 0.9). To further improve the uniformity of nickel deposition, Nielsch et al. developed a pulsed electrodeposition (PED) method, which shows that nearly 100% of the pores were filled with nanocrystalline nickel with a very small fluctuation in growth rate.

Although the uniform deposition of nickel into porous alumina had been investigated before by using the PED method, the direct connection between porous geometry and surface optical properties has not been previously investigated. Also, by using more modern equipment (e.g. SEM, FIB) with higher resolution, details inside the materials can be characterized with higher accuracy. Understanding this connection and the detailed microstructure of Al₂O₃-based selective solar absorbers will lead to a better understanding and further improvement in solar conversion efficiency.

In this study, we refined the nickel deposition by using PED method and investigated the effects of various nickel deposition parameters on the optical properties of selective solar absorbers.

NM04.06.07

Microkinetic Analysis of Hydrogen Evolution Reaction on Graphene Coupled Molybdenum Carbide Heterostructure Timothy T. Yang and Wissam Saidi; Materials Science, University of Pittsburgh, Pittsburgh, Pennsylvania, United States.

Molybdenum carbides have shown high catalytic activity towards hydrogen evolution reaction (HER) by coupling with graphene supports. However, the atomistic mechanism for the enhanced activities is still lacking. Herein, we use first-principles calculations in conjunction with *ab initio* thermodynamics to investigate the HER on Gamma-phase MoC coupled graphene. Analyzing the reaction pathways and charge transfer events from first principles results, we develop a novel model to predict linear sweep voltammetry in electrochemical conditions based on Volmer-Butler kinetics. Particularly, this model shows that the heterostructure with graphene divacancies reaches its optimum for HER resulting in an overpotential of -0.1 V vs. SHE for 10 mA/cm² current density. We validate this kinetic model by demonstrating that the Volmer-Heyrovsky pathways on the heterostructure are mainly controlled by hydrogen adsorption Gibbs free energy, the descriptor which has been widely used to measure HER activities in the catalyst community.

NM04.06.08

IR-Driven Photoelectrochemical Properties and Band Structures of CdSe/ZnO Heterostructures Fabricated on the Up-Conversion Glass-Ceramics Joo-Won Lee, Joon-Soo Yoon and Yun-Mo Sung; Korea University, Seoul, Korea (the Republic of).

We report the new approach for utilizing infrared (IR) light, which is differentiated from the established routes using heterostructures of up-conversion (UC) fluoride nanoparticles and semiconductor photocatalysts. We introduced the IR-driven photoelectrochemical (PEC) cells using UC glass-ceramics as substrates and this enabled the overcome of the natural instability of UC fluoride nanoparticles, the blockage of incident light, and the restricted exposure of photocatalysts to liquid electrolytes.

Oxyfluoride glass-ceramics containing (Yb,Er)-doped and (Yb,Tm)-doped YF₃ nanoprecipitates were verified to radiate UC green and UC ultraviolet/blue emissions, respectively under 980 nm illumination. High-density ZnO nanorod arrays were fabricated on the UC glass-ceramics substrates via the hydrothermal method and subsequently CdSe/ZnO heterostructures were realized with the chemical bath deposition method.

CdSe nanoparticles with the bandgap of ~1.8 eV were activated by both the UC ultraviolet emission from Tm³⁺ ions and the UC visible emissions from Er³⁺ and Tm³⁺, whereas ZnO nanorod arrays with the bandgap of ~3.2 eV absorbed the UC ultraviolet emission from Tm³⁺ mostly. Two distinct carrier transport mechanisms, so called sensitization and type-II cascade, turned up in the identical CdSe/ZnO photocatalysts originated from the difference in the UC emissions from Er³⁺ and Tm³⁺ ions. Eventually, the CdSe/ZnO fabricated on the UC glass-ceramics containing (Yb,Tm)-doped YF₃ exhibited increased photocurrent density compared to that on the UC glass-ceramics containing (Yb,Er)-doped YF₃ because of the charge separation activated by the type-II cascade transport mechanism.

NM04.06.09

Optically Transparent, Thermally Insulating Aerogels for Energy Efficient Window Applications Elise M. Strobach¹, Bikram Bhatia¹, Lin Zhao¹, Sungwoo Yang², Shaoting Lin¹, Xuanhe Zhao¹ and Evelyn N. Wang¹; ¹Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; ²Civil and Chemical Engineering, The University of Tennessee at Chattanooga, Chattanooga, Tennessee, United States.

The United States uses 14% of the total annual energy produced on heating, ventilation, and air conditioning in buildings. A large portion of this energy is lost through windows, a necessary but lossy portion of the building envelope. High-performance windows use exotic low conductivity gases, large frame footprints, low-emissivity coatings, and complex sealing strategies to achieve high performance, often leading to long payback periods. We propose using high-transparency silica aerogel developed in our lab to reduce energy losses via the super-insulating properties of its nanoporous structure. In this work, we have shown that by controlling density and pore/particle size, we can achieve a visible transmission of >98%, a visible haze <3.0%, and a thermal conductivity of <0.02 W/mK through a 3 mm monolithic slab in ambient conditions. This exceeds the highest clarity reported in literature for silica aerogels, allowing the material to be competitive with traditional window insulating materials at a relatively low cost (\$2 per square foot). We also present an approach to optimize the high-transparency aerogel structure for optical, thermal, and mechanical performance critical to window applications. This is done using structure-property relationships developed in combination with a center-of-pane window performance model to identify the ideal achievable aerogel structure. This optimization approach creates a framework that allows the aerogel to maximize energy efficiency in windows for the varied

performance needed in many different buildings and climates.

NM04.06.10

SnS₂ Nanoparticles and P3HT Blends for Hybrid Solar Cells [Maria E. Perez Barthaburu](#)¹, Daniela Oreggioni¹, Loengrid Bethencourt¹, Mauricio Rodríguez Chialanza¹, Ricardo Santana², Lauro Maia² and Laura Fornaro¹; ¹Departamento de Desarrollo Tecnológico, CURE - Universidad de la Republica, Rocha, Uruguay; ²Instituto de Física, Universidade Federal de Goiás, Goiania, Brazil.

Hybrid solar cells are among the studied technologies for the generation of electric energy from solar energy. In these solar cells, an inorganic electron acceptor of nanometer size must be developed, while a polymer is generally used as donor, being P3HT the most common one. SnS₂ is a semiconductor with an energy band gap of 2.35 eV adequate for its use in hybrid solar cells. Many studies were performed for its application as sensor, in lithium ion batteries, photocatalysis, etc. In the present work, we synthesized SnS₂ nanoparticles (NPs) by the hydrothermal method. SnCl₄·5H₂O and Thioacetamide were used as Sn and S sources. In all the syntheses citric acid was used as capping agent (CA). The ratio Sn:S (1:2) was kept constant, while the ratio Sn:CA was varied to study its influence in morphology and size of NPs. For this purpose, the ratios [2:1], [1:10] and [1:15] were tested. All obtained samples were centrifuged with water and ethanol. The sample with a Sn:CA [1:10] ratio yielded the best results, with hexagonal NPs of 15-50nm and rounded NPs of 2-4nm in size, observed under Transmission Electron Microscope. This sample was selected to perform an exchange of CA. The sample was refluxed in pyridine or aniline during 6 hours (samples S-Py and S-Ani, respectively). They were washed following the same procedure described before. The success of CA exchange was studied by FTIR, confirming the presence of aniline in sample S-Ani and pyridine in sample S-Py. The stability of NPs suspension in chloroform was studied, being important for the preparation of P3HT/SnS₂ blends. It was proved that NPs capped with aniline were more stable than the pyridine ones, presenting a decanting coefficient of 0.02g/L.min. Blends and then layers of SnS₂/P3HT were obtained with both samples, S-Ani and S-Py. Layers were deposited onto glass covered with ITO/PEDOT:PSS substrates, using the spin coating technique. The layers LS-Ani and LS-Py were studied by Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS). EDS results confirmed presence of SnS₂ NPs, while SEM showed that both layers have uniform distribution of NPs. Photoluminescence studies were performed on S-Ani, S-Py, LS-Ani and LS-Py samples. Emission peaks of CA were observed for the samples S-Ani and S-Py. SnS₂ emission is possibly included in these peaks. The layers also showed the characteristic emission peaks of P3HT. UV-Vis spectroscopy studies were carried out to the same samples and to substrates covered with P3HT only, observing two bands of P3HT. Results of layers prepared with different proportions of nanoparticles, proved that there is an electronic coupling between the polymer and the NPs. Our results show that the presence of aniline or pyridine are necessary for the suspension of SnS₂, being aniline the best. Moreover, the spectroscopy results encourage us to further study the photovoltaic properties of layers for the development of hybrid polymeric-inorganic solar cells.

NM04.06.11

Gold Deposited Flexible Nickel Micro-Pillar Structured Substrate for Solar Steam Generator [Soomin Son](#), PilHoon Jung, Jaemin Park, Dongwoo Chae, Sucheol Ju and Heon Lee; Korea University, Seoul, Korea (the Republic of).

Solar steam generators are potential technologies that can be used in a variety of applications such as desalination and sterilization, and are emerging as promising technologies for solar energy harvesting. In recent years, various artificial structures have been developed for the purpose of improving the energy conversion rate by improving solar absorption, thermal localization, water supply and steam transportation. In this research, a solar steam generator was fabricated by depositing plasmon metal particles that can efficiently convert light into heat under sunlight, such as gold on a nickel micropillar (NiMP) structured substrate. The NiMP substrate was confirmed to have a high absorption of 98% or more in the broad spectrum of 300-2500 nm. As a result, we have fabricated the steam generator with high solar conversion efficiencies using high absorbance and light-to-heat efficient conversion under solar light illumination. This structure demonstrates the potential for future regeneration functions, portable solar energy generation and phase change applications, and solar energy based desalination.

NM04.06.12

Improving Ni-YSZ Cermet Anode Performance by Liquid Infiltration of Nickel Catalyst Particles with LSCM [Yanchen Lu](#), Paul Gasper, Boshan Mo, Uday Pal, Srikanth Gopalan and Soumendra Basu; Boston University, Brookline, Massachusetts, United States.

Hydrogen generation and storage are a critical part of a sustainable energy future; a key technology for the production of energy from hydrogen fuel is the solid oxide fuel cell (SOFC). Impregnation of nanoscale metallic catalysts into the anode electrode has been shown in many studies to improve SOFC performance in various ways, such as increase catalytic performance, improve sulfur tolerance, and mitigate coking. The goal of this study is to infiltrate nickel nanoparticles into both anode symmetric cells and anode supported button cells to increase electrochemical active site density and improve anode catalytic performance. The microstructure of infiltrated nickel is engineered by co-infiltrating or sequentially infiltrating an additional electronically conductive phase (La_{0.8}Sr_{0.2}Cr_{0.5}Mn_{0.5}O_{3-δ}). The in-situ formed oxide phase connects nickel nanoparticles, enabling them to be electrochemically active and stabilizes them to mitigate coarsening during operation at high fuel utilization conditions. Electrochemical I-V and EIS results will be utilized to measure performance, and fracture cross-section SEM and TEM analysis used to characterize the infiltrated microstructure and quantify particle degradation.

NM04.06.13

Spray-Flame Synthesis (SFS) of the Nanosized LaMO₃ (M = Fe, Co) Perovskites from Metal Nitrate Precursors—Influence of the Mixture of Ethanol and 2-Ethylhexanoic Acid on Materials' Homogeneity [Steven Angel](#)^{1,2}, Mira Klinge³, Hermann Nirschl³, Klaus Friedel-Ortega⁴, Yuan Wang⁵, Hamidreza Arandiyani⁶, Hartmut Wiggers^{1,2} and Christof Schulz^{1,2}; ¹IVG, Institute for Combustion and Gas Dynamics, University of Duisburg-Essen, Duisburg, Germany; ²CENIDE, Center for Nanointegration, University of Duisburg-Essen, Duisburg, Germany; ³Institute of Mechanical Process Engineering and Mechanics, Karlsruhe Institute of Technology, Karlsruhe, Germany; ⁴Faculty of Chemistry, Inorganic Chemistry, University of Duisburg-Essen, Essen, Germany; ⁵Particles and Catalysis Research Group, University of New South Wales, Sydney, New South Wales, Australia; ⁶Laboratory of Advanced Catalysis for Sustainability, The University of Sydney, Sydney, New South Wales, Australia.

Perovskite nanomaterials composed of LaMO₃ (M = Fe, Co) are of current interest for environmental catalysis applications, e.g., oxidation of CO and CH₄, and for catalytic energy conversion reactions such as water splitting. The synthesis of such compounds is commonly done in time and energy consuming batch processes. Alternatively, spray-flame synthesis (SFS) allows the formation of functional perovskite nanoparticles in a single step. Cost-efficient production requires the utilization of cheap and abundant precursors such as metal nitrates, which are more attractive than the organometallic precursors (acetates, carboxylates). However, the use of metal nitrates in SFS is often associated with the formation of particles non-homogeneous in size¹. Furthermore, the different melting/decomposition mechanisms and their different solubility in solvents such as ethanol cause the formation of undesired phases, e.g., La₂CoO₄, La₂O₃ and Co₃O₄, which are often obtained in parallel to the main perovskite phase. In order to improve the perovskite homogeneity in size and composition, mixtures containing the metal nitrate precursors and two different solvents, ethanol and 2-ethylhexanoic acid (2-EHA), were employed in this study. The incorporation of 2-EHA has been previously investigated and a positive effect toward narrow particle-size distributions has been observed. It is suggested that the addition of 2-EHA leads to the formation of micro-explosions in the droplets through superheating of ethanol and the formation of volatile metal carboxylates², which is investigated in this study.

LaCoO₃ and LaFeO₃ nanoparticles were synthesized from solutions of the respective nitrates in ethanol/2-EHA. To understand the effect of 2-EHA on the product properties, temperature-dependent liquid-phase ATR-FTIR studies were performed. It was found that an esterification of 2-EHA with ethanol occurred forming ethyl-2-ethylhexanoate (verified by GC/MS). We assume that the metal nitrates act as catalysts as reported for similar reactions^{3,4}. The nanoparticle products were characterized using XRD, XPS, TEM, SAXS, and Mößbauer spectroscopy. The measurements confirm that the incorporation of 2-EHA in the solution was effective for obtaining homogeneous, single-phase, and high-surface-area products (LaCoO₃: $d_p = 11$ nm, SSA > 90 m²/g, LaFeO₃: $d_p = 15$ nm, SSA > 88 m²/g). The LaFeO₃ and LaCoO₃ perovskites were evaluated for the catalytic oxidation of carbon monoxide, reaching a 50% CO conversion at temperatures lower than 206°C.

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NM04.06.14

Spray-Flame Synthesis of Ba_{1-x}Sr_xTiO₃ Nanoparticles for Photocatalytic Hydrogen Production Alexander Tarasov^{1,3}, Marco Rehosek², Frank Marlow² and Hartmut Wiggers^{1,3}; ¹Institute for Combustion and Gas Dynamics – Reactive Fluids (IVG), University of Duisburg-Essen, Duisburg, Germany; ²Max-Planck-Institut für Kohlenforschung, Mülheim, Germany; ³Center for Nanointegration Duisburg-Essen, CENIDE, Duisburg, Germany.

Barium titanate (BaTiO₃) and strontium titanate (SrTiO₃) are oxides perovskites with large band gap values (~3.2 eV) suitable for hydrogen production via water splitting under UV light. These materials show high thermal and chemical stability, and the flexibility of the ABO₃ perovskite structure offers the possibility of substituting cations on both, A and B sites, therefore allowing to selectively adjust properties of interest such as band gap width and particle size. While nanoscale cubic SrTiO₃ has been shown a promising catalyst, BaTiO₃ is afflicted by the existence of multiple phases over a narrow temperature range. The cubic phase of BaTiO₃ can be stabilized by the introduction of smaller Sr-atoms, however, the influence on the catalytic activity is not known so far. Therefore, the formation of Ba_{1-x}Sr_xTiO₃ and its catalytic properties was investigated.

Nanosized barium strontium titanate was synthesized in the gas phase by means of spray-flame synthesis (SFS). This scalable method allows a continuous production of oxide nanoparticles and provides a good control over size, crystallinity, and phase composition. The SFS method is essentially a combustion process, whereby high temperatures of the burning spray lead to the evaporation of the dissolved metal precursors, gas-phase reactions, and subsequent particle formation. The applicability of the SFS technique to nanoparticle synthesis has been already demonstrated for many simple oxides (e.g., TiO₂, Al₂O₃ etc.) and has been extended to encompass more complex systems. Additional strength of the SFS technique is a reliable and straightforward doping/substitution as a part of a continuous process.

Ba_{1-x}Sr_xTiO₃ nanoparticles with the following $x = 0, 0.5$ and 1 were synthesized using barium acetate and titanium isopropoxide in propionic acid and isopropanol. X-ray diffraction (XRD) analysis shows a multi-phase system in the case of BaTiO₃, whereas the rest of the powders were found to be phase-pure. Transmission electron microscopy (TEM) suggests an average particle size below 20 nm for all powders. The powder surface was characterized by infrared and X-ray photoelectron spectroscopies (IR-FTIR and XPS), both showing a surface contamination with organics resulting from the imperfect combustion of solvents and precursors. Based on results from thermogravimetric measurements (TGA), a subsequent heat-treatment was applied (800°C) for three hours to remove adsorbed organic carbon species from the surface.

As-produced (AP) and heat-treated powders (HT) were tested in UV light water splitting reaction with methanol and compared with commercially available BaTiO₃ powder. On average, the Sr-containing AP powders show 15% higher hydrogen production rate than the commercial sample. Surprisingly, HT samples show similar activity despite having less surface available as suggested by BET measurements. We attribute this to an initial decomposition of the adsorbents, which no longer hinder the catalytic reaction.

NM04.06.15

High-Efficiency, High-Temperature Cu and Mn Oxides Nanoparticle-Pigmented Anti-Oxidation Solar Selective Coatings via Spray-Coating Method Can Xu, Eldred Lee, Xiaoxin Wang and Jifeng Liu; Dartmouth College, Hanover, New Hampshire, United States.

As an important component of concentrating solar power (CSP) systems, solar selective absorber coatings can help enhance the absorbance in the solar spectrum regime and reduce the emittance loss in the infrared (IR) range [1]. However, many of the current coating products are not capable of maintaining the solar selectivity as well as satisfying the thermal efficiency requirement (>90%) when undergoing high operating temperature [2]. Herein, we report Cu and Mn oxides nanoparticle (NP)-pigmented silicone solar selective coatings on Inconel substrates via a simple hot spray-coating method. The coatings can withstand a high temperature of 750 degrees C for future generations of CSP systems [3], and hence improve the thermal efficiency according to Carnot's Theorem. Based on theoretical modeling [4] and verified by experiments, these NP-pigmented coatings can tolerate a relatively large variation in the pigment NP concentration, diameter, as well as coating thickness, thereby enabling facile spray coating method without the need of stringent thickness control. By adequately selecting silicone precursors with low emissivity and high enough viscosity, the pigment NPs can be well dispersed in the solution for spray coating with excellent stability against precipitation of NPs. To further explore the impact of relevant factors, we varied parameters including types of silicone precursors, organic solvents, compositions and concentrations of NPs, and the thickness of the coatings. Our preliminary optimization effort has already achieved a high solar absorbance of 96.7%, a thermal emittance of 59.1%, and a record-high overall optical-to-thermal energy conversion efficiency of 93.0% for 1000x solar concentration ratio at 750 degrees C, exceeding that of the state-of-the-art Pyromark 2500 black paint (ε90%) at the same temperature [4]. These coatings also block the IR emittance losses of the thermal oxide layers on the Inconel substrates found in previous research [5]. Furthermore, they have already passed 100 h endurance testing at 750 degrees C in air without deterioration in efficiency or mechanical integrity, promising for long-term thermal stability at high temperatures. The high efficiency, high-temperature thermal stability, and simple and facile fabrication process make these Cu and Mn oxide NP-pigmented solar selective coatings especially promising for scaling up in CSP industry.

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NM04.06.16

Cellulose Based Nanomaterials Synthesis for Sustainable Energy Conversion Anand Kumar¹, Jesna Ashraf¹ and Anchu Ashok²; ¹Department of Chemical Engineering, Qatar University, Doha, Qatar; ²Department of Mechanical and Industrial Engineering, Qatar University, Doha, Qatar.

Fuel cells (FCs) have long been considered as an alternative to fossil fuel energy for a sustainable growth and the protection of the ecosystem from harmful emissions. Direct methanol fuel cells (DMFCs) among various types of FCs, have been intensively studied because of their low-operating temperature,

high-energy conversion efficiency, and environmental-friendly nature for micro-power energy strategy. However, Pt is the only commercially available anodic materials, that is reasonably active and stable, as it has shown low CO-poisoning in alkaline media. Alternative materials with low costs are still being sought as suitable catalysts to enable commercialization and widespread application of DMFCs. Here we explore a more sustainable approach that is based on the application of cellulosic materials for large-scale synthesis of transition metals and their alloys with noble metals for various catalytic applications, in particular, fuel cells. In this technique, an aqueous solution of metal nitrate and a reducing agent is impregnated on a thin cellulose paper. The paper is dried and locally ignited at one end to start combustion reaction that is self-sustained under optimum loading of reactive solution, continuously producing nanoparticles. The thin film helps in generating a quenching effect and limits nanoparticles sintering in post-combustion stages. This paper describes the synthesis of Cu, Ni and Co based nanomaterials that are found to be active for sustainable hydrogen production from bioethanol, methanol that can be generated from bio-wastes. A detailed mechanistic study of nanoparticle evolution during synthesis process was conducted along with the reaction pathway analysis for hydrogen production from bioethanol. In-situ FTIR (DRIFTS) studies on the metal surfaces reveal the differences in their catalytic performance and help in explaining the observed product distribution.

ACKNOWLEDGMENTS

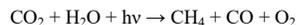
This publication was made possible by NPRP grant (NPRP8-509-2-209) from the Qatar national research fund (a member of Qatar foundation). The statements made herein are solely the responsibility of the author(s).

NM04.06.17

Sustainable CO₂ Conversion Over Visible-Light-Responsive Perovskites via Artificial Photosynthesis Eduardo Morais¹, Kristy Stanley¹, James Sullivan¹ and Ravindranathan Thampi²; ¹School of Chemistry, University College Dublin, Dublin, Ireland; ²School of Chemical and Bioprocess Engineering, University College Dublin, Dublin, Ireland.

The bulk of energy generation on Earth derives from combustion of fossil fuels. This has undesired consequences including the depletion of fossil fuel resources (which are also the principal feedstock of the chemical industry) and the generation of CO₂ (a greenhouse gas which has recognised the generation of which has implications for climate change implications). This reliance on fossil fuels is unsustainable and therefore it is imperative to find alternative cleaner energy sources¹.

This work aims to harness the energy available in solar radiation using photo responsive catalysts to carry out the reduction of CO₂ into CO and/or CH₄ using H₂O as a co-reactant (*i.e.* the artificial photosynthesis reaction). The materials studied are a range of semiconductor Bi₂WO₆ quasi-perovskites Bi₂WO₆. These were prepared *via* facile solvothermal methods at low temperatures and the use effects of surfactants, template agents and microwave radiation within the preparation mixture and surface modifications with amine groups on reactivity was investigated. Also, surface modifications with terminal amine moieties and doping were carried out on the parent materials with the aim of enhancing the photocatalytic activity^{2,3}. All the plain and modified catalysts were characterised using a range of techniques and applied in a batch reactor in the artificial photosynthesis reaction.



The characterization techniques included XRD, UV Visible spectroscopy, SEM and TEM, adsorption/desorption of probe molecules (CO₂ and H₂O), BET and XPS. X-ray diffraction showed both crystalline and amorphous Bi₂WO₆ depending on the synthetic route adopted. SEM and TEM studies revealed that nanoparticle morphologies also depended on the synthesis. The materials had relatively large BET surface areas and TPD experiments confirmed the adsorption / desorption of both CO₂ and H₂O on (and from) the catalyst surface.

The catalysts were tested in the CO₂ + H₂O reaction under simulated solar radiation, evolving CO and CH₄ as products. CO₂ conversion and CO/CH₄ product ratios were dependent on aspects such as surface area and functionalization and light absorption properties (which in turn were dependent on the morphology of the particles).

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NM04.06.19

Photovoltaic and Photocatalytic Properties of Bismuth Oxyiodide-Graphene Nanocomposites Candy C. Mercado, Levannie A. Mabuti and Ian Kenneth Manding; Department of Mining, Metallurgical, and Materials Engineering, University of the Philippines Diliman - ANSYD Lab, Quezon City, Philippines.

Solar energy is considered to be the most viable solution for the future energy crisis and water pollution. In this study, we evaluate the photovoltaic and photocatalytic properties of chemical vapor deposited bismuth oxyiodide (BiOI) and bismuth oxyiodide-graphene (BiOI-GR) nanocomposite thin films. They were characterized using XRD, SEM, UV-Vis spectrophotometer, and EIS. The BiOI thin film has an average thickness of 574 nm and a bandgap of 2.12 eV. The BiOI and BiOI-GR thin films exhibited nanoflake morphology. It was found that addition of graphene increases absorbance by causing vertical growth of nanoflakes, imparting anti-reflectance and light trapping and also suppresses recombination due to its electron accepting nature. The photocatalytic activities of the thin films were evaluated by examining methylene blue (MB) degradation under visible light irradiation. BiOI-GR degraded 56.42% of MB in two hours while BiOI degraded 44.16%. Afterwards, FTO | BiOI | Graphite | Al and FTO | BiOI-GR | Graphite | Al solar cell devices were fabricated with photocurrent density values of 0.20 μA/cm² and 0.27 μA/cm², respectively. The improved properties of BiOI-GR are attributed to the anti-reflecting and light trapping properties of vertical BiOI-GR nanoflakes and the enhanced carrier separation due to graphene.

NM04.06.20

Oxide Anchored, Carbide Supported Pt Nanoparticles for Oxygen Reduction Reaction Zishuai Zhang¹, Amin Sadeghi¹, Nicolas Brodusch¹, Raynald Gauvin¹, Jeff Gostick², Siyu Ye³, Geraldine Merle¹ and Jake Barralet¹; ¹McGill University, Montreal, Quebec, Canada; ²University of Waterloo, Waterloo, Ontario, Canada; ³Ballard Power System Inc., Burnaby, British Columbia, Canada.

Transition metal carbides have attracted increasing attention recently as low-cost electrocatalyst supports for the oxygen reduction reaction (ORR) due to some conductivity and relative stability. Furthermore, transition metal carbides can promote electron transfer between the catalysts and supports.^[1] To further improve the carbide conductivity and stability, especially at higher potentials (TIC>1.5V), we developed a process for the formation of a cobalt oxide protective shell on Pt decorated TiC. The oxide was removed selectively at the location of the Pt thereby creating a protective layer for the carbide only. It had the unexpected advantage of physically anchoring the Pt to the carbide. We examined ORR activity and stability of these composite particles by chronoamperometry analysis in oxygen-saturated 0.1M KOH for 15h.

Here, we reported the synthesis of anchoring Pt nanostructured catalysts for ORR. The approach includes the deposition of a thin layer of uniform cobalt (oxide) nanoparticles on the TiC/Pt (40 wt% Pt) core by the cobalt citrate (formed the reaction between citrate acid and cobalt nitrate) crystallination process. The method consists in depositing platinum before the cobalt layer, and 5 wt% hydrogen peroxide was used to burst the cobalt shell to expose platinum nanoparticles.

Electron microscopy confirmed that the platinum nanoparticles were in contact with both the carbide core and cobalt shell. These coated carbide nanomaterials had greatly improved stabilities as supports compared with pristine carbides (chronoamperometry curve showed no activity loss at 0.6V vs RHE after 15h) without compromising their catalytic activities. Additionally, the core-shell mathematical diffusion model simulation confirmed experimental results: the cobalt oxide shell acts as a strong diffusion barrier for the oxygen diffusion, which can dramatically slow down the carbide oxidation process. Very good agreement was found between the simulated and experimental data indicating that *in silico* experiments may optimize the approach further.

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NM04.06.21

Dissolution and Redesign of Complex Metal Oxides—How the Thermodynamics of Transformations Can Guide Sustainable

Nanotechnology Joseph W. Bennett¹, Diamond Jones¹, Christy L. Haynes², Robert J. Hamers³ and Sara E. Mason¹; ¹Department of Chemistry, University of Iowa, Iowa City, Iowa, United States; ²Chemistry, University of Minnesota, Minneapolis, Minnesota, United States; ³Chemistry, University of Wisconsin–Madison, Madison, Wisconsin, United States.

Nanoscale complex metal oxides have transformed how technology is used worldwide. The most widespread examples are the electroactive components of Li-ion batteries found in portable electronic devices. As the number of portable devices is projected to increase, so too will the inadvertent release of complex metal oxide nanomaterials into the environment. This is a pressing problem because the environmental and biological impact of complex metal oxide nanomaterials are most times unknown, since they are subject to transform rapidly with changes in pH and concentration. This brings us to a looming problem that needs to be solved on a global scale. There is a fundamental knowledge gap in developing sustainable nanotechnology because there is not yet a systematic method to predict how the properties of a complex metal oxide will change with changes in chemical environment. We have developed an analysis, based on Hess's Law, which combines DFT-computed total energies and experimentally adjustable reaction conditions to compute the surface dissolution of complex metal oxides. We focus on the materials found in a Li-ion battery cathode, namely LiCoO₂ and compositionally tuned variants with general chemical formula Li(Ni_xMn_yCo_z)O₂. We find that adjusting surface terminations, compositions and pH will change the dissolution properties of this family of materials, and yields insights into the nanoscale transformations that may take place under a given set of conditions. Not only can these results be used to improve environmental fate and toxicity models, but we are able to use the results of our analysis to create a set of rational design rules to govern the creation of the next-generation of Li-ion battery cathodes that will be benign by design.

NM04.06.22

Internal Polarization Modulation in Nanostructured Bi₂MoO₆ for Photocatalytic Performance Enhancement Under Visible Light

Illumination Yan Chen¹, Weiyi Yang¹, Shuang Gao², Linggang Zhu³, Caixia Sun⁴ and Qi Li¹; ¹Institute of Metal Research, Chinese Academy of Sciences, Shenyang, China; ²Graduate School at Shenzhen, Tsinghua University, Shenzhen, China; ³Beihang University, Beijing, China; ⁴Qingdao Binhai University, Qingdao, China.

Recently, the introduction of a built-in electric field inside polar photocatalysts was proved effective for the improvement of their photocatalytic performances because the internal electric field could provide the driving force for electrons and holes to move in opposite directions for their enhanced separation. Most research in polar photocatalysts is now focused on exploring polar semiconductors as novel photocatalysts, including GaN, ZnO, BaTiO₃, NaNbO₃, Sr₂(Ta,Nb)O₇, Cu₂(OH)PO₄, BiOCl, BiOF, BiOIO₃, Na₃VO₂B₆O₁₁, and Bi₇Fe₃Ti₃O₂₁, while fewer efforts had been made on the modulation of their internal polarization through the precise control of their structure to modulate their photocatalytic performances.

Bi₂MoO₆ is one of the simplest members of the Aurivillius family, which is composed by [Bi₂O₂]²⁺ layers sandwiched between MoO₄²⁻ slabs. The strong covalent bonding within these layers and the weak interlayer van der Waals interaction give rise to a highly anisotropic structure of Bi₂MoO₆. It had been found that the internal electric field formed between the [Bi₂O₂]²⁺ and MoO₄²⁻ layers in Bi₂MoO₆ could effectively separate photogenerated charge carriers, while the hybridization between its O 2p and Bi 6s states could narrow its band gap to enable the absorption of visible light. Thus, it had drawn research attentions as an efficient visible-light-activated photocatalyst for various applications. More interestingly, its layered structure with weak interlayer interaction could provide the potential to be modulated, which could subsequently change its internal polarization and open up an unexplored avenue to further enhance the photocatalytic performance of a polar photocatalyst.

Herein, we report the modulation of internal polarization in nanostructured Bi₂MoO₆ by the precise control of its structure through both the theoretical and experimental approaches for the first time. Theoretical calculation based on density function theory (DFT) discovered that the internal polarization in Bi₂MoO₆ could be increased by shortening its crystal lattice parameter *b*. Subsequently, a simple, one-pot template-free solvent-thermal process was developed for the synthesis of nanostructured Bi₂MoO₆ photocatalyst, and the addition of NaOH in the reaction solution was found to be effective to shorten its crystal lattice parameter *b*. With shortened crystal lattice parameter *b*, the nanostructured Bi₂MoO₆ photocatalyst demonstrated improved photogenerated charge carrier separation efficiency due to its increased internal polarization as demonstrated by the powder second-harmonic generation (SHG) signal measurement, and subsequently possessed a largely enhanced photocatalytic performance as demonstrated in its photocatalytic degradation of organic pollutants and disinfection of *staphylococcus aureus* bacteria under visible light illumination.

NM04.06.25

Top Emitting InP Quantum Dot Light Emitting Diodes with High Efficiency Through Improved Charge Balance Taesoo Lee and Changhee Lee; Seoul National University, Seoul, Korea (the Republic of).

Top emitting quantum dot light emitting diodes (TQLEDs), which emits light in the direction to the top electrode, is being researched due to its advantages of higher current efficiency, higher aperture ratio, narrow full-width-half-maximum (FWHM) than bottom emitting QLEDs, and its applicability to industry[1-3]. On the other hand, there is an environmental issue when using cadmium based quantum dots as an emissive layer. For this reason, Cd-free QLEDs such as indium phosphide (InP) QLEDs are being actively researched. [4] The InP QLEDs, however, needs further improvement in their performances, which are quite inferior to Cd-based ones until now. In this work, we simulated and enhanced the efficiency of the InP QLEDs by changing the device structure from bottom emission to top emission type. In addition, we introduced thin semi-insulating interlayer between emissive layer and hole transport layer (HTL) for optimized electron/hole balance. Compared to the bottom emitting counterparts, top emitting device showed remarkable improvements in its current efficiency, maximum luminance and FWHM. The current efficiency improved from 6.9 cd/A to 10.4 cd/A, maximum

luminance from 3,300 nit to 31,700 nit, and FWHM from 41 nm to 37 nm. Refining the device structure by inserting hole suppressing interlayer further increased the device efficiencies. The top emitting device with 5 nm interlayer between QDs and HTL showed its maximum current efficiency of 21.6 cd/A, maximum luminance of 17,400 nit, and FWHM of 37 nm, which is the highest current efficiency for InP QLEDs reported to date. This breakthrough is attributed not only to the enhancement of light extraction by introducing top emitting structure, but also to the balanced charge densities inside QDs by suppressing hole injection from HTL to QDs. We believe that our result is a step forward to make highly efficient InP QLEDs.

SESSION NM04.07: Nanocomposites I
Session Chairs: Ray Baughman and Yury Gogotsi
Wednesday Morning, November 28, 2018
Sheraton, 2nd Floor, Back Bay C

9:00 AM NM04.07.01

Strong Covalent Bonding Modulated Graphene Oxide/Epoxy Interfacial Enhancement and Advanced Corrosion Resistance Haihua Wang^{1,2}, Jingyi Li¹, Guiqiang Fei¹ and Ke Zhu¹; ¹Shaanxi University of Science and Technology, Xi'an, China; ²Department of Material Science and Engineering, Northwestern University, Evanston, Illinois, United States.

Chemically functionalized graphene oxide (MAGO) was achieved by building covalent bonds between graphene oxide (GO) and a small molecule containing benzene structure and multi-amino groups. FT-IR, XRD, X-ray photo electron spectroscopy and TEM-EDX results certified that the molecule was successfully grafted onto GO nanosheets. Subsequently, functionalized GO was incorporated into waterborne epoxy (EP) coating through ball-milling method. This molecular design can significantly improve the dispersion of MAGO in EP matrix, as well as the compatibility and interaction between MAGO and EP. Compared with GO/EP, the water absorption of MAGO/EP decreased from 4.38% to 2.59%, the adhesion strength of MAGO/EP increased from 4.72 MPa to 6.32 MPa after immersion of 40 days in 3.5 % NaCl solution. Incorporation of 1 wt% of MAGO into EP matrix prominently improved the long-term corrosion resistance. The impedance modulus of GO/EP coating decreased by four orders after 40 day immersion, while that of MAGO/EP coating only decreased by one order. The impedance modulus was still $1.47 \times 10^8 \Omega \cdot \text{cm}^2$, and two-time constant wasn't detected for MAGO/EP coating. This research developed a facile approach to prepare green anticorrosion coating with enhanced durability for metal protection. MAGO can also be utilized as nanofillers for other waterborne polymer matrixes to fabricate green anticorrosion coatings of high performance.

9:15 AM NM04.07.03

Real-Time Observation of Single CNT Fiber Subjected to Transverse Ballistic Impact Jae-Hwang Lee¹, Wanting Xie¹, Robert Headrick², Runyang Zhang³, Lauren Taylor², Matteo Pasquali² and Sinan Müftü²; ¹University of Massachusetts, Amherst, Massachusetts, United States; ²Rice University, Houston, Texas, United States; ³Northeastern University, Boston, Massachusetts, United States.

Carbon nanotubes (CNTs) are promising constituents as high-performance mechanical materials due to the high intrinsic strength and low density. CNTs have displayed high strength and stiffness combined with low density, they are very promising, with much higher theoretical tensile strength over polymeric fibers. Up to now, mechanical tests on CNT fibers have mostly been within the quasi-static regime, which is inadequate for assessing the high-strain-rate performance of CNT fibers.

We demonstrate supersonic impacts of a micro-projectile on a CNT fiber. Three other fibers, Kevlar KM2 filaments, Nylon 6,6 filaments, and pure aluminum filaments, are also investigated under the same conditions for comparison. The fiber (~10 μm in dia.) is mounted in air using two epoxy supports and individual glass spheres (~30 μm in dia.) impact on the fiber perpendicular to the fiber's axial direction at ~500 m/s. The real-time deformation process is recorded using a microscope system using ultrafast white light generated by the nonlinear conversion of femtosecond pulses. This microscopic ultrafast imaging technique provides accurate kinetic information of the impacting micro-projectiles and the responding fiber. We observe the characteristic deformation of each fiber during the impact, and measure instantaneous velocity and acceleration of the projectile. In terms of the specific energy dissipation rate of the micro-projectile interacting with the fiber, the CNT fibers demonstrate superior impact mitigation performance to the other three fibers, including Kevlar KM2, primarily due to the highest transverse wave speed of the CNT fibers. Scanning electron microscopy is used to study the post-impact damage features of the fibers. For the CNT fibers, Raman spectroscopy mapping is used to reveal the impact-induced lattice damage of CNTs.

9:30 AM NM04.07.04

Intragranular Dispersion of Carbon Nanotubes Comprehensively Improves Aluminum Alloys Kang Pyo So¹, Akihiro Kushima², JongGil Park³, Xiaohui Liu⁴, Dong Hoon Keum⁵, Hye Yun Jeong³, Fei Yao³, Soo Hyun Joo⁵, Hyoung Seop Kim⁵, Hwanuk Kim⁶, Ju Li¹ and Young Hee Lee³; ¹Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; ²University of Central Florida, Orlando, Florida, United States; ³Sungkyunkwan University, Suwon, Korea (the Republic of); ⁴Shanghai Jiao Tong University, Shanghai, China; ⁵Pohang University of Science and Technology, Pohang, Korea (the Republic of); ⁶Korea Basic Science Institute, Daejeon, Korea (the Republic of).

One-dimensional carbon nanotubes (CNTs), which are mechanically strong and flexible, possess better structural properties than their counterpart nanoparticles/nanowires. Well-dispersed CNTs act like forest dislocations, therefore it can harden the metal pretty much like stored dislocation line density, *as well as* still acting like a composite filler and transmitting load directly. We report an intragranular dispersion strategy of CNTs in Al matrix that leads to comprehensively improve mechanical, electrical/thermal properties of Al alloys. This was in turn rationalized by "cold welding" and rapid surface diffusion of Al atoms in vacuum-environment mechanical ball milling, which buried the MWCNTs *inside* the master alloy particles. This cold welding and burying process were revealed by in situ transmission electron microscopy (TEM) experiments under similar vacuum conditions. Our way of producing master alloy and dispersing them are thus key for the comprehensive superiority of the properties over other methods of making Al+CNT nanocomposites.

9:45 AM NM04.07.05

Axial Reinforcement of Unidirectional Composites by Self-Aligned Graphene Robert Young and Zheling Li; University of Manchester, Manchester, United Kingdom.

The modern structures employed in aerospace and automotive applications are becoming lighter and thinner, but still require high levels of aerodynamic and vibration stability, leading to the stiffness becoming a dominate design driver. Since graphene has high levels of stiffness and strength its use as a reinforcement in polymer composites shows huge potential of further enhancing the mechanical properties of composites. Although there has been a rapid growth of interest in graphene-based polymer nanocomposites for structural applications, the mechanics of reinforcement in such materials has only recently become understood [1,2].

It is shown that the addition of approximately 2% by weight of graphene to the matrix of a unidirectionally-reinforced carbon fiber epoxy composite can lead to a significant enhancement in mechanical properties. In particular, it is found that the axial stiffness of the composites can be increased by the order of 10 GPa accompanied by an increase in axial strength of 200 MPa. X-ray computed tomographic imaging and polarized Raman spectroscopy have demonstrated that the graphene is predominately aligned parallel to the axes of the carbon fibers. Moreover stress-induced Raman band shifts showed that the self-aligned graphene is subjected to high levels of stress during axial deformation of the composite. The graphene is found to have an effective Young's modulus in the composite of around 825 GPa, approaching its theoretical value of 1050 GPa. This behavior has been modelled using the rule of mixtures and shear-lag analysis and it is demonstrated that highly-aligned graphene in a constrained environment between high-modulus fibers can give significantly better mechanical reinforcement than graphene in conventional polymer-based nanocomposites. It has been demonstrated the enhancement is due to three effects: (a) the alignment of graphene around the fiber by a 'filtering' effect; (b) confinement of graphene between the fiber gaps and (c) the matrix being stiffened by the carbon fibers. It shows the considerable potential of using graphene to enhance the mechanical properties of conventional carbon fiber composites even in the high-stiffness fiber direction.

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10:00 AM BREAK

10:30 AM *NM04.07.06

Strong, Tough Graphene Sheets by a Low Temperature Sequential Bridging Process Sijie Wan², Qunfeng Cheng² and Ray H. Baughman¹; ¹The University of Texas at Dallas, Richardson, Texas, United States; ²School of Chemistry, Beihang University, Beijing, China.

We here show that infiltrated bridging agents can convert inexpensively fabricated graphene platelet sheets into high performance materials, thereby avoiding the need for a polymer matrix. Two types of bridging agents were investigated for interconnecting graphene sheets, which attach to sheets by either π - π bonding or covalent bonding. When applied alone, the π - π bonding agent is most effective. However, successive application of the optimized ratio of π - π bonding and covalent bonding agents provides graphene sheets with the highest strength, toughness, fatigue resistance, electrical conductivity, electromagnetic interference shielding efficiency, and resistance to ultrasonic dissolution. Raman spectroscopy measurements of stress transfer to graphene platelets allow us to decipher the mechanisms of property improvement. In addition, the degree of orientation of graphene platelets increases with increasing effectiveness of the bonding agents, and the interlayer spacing increases. When compared with other materials that are strong in all directions within a sheet, the realized tensile strength (945 MPa) of the resin-free graphene platelet sheets was higher than for carbon nanotube or graphene platelet composites, and comparable to that of commercially available carbon fiber composites. The toughness of these composites, containing the combination of π - π bonding and covalent bonding, was much higher than for these other materials having high strengths for all in-plane directions, thereby opening the path to materials design of layered nanocomposites using multiple types of quantitatively engineered chemical bonds between nanoscale building blocks. Y. Li, J. Mu, A. Aliev, S. Fang, N. A. Kotov, and L. Jiang also collaborated on this work.

11:00 AM NM04.07.07

Preparation and Nanostructure Analysis of Graphitic Carbon Infused Copper Alloys Beihai Ma¹, Uthamalingam Balachandran¹, Steve Dorris¹, Tae Lee¹, Jie Wang¹, Jianguo Wen¹, Yuzi Liu¹, Jonathan Poplawsky² and Adam J. Rondinone²; ¹Argonne National Laboratory, Lemont, Illinois, United States; ²Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

We prepared graphitic carbon nanostructure infused copper alloys by electron-beam melting. This new class of materials, known as copper covetics, exhibit enhanced electrical and thermal conductivities. We observed up to 30% enhancement in electrical conductivity in covetic copper thin films deposited by electron-beam evaporation. Our results revealed remarkable promise for applications as interconnects in the next generation integrated circuits and memory devices. Understanding the nature of interaction between the carbon nanostructures and their host metal is critical to elucidate the origins for superior properties. We utilized atom probe tomography (APT), helium ion microscopy (HIM), high-resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM) in the study of carbon nanostructures in copper covetics and thin films. APT revealed 3D distribution of carbon-rich nanoclusters; HIM provided unique opportunity to visualize carbon nanostructures in metal matrix due to its superior contrast and resolution; HRTEM and STEM elemental mapping verified the existence of carbon nanoparticles and networks in the copper metal hosts. Details of experimental results will be presented in this talk.

This work was supported by the U.S. Department of Energy (DOE), Energy Efficiency and Renewable Energy, Advanced Manufacturing Office, under Contract DE-AC02-06CH11357. HRTEM and STEM were performed at the Center for Nanoscale Materials at Argonne, a DOE Office of Science User Facility. APT and HIM experiments were conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

11:15 AM NM04.07.08

Water-Processable Cellulose-Based Resist for Green Nanofabrication Camilla Dore¹, Johann Osmond² and Antonio Agustín Mihi¹; ¹ICMAB-CSIC, Bellaterra, Barcelona, Spain; ²ICFO–The Institute of Photonic Sciences, Barcelona, Spain.

Cellulose is the most abundant polymer on Earth and for centuries has had a wide technological impact in areas such as textile, packaging or knowledge storage. Cellulose is biodegradable, biocompatible and possesses excellent mechanical characteristics that have raised the interest of many engineering fields. In our manuscript, we introduce an exciting new path for cellulose derivatives. We report a new lithographic process employing hydroxypropyl cellulose (HPC), a biocompatible and biodegradable cellulose derivate, and water as only chemicals. We use hydroxypropyl cellulose as a nanoimprinting and electron beam lithography resist and demonstrate its potential by fabricating photonic crystals and 2D metal nanoparticle arrays with up to 100 nm resolution over 1 cm² areas. Beyond its biocompatibility and abundance, we combine this cellulose with traditional resists non-soluble in water (PMMA), leading to advanced fabrication possibilities. We fabricated alternating stacks of HPC and PMMA in which each material is selectively removed with the proper solvent. Furthermore, when combined with nanoimprinting, sub-micrometric air cavities are left inside the PMMA, enabling a straightforward nanofabrication strategy for novel optofluidic devices.

11:30 AM RAPID FIRE PRESENTATION

1:30 PM NM04.08.01

Additive Manufacturing of Cellulose Nanofibril Materials Kevin T. Turner¹, Lisa M. Mariani¹ and John M. Considine²; ¹University of Pennsylvania, Philadelphia, Pennsylvania, United States; ²USDA, US Forest Service, Forest Products Laboratory, Madison, Wisconsin, United States.

Cellulose nanofibrils (CNFs) are high aspect ratio nanofibers (dia. ~10 nm) that have high specific stiffness and strength, and are also optically transparent and biodegradable. These properties make them attractive building blocks for bulk structural materials. However, to date, the overall dimensions of bulk materials comprised of CNFs are significantly limited by the development of residual stresses generated during the drying process. CNF solutions gel at low volume fractions (~1%), thus a significant amount of water must be removed during drying. Here, we overcome these issues by producing CNF films and structures by additive manufacturing (i.e., 3D printing) of a shear thinning aqueous CNF suspension under controlled drying conditions. The multistep layer-by-layer manufacturing process allows for control of drying and management of residual stresses. The fabricated materials have Young's moduli and fracture strengths greater than 10 GPa and 70 MPa, respectively. Mechanical characterization is supported by additional characterization via atomic force, optical, and electron microscopy. This study demonstrates the ability to additively manufacture stiff, strong, and uniform materials comprised of sustainable cellulose nanofibril materials.

1:45 PM NM04.08.02

From Sol Gel Electrospun Composite Nanofibers to Ultralight and Flexible Aerogels Tahira Pirzada and Saad A. Khan; Chemical & Biomolecular Engineering, North Carolina State University, Raleigh, North Carolina, United States.

We present a facile and sustainable solid templating approach to fabricate highly porous and superhydrophobic aerogels of composite nanofibers of cellulose diacetate and silica which are produced through sol gel electrospinning. Scanning electron microscopy, contact angle measurement and attenuated total reflection-Fourier transform infrared spectrometry are used to understand the structural features of the resultant aerogels while thermogravimetric analysis and differential scanning calorimetry demonstrate their thermal stability as compared to cellulose diacetate. These aerogels exhibit a self-supportive three-dimensional network abundant in large secondary pores surrounded by primary pores resulting in a highly porous structure. Thermal crosslinking of the aerogels has further stabilized their structure and flexibility without compromising on the porosity. Ease of processing, thermal stability, high porosity and superoleophilic nature of these aerogels make them promising candidate for applications like thermal insulation and oil and water separation.

2:00 PM NM04.08.03

A High Concentration Approach to Magic-Sized Cluster Scale-Up Curtis Williamson¹, Richard Robinson¹, Tobias Hanrath¹, Douglas Nevers¹, Lena Fitting Kourkoutis¹, Benjamin H. Savitzky¹, Ido Hadar² and Uri Banin³; ¹Cornell University, Ithaca, New York, United States; ²Chemistry, Northwestern University, Evanston, Illinois, United States; ³The Hebrew University of Jerusalem, Jerusalem, Israel.

Magic-sized clusters (MSCs) are renowned for their identical size and precise composition, existing at an intermediate length scale between small molecule and conventional nanocrystal. Nanocrystal systems have been extensively studied and modeled to understand the synthesis, yet this knowledge does not directly translate upon scale-up and current production yields are miniscule. Furthermore, despite efforts, nanocrystals still possess a disparity in size, shape, and composition (although small) that in essence is a distribution of products. Hence, MSCs provide a quintessential framework to understand colloidal synthesis and assembly across length scales. Traditionally, the origin of the MSC stability was thought to derive from the "closed-shell" arrangement of atoms; this inhibits the continuous growth that is typically seen with nanocrystals. However, in semiconductor MSCs, we report that the MSC stability is strongly coupled to an organic-inorganic mesophase: a fibrous self-assembly of inorganic clusters passivated with organic ligands that form during high concentration (1000 mM) synthesis. This mesophase behaves as a large suspended network (>100 nm grains) that stabilizes and promotes a well-defined reaction pathway for the formation of high-purity MSC. Conversely, diluting precursor concentration (<500 mM) impedes mesophase formation and thus inhibits MSC formation. To identify the hexagonal mesophase where these MSCs persist, we utilized in-situ small and wide angle x-ray scattering, which also revealed that the rate of mesophase formation is proportional to the MSC nucleation rate. The MSCs still preserve their fibrous mesophase assembly after separation and purification. Akin to protein systems, these fibrous assemblies (secondary structure) of MSCs (primary structure) align into bundles (tertiary structure) that form banded (quaternary) structures under uniaxial shearing and drying. Polarization spectroscopy revealed that not only are the individual clusters strongly anisotropic with polarized emission, but also their assembly into highly ordered banded structures at the millimeter length scale yield polarized absorption. This high degree of polarization across magnitudes of self-assembled length scale enables investigation into novel optical properties, which previously has only been accomplished in metamaterials. The high concentration synthesis of magic-sized clusters not only produces larger quantities of single-sized nanomaterials, but also deepens the understanding of nanosynthetic pathways and enables novel property development.

2:15 PM NM04.08.04

Lightweight Organosilica Foams Prepared from a Surface-Active Aminosilane and Cellulose Nanofibrils Korneliya S. Gordeyeva, Hugo Voisin, Niklas Hedin, Lennart Bergström and Nathalie Lavoine; North Carolina State University, Raleigh, North Carolina, United States.

Organosilica foams are widely used for applications such as thermal and acoustic insulation, CO₂ adsorption and water purification. Organosilica foams are commonly obtained by elaborate multistep processes involving hydrolysis and condensation of organosilanes followed by solvent exchange and *e.g.* supercritical CO₂ drying.

Here, we report a novel, simple and energy-efficient approach for the preparation of hybrid organosilica foams from aqueous mixtures of a surface-active aminosilane (AS) and TEMPO-oxidized cellulose nanofibrils (TCNF) that introduces air bubbles in the TCNF/AS dispersion by mechanical blending followed by ambient pressure drying to obtain the solid foam. The dry foams displayed low densities (25-50 kg/m³) and high porosities (96-99 %) with monodisperse macropore sizes of 150-300 μm. NMR showed that the hydrolysis and condensation of the surface-active AS was triggered by the increase of the temperature and solvent evaporation during the drying step. The influence of the pH and AS concentration on the foaming behavior and foam stability will be presented and correlated to the rheological properties and the interactions between the AS and TCNF. We will demonstrate that by variation of pH and AS concentration foams with defined density, homogeneity and porosity can be prepared.

2:30 PM BREAK

3:30 PM *NM04.08.05

Nanocomposite Sensing Skins for Human and Structural Monitoring [Kenneth J. Loh](#); Department of Structural Engineering, University of California, San Diego, La Jolla, California, United States.

Both physical structures and human assets are susceptible to *deterioration* and *damage* that can degrade their performance, especially in challenging operational conditions. For example, the safety of aerospace, civil, and marine structures are jeopardized by damage due to excessive loading, corrosion, and impact. On the other hand, monitoring the health and physiological performance of the warfighter is necessary for ensuring their combat readiness. Therefore, the objective of this research is to develop a sensing platform that can be used for both structural health monitoring and human performance assessment. The approach is to design flexible and scalable coatings that are designed whose electrical properties are selectively sensitive to a certain type of external stimulus and can be deposited onto various structural surfaces. Here, these sensors are designed from a materials perspective stemming from a "bottom-up" design methodology. Nanomaterials and conductive polymers are judiciously chosen, and then assembled, to realized nanocomposite thin films that are sensitive to parameters such as strain or pH. First, this work begins with a discussion of how carbon nanotubes (CNT) and graphene nanosheets (GNS) could be used during spray-coating, micro-plotting, and screen-printing to form thin film strain sensors. Second, tensile-compressive tests were performed to validate their sensing behavior. Third, a percolation-based model was implemented to explain the nano-/micro-scale mechanisms that enable their bulk film behavior, and the model was employed for determining fabrication parameters that enhanced sensing performance. However, even after optimization, a fundamental limitation was that they remained as discrete sensors, where one could only obtain information about the physical or human structure at the location where the sensor was instrumented. Thus, by coupling the films with an electrical impedance tomography (EIT) measurement strategy and algorithm, reconstruction of the two-dimensional resistivity or conductivity distribution of these materials was possible. These "sensing skins" could then be implemented to sense and localize *damage* features over large spatial domains. Distributed strain, impact, crack, and pH sensing was successfully validated.

4:00 PM RAPID FIRE PRESENTATION

SESSION NM04.09: Poster Session III: Nanocomposites
Session Chairs: Babak Anasori, Monica Jung de Andrade and Maria Perez Barthaburu
Wednesday Afternoon, November 28, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

NM04.09.01

Impact of Graphene Oxide Dispersity on Its Applications [Harish V. Kumar](#), Thomas Francnis and Douglas Adamson; Polymer Program- Institute of Materials, University of Connecticut, Storrs, Connecticut, United States.

Graphene oxide (GO) is used in various applications due to its unique surface properties. One of the important features of GO is that it stabilizes oil-in-water emulsions by staying at the interface of the two phases. We harness this property of GO to act as a surfactant in order to characterize, fractionate, and use the system for various applications. Different batches of GO are composed of graphene sheets with different degrees of oxidation. We divide graphene oxide sample into differently oxidized fractions using emulsion based fractionation method. In this emulsion based method, more oxidized GO sheets suspend in a water phase, while the less oxidized material stabilizes the emulsion phase. This method provides the ability to control different properties of GO. These GO fractions are characterized by different techniques including XRD, UV/vis, elemental analysis, and Raman spectroscopy. Further, we explore the property changes of polymer/graphite oxide (GO) nanocomposites as the degree of GO oxidation is changed. We have found that emulsifying a sample of GO separates the sheets into fractions of differing degrees of oxidation and we have demonstrated that this variation in degree of oxidation of GO plays a role in the improvement of tensile properties of GO based polymer nanocomposites. The interaction of GO sheets with the polymer matrix plays an important role in the mechanical properties of the nanocomposites. In addition, the mechanical properties are also dependent on the hydrophilic or hydrophobic nature of the polymers. We further investigate polymer nanocomposites made from oil-in-water emulsion systems stabilized by GO. The nature of the emulsion systems can be controlled by replacing a part of GO with graphene sheets as well as by altering the type of GO used. This approach provides a route to control the shape and conductivity of these polymer nanocomposites. In addition, we describe further merits of the fractionation method, as well as explain the impact controlling the extent of oxidation has on various other GO based applications.

NM04.09.02

Ultrasonic Deacetylation—A Rapid Method to Covert Cellulose Acetate into Cellulose Nanofibers [Muzamil Khatri](#), Ick Soo Kim and Zeeshan Khatri; Shinshu University, Ueda City, Japan.

Electrospun nanofibers are getting more attraction because of their prominent applications such as light weight, permeability, breatheability, filtration, biomedical, apparel and functional applications. Cellulose nanofibers because of high absorbency and high surface area is also considered one the efficient material for potential applications. Getting electrospun cellulose nanofibers is highly time consuming, conventionally deacetylation process takes upto 30 hours to convert cellulose acetate into cellulose.

We attempted to use ultrasonication to enhance efficiency of deacetylation process. We successfully deacetylated cellulose acetate by using ultrasonic method which only took 1 hour instead of 30 hours. SEM showed smooth morphology before and after ultrasonic deacetylation. XRD showed increased crystallinity after deacetylation because cellulose substrate has more crystalline region. Wicking behaviour was also enhanced after deacetylation which is another evidence to justify conversion. FTIR showed chemically converted cellulose after deacetylation process.

NM04.09.03

Surface-Modified Cellulose Nanofibers for the Effective Reinforcing Materials of Poly(ϵ -caprolactone) Composites [Hiroki Ichimura](#), Naruki Kurokawa and Atsushi Hotta; Keio University, Yokohama-shi, Japan.

Poly(ϵ -caprolactone) (PCL) is one of the leading biocompatible and biodegradable polymers, having the great potential for an alternative material of polyolefins such as polyethylene and polypropylene. However, the mechanical property of PCL is relatively poor as compared with that of polyolefins, which has limited the active applications of PCL for an industrial material. In this study, to enhance the mechanical property of PCL, cellulose nanofibers (C-NF), compounding agents of several composites due to their high mechanical property, were investigated for the reinforcement material of PCL. The C-

NF were fabricated via the electrospinning of cellulose acetate (CA) before the saponification of CA. The spinning solution was prepared by dissolving CA in the mixed solvent of acetone/dimethylacetamide (6/4 wt/wt) and the concentration of CA was set at 20 wt%. The electrospun CA nanofibers were saponified in a 0.05 M NaOH/ethanol solution to finally obtain C-NF. For the enhancement of the mechanical property of the PCL composite, the compatibility of C-NF and PCL was studied. The surface modification of C-NF was performed by the ring-opening polymerization to graft PCL onto C-NF (C-NF-g-PCL) as follows: C-NF, tin(II) 2-ethylhexanoate, ϵ -caprolactone, and super-dehydrated toluene were added to a flask under argon atmosphere in a glove box. Then the flask was set into an oil bath and the polymerization was allowed to proceed in the flask at 130°C for 1 hour to obtain C-NF-g-PCL. The morphology of the C-NF and the C-NF-g-PCL was analyzed by the scanning electron microscopy (SEM). It was found by the image analysis that the diameters of the nanofibers increased after the surface modification. The Fourier transform infrared (FTIR) spectroscopy was used to determine the structures of the C-NF and the C-NF-g-PCL. As a result of the FTIR analysis, the carbonyl-bond peak derived from PCL appeared at $\sim 1720\text{ cm}^{-1}$, indicating the success in the grafting process. Then the synthesized C-NF or C-NF-g-PCL was inserted between two PCL sheets and pressed at the pressure of 8 MPa at 80°C to obtain C-NF/PCL or C-NF-g-PCL/PCL composite films. Tensile testing was performed to examine the mechanical properties of the C-NF/PCL and the C-NF-g-PCL/PCL. At the fiber concentration of 15 wt%, the Young's modulus of PCL compounded with neat C-NF was found to increase by 215% compared to that of PCL, while, compounded with C-NF-g-PCL, it reached 251%. The fracture surfaces of the composites were analyzed by SEM. Through the image analyses, it was confirmed that the interfacial adhesion between PCL and C-NF was successfully improved by the surface modification. The results demonstrated that the effective surface modification of C-NF fabricated via electrospinning was realized by the C-NF-g-PCL/PCL composites.

NM04.09.04

Enhancement of the Mechanical Property of poly(ϵ -caprolactone) Composites with Surface-Modified Cellulose Nanofibers Hiroki Ichimura, Naruki Kurokawa and Atsushi Hotta; Keio University, Yokohama-shi, Japan.

The use of natural products as reinforcement materials of composites has recently been actively studied. Among the reinforcement materials, cellulose is attracting considerable interest because of its high mechanical property and high biocompatibility. In fact, the meaningful enhancement of the mechanical properties of the composites by compounding cellulose nanofibers (C-NF) has already been reported. In this study, C-NF fabricated via the electrospinning of cellulose acetate (CA) before the saponification of CA, were compounded into poly(ϵ -caprolactone) (PCL) to improve the mechanical properties. In the electrospinning method, the spinning solution with CA in the mixed solvent of acetone/dimethylacetamide (6/4 wt/wt) at the concentration of 20 wt% was prepared and added to a syringe with a stainless needle. Then a high voltage of 12 kV was applied between the spinning needle and a ground collector to fabricate CA nanofibers. The obtained CA nanofibers were dried under vacuum at 50°C for 24 h and saponified in a 0.05 M NaOH/ethanol solution for 24 h to convert CA nanofibers into C-NF. In addition to the fabrication of C-NF, the surface modification of the C-NF was also performed to improve the compatibility of the C-NF and the PCL for the enhancement of mechanical property of the composites. In order to graft PCL onto the C-NF to make C-NF-g-PCL, the ring-opening polymerization was carried out as follows: C-NF, tin(II) 2-ethylhexanoate (a commonly used catalyst for the polymerization of lactones), ϵ -caprolactone, and super-dehydrated toluene were all added to a flask in a glove box under argon atmosphere. The flask was then set into an oil bath and the polymerization was allowed to proceed in the flask at 130°C for 1 hour to obtain C-NF-g-PCL. The Fourier transform infrared (FTIR) spectroscopy was used to determine the structures of the C-NF and the C-NF-g-PCL. The FTIR results indicated that the polymerization was successfully conducted. The compression molding method was employed to fabricate C-NF/PCL or C-NF-g-PCL/PCL composite films. C-NF or C-NF-g-PCL was inserted between two compression-molded PCL sheets, which was thermally compressed at the pressure of 8 MPa at 80°C. Tensile testing was performed to examine the mechanical property of the C-NF/PCL and the C-NF-g-PCL/PCL. At the fiber concentration of 15 wt%, the Young's modulus of PCL compounded with C-NF-g-PCL increased by 17% compared to that of the composite with neat C-NF. The fracture surfaces of the composites were analyzed by the scanning electron microscopy (SEM). The image analyses confirmed that the interfacial adhesion between the PCL and the C-NF was substantially improved by the surface modification.

NM04.09.05

Mechanical Properties of Poly(vinyl alcohol) Composites with Electrospun Cellulose Nanofibers Annealed at Different Temperatures Shunya Inukai, Naruki Kurokawa and Atsushi Hotta; Keio University, Yokohama, Japan.

We synthesized highly crystallized regenerated cellulose nanofibers (RC-NF) through the annealing and the subsequent saponification of cellulose-acetate nanofibers (CA-NF) that were used as reinforcement materials for poly(vinyl alcohol) (PVA). We especially focused on the studies of the effects of the annealing temperature on the mechanical property of RC-NF/PVA composites. To enhance the mechanical properties of the RC-NF/PVA composites, annealing was first carried out for the RC-NF to raise the crystallinity. However, it was found that the direct annealing of the RC-NF did not affect the crystallinity. It was considered that the hydrogen bonding of the hydroxyl groups (-OH) in the RC-NF could be too strong to maintain the molecular movement of the cellulose required for the increase in the crystallinity. In this study, we synthesized highly crystallized RC-NF through the annealing and the subsequent saponification of CA-NF. Cellulose-acetate (CA), a derivative of cellulose, possesses a smaller amount of hydrogen bonding as compared with cellulose, thus maintaining a sufficient molecular movement to obtain higher crystallinity. Therefore, highly crystallized RC-NF could be obtained via the saponification of the annealed CA-NF. CA-NF were fabricated by electrospinning, subsequently annealed at 50, 75, and 100°C for 0-12 h above the glass transition temperature of the CA. The annealed CA-NF were then saponified to obtain highly crystallized RC-NF. The crystallinity of the RC-NF was measured by the X-ray diffraction (XRD). The RC-NF were compounded into poly(vinyl alcohol) (PVA) by the film-casting method to fabricate RC-NF/PVA composites. The mechanical properties of the RC-NF/PVA were investigated by tensile testing. It was found that the CA-NF annealed at 50°C, the crystallinity of the resulting RC-NF increased from 37 to 41% up to the annealing time of 12 h, which became constant after 12 h. The CA-NF annealed at 75°C for over 4 h and at 100°C for over 0.5 h produced highly crystalline RC-NF reaching 41% in crystallinity at the maximum. The Young's modulus of PVA with non-annealed RC-NF was ~ 2.1 GPa, which increased as the CA-NF annealing time increased. The Young's modulus eventually reached ~ 3.0 GPa at the maximum, becoming constant after 12 h of the annealing time at 50°C. It also reached ~ 3.0 GPa, when CA-NF were annealed at 75°C for over 4 h or annealed at 100°C for over 0.5 h. By considering the Helpin-Tsai equation, it was found that the Young's modulus of the RC-NF increased from 11.2 to 28.0 GPa. The correlation coefficients between the crystallinity and the Young's modulus of the RC-NF fabricated from the CA-NF annealed at 50, 75, and 100°C, were 0.970, 0.945, and 0.991, respectively. It was concluded that the maximum crystallinity and Young's modulus could be gained at shorter annealing time when annealed at higher temperature.

NM04.09.06

Annealing and Saponification of Electrospun Cellulose Nanofibers for a Reinforcement Material of Poly(vinyl alcohol) Composites Shunya Inukai, Naruki Kurokawa and Atsushi Hotta; Keio University, Yokohama, Japan.

Compounding relatively strong fibers into polymer materials has been one of the effective ways to enhance the mechanical properties of the polymers. It is well known that the higher aspect ratio of nanofibers in polymer composites could result in the increase in the specific surface area of the nanofibers, thus eventually improving the adhesion between the polymer matrix and the fibers. Electrospinning is also known as an effective way to make polymer nanofibers with high aspect ratios. Among the electrospun cellulose nanofibers, regenerated cellulose nanofibers (RC-NF) fabricated by the saponification

of electrospun cellulose-acetate nanofibers (CA-NF), are attracting considerable interest as reinforcement materials. In fact, improvement of the mechanical property of RC-NF is the key to generate polymer composites with excellent mechanical property. For this purpose, an annealing process is an effective way to raise the crystallinity of the targeted polymers, hence improving the mechanical property, leading to the fabrication of fibers with higher tensile modulus. However, it was found that the direct annealing of RC-NF resulted in no effect in increasing the crystallinity of the RC-NF. It was considered that the hydrogen bonding of the hydroxyl groups (-OH) in the RC-NF was too strong, inhibiting the enough molecular movement of the cellulose required for the improvement of the crystallinity.

In this study, we, therefore, synthesized highly crystallized RC-NF through the annealing and the saponification processes of CA-NF. Cellulose-acetate (CA), a derivative of cellulose, possesses a smaller amount of hydrogen bonding as compared with cellulose, thus carrying sufficient molecular-movement characteristics to obtain higher crystallinity. In more detail, the CA-NF were first annealed, and acetyl groups (-OCOCH₃) of the annealed CA-NF were then replaced with hydroxyl groups (-OH) to obtain highly crystallized RC-NF. The annealing time was changed, while the annealing temperature was kept constant at 50°C, which was above the glass transition temperature of CA.

The CA-NF were fabricated by electrospinning, which were then annealed and saponified to obtain highly crystallized RC-NF. The crystallinity of RC-NF was measured by the X-ray diffraction (XRD). By increasing the annealing time of CA-NF from 0 to 12 h at 50°C, the crystallinity of RC-NF increased from 37 to 41%, which became constant after 12 h. It indicated that highly crystallized RC-NF were successfully obtained by the annealing and the saponification of CA-NF. Finally, the RC-NF were compounded into poly(vinyl alcohol) (PVA) by the film-casting method to fabricate RC-NF/PVA composites. The mechanical properties of the RC-NF/PVA were investigated by tensile testing. The Young's modulus of the RC-NF/PVA increased from 2.1 to 3.0 GPa by raising the annealing time from 0 to 12 h, after which it became constant, whereas that of pure PVA was 1.5 GPa.

NM04.09.07

Highly Stable Photoconductive Cellulose Paper—A Bright Future for Flexible Paper Electronics [Naveed ul Hassan Alvi](#), Samim Sardar, Xavier Crispin and Magnus Jonsson; Laboratory of Organic Electronics, ITN, Linköping University, Norrköping, Sweden.

These days cellulose paper is ubiquitous in our daily life. For thousands of years, cellulose paper has been a major medium for displaying and transmitting information in many parts of the world. Its chemical and mechanical stability under atmospheric conditions and ability to absorb ink readily remain unmatched by other materials used in large abundance. Cellulose, the major component of paper, can be obtained from plants and represents one of the most abundant organic materials on earth. Cellulose by itself is usually limited in functionalities. Recently, research on organic/inorganic cellulose composites has increased dramatically due to the potential applications in electronics, biosensors, and energy storage devices [1–4].

The integration of functional micro and nanostructures into the paper, such as zinc oxide tetrapods or nanoparticle powders, has opened up many opportunities for applications in advanced energy harvesting systems and electronic devices [5-6]. In this respect, one of the major challenges is to avoid leakage of the micro- and nanoparticles from the paper over time. This is a serious problem that is limiting their applications into the practical devices.

In this work, we present a novel, environmentally friendly and fully scalable approach enabling the production of highly stable paper functionalized with zinc oxide nanostructures. Small (0.5 cm²) two-probe interdigitated carbon electrodes are printed on the paper to form a complete electronic device. It exhibits excellent photosensing properties over a wide range of light irradiances (0.01-1 Sun), with excellent long-term stability. At a bias voltage of 1 V, the device shows a strong and repeatable 65 μA photocurrent signal under simulated sunlight. This is more than 100 and 10,000 times better than the photocurrent of our control samples fabricated using zinc oxide tetrapods and nanoparticles, respectively. In addition to the superior photoconductive properties, our paper is smooth and mechanically strong, allowing its applications in a range of flexible energy and electronics devices.

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NM04.09.08

Effect of Surface Nanocrystallization on the Mechanical Properties of AISI 304 Stainless Steel Wire [Temitope O. Olugbade](#) and Jian Lu; City University of Hong Kong, Hong Kong, Hong Kong.

The effect of surface mechanical attrition treatment (SMAT) on the mechanical properties of 304 stainless steel (SS) wire was investigated using different ball materials and wire diameter. The surface characterization after SMAT was observed by scanning electron microscope (SEM) and X-ray diffraction (XRD). The mechanical properties were studied through yield stress, ultimate tensile stress, and fracture elongation. At different treatment time, the SMAT operation using the same amount of Tungsten Carbide (WC) and 304 SS balls significantly enhanced the strength of the material as well reduced the fatigue damage and other material related failures such as crack. The tensile test, with a tensile speed of 1.5 mm/min at room temperature, indicated a markedly increase in strength after SMAT. Compared to the untreated sample, the 304 SS wire subjected to SMAT experienced a great improvement in yield stress, ultimate tensile stress, and reduction in fatigue fracture. The type of ball used, and the wire diameter also has a significant effect on the mechanical properties. The surface characterization by SEM and XRD revealed an improvement in the yield and ultimate tensile stress of the SMATed samples using WC balls and 1.5 mm wire. The nanostructured material will find applications in biomedical and nanomanufacturing sectors.

NM04.09.09

Flame Retardant and Antiwetting Cellulose-Based Composite Aerogels as Sustainable Engineering Materials for Sound Adsorption [Application Xianjing Gong](#); Materials Science and Engineering, City University of Hong Kong, Hong Kong, SAR, Hong Kong.

Cellulose nanofiber (CNF) is an attractive bio-material and has advantageous properties such as light weight, excellent mechanical property, high aspect ratio, good thermal stability, as well as relatively low cost. In this study, we demonstrate a sustainable composite aerogel with sound adsorption, flame retardant and antiwetting abilities, the structure of which is composed of modified CNF and aluminium hydroxide (Al(OH)₃). Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) were used to confirm the modification of CNF and the formation of Al(OH)₃. Then scanning electron microscopy (SEM), sound-adsorption test, thermogravimetric analysis (TGA) and contact angle test were conducted. These results imply promising applications for practical engineering materials.

NM04.09.10

Strong, Flexible and Transparent Films of Lignocellulose Produced by Tailoring the Electrostatic Interactions [Yingxin Liu](#); Department of Materials and Environmental Chemistry, Stockholm University, Stockholm, Sweden.

The assembly of nature-based nanomaterials into complex architectures is both a design principle of biological composites, e.g., nacre with outstanding properties and a promising route for developing functional macroscopic materials. Our study aims to investigate the colloidal assembly behavior of

nanocellulose in aqueous dispersions. Moreover, composite films of nanocellulose and nanoclay/lignin with diverse functionalities are fabricated by tailoring the electrostatic interactions of these building blocks.

Initially, optically transparent films of synthetic aminoclay (50 wt%) and cellulose nanofibril (CNF) were fabricated, of which tensile strength and strain to failure (205 MPa and 7.5%) were significantly higher than previously reported nacre-mimicking nanocellulose-based materials, e.g., montmorillonite-CNF films, due to the formation of ionic bonding between the cationic clay and anionic CNF. On the other hand, anionic lignin nanoparticles were testified to enhance the colloidal stability and dispersity of carboxylated CNF in dispersions, and showed a remarkable strengthening and stiffening effect on the matrix of CNF. The mechanical properties of lignin-CNF films were superior to previously reported polymer/nanoparticle-CNF composites, such as polyvinyl alcohol-CNF films and even reduced graphene oxide-CNF films. The low cost of nanocellulose in combination with the excellent mechanical performance and functionalities of above composite films sheds light on potential applications such as substrates for optoelectronics.

NM04.09.11

Mechanical and Microstructural Characterisation of Graphene Oxide Reinforced Aluminium Matrix Nanocomposites Fei Lin¹, Ian A. Kinloch¹, Robert Young¹, Shaojiu Yan², Qihu Hong², Xiang Chen², Xiaoyan Zhang² and Shenglong Dai²; ¹Advanced Nanomaterials Group, National Graphene Institute and School of Materials, The University of Manchester, Manchester, United Kingdom; ²Beijing Institute of Aeronautical Materials, Beijing, China.

Due to its low density and high Young's modulus, graphene is able to make Aluminium (Al) matrix composites lighter and stronger. These materials are in demand for structural materials in airplanes, automobiles and other transportation applications. These structural materials can contribute to low carbon emissions, sustainable development and the overall economy. Al matrix nanocomposites reinforced with graphene related materials, have been developed well in the last decade. We have investigated the relationship between the mechanical properties and microstructure for Graphene Oxide (GO) reinforced Al matrix nanocomposites.

A powder metallurgy (PM) method was employed to produce GO reinforced Al matrix composites. We fabricated Al matrix composites with 0.3, 0.5, 1.0 wt. % loadings of GO, and pure Al as well for comparison.

By using large area Raman mapping and SEM respectively, we found the GO flakes to be dispersed well and located at the grain boundaries of the Al matrix in the composite. In addition, GO was aligned well in the direction of extrusion, indicated by Raman orientation investigations. Interestingly, the GO can even hinder grain growth of the Al matrix. Grain refinement was observed in the composite, caused by the barrier effect of GO. Quantitative information of the grain orientation and grain size was obtained from the analysis of EBSD (Electron Backscatter Diffraction) results. Aluminium carbides were not detected by either X-Ray Diffraction (XRD) or Raman spectroscopy, and thus chemical reaction at the interface did not take place.

Nanoindentation experiments were conducted to determine the mechanical properties of the pure Al and reinforced Al matrix composites as well. For macro mechanical properties, Young's modulus and hardness of the Al matrix composite were improved by adding 0.3, 0.5 and 1.0 wt. % GO in comparison with pure Al. GO has the ability to improve the mechanical properties of Al matrix composite when it is dispersed uniformly in the composite. However, the composite with a loading of 0.5 wt. % GO, rather than with 1.0 wt. %, was found to have the most strengthening effect. We observed some agglomeration in the composite reinforced with 1.0 wt. % GO from SEM images, which induced more defects, more pores, less interfacial area, and a lower effective modulus. We believe these factors may explain why its Young's modulus was not as high as expected. In addition, SEM (Scanning Electron Microscopy) was used to observe the microstructure around the indented areas. Indeed, the mechanical properties of the composites are closely linked to the microstructure. After indentation, we can see that the GO flakes between grain boundaries hinder the movement of the dislocations. Al matrix grains experienced their plastic deformation by slipping or twinning when the dislocations cannot move further due to obstruction by the GO. These microstructural changes resulted in better mechanical performance of the composites.

NM04.09.12

A Novel Process to Fabricate Nano Carbon Reinforced Copper Matrix Composites Utilizing Self-Assembly of Bioinspired Polydopamine Yao Zhao, Filippo Di Carlo, Bosen Qian, Haoqi Li, Zhuolei Zhang and Fei Ren; Mechanical Engineering, Temple University, Philadelphia, Pennsylvania, United States.

Introduction of nanocarbons, such as graphene and carbon nanotubes, to metal matrices may enhance the electrical and thermal transport and mechanical properties of the composite materials. In this study, copper (Cu)-polydopamine (PDA) composite was fabricated by coating Cu powders with the bioinspired PDA polymer, which was then converted to graphite-like structure during the subsequent sintering. Structural characterization using SEM, TEM, and Raman spectroscopy demonstrated the formation of the graphite-like structure in the composite. Compared to the pure Cu sample, the Cu-PDA composite showed increased electrical conductivity, higher microindentation hardness, and enhanced wear resistance. These findings suggest inclusion of nanocarbon phase converted from PDA can simultaneously improve the electrical and mechanical properties of sintered Cu materials. Effect of coating time (carbon content) on the microstructure and properties of the composites will also be discussed.

NM04.09.13

Mechanical Properties of Polydopamine Thin Films Haoqi Li, Qian Dong, Qiuting Zhang, Yao Zhao, Zhuolei Zhang, Haijun Liu, Jie Yin and Fei Ren; Temple University, Philadelphia, Pennsylvania, United States.

Polydopamine (PDA) is a recently discovered bioinspired polymer. Coating and freestanding films of PDA can be fabricated via the self-assembly process of dopamine molecules in mild conditions. Many interesting properties of PDA have been reported. One potential application of PDA thin film is in soft and flexible devices, where the mechanical property of the film and adhesion to substrate are critical. By adding dopamine hydrochloride into alkaline solution, freestanding PDA films were synthesized at the air/solution interface, which was then transferred onto capillary tubes. The vibrational response of PDA freestanding film was investigated using acoustic impulse method, from which the elastic modulus was determined. Meanwhile, by studying the surface buckling behavior of PDA coating on PDMS substrate, the adhesion between the two materials was obtained. Furthermore, wear resistance of PDA films was evaluated using nanoscratch test. Effects of film thickness and metal ion doping were also investigated.

NM04.09.14

Effect of Encapsulation of Citric Acid with Zeolite Nanoparticles on Its Heat Resistance in Polymer Composite Hye Mi Choi¹, Young Min Lim¹, Dong Soo Shin², Gun Young Kwak³ and Tae Hwan Oh¹; ¹Yeungnam University, Gyeongsan, Korea (the Republic of); ²Clavis, Gyeongsan, Korea (the Republic of); ³Dyotec, Daegu, Korea (the Republic of).

Citric acid having low heat resistance was encapsulated by zeolite nanoparticles and zeolite/citric acid capsules were coated by titanium oxide (TiO₂) to enhance the heat stability of the citric acid during melt processing of polymer/citric acid composite. The conditions to maximize adsorption of the citric acid were investigated for citric acid concentration, adsorption temperature and time. Reaction conditions for TiO₂ coating onto zeolite were also investigated for enhancing the heat resistance of the citric acid during melt processing of polymer/citric acid composite.

The presence of the citric acid after its adsorption into zeolite was measured by electrical conductivity change with concentration. By coating TiO₂ on

zeolite, the heat resistance of the citric acid increased and hence after melt extrusion, we could observe the survival of the citric acid after melt extrusion.

NM04.09.15

Synthesis of Eco-Friendly Nano-Structured Biosurfactants from Vegetable Oil Sources and Characterization of Their Interfacial Properties for Cosmetic Applications [JongChoo Lim](#), DaNan Yea and SeonHui Jo; Dongguk University, Seoul, Korea (the Republic of).

The enormous market demand for surfactants is currently met by numerous synthetic, mainly petroleum-based, chemical surfactants. These compounds are usually toxic, non-biodegradable and environmentally hazardous. Tightening environmental regulations and increasing awareness for the need to protect the ecosystem have effectively resulted in an increasing interest in biosurfactants as possible alternatives to chemical surfactants. They have advantages over their chemical counterparts in specificity, relative ease of preparation, mildness, and effectiveness even at extreme temperature or pH. Biosurfactants also have the merit of diversity, environment friendly nature such as nontoxicity and excellent biodegradability, possibility of large-scale production, selectivity, performance under extreme conditions, and potential applications in environmental protection. Due to their unique functional properties, biosurfactants have been used in various industries including agriculture, fertilizers, petroleum, petrochemicals, cosmetics, pharmaceuticals, personal care products, food processing, beverages, textile manufacturing, metal treatment and processing, pulp and paper processing, paint industries and many others. They can be used as emulsifiers as well as demulsifiers, wetting agents, foaming agents, spreading agents, environmental cleanup of pollutants, functional food ingredients and detergents. In this study, 3 types of zwitterionic phospholipid biosurfactants were prepared using 3 different raw materials such as rapeseed oil, coconut oil, and cottonseed oil respectively and the structure of the resulting products was elucidated by FT-IR, ¹H NMR, and ¹³C NMR spectroscopies. Biodegradability, acute oral toxicity (LD₅₀), acute dermal irritation and acute eye irritation tests revealed that the newly synthesized biosurfactants possess excellent mildness and superior environmental compatibility as well as superior interfacial properties, indicating the potential applicability in cosmetic product formulations. The patch test has been performed with 0.1 mL of 0.5 wt% surfactant solution and the result has shown that the newly prepared biosurfactants indicated no allergic inflammation on a skin during 48 hrs. The prescription test in shampoo formulation prepared with the newly synthesized biosurfactants indicated excellent sensory feeling and foam ability compared with conventional hydrocarbon and silicon surfactants. In particular, CDP(S) biosurfactant can be considered as a strong candidate for the potential applicability in cosmetic product formulations since the newly synthesized CDP(S) surfactant is highly surface active, mild, nontoxic, non-irritating and readily biodegradable.

ACKNOWLEDGEMENTS

This work was supported by "the Technology Innovation Program"(10063387, Development of aryl phenol surfactants and paint additives for the replacement of nonyl phenol) funded by the Ministry of Trade, Industry & Energy, Korea.

NM04.09.16

Mechanical Properties of Rubber Composite Reinforced by Cellulose Nanofiber [Tomoyuki Sakai](#); The Yokohama Rubber Company Ltd, Kanagawa, Japan.

Yokohama Rubber Company Ltd. has been researching on sustainable materials for rubber as an environmentally friendly company. We prepared NR and SBR reinforced with TEMPO oxidized cellulose nanofibers (TOCN), which were modified from wood pulp, instead of traditional carbon black derived from petroleum. The Wood-derived TOCN can contribute to an effective use of forests and to a recycling-based society. They have average 3 nm in diameter and high aspect ratio. The wear resistance and viscoelasticity of the rubber-TOCN composites were investigated for the application of pneumatic tires. Their tensile stress was larger than that of the same amount of carbon black reinforcement. We will discuss how to improve their mechanical property by examining the bound rubber on the interface of cellulose nanofibers.

This research was supported by grants from the Project of the NARO Bio-oriented Technology Research Advancement Institution (R&D matching funds on the field for Knowledge Integration and innovation)

NM04.09.17

Manganese Incorporation on Structural, Optical and Photocatalytic Properties of ZnO Nanofibers [Ilyas Savkliyildiz](#)^{2,1}, [Elif Baylan](#)^{2,1} and [Ozlem A. Yildirim](#)^{2,1}; ¹Selcuk University, Konya, Turkey; ²Konya Technical University, Konya, Turkey.

There is currently intense interest in the elimination of the organic dye compounds in the water via photocatalytic reactions. Zinc oxide (ZnO) nanostructures have drawn attention as a promising photocatalyst for its high catalytic activity, low cost, and environmental friendliness. Visible-light photocatalytic properties of ZnO nanostructures can be improved with metal doping. To improve photocatalytic activity of ZnO nanostructures, manganese-doping (ZnO:Mn) is appreciable because manganese behaves highly reactive catalyzer in the photocatalytic reactions. Furthermore, synthesis of ZnO:Mn nanostructures with well-controlled size and morphology have been also attracted great attention to enhance photocatalytic efficiency. In this study, we aimed to improve visible-light photocatalytic activity of Mn doped ZnO nanofibers via electrospinning technique to eliminate interparticle interactions. The effects of doping level and aspect ratio of nanofibers, on the band structure of ZnO and finally photocatalytic properties of ZnO:Mn nanofibers were investigated through XRD, XPS, HRTEM, FESEM and UV-Vis spectroscopy. The results showed superior photocatalytic activity for 1.5 at.% Mn doped ZnO nanofibers and the complete decomposition of Methylene Blue has been achieved after 120 minutes UV illumination.

NM04.09.18

Polymerization of Valerolactone Derived from Biomass for Eco-Friendly Powder Coating [Lim Hanwhuy](#)^{2,1} and [Baekjin Kim](#)²; ¹Yonsei University, Seoul, Korea (the Republic of); ²Green Chemistry and Materials Group, Korea Institute of Industrial Technology, Cheonan, Korea (the Republic of).

Valerolactone is a biomass material that can be obtained through catalysis from mevalonic acid obtained by fermentation of glucose. It is used as an environmentally friendly application material and it also can be applied as powder coating material without organic solvent. In order to use valerolactone as a coating material, it is necessary to polymerize by ring opening transesterification polymerization (ROTEP) reaction, and it have to be optimized according to the type, amount of catalyst and reactant conditions. As a result, ROTEP polymer was successfully synthesized using valerolactone using 0.75 wt% TBD catalyst. The result is 30,000 g/mol, Mw and PDI = 1.2 confirmed by GPC. Furthermore, we also discussed the application of additional functional groups to enhance the biomass ratio. After replacing the terminal of the polymerized polymer with hydroxyl groups, molecular weight could increase with biobased content. The synthesized compounds were applied to coating material as the powder form.

NM04.09.19

Flammability and Structural Characterization of LDPE/EVA Blend Composites Containing Keratin Fibers and DNA as a Flame Retardant Combinations [Saul Sanchez](#), Eduardo Ramirez, Jorge Albite, Yuresis Nuñez and Rogelio Ramirez; CIQA, Saltillo, Mexico.

The combination of keratin fibers obtained from feathers, with deoxyribose nucleic acid (DNA) applied as a coating with a segregated structure on filler dispersion and flame retardant properties of low-density polyethylene-ethylene vinyl acetate (LDPE/EVA) blends was investigated. A maleic anhydride modified polyethylene (PEgMA) was used as compatibilizer. The thermal stability and flame retardant properties were evaluated by Limiting Oxygen Index (LOI), Cone calorimeter determinations and Flammability test (Underwriters Laboratory - UL-94). The structural characterization was carried out by FTIR and scanning electron microscopy in transmission mode (STEM). The mechanical properties were also evaluated. The effect of coating procedure, direct melt compounding or segregated structure deposition, on DNA dispersion and flame-retardant behavior was discussed. The results indicated that the DNA deposition method of segregated structure promoted the best flame retardant behavior and that the incorporation of keratin fibers enhanced the mechanical performance of the nanocomposites. It was demonstrated that DNA induced a char foamed layer that was able to quite efficiently protect the blend polymer matrix against heat, reducing the combustion kinetics. The thermal stability of PE/EVA blends increased to a higher extent when using these filler combinations.

NM04.09.20

Materials Engineering—Controllable Defect Nanomaterials for Electrical and Biological Application Li Wei Huang¹, Chun-Yen Lai², Lin M. Ling¹, Ping-Hung Yeh¹ and Wen-Wei Wu²; ¹Tamkang University, New Taipei City, Taiwan; ²National Chiao Tung University, Hsinchu City, Taiwan.

For materials engineering, the various electrical properties of Poly-SnO₂ nanofiber can be obtained by controlling fabrication processes. By well controlling fabrication processes, there are several specific materials can be found, such as defect-free, defect-rich and defect-controlled SnO₂ nanofiber. In this research work, defect-free sample has strong reaction with UV light. But if the defect amount was increased by changing formation process, the defect-rich poly crystal nanofibers can be obtained to make an ultra-sensitive nano-sensor. Because the nano-sensor has huge defect that will give the device to has ultra-high sensitivity; the current of the nano-sensor can be easily varied by light and surrounding gas. This property can make our nano-sensor as room temperature gas (50 ppb NO) detector. This nanomaterial also can control the defect amount to fit the biological antibacterial purpose by well controlled the fabrication process. In a well-controlled defect amount, the nanomaterial can provide Hydroxyl by specific light in moisture solution to prevent bacterial infections. In our work, the E-coli can be effectively reduced by our nanomaterials substrate due to the Hydroxyl.

SESSION NM04.10: Toxicology, Monitoring and Depollution I

Session Chairs: Ivana Aguiar and Benjamin Hsiao

Thursday Morning, November 29, 2018

Sheraton, 2nd Floor, Back Bay C

8:30 AM *NM04.10.01

Nanotoxicology and Environmental Impact of Carbon Nanomaterials—A Focus on Double-Walled Carbon Nanotubes Emmanuel Flahaut¹, B. Paudyal², U. Kishore², E. Meunier³, S. Fiorito⁴, A-M. Galibert¹, B. Soula¹, L. Evariste⁵, A. Mottier⁵, F. Mouchet⁵, E. Pinelli⁵ and L. Gauthier⁵; ¹CIRIMAT UMR5085 CNRS/University Paul Sabatier/INPT, Toulouse, France; ²Brunel University, London, United Kingdom; ³IPBS, CNRS, University Paul Sabatier, Toulouse, France; ⁴Istituto di Farmacologia Traslazionale, CNR, Roma, Italy; ⁵ECOLAB, CNRS, University Paul Sabatier, INPT, Toulouse, France.

Carbon nanotubes (CNTs) are often the emblematic figure of nanoparticles in general, promoted by many for their exceptional physico-chemical properties which have led to applications in almost all fields, and criticized by the others for their potential toxicity toward human health and the environment. After a general introduction to the toxicity of nanoparticles, we will focus on the case of CNTs and in particular of double-walled CNTs (DWCNTs) [1] which represent a unique category at the interface between single-wall CNTs and multi-walled CNTs. The interaction of DWCNTs with the immune system [2, 3] will be described, showing that if these CNTs activate this defence mechanism, there are also potential ways to moderate this through appropriate surface functionalisation. Some examples of interaction of DWCNTs with cancer cells [4] or bacteria [5] will also be given as illustrations of potential biomedical applications.

Finally, we will summarise our recent work on the question of the choice of the most appropriate metric in order to allow the comparison of the results obtained for different kinds of nanocarbons (different carbon nanotubes, few-layer graphene, nanodiamonds) as well as a sample of carbon black, in the case of their environmental impact [6]. Experimental results obtained using an amphibian larvae model (xenopus), very relevant for the aquatic compartment and especially the water column, clearly show that only the specific surface area allows the plot of all the data on the same "master curve", even making possible to become predictive and to propose a "Surface effective concentration" SEC50. These results have also been recently extended to the comparison of nanocarbons dispersed in water by either covalent (oxidation) or non-covalent (addition of a surfactant) functionalisation, confirming that the specific surface area is still the relevant parameter.

Acknowledgement

The research received funding from the European Union 7th Framework Program under grant agreement N°785219 Graphene flagship.

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9:00 AM NM04.10.02

The Toxicity of Carbon and Gold-Based Nanomaterials Against Human Cells and Aquatic Organisms Jaqueline Souza^{1,2}, Juliana Cancino^{1,2}, Valeria Marangoni^{1,2}, Fabricio Santos^{1,2}, Adrislaine Mansano^{1,2}, Francine Venturini^{1,2} and Valtencir Zucolotto^{1,2}; ¹University of Sao Paulo, Sao Carlos, Brazil; ²Nanomedicine and Nanotoxicology Group, USP, Sao Carlos, Brazil.

The specific properties of nanomaterials have allowed their application in different areas including electronics, energy storage, nanomedicine, and environmental remediation. Carbon and gold-based nanomaterials, for example, are commercially available, with prediction for increasing their production in the next years. However, the use and discard of these nanomaterials can result in accumulation in aquatic compartments, where the subsequent possible

damages for human health and aquatic organisms are not completely understood. To understand the mechanisms responsible for the toxicity exhibited by nanomaterials against human cells and aquatic organisms, several strategies have been applied. Cell membrane models, in particular, have been recently introduced as a novel platform to investigate the interactions between the nanoparticles and biological systems at the molecular level, which can be useful to understand the influence of membrane composition in the uptake process. In this study, we investigated the influence of morphology and size of gold nanostructures (including gold nanoparticles, AuNPs, and nanorods, AuNRs) using real and mimetic membrane models. The interaction of the nanomaterials with the lipidic membrane models was studied using Langmuir monolayers, revealing that incorporation of AuNRs into the mimetic cell membrane was more pronounced compared to nanospheres (AuNPs), as revealed by the adsorption kinetics and surface pressure measurements. We also evaluated the toxic effects of graphene-oxide (GO) on aquatic organisms, in vivo, after exposure to sub-lethal concentrations. Flow cytometric analysis showed that sub-lethal GO exposure led to an increase in the number of gill cells that were in early apoptotic and necrotic stages in zebrafish. The toxic mechanism of GO to zebrafish was attributed to an increase in the oxidative stress level, as observed by the enzymatic biomarkers that showed significant increases in the activity of superoxide dismutase (SOD), catalase (CAT) and lipid peroxidation after sub-lethal exposure. We showed that both gold and carbon-based nanostructures may be harmful to human cells and aquatic species. In the latter, such effects could be permanent, threatening the aquatic food chain balance. Our results may help in the determination of environmentally safe concentrations of nanomaterials for regulatory purposes.

9:15 AM NM04.10.03

Design Criteria for Sustainable Nano Materials (DENANA) Philipp Altmann¹, Juliane Filser², Bernd Giese³, Martin Hoppe⁴, Tim Huelsner⁵, Marcus Lukas⁶, Lutz Mädler⁷, Suman Pokhrel⁷, Karsten Schlich⁸ and Sophie M. Schnurre⁵; ¹Klüber Lubrication München SE & Co. KG, Munich, Germany; ²Center for Environmental Research and Sustainable Technology (UFT), University of Bremen, Bremen, Germany; ³Department of Technology Development and Design, University of Bremen, Bremen, Germany; ⁴Federal Institute of Geoscience and Natural Resources (BGR), Hannover, Germany; ⁵Particle Process Technology and Characterization, Institute of Energy and Environmental Technology e.V., Duisburg, Germany; ⁶Federal Environment Agency (UBA), Berlin, Germany; ⁷Foundational Institute of Materials Science (IWT), Bremen, Germany; ⁸Ecotoxicology, Fraunhofer Institute for Molecular Biology and Applied Ecology IME, Schmallenberg, Germany.

Sustainability should be an objective of every future technology. Especially nanotechnology has shown that worries and concerns of consumers may hamper the development of nanomaterials. In the face of the conflict between immediate marketing of innovative products containing engineered nanoparticles (ENP) and the precautionary principle regarding the potential environmental and human risks we established a multidisciplinary consortium of 10 academic, industrial and regulatory partners, which worked on manifold questions within project. For a sustainable production of goods containing ENPs it is crucial to have no adverse effects on the environment.

Therefore, the project focused on the study of the long-term characteristics of ENPs under various environmental conditions. Silicon dioxide nanoparticles (SiO₂-NP) and cerium dioxide nanoparticles (CeO₂-NP) were selected because of their prevalence and commercial relevance. Utilization oriented aspects were studied on SiO₂-NP spiked lubricants as an exemplary application.

On the one hand innovative functionalized variations of SiO₂-NP and CeO₂-NP (e.g. doped) are produced by lab- and pilot scale gas phase reactors. For these materials an enormous marketing potential is expected due to their presumed low toxicity and multiple application possibilities.

On the other hand we detected, tracked and modeled the life cycles of the ENPs in the lab and the near-natural environment to enlarge the knowledge of ENPs ecotoxicological potentials and to fill methodological gaps concerning their environmental exposures. The environmental fate and pathways of the ENPs were studied using numerous methods on different levels: characterization of the ENPs, environmental exposure and fate modeling. The effects of ENPs on organisms representing different trophic levels and environmental compartments were addressed for the identification of early warning indicators required for the long-term risk assessment of ENPs.

The bilateral approach of DENANA addresses the interests of all stakeholders (producer, user and consumer). The identification of early warning indicators of the long-term risk potential supports the progress in the statutory approval of new ENPs; the generation of data on the environmental exposure provides a basis for regulatory measures and, finally, materials risk quantification. We present methods (e.g. Europium doping) to tune particle morphology, which allows to trace, track and identify particles in biological systems. Furthermore, the exposure of nanoparticle into soils and the effect of plant growth are shown. Results of end of life cycle assessment using new models of nano particle distribution scenarios are displayed. The project ended with the collective evaluation of obtained results required for the identification of design criteria of sustainable ENPs. Finally, the selected test materials did not reveal any ecotoxicological potentials to organisms.

9:30 AM NM04.10.04

Challenges in Characterizing Nanocellulose for Toxicological Studies Zhenyuan Zhang¹, Georgios Pyrgiotakis¹, Dimitrios Bitounis¹, Ana Stavanovic¹, Wing Luu², Douglas Bousfield² and Philip Demokritou¹; ¹Center for Nanotechnology and Nanotoxicology, Harvard University, Boston, Massachusetts, United States; ²Department of Chemical and Biological Engineering, University of Maine, Orono, Maine, United States.

Cellulose is the most abundant natural polymer, is readily available, biodegradable, and inexpensive. Recently, interest is growing around nano-scale cellulose due to the sustainability of these materials, the novel properties, and the overall low environmental impact. The rapid expansion of nanocellulose uses in various applications makes the study of the toxicological properties of these materials of great importance to public health regulators. However, most of the current toxicological studies are highly conflicting, inconclusive, and contradictory. The major reason for these discrepancies is the lack of methods to and to characterize nanocellulose in various forms. In order to address these issues, industry-relevant synthesis platforms were developed to produce nanocellulose with controlled properties that can be used as reference materials in toxicological studies. In this work we report the synthesis and characterization of CNF and CNS reference ENMs and outline some of the most important challenges in our efforts. Among the greatest challenges is to characterize the CNF length and thus to obtain the complete morphology of CNF. We developed a new method that utilizes Scanning Electron Microscopy (SEM) to resolve these issues. Furthermore, another issue is the characterization in liquid in particular when DLS is not suitable. In our work we have developed a method to image the cellulose aggregates in various biological media.

9:45 AM NM04.10.05

Portable Ultra-low Power Smart Electronic Nose System Based on Three-Dimensional Tin Dioxide Nanotube Arrays for Multiple Gases and Mixture Detection Jiaqi Chen¹, Zhuo Chen¹, Farid Boussaid², Chi-Ying Tsui¹, Amine Berkak^{1,3} and Zhiyong Fan¹; ¹HKUST, ECE Department, Hong Kong, Hong Kong; ²The University of Western Australia, Perth, Western Australia, Australia; ³Hamad Bin Khalifa University, Doha, Qatar.

Here we present a wireless and room-temperature high performance smart electronic nose (E-nose) system for air quality monitoring. The battery-driven system consists of a monolithic and multiplexed tin dioxide (SnO₂) nanotube sensor array, a read-out circuit, a wireless data transmission unit, a mobile phone receiver and a data processing application (App). The proposed SnO₂ nanotube array was fabricated through conformal deposition of SnO₂ nanoparticle on a freestanding open-ended porous aluminum membrane. By adjusting the specially designed pore size of the SnO₂ nanotube array, Knudsen diffusion effect could be utilized for enhancing the sensitivity of the device. The surface modification was conducted through noble metal decoration to enhance the performance. Using the nanotube device in conjunction with multiple electrode materials deposited on both ends of the nanotube to form a "sandwich" sensor structure, a highly compact monolithic array with sixteen different sensors was prepared. A high sensitivity gas detection has been achieved at room

temperature, enabling a 1,000 times reduction of sensor's power consumption as compared to a conventional thin film SnO₂ gas sensor device which needs to be operated with an energy-hungry heater. Addition to the ultra-low power monolithic sixteen sensor array, a readout circuit and a wireless transmission unit was designed. Powered by two button batteries, the portable system was able to mobile detection of the air quality or gas leakage. Moreover, with the assorted mobile phone receiver, the detection results from the sixteen different sensors could be analyzed through advanced classification algorithms for the target gas or gases mixture discrimination. Multiple gases (H₂, NO₂, benzene and water vapor) and gases mixtures (H₂ and ethanol, H₂ and acetone, H₂ and methanol) have been tested, and benefitting from the excellent repeatability of the sensor array, the developed classification algorithm, bagging decision tree, could reach a very satisfied classification performance (more than 95%) for both single gas and gases mixtures. Such a robust smart E-nose system can address the imperative needs for distributed environmental monitoring in smart homes, smart buildings and smart cities in the form of a portable or wearable device.

10:00 AM BREAK

10:30 AM NM04.10.06

Highly Selective Formaldehyde Detection with Microporous Zeolite Membranes for Environmental Monitoring [Andreas T. Güntner](#), Sebastian Abegg, Jan van den Broek, Karsten Wegner and Sotiris E. Pratsinis; ETH Zurich, Zurich, Switzerland.

A major challenge in environmental sensing is the detection of trace-level pollutants (e.g. carcinogenic formaldehyde¹) in complex gas mixtures. Devices based on chemo-resistive gas sensors would offer sufficient sensitivity and low detection limit down to ppb, but lack selectivity². Here, we combine nanomanufactured sensors with highly selective zeolite membranes pre-separating gas mixtures³. Zeolites - broadly applied in catalysis and gas separation - effectively separate molecules based on kinetic diameter, sorption and diffusion characteristics⁴. Therefore, zeolite membranes are suitable filters for gas sensors removing undesired species from indoor air. As proof-of-concept, a zeolite MFI/Al₂O₃ membrane is placed upstream a highly sensitive but weakly selective Pd-doped SnO₂ sensor. Their combination exhibits exceptional selectivity (>100) for formaldehyde down to 30 ppb at 90% relative humidity, outperforming state-of-the-art detectors by more than an order of magnitude. This novel concept is readily extendable to other tracers, as manifold combinations of widely tunable microporous membranes and gas sensor types can be realized in the modular sensing device. This could enable a new class of highly sensitive and selective environmental monitors.

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10:45 AM NM04.10.07

Environmental Transformation and Biological Impact of LiCoO₂ and LiNi_xMn_yCo_(1-x-y) (NMC) Lithium-Ion Battery Cathode Nanomaterials [Robert J. Hamers](#)¹, Christy L. Haynes², Sara E. Mason³, Joseph W. Bennett³, Mimi Hang¹, Natalie V. Hudson-Smith², Rebecca Klaper⁴, Jared Bozich⁴ and Elizabeth Laudadio¹; ¹University of Wisconsin-Madison, Madison, Wisconsin, United States; ²Chemistry, University of Minnesota Twin Cities, Minneapolis, Minnesota, United States; ³Dept. of Chemistry, The University of Iowa, Iowa City, Iowa, United States; ⁴Great Lakes Freshwater Research Center, University of Wisconsin-Milwaukee, Milwaukee, Wisconsin, United States.

The rapidly increasing use of LiCoO₂ (LCO) and LiNi_xMn_yCo_(1-x-y) (NMC) as cathode materials in lithium ion batteries raises questions about the potential environmental impact associated with unintentional release of these materials into the environment. We have investigated the interaction of nanoscale LCO and NMC materials with several model organisms that lie at the base of the food chain in soil, aquatic, and sediment environments. In aqueous media, NMC materials release transition metals incongruently, with release rates in the order Li > Ni > Co > Mn. Using *Shewanella oneidensis* MR-1 as a model soil bacterium, we find that most (but not all) of the biological impact arises from release of transition metal ions, with some contribution from reactive oxygen species. In *Daphnia magna*, however, there are nanoparticle-specific effects and significant direct interaction with the nanoparticles. At low concentrations, NMC can induce significant changes in gene expression at concentrations much lower than those where viability is reduced. Our work investigating the influence of composition and nanoparticle morphology reveal new mechanistic insights into the chemistry of these materials relevant to understanding their potential environmental impact.

11:00 AM NM04.10.08

PEOx-EI/PAA Complex Nano-Filtration Membrane for Dye/Salt Separation Xiaowei Xu^{1,2}, Liping Zhu¹ and [Shuguang Yang](#)^{1,2}; ¹Center for Advanced Low-dimension Materials, Donghua University, Shanghai, China; ²State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai, China.

The mixture of dye/salt generated from digital ink-jet printing industry is not only a crucial source of pollution but also a huge waste of materials. Recently, polymer complex membranes (PCMs), as a nano-filtration membrane, have drawn a considerable attention in treatment of the dye/salt mixture in order to recycle dye due to its inherent ionic cross-linking structures and high hydrophilic property. The preparation of polymer complex membrane usually requires the protonation and de-protonation of certain functional groups to make the solution homogeneous and processable in a large scale. In this work, in order to avoid the adjustment in the amount of ionic groups after complexation, a new solution preparation method is developed to maintain the viscosity and homogeneity of solution, and thus to skip the common and necessary precipitation process existed in most of the membrane preparation methods. Partially hydrolyzed poly (2-ethyl-2-oxazoline) (PEOx-EI) which is consisted of poly (2-ethyl-2-oxazoline) and polyethyleneimine (PEI), as cation polyelectrolyte, and poly(acrylic acid) (PAA), as anion polyelectrolyte, are selected to prepare PCMs by solution-casting first, then followed by an interfacial polymerization process. The structural characteristics and surface properties are then systematically investigated. The number of hydrogen-bonding sites can be easily manipulated with solution pH, which provides an opportunity to efficiently clean the membrane and make it reusable under extremely conditions. A high water permeability and good antifouling ability are expected due to the hydrophilicity of membrane provided by the excess amount of carboxyl groups. Though the dye barrier ability is currently lower than the commercialized nano-filtration membrane systems, the overall performance of the as prepared PCMs, including facile fabrication process, good selectivity for the dye/salt mixture, high permeability and good antifouling ability, find them a promising future in separation of dye/salt mixture.

11:15 AM NM04.10.09

Silica Based Hybrid Colloidosomes and Pickering Emulsions and Their Implantation For Single Cell Microencapsulation [Guy Mechrez](#); Volcani Center, ARO, Rishon LeZion, Israel.

This research presents an *in-situ* functionalization of silica nanoparticles in oil-in-water (o/w) biphasic system with two equimolar organosilanes of antagonistic polarity. Homogeneous and stable Pickering emulsions have been obtained, where droplet size can be tuned according to the silica particle concentration and the o/w ratio used. The micro and nano-structure was analysed by optical and fluorescence microscopy and cryo-SEM. The introduction

of carbon nanotubes (CNT) to the silica based Pickering emulsion enabled us to prepare electrically conductive CNT/silica nanohybrid colloidosomes with controlled porosity. CNTs and silica nanoparticles both are located in the interface, as evidenced by confocal laser scanning microscopy and cryo-SEM. After drying, hierarchical porous structures have been generated spanning the micro, nano, and macropore range. The emulsions have shown high stability against coalescence and sedimentation. Additionally, a highly tunable biocompatible Pickering emulsion system enabled us to develop a new approach for successful single cell encapsulation of fungal spores of *Metarhizium anisopliae*, which is implemented in efficient biopesticide formulation for arthropod pest control in agricultural applications. This successful single cell encapsulation system led to a significantly higher distribution of conidia cells on the leaves. The Pickering emulsion based formulation exhibited significantly higher pest control against *Spodoptera littoralis* larvae, thus making it a promising cost effective, innovative approach to tackling the pest control challenge.

11:30 AM RAPID FIRE PRESENTATION

SESSION NM04.11: Toxicology, Monitoring and Depollution II
Session Chairs: Emmanuel Flahaut and Jean Gaumet
Thursday Afternoon, November 29, 2018
Sheraton, 2nd Floor, Back Bay C

1:30 PM *NM04.11.01

Advancing Nanocellulose Technologies for Water Purification Benjamin S. Hsiao; Stony Brook University, Stony Brook, New York, United States.

The fabrication of nanocellulose can be accomplished by chemical and mechanical treatments of any natural biomass, including agricultural waste, weeds and shrubs, where some sources can provide “effortless extractability” with very low energy consumption. Nanofibrous scaffolds have very unique properties including interconnected pores, a very large surface-to-volume ratio and a high capacity for surface modifications, making them ideal candidates for fabrication of high throughput separation membranes (e.g. microfiltration and ultrafiltration) and/or highly efficient sorptive media. Directed water channels in the barrier layer of reverse osmosis and nanofiltration membranes can also be formed through the formation of interface between the nanofibers and barrier layer polymer matrix, while the gap thickness can be regulated by physical interactions or chemical bonding. In the present context, advances in fundamental studies on cellulose microfibrils, the building blocks from the cell wall of any plant, and their interactions with metal ions by means of synchrotron x-ray and neutron techniques have provided us with new insight into the design and fabrication of highly permeable nanofibrous membranes, having a hierarchically tiered structure, that can enable higher flux, higher retention and lower energy consumption water purification. Nanocellulose may serve as a revolutionary platform technology for the design and fabrication of low cost, sustainable and highly efficient filtration and sorptive media.

2:00 PM NM04.11.02

Design and Development of Process for Wastewater Treatment Using Sustainable Adsorbents Nathan Grishkewich¹, Nishil Mohammed¹, Richard Berry² and Michael K. Tam¹; ¹Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada; ²Celluforce, Montreal, Ontario, Canada.

This study describes the design and development of a continuous process for use in textile effluent remediation. The system utilizes an adsorbent prepared from eco-friendly materials derived from renewable sources, cellulose nanocrystals (CNCs) and sodium alginate (ALG). The ability of the adsorbent to remove a model cationic dye, methylene blue (MB), was studied in detail.

Equilibrium batch adsorption experiments provided information on the equilibrium uptake of MB dye from water as well as the adsorption kinetics. In addition, the impact of ionic strength, pH, and temperature on the equilibrium uptake were examined. Continuous experiments were conducted in a fixed bed vessel to study the impact of flow rate, initial MB concentration and packing height on the capability of the process to remove MB. A self-sustained system that could produce this adsorbent in-situ was also developed.

From the batch experiments we determined a theoretical maximum adsorption capacity for MB by the adsorbent to be 431.6 mg/g, and additional experiments demonstrated that the adsorbent could undergo repeated adsorption-desorption cycles, achieving ~97 % dye removal efficiency after 5 cycles. From lab scale continuous experiments we determined the influence of flow rate, initial MB concentration and packing height on breakthrough time and shape of the breakthrough curve, allowing for the scale-up of the system for field tests. Continuous tests also validated theoretical predictions of maximum adsorption capacity obtained from batch adsorption experiments, achieving an MB loading of 391.7 mg/g.

Following this, a pilot scale fixed bed was developed to treat wastewater generated at a batik textile mill in Yogyakarta, Indonesia. However, the influence of other contaminants in the wastewater impacted the adsorption of MB onto the adsorbent, resulting in a lower projected performance. Following this, the influence on divalent salts during the start up of the fixed bed process on the adsorption of MB dye and the swelling of the adsorbent was studied. The CNC-ALG hydrogel beads were determined to be effective adsorbents for the removal of organic dyes from wastewaters in both batch and continuous processes, and their development for use in industrial water treatment systems is progressing well.

2:15 PM NM04.11.03

Tension Gradient Self-Assembly to Facilely Fabricate Polytetrafluoroethylene Nanofibrous Coating for Oil-Water Separation Dong Feng, Jiadao Wang and Ding Weng; Tsinghua University, Beijing, China.

Oil-water mixtures, which result from food processing, metal finishing, petrochemical and so on, have become the most common contaminant all over the world. Thus, oil-water separation is an important challenge in the field of scientific research and environment protection. Traditional methods for the oil-water separation, including air flotation, ultrasonic separation and biological treatment, have difficulty in practical applications due to the limitations of low separation efficiency and the generation of secondary pollutants. Recently, the superhydrophobic and superoleophilic materials for selectively adsorbing or filtrating oil from oil-water mixtures have flourished with advantages of high separation efficiency and wide applicability. Numerous preparation methods are developed, such as electrochemical deposition, electrospinning and vapor phase deposition. However, they are complex, high-cost, or inapplicable for large-area fabrication.

Here, we present a facile method to create durable superhydrophobic and superoleophilic coating on the porous metal fiber sintered felt (PMFSF) via tension gradient self-assembly. Firstly, PMFSF was immersed into ethanol and then pulled out vertically. A thin film of ethanol formed on the surface of PMFSF. Secondly, PMFSF was vertically placed into polytetrafluoroethylene (PTFE) solution (6 wt%) at a speed of 1 cm/s. The tension gradient appeared

as a result of the dissolution of ethanol into water, and induced the Marangoni convection and the relative motion between the solution and the PTFE nanoparticles. The particles moved towards the surface of PMFSF and a PTFE nanoparticle coating formed. Thirdly, the sample was heated to 380 °C for 40 min, followed by cooling down in air. During the sintering process, the PTFE particles melted and rearranged to form nanofibers. As a result, the PTFE nanofibers not only offered low surface energy, but also provided nanoscale roughness, which was beneficial for the oil-water separation. After a series of tests, the PMFSF coated with nanofibers could separate a series of oil-water mixtures with an efficiency over 98%. The separation efficiency was still stable after the sample was reused for oil-water separation over 30 times. Moreover, the sample worked well under extreme environmental conditions of strong acidic or alkaline solution, high temperature and ultraviolet irradiation.

In summary, we have demonstrated a simple, low-cost and rapid method to fabricate larger-area PTFE nanofibrous coating on PMFSF for oil-water separation based on tension gradient self-assembly. The coated PMFSF has the advantages of high-efficiency, durability and good environmental adaptability, which is suitable for industrial application.

2:30 PM BREAK

3:00 PM NM04.11.04

Nanofluidic Channels and Electrokinetic Energy Generation on Two-Dimensional Boron Nitride Membrane Si (Alex) Qin, Zhiyu Wang, Dan Liu, Weiwei Lei and Joselito Razal; Deakin University, Geelong, Victoria, Australia.

Recent research show that two-dimensional (2D) membrane can provide unprecedented large number of nanofluidic ion channels through economic and easy fabrication processes. However, constructing a 2D membrane suitable for harsh environment such as highly acidic or alkaline solutions is still a challenge. Boron nitride (BN) membranes constructed from highly stable, acidic and alkaline resistant functionalised BN nanosheets are promising alternatives for organic or GO membrane. Herein we show BN membranes which allow ions to pass through intra-layer spaces. Measurement across the BN membrane showed a surface-charge-governed ionic conductivity in a variety of salt solutions (KCl, NaCl and CaCl₂) at low salt concentrations (<10⁻⁴ M). Moreover, due to outstanding chemical and thermal stability of BN nanosheets, the ionic channels remain fully functional in harsh conditions and at elevated temperatures. The BN membrane can operate in highly acidic and basic environments, and does show degradation after immersing in solutions with extreme pH (pH close to 0 or 14) for one week. More interestingly, pressure gradient results in a current response across the membrane. Current in the range of 8–13 nA can be generated on a 5 mm² membrane with a pressure gradient of 5 kPa in 0.1 M NaCl solution. The electrokinetic electric generation can be scale up by connecting multiple devices. Those excellent properties make the BN membranes suitable alternative to organic or GO membranes and attractive for applications in nanofluidic devices and membrane separation.

3:15 PM NM04.11.05

Ultrahigh Performance of Novel Energy-Efficient Capacitive Deionization Electrodes Based on 3D Nanotubular Composites Nageh K. Allam; American University in Cairo, New Cairo, Egypt.

Capacitive deionization (CDI) is being progressed as an auspicious ions removal technique from brackish and seawater. Herein, we introduce a novel one-step facile chemical approach to fabricate tubular architected composite electrodes made of both Titania and Multi-walled carbon nanotubes (TNTs/MWCNTs). The composites have been exploited, for the first time, as the electrode materials for capacitive deionization. The composite electrodes were fully characterized via Field Emission Scanning Electron Microscopy (FESEM), Raman spectroscopy, X-Ray Diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS) techniques, and Nitrogen Sorption. The electrochemical response was investigated by using Cyclic Voltammetry (CV), Galvanostatic Charge and Discharge (GCD), and Potentio-Electrochemical Impedance Spectroscopy (PEIS) measurements. The fabricated composite electrodes containing 5 wt% TiO₂ nanotubes showed a remarkable specific capacitance, conductivity, reversibility, and durability compared to pristine MWCNTs and other MWCNTs-based composite electrodes reported in the literature. The desalination capability of the composite electrode was investigated using batch mode operation. The electrosorption capacity of the composite electrode containing 5 wt% TiO₂ nanotubes (13.2 mg/g) is approximately two folds of magnitude larger than that of pristine MWCNTs (7.7 mg/g), indicating an improved desalination efficiency. Therefore, the fabricated TNTs/MWCNTs composite electrode is a promising candidate for CDI technology.

3:30 PM NM04.11.06

Using Nickel Sulfide Nanoparticles Incorporated PMMA-Zirconia Membranes as Efficient Adsorbent for Ultra Deep Desulfurization of Thiophenes Adnan Mujahid¹, Tuba Choudhary¹, Tajamal Hussain¹ and Sadia Zafar Bajwa²; ¹Institute of Chemistry, University of the Punjab, Lahore, Pakistan; ²National Institute of Biotechnology and Genetic Engineering, Faisalabad, Pakistan.

Ultra deep desulfurization of liquid fuels such as gasoline/diesel has attracted considerable attention of modern clean fuel research due to strict environmental regulations. Apart from that, SO_x produced during combustion, poison the catalytic converter and exhaust emission system. Comparing to conventional catalytic and hydrodesulfurization techniques, adsorptive method for removal of sulfur bearing compounds e.g. thiophene derivatives is a promising approach which does not require hydrogen, or high temperature and pressure. In this study, we used nickel sulfide nanoparticles as a potential affinity material for adsorptive extraction of thiophene derivatives i.e. thiophene, benzothiophene and dibenzothiophene from n-hexane. The functionality and surface morphology of synthesized material was examined by Fourier transformation infrared (FTIR) and atomic force microscopy (AFM) images, respectively. The quantitative data regarding adsorptive removal of thiophene derivatives was determined by monitoring the absorbance values of their standard solutions before and after treating with synthesized material under ambient conditions. It was noticed that nickel sulfide nanoparticles exhibited excellent rebinding response for removal of dibenzothiophene down to 0.5ppm which is useful concerning ultra deep desulfurization. The prepared nickel sulfide nanoparticles were incorporated in polymethylmethacrylate-zirconia matrix for adsorptive desulfurization of tedious thiophenes from liquid fuels without using hydrogen gas or any other catalyst.

3:45 PM NM04.11.07

Chemically Functionalized Laminar MoS₂ Membranes for Nanofiltration Mark A. Bissett, Wisit Hirunpinoyopas, Eric Prestat and Robert A. Dryfe; University of Manchester, Manchester, United Kingdom.

Environmental pressures, along with the discovery of two-dimensional (2D) materials such as graphene, have combined to provide renewed interest in the development of membrane technologies. Laminar membranes of two-dimensional materials are excellent candidates for applications in water filtration due to the formation of nanocapillaries that can exhibit a size and charge sieving effect, while allowing high water flux. Laminar membranes of 2D materials have been demonstrated previously in the case of graphene oxide, however these membranes suffer from swelling when exposed to liquid water, leading to low ionic rejection and reducing their applicability for desalination applications.

In this work, we demonstrate that thin (~5 μm) laminar membranes of exfoliated molybdenum disulfide (MoS₂) can be modified by a simple chemical functionalization step and can efficiently reject (~99%) of the ions commonly found in sea water (e.g. Na⁺, K⁺, Ca²⁺, and Mg²⁺), while maintaining water fluxes significantly higher (~5 times) than those reported for graphene oxide membranes.¹ These chemically functionalized MoS₂ membranes exhibit long-

term stability with no swelling, and consequent decrease in ion rejection, when immersed in water for periods exceeding 6 months. Similar stability is observed when exposed to organic solvents, indicating that they are ideal for a variety of technologically important filtration applications.

We also performed ion transport measurements through the chemically functionalised MoS₂ membranes as a function of applied electric potential to differentiate between the effects of size and charge. Hydrated and non-hydrated cation permeability was measured for various mono-, bi-, and trivalent ions, demonstrating that higher charge density has a greater effect on the permeability of the inorganic cations than the organic cation of comparable radii. The method presented here, based on non-toxic organic-functionalized MoS₂ laminar membranes, demonstrates impressive potential for application in water purification technologies such as desalination, ion exchange, electrodialysis, reverse osmosis, and electrodeionization (EDI).

[1] W. Hirunpinyopas, E. Prestat, S.D. Worrall, S.J. Haigh, R.A.W. Dryfe, M.A. Bissett, ACS Nano 11(11) (2017) 11082–11090.

4:00 PM RAPID FIRE PRESENTATION

SESSION NM04.12: Poster Session IV: Toxicology, Monitoring and Depollution
Session Chairs: Babak Anasori, Monica Jung de Andrade and Maria Perez Barthaburu
Thursday Afternoon, November 29, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

NM04.12.01

Coffee Waste as Biocleaning Agent for Polluted Water Reservoirs Pedro Perdigon Lagunes¹, Sofia Aguilera-Barraza², Alejandro Isaza-Orozco², Pablo A. Cano-Martínez², Lorena Arreguín-Lozano², Humberto Pro White², Daniel Dalma Nehmad², Diego Delgado Fajardo² and Raul Herrera-Becerra¹; ¹Universidad Nacional Autónoma de México, México City, México; ²Instituto Tecnológico y de Estudios Superiores de Monterrey, Ciudad de México, México.

Fresh water reserves are being depleted quickly in the last century and the rest of them are being contaminated. Different types of pollutants are released in the environment from various industries, specially, heavy metals in water reservoirs are a harsh task to solve. This is because these types of materials bound strongly to water molecules; hence, it is necessary to use different methods such as electro-Fenton reactions, advanced oxidation processes and nanotechnology to remove them [1]. An interesting approach is to use living microorganisms or fungi as bioremediation agents, because in the nature these organisms work as caretakers of water and soil. However, in this case the contaminants surpass their resilience to toxic waste. In our case, we decided to solve this problem using nanotechnology approach [2], utilizing a common waste as our main reduction agent: Coffee waste. Despite the fact it is used as a compostable waste, we used it as a biocleaning agent instead. Coffee extracts have demonstrated their capability to bioreduce metals into nanostructures [3]; therefore, we obtained a bioactive extract from used coffee capable of quickly reducing metallic ions into nanoparticles. Then, we tested our extract to collect heavy metals from polluted water. In this experiment, metal-oxide nanoparticles of different composition were precipitated at the bottom of the test tubes. Then those nanoparticles were analyzed to determine their composition. This technique is a promising one, because it is simple to escalate, it uses waste products as their main reagents, and small nanoparticles can be recovered to be used in technological applications.

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NM04.12.02

Synthesis of Nanoporous Adsorbents Showing High CO Selectivity to CO₂ and High CO₂ Selectivity to CH₄, Based on Systematic Study on Effect of Physico-Chemical Properties of Nanoporous Materials to Adsorption of Each Component Kanghee Cho, Hyung Chul Yoon, Taesung Jung, Dongwoo Cho, Jong-nam Kim, Sang Sup Han, Jong-ho Park, Hee Tae Beum, Jongkee Park and Sun Hyung Kim; Korea Institute of Energy Research, Daejeon, Korea (the Republic of).

We synthesized two types of nanoporous adsorbents: one for CO-selective separation from CO/CO₂ mixture, and the other for CO₂-selective separation from CO₂/CH₄ mixture. For the synthesis of the CO-selective adsorbent, we impregnated CuCl species which shows strong interaction with CO on suitable alumina-type nanoporous supporting material. The driving force of CO-selective adsorption is strong interaction between the CuCl species and CO molecules. For the synthesis of the CO₂-selective adsorbent, we modified zeolite to tune finely the size of micropore aperture of the zeolite to certain size between the molecular sizes of CO₂ (0.33 nm) and CH₄ (0.39 nm). The driving force of the CO₂-selective adsorption is the size-selective effect (molecular sieving effect) of the micropores in the zeolite. For both cases of the adsorbent syntheses, it is highly important to choose suitable nanoporous supporting material and to modify the nanoporous supporting material, in order to enhance adsorption capacity and selectivity of target component. For this purpose, it is necessary to understand the effect of the physico-chemical properties of the nanoporous materials to the adsorption of each adsorbate. In the case of the CO-selective adsorbent, nanoporous supporting material is desired to disperse well the CuCl species to increase CO adsorption capacity, and it is simultaneously desired to show weak interaction with CO₂ to enhance CO selectivity. Zeolite 13X which has been normally used for the preparation of CO-selective adsorbent shows high CO₂ adsorption capacity owing to electro-static interaction with CO₂ and zeolitic microporosity, even though it shows high surface area which is good for high dispersion of CuCl. We used mesoporous alumina as a supporting material for the CuCl, and the mesoporous alumina has weaker electrostatic interaction than zeolite and no microporosity. We confirmed that our new CO-selective adsorbent 35 cm³ g⁻¹ of CO adsorption but only 2.9 cm³ g⁻¹ of CO₂ adsorption at 293 K under 100 kPa of each gas. In the case of the CO₂-selective adsorbent, the adsorbent is desired to show nanopore size between the sizes of CO₂ and CH₄ to have size-selective effect. When the size of micropore aperture of the zeolite is reduced to desired range, CH₄ molecules cannot enter the micropore aperture. However, the adsorption speed of CO₂ becomes inevitably too low to use fully the size-selective effect of the zeolite in CO₂ separation. In order to resolve such a problem of slow adsorption, we generated additional mesopores in the zeolite crystals by using organosilane surfactant as a mesopore generating agent. The adsorption of CO₂ into the micropores is still slow in the case of the mesoporous zeolite, but the mesopore generation increases the number of micropores exposed to external surface. The mesoporous zeolite shows high CO₂/CH₄ selectivity, and it shows much higher CO₂ adsorption rate than solely microporous zeolite counterpart.

NM04.12.03

Dielectric Mirrors for Vapor Sensing and the Study of Time-Resolved Response Shuai Gao, Karen Forberich and C. Brabec; University of Erlangen-Nuremberg, Erlangen, Germany.

Organic solvent and water vapors detection plays an important role in industrial and life areas. Predictable and selective sensing shows a large number of applications. Dielectric mirrors (DMs), also known as Bragg stacks or one-dimensional photonic crystals, have certain reflection bands, and the position of the reflection band can be controlled by changing the thicknesses or the refractive index of the stacked layers. Polymers or organic-inorganic materials are popular in vapor sensitive dielectric mirrors, and the variation of refractive index or thickness is easily controlled because polymers show the property of swelling. The tunable reflection bands enable the mirrors to work as vapor sensors. In most research, polymers are deposited as the active layer and oxide nanoparticles are deposited as the other porous layer to improve the permeability and increase the refractive index contrast in the bilayer structure. However, due to the specific properties of the polymers, they can only respond to either water or organic solvents.

In this work, dielectric mirrors based on bilayers are fabricated for the purpose of vapor sensing, which are made of polystyrene-block-poly (ethylene-ran-butylene)-block-polystyrene (SEBS) and polyvinyl alcohol (PVA)-zirconium dioxide (ZrO₂) nanocomposites. The specific reflection bands of dielectric mirrors depend on the refractive indices and thicknesses of the alternating layers. When dielectric mirrors are exposed to solvent vapor, layers swell which causes a shift of the reflection band. Since SEBS and PVA respond to organic solvents and water, respectively, these mirrors can be used as sensors for a large variety of different solvents. Hydrophilic ZrO₂ nanoparticles are introduced to increase the porosity of the PVA layers, and the ratio of ZrO₂ nanoparticles was optimized to achieve the optimum effect. The time-resolved response is studied to understand the swelling processes. Time-resolved measurements show that the mirrors with nanoparticles have a significantly faster response compared with those without nanoparticles. Due to the different Flory-Huggins interaction parameters between materials and solvents, the dependence of the responses on the relative humidity and on the type of solvents is studied, which provides an approach to make responses predictable and selective. The swelling of the mirrors is reversible upon thermal annealing so that the response of the vapors sensors shows good reproducibility. The combination of good properties such as selectivity, predictability, and reversibility with the simple fabrication procedure is promising in the development and application of the dielectric mirrors as vapor sensors.

NM04.12.04

TiO₂ Encapsulated AIOOH Dual Nanostructures with Robust Anti-Oil Fouling Sun Mi Yoon^{1,2}, Hyebin Lee¹, Young Cheol Park¹, Sahn Nahm² and Myoung-Woon Moon¹; ¹Materials and Life Science Research Division, Korea Institute of Science and Technology, Seoul, Korea (the Republic of); ²Department of Materials Science and Engineering, Korea University, Seoul, Korea (the Republic of).

More researches are under progress for developing an oil-water separation or recovery method as oil spillage accidents continuously occurs. Technology for removing oil spilled in the sea or the river includes adjusting surface energy like hydrophilicity and hydrophobicity as well as the structures in nano- or microstructures or their hybridization. Among functional materials, the hydrophilic/underwater oleophobic materials have advantages in the various applications such as self-cleaning, oil transportation or oil-water separation. However, the hydrophilic or superhydrophilic surfaces are still required for the long-term durability in mechanical and chemical stability.

In this work, we present a durable superhydrophilic and underwater superoleophobic mesh filter with dual nanostructures of nanoflake and nanoparticle clusters. The aluminum (Al) mesh surfaces show the long-term superhydrophilicity/underwater superoleophobicity induced by hydrothermal treatment in containers having Al mesh and TiO₂ nanofluid. As Al is immersed in boiling TiO₂ nanofluid, the Al surface reacts hydroxyl ion decomposed water to form flake-like AIOOH nanostructure encapsulating TiO₂ nanoparticles inside. Al ions are diffused out from the Al₂O₃ matrix, leaving Al depletion zone, then the Al ions in TiO₂ nanofluid can be precipitated on the both surfaces of Al depletion zone and TiO₂ nanoparticles. Pristine Al mesh filter without TiO₂ nanoparticles showed mild hydrophilic but not lasted for longer duration, while the mesh filter with dual nanostructures has long-term stability in superhydrophilicity more than 10 weeks due to dual scale roughness in nanoscale as well as TiO₂ effect. The hybrid nanoclusters have very low wetting angle of near 0 degree in air and superoleophobic underwater long-lasting anti-oil property. We applied this surface to oil collecting filter by separating oil/water, which are required for the spontaneous oil detachment at the water surface for cyclic oil-water collection-separation-release process with the crude oil over 5,000 times.

NM04.12.05

Cost-Effective Fabrication of Metal Oxide Nanoparticles (WO₃, ZnO) Based Gas Sensor for Selective Detection of NO₂ and CO Environmentally Hazardous Gases Sapana Ranwa, Vikas Sharma, Habeebur Rahman and Bodh R. Mehta; Department of Physics, Indian Institute of Technology Delhi, New Delhi, India.

In today's era, real-time monitoring of environmental pollutant toxic gases is vital for domestic sector as well as automobile sector to uphold human health and safety. The selective detection of most common and hazardous gases CO and NO₂ at low operating temperature is one of the critical challenges in the area of commercially environmental sensors. Metal oxide nanoparticles (ZnO, WO₃) based gas sensor provides an opportunity to fabricate cost-effective environmental gas sensor with low concentration gas detection possibility even at moderate operating temperature. In this study, a WO₃ nanoparticles based sensor able to give ~ 36.3% sensor response towards 10 ppm NO₂ gas even at 50 °C operating temperatures. This sensor shows highly selective sensor response towards 10 ppm NO₂ gas in comparison to other air pollutant gases (10 ppm CO ~ 2% and 10 ppm NO ~ 3%) at a low operating temperature (50 °C). Furthermore, doping of Ga (1% to 5%) into ZnO based sensor could provide the possibility to solve the selectivity problem for NO₂ gas concentration among other common environmental pollutants (CO, NO). 2.5% Ga doped ZnO based sensor able to depicts 10 fold increased sensor response with high selectivity towards 10ppm NO₂ gas at 150 °C operating temperature in comparison to pristine ZnO based sensor for other hazardous gases (CO, NO). ZnO nanoparticles and Ag loaded ZnO Nanoparticles based chemical sensor performance have been further studied for selective detection of 10 ppm CO gas concentration at operating temperature ranging from 50 °C to 150 °C. Functionalization of ZnO sensor with surface decoration of Ag nanoparticles (5-20 nm) has been achieved by a continuous gas phase deposition method. Gas sensing response of Ag loaded ZnO sensor shows significantly enhanced sensor response ~40% in comparison to ZnO sensor response ~9% for 10 ppm CO gas concentration at 150 °C operating temperature. This improved sensor response towards reducing gas (CO) for Ag loaded ZnO sensor could be explained by electronics as well as chemical gas sensing mechanism. Ag loaded ZnO sensor also has been able to depict selective sensor response towards 10 ppm CO gas with ~ 40% sensor response in comparison to other air pollutants (10 ppm NO with ~ 10% and 10 ppm NO₂ with ~20%) at 150 °C operating temperature. This current approach enables us to fabricate cost-effective and low operative temperature environmental gas sensor with high selectivity for the detection of CO and NO₂ gases. These studies also motivate us to record both WO₃ and Ag loaded ZnO based sensor response at the same time which gives selective detection of NO₂ and CO gases without changing sensor from the chamber.

NM04.12.06

Photocatalytic activity of Ce doped SnO₂ nanoparticles for the degradation of organic toxic pollutants Akanksha Gupta¹, Sanjeev K. Yadav², Prateek Saini², Ayesha Seth² and Vinod Kumar³; ¹Chemistry, Sri Venkateswara College, Delhi, India; ²Chemistry, Kirori Mal College, Delhi, India.

Water pollution by different harmful compounds is becoming an increasing global concern. Most industrial dyes, pesticides are toxic, carcinogenic, and

mutagenic, and have low biodegradability. Moreover, dye-containing effluents are highly colored, so discarding these effluents into natural water bodies affects the balance of aquatic ecosystems because they can prevent the penetration of sunlight into the water, which results in a reduction in dissolved oxygen content. Therefore, the removal of dyes and pesticides prior to the discharge of wastewater from industries is of great importance. The inadequate treatment and inappropriate disposal of these toxic carcinogenic organic compounds pose a considerable threat to the environment [1].

Several binary oxides such as TiO_2 , ZnO , SnO_2 etc. have been recognized as preferable materials for photocatalytic activities due to their high photosensitivity, low cost, and chemical stability and hence, they have been investigated for the degradation of these pollutants in waste water [2]. Little information is available in the literature regarding the SnO_2 -RE (RE=rare earth) system [3].

Tin dioxide (SnO_2) is a n-type semiconductor that has a wide range of potential applications in gas sensors, catalysts, batteries, transistors, and transparent electrodes. The structure, band gap, and chemical stability of SnO_2 are similar to those of titanium dioxide (TiO_2), which is a widely used photocatalyst. Moreover, SnO_2 has no adverse health effects and is poorly absorbed by the human body when injected or inhaled. Thus, SnO_2 is potentially an ideal photocatalyst and possess large surface area. Semiconductor photocatalytic processes are based on the generation of electron-hole pairs by means of band gap radiation. SnO_2 has also been used as a component of composite photocatalysts such as $\text{SnO}_2/\text{TiO}_2$, SnO_2/ZnO , and $\text{SnO}_2/\text{ZnO}/\text{TiO}_2$ [4]. Doping of rare earth ion in metal oxide introduce defects lowering the effective optical gap and hence leading to a better photoactivity. Ce doped SnO_2 is a promising material and several scientists have reported its gas sensing properties for various harmful gases but to the best of our knowledge its photocatalytic activity has not been explored much.

Herein, we present the synthesis and structural characterization of varying concentration of Ce-doped SnO_2 nanoparticles. Detailed characterization are attempted based on the PXRD measurements, FTIR, Raman, UV-visible spectroscopy etc. We have successfully degrade the organic dyes and pesticides under UV irradiation, which might be helpful for the wastewater treatment in future.

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NM04.12.07

High Performance Single Magnéli Phase Reactive Electrochemical Nanoporous Membrane for Waste Water Treatment Sasmita Nayak and Brian P. Chaplin; University of Illinois at Chicago, Chicago, Illinois, United States.

Reactive electrochemical membrane (REM) based on Magnéli phase titanium oxides ($\text{Ti}_n\text{O}_{2n-1}$, $n = 4$ to 10), are attractive, because of their high conductivities, chemical stability, and low cost with unique functionality to produce OH via water oxidation. Most of the present Magnéli phases based REM are limited to formation of high-quality, the most conductive and single magnéli phase, i.e., Ti_4O_7 . This study reports the synthesis and electro-oxidation capabilities of Magnéli Ti_4O_7 REM using probe molecules and organic compounds through both direct oxidation (oxalic acid) and interaction with OH (terephthalic acid). High membrane fluxes of ($1736 \text{ LMH bar}^{-1}$) resulted in a convection-enhanced rate constant for $\text{Fe}(\text{CN})_6^{4-}$ oxidation of $8.13 \times 10^{-4} \text{ m s}^{-1}$ and that for $\text{Fe}(\text{CN})_6^{3-}$ reduction of $10.84 \times 10^{-4} \text{ m s}^{-1}$ that approaches the kinetic limit. Batch experiments were also performed for electrochemical destruction of N-nitrosodimethylamine (NDMA) in flow-through electrode for single-pass sequential reduction-oxidation.

NM04.12.08

Highly Efficient Adsorption of Heavy Metal Ion from Wastewater Using Hollow Carbon Coated with Fe_3O_4 Hybrid Composites Byeong Seok Lim, Bongkyun Kang and Woo Seok Yang; Korea Electronics Technology Institute, Seongnam-si, Korea (the Republic of).

The presence of hazardous heavy metals in water is an important issue in environmental pollution management with crucial effects on human health. Heavy metal can cause several serious health problems and skin cancer. Iron oxide based materials are very effective in the removal of heavy metal. However, Fe_3O_4 nanoparticles are actually prone to aggregate by spontaneous magnetization that decreases specific surface area. Additionally, heavy metal adsorbed Fe_3O_4 nanoparticles are difficult to separate in water owing to their low magnetic properties and nanosize.

In this work, we synthesized the hollow carbon coated with Fe_3O_4 hybrid composites via SiO_2 @dopamine core shell. The hollow carbon coated with Fe_3O_4 hybrid composites did not aggregate well compared to other Fe_3O_4 materials because the hollow carbon structure had a three dimension (3-D) sphere shape and high outer surface area with inner surface. Consequently, the hollow carbon coated with Fe_3O_4 hybrid composites exhibited more heavy metal adsorption capacity compared to pure Fe_3O_4 and other materials with Fe_3O_4 .

NM04.12.09

An Intelligent Dual Mode Reversible Filtration Device for Separation of Immiscible Oil/ Water Mixtures and Emulsions Parul Raturi and Jitendra P. Singh; Physics, Indian Institute of Technology Delhi, Delhi, India.

For the treatment of oily wastewater strategies used for oil/water separation, including immiscible light/heavy oil water mixture, both oil in water and water in oil emulsions are of great demand. Recently, materials having specific wettability properties have become interesting due to their importance in the field of oil/water separation. Herein, we report an intelligent mesh for dual mode reversible separation of immiscible heavy/light oil water mixture and both oil-in-water as well as water-in-oil emulsions. ZnO nanowires coated stainless steel mesh with pore size of $50 \mu\text{m}$ and $10 \mu\text{m}$ were fabricated successfully. The wettability of mesh can be reversibly switched between “oil-blocking” and “water-blocking” modes by alternative exposure and removal of low surface energy material. The “oil-blocking” mode was suited for the efficient separation of light oil/water mixture and oil-in-water emulsion, while “water-blocking” mode was found to be suitable for the separation of heavy oil/water mixture and water-in-oil emulsion. This work provides a simple, cost effective, eco-friendly and time saving approach applicable for separation of both form of oil/water mixture, free as well as surfactant stabilized emulsions, irrespective of the types of oil involved. The separation efficiency of the mesh was found to be more than 99% for free as well as emulsified mixtures. Even after cyclic usage in both modes alternatively, the separation efficiency of the mesh remained relatively unchanged, showing antifouling property and excellent recyclability of the mesh.

NM04.12.10

Recyclable and Multifunctional 3D Hybrid Networks for Adsorption, Detection and Decomposition of Environmental Pollutants Yunjeong Lee, Seungki Lee, Chang Min Jin, Hyo Sil Kim and Inhee Choi; Department of Life Science, University of Seoul, Seoul, Korea (the Republic of).

Monitoring and removal of environmental pollutants have been regarded as important tasks nowadays due to global and public health issues. For this purpose, efficient materials that can adsorb, detect, and decompose such pollutants have been consistently sought after. Even for such an essential necessity, there are only a limited number of reports on suitable platforms or materials that can allow combining multiple roles of adsorption, detection, and decomposition of VOCs. Herein, we present a simple, inexpensive and eco-friendly fabrication method of recyclable and multifunctional three-dimensional (3D) network with functional nanoparticles (hybrid network). Water-soluble crystals (e.g., sugar and salt) and photocatalytic nanoparticles (e.g., TiO_2 nanoparticles) are utilized to construct porous templates where liquid polydimethylsiloxane (PDMS) mixture (base and curing agent) is filled. For

more sensitive detection of pollutants, metal precursors (e.g., HAuCl_4 and AgNO_3) can be added into the liquid PDMS mixture to form the plasmonic nanoparticles such as Au and Ag nanoparticles in the porous PDMS network. After curing the PDMS, porous network structures with the self-integrated nanoparticles are finally obtained by dissolving the templates by water. To demonstrate the performance of the hybrid network, we quantitatively and qualitatively detect the pollutants such as organic dyes and volatile organic compounds (VOCs) via molecular-specific and label-free Raman scattering. Furthermore, we show the recyclability by achieving photocatalytic decomposition of the adsorbed pollutants by using the TiO_2 hybrid networks. We believe that the developed hybrid 3D networks could be widely utilized in managing organic pollutants in aquatic and atmospheric environments.

NM04.12.11

Enhanced Aqueous Copper(II) Ion Adsorption Efficiency of Polyaniline Nanofibers via Phytic Acid Doping Hyeong Jin Kim and Young Joon Hong; Department of Nanotechnology and Advanced Materials Engineering, Sejong University, Seoul, Korea (the Republic of).

Scavenging discarded metal in aquatic environment has been of note in both polluted water purification and mineral mining, which have been usually processed using various methods. Among the diverse methods, adsorption/metal-organic complexation by ion exchange has gained a great deal of interest for low processing cost, energy saving, and greener chemical technology. Because of the ability of the technique to reuse the adsorbent and the discarded metal, as of late, many types of meso-porous and nanostructured have been developed for high efficiency collection of aqueous metal ions, due to the high surface-to-volume (s/v) ratio. In particular, nanostructure adsorbents are thought to be ideal for high-efficiency metal adsorption, but high density surface ionic functional groups are further needed to strongly attract aqueous metal. Especially, polymer has a structural advantage of being viable to modify surface chemical properties via doping chemical functional groups to backbone, enabling it to substantially raise the aqueous metal adsorption efficiency. Also, many polymers are deformable such that they can be structurally designed to form desirable shapes in demand. In addition, considering the significance of reuse of adsorbed metals.

Here, we report on radical polymerization synthesis of phytic acid-doped polyaniline nanofibers (Ph-PANI NFs) and enhanced adsorption of aqueous Cu^{2+} after the doping. To pose a higher negative charge, the dopant of phytic acidic molecules with phosphoric acid functional groups was employed. The Cu^{2+} adsorption efficiency of Ph-PANI NFs was markedly increased after the doping, presumably due to high ionic attraction feature of phosphoric acid group in phytic acid. The adsorption efficiency of Ph-PANI NFs is discussed in terms of Langmuir and Freundlich adsorption models. We further investigated the pH-dependent adsorption efficiency of Ph-PANI NFs and found much higher Cu^{2+} adsorption capability under high pH conditions owing to spontaneous deprotonation by the basic solution. Furthermore, Ph-PANI NFs showed stable, high Cu^{2+} adsorption efficiency, irrespective of Co^{2+} concentration in the bi-metallic Cu and Co aqueous solution. Surface modification and/or doping to enhance the adsorption efficiency of Cu(II) introduced in this study will provide a great venue for expanding the use of many other polymeric nanostructures for reclamation in metal mining as well as the conventional environmental applications such as water purification.

NM04.12.12

Smart Metal Mesh to Simultaneously Harvest Atmospheric Fog and Remove Pollutants Ritwick Ghosh^{4,2,3}, Rakesh P. Sahu⁴, Igor Zhitomirsky¹, Ranjan Ganguly² and Ishwar K. Puri^{4,1}; ¹Materials Science and Engineering, McMaster University, Hamilton, Ontario, Canada; ²Power Engineering, Jadavpur University, Kolkata, India; ³Mechanical Maintenance, NTPC Ltd., Farakka, India; ⁴Mechanical Engineering, McMaster University, Hamilton, Ontario, Canada.

Water harvesting from fog-laden atmospheric and industrial wind streams is finding increasing application. Since fog often contains SO_x , NO_x , and VOCs, use of the harvested water is limited by its quality. We describe an integrated approach that simultaneously harvests fog and removes pollutants from the collected water. A stainless steel (SS) mesh is coated with TiO_2 / ZnO nanoparticles through electrophoretic anodic deposition. These two types of nanoparticles exhibit photocatalytic properties when they are exposed to UV radiation, which alters the mesh wettability and decomposes organic compounds. The applied voltage, deposition time, dispersant concentration, specific binder material and nanoparticle composition are systematically adjusted to develop a uniform and durable coating on the surface of the mesh. A correlation is established between the applied voltage, and nanoparticle deposition time and mass deposited on the mesh. For the right deposition conditions, the nanoparticle layer on the mesh is free of surface cracks and resistant to mechanical stress. To determine the photocatalytic decomposition efficacy of various meshes, methylene blue (MB) solution is used as a VOC surrogate. While exposed to UV radiation that induces photocatalytic cleansing, functionalized SS meshes of various wettabilities are inserted into flows to intercept fogs generated from MB solutions, and their photocatalytic efficacies are evaluated. The MB solution that is harvested is characterized using UV-Vis spectroscopy to determine the extent of its photocatalytic degradation. The UV intensity, duration of fog collection, and quantity of deposited nanoparticles used to coat the meshes are correlated with this mesh efficacy. This technology can potentially be used to improve the local air quality by arresting smog in large complexes, such as hospitals, schools and public arenas.

NM04.12.13

Gas-Phase Interrogation Module For Lower-Power Chemical Collection (GIMLI) Myeongseob Kim, Michael J. Bowers, Don Ahmasi Harris and Pierre-Alain Auroux; FAST Labs, BAE Systems, Columbia, Maryland, United States.

In this presentation, we provide partial results of IARPA supported MAEGLIN (Molecular Analyzer for Efficient Gas-Phase Low-Power Interrogation) program. The MAEGLIN program intends to develop an ultra low power chemical analysis system for remote site detection and identification of explosives, chemical weapons, industrial toxins and pollutants, narcotics, and nuclear materials in the presence of significant background and interferents. The system should be traceable to a package fitting within 0.5 L and 2.5 kg. The power threshold is < 7.5 J per analysis run with a goal of < 1.5 J per analysis run. The autonomy of the systems shall be at least 730 cycle sampling performance (one sample per day for two-year use). To accomplish this task, BAE SYSTEMS utilized its open cell proprietary foam as a low pressure drop broad-based adsorbent medium which enables sampling at high rates (liters per minute or lpm) utilizing a computer fan or blower. Upon collection the analytes are thermally desorbed from the foamed sorbent material and delivered directly to a GC column without use of a cryo-focusing system. Currently our system is able to collect over 50 targets (among 100 background compounds and with 5 true unknowns) with a compound mass range of 30-350 amu. With energy per sample 1.248J, system volume 0.82 L, and reusability is >730 times.

NM04.12.14

Ultra-Durable Superhydrophobic/Superoleophilic Mesh Prepared by Spray-Coating for Oil/Water Separation Chaolang Chen, Ding Weng, Awais Mahmood and Jiadao Wang; Tsinghua University, Beijing, China.

Nowadays, the efficient separation of oil/water mixtures has become an urgent challenge all over the world. Superhydrophobic/superoleophilic materials have been widely employed to separate oil/water mixtures due to its high efficiency, high flux and high selectivity. However, the poor mechanical durability of superhydrophobic materials has always been a common drawback, which limits their applications in real industry. Here, we propose a facile method to fabricate superhydrophobic mesh by spraying commercial adhesives and PTFE nanoparticles. The adhesives were used to bond the PTFE nanoparticles to the substrates and enhance its durability. The PTFE nanoparticles were used as building blocks to decrease the surface energy of substrates and promote hydrophobicity. The coated mesh exhibited superhydrophobic/superoleophilic properties with water contact angle of above 155° and oil

contact angle of 0°. Moreover, the as-prepared mesh can be applied to separate not only immiscible oil/water mixtures, but also water-in-oil emulsion with high separation efficiency. The coated mesh also exhibited good hydrophobicity and possessed high separation efficiency for various oil/water mixtures even after over 600 abrasion cycles, showing ultra-durable property. Furthermore, this method could be flexibly applied to almost any soft and solid substrate such as fabric, sponge, glass and so on, which could have significant application in industries.

NM04.12.15

Toxicity Evaluation of Boron- and Phosphorous- Doped Silicon Nanocrystals Towards *Shewanella oneidensis* MR-1 [Bo Zhi](#)¹, Sadhana Mishra², Natalie V. Hudson-Smith¹, Uwe R. Kortshagen² and Christy L. Haynes¹; ¹Chemistry, University of Minnesota Twin Cities, Minneapolis, Minnesota, United States; ²Mechanical Engineering, University of Minnesota Twin Cities, Minneapolis, Minnesota, United States.

Silicon nanocrystals, also known as silicon quantum dots, are regarded as green alternatives to traditional quantum dots composed of heavy metal elements. While the semiconductor properties of these materials can be tuned by doping with p/n-type dopants (*i.e.*, boron and phosphorous), little is known about the potential environmental impacts of these doped nanocrystals. This work demonstrates that introduction of dopants, especially phosphorus, causes the doped silicon nanocrystals to produce reactive oxygen species, resulting in significant toxicity to a model microorganism, *Shewanella oneidensis* MR-1. In addition, the interaction between bacteria cells and silicon nanocrystals was investigated using hyperspectral dark field microscopy and TEM. Interestingly, likely due to Lewis acid-base interactions, the boron-doped silicon nanocrystals tend to attach to the bacterial cell surface while this phenomenon was not observed for undoped or phosphorous-doped silicon nanocrystals. This mechanistic understanding of nanocrystal-bacteria interactions yields critical insight for future design of sustainable nanomaterials.

NM04.12.16

Surface Modification of Polymer Filters by Etching and a PDA Coating for Oil-Water Separation [Pei Zhao](#), Ning Qin, Carolyn Ren and John Wen; Department of Mechanical and Mechatronics Engineering, University of Waterloo, Waterloo, Ontario, Canada.

Oil-water separation has been a global challenge due to extensive oily wastewater from industry and oil leakage. The polymer filters possessing underwater oleophobicity have been used for oil-water separation, which selectively allow water to flow through while resist oil. Those filters have been achieved either by the surface etching or by using novel coatings, as the wettability depends on the nature of the surface materials as well as the topography. Here, we developed a two-step strategy to modify polymer meshes and nonwoven fabrics for oil-water separation, where an underwater oleophobic PDA bio coating was applied onto a pre-etched polymer surface that had a large roughness. This strategy combines the required wettability of the coating and the large roughness that could further enhance the wettability.

Such modified polymer filters possessed superoleophobicity (>150°) in water and were capable of separating various oil-water mixtures with a high efficiency (>98.5%). These filters also showed increased intrusion pressure than the only coated or only plasma treated filters. The rugged surface created by the etching reinforced the coating stability and prevented the coating from peeling out of the substrate. Then the two-step modified filters were more durable than the only coated ones. Different from other durability investigations, in our work, for each cycle of use the filter was intruded (contaminated) by oil in order to measure its intrusion pressure. After 6 cycles of uses, the nonwoven filter was no longer underwater oleophobic due to severe oil contamination, and thus came to a failure in oil-water separation. After 19 repeated uses, the mesh filter was still capable of separating a certain amount of oil-water mixture but presented a decreased intrusion pressure due to slight oil fouling. Filters with different structures had different oil fouling levels during repeated uses that affected their durability for oil-water separation. The nonwoven with complex layers of pores was less durable than the mesh with a simple one layer porous structure, due to the much heavier oil fouling of the nonwoven. A way to efficiently clean the viscous oil residual in the filters could benefit the durability. The recoverability of the filter from oil fouling should be considered for practical applications. The two-step method of surface modification for polymer filters and the durability investigations give a new insight for filter design.

NM04.12.17

Electroimpedance Sensor for Detection of Cd with a Low-Cost Solution-Processed Sensing Layer [Priya Vinayak](#), Henam Sylvia Devi, Soumen Saha, Madhusudan Singh and Bhaskar Mitra; Indian Institute of Technology Delhi, New Delhi, India.

Cadmium is a trace metal in the Earth's environment that presents with significant toxicological and carcinogenic effects in multiple organs in humans. The Centers for Disease Control (CDC) prescribe a maximum daily Cd exposure limit of 9 mg/m³. In this work, we have used chemical bath deposition to deposit CdS on gold for sensing Cd ions in test solutions. A Cr/Au layer (15nm/40nm) was deposited on glass under vacuum (4.2 x 10⁻⁶ Torr) using thermal evaporation. Subsequently, this substrate was immersed in an aqueous solution consisting of triethanolamine, cadmium acetate and thiourea (sulfur excess) at a pH of 12 using ammonium hydroxide, for over one hour at 50°C under constant stirring. Thin film X-ray diffraction (XRD) revealed CdS (111) deposition, while the absorption of resulting film was consistent with published data. The composition of the film was verified using energy dispersive X-ray spectroscopy (EDX) to reveal a Cd:S ratio of approximately 1:1. Electroimpedance measurements were carried out using a Biologic SP-150 potentiostat, using an AC bias of 50 mV peak to peak on a DC ramp, with a Pt counter electrode and Ag/AgCl reference. Spiked Cd(NO₃)₂·4H₂O solutions with concentrations 1M to 10⁻⁸M were used to characterize the operation of the sensor. The sensor showed linearity below 10⁻⁶M, with a detection limit of ~0.3 ppm. This compares favourably with the established exposure limit (~15 ppm) for Cd. As a result, this sensor is expected to be suitable for low-cost sensors for the screening of drugs, drinking water, and other comestibles.

NM04.12.18

Functionalized Single Walled Carbon Nanotubes as Novel Nanoresin for Fast, Safe and Sustainable Water Purification [Abhispa Sahu](#) and Jordan C Poler; Chemistry, University of North Carolina at Charlotte, Charlotte, North Carolina, United States.

Ground water & surface water quality in rural & urban areas are affected by natural & anthropogenic contamination. These water resources are being contaminated by pervasive Low Molecular Weight Organic Compounds (LMWOCs) which are not effectively removed by the current wastewater technologies. The US Environmental Protection Agency (USEPA) is focused on the removal of many classes of LMWOCs from drinking water & wastewater including: disinfection byproducts (DBP) precursors, pharmaceuticals, personal care products, heavy metals & perfluoroalkylated substances. In order to address removal of these pervasive compounds, an anion exchange resin polymer (AEP) functionalized Single Walled Carbon Nanotubes (SWCNTs) in the form of nanoresin has been developed. The large surface area of SWCNTs increases the availability of active ion exchange sites of the AEP. These nanoresins have higher & faster adsorption capacity compared to other current commercialized materials like magnetic ion exchange resins, DOWEX, etc.

This nanoresin was synthesized by modified activator regenerated electron transfer atom transfer radical polymerization technique in aqueous media. The hydrodynamic diameter of the purified AEP & nanoresins were 1.660 ± 0.10 nm & 194.9 ± 11.3 nm, respectively. The ratio between D & G bands, measured using Raman Spectroscopy, increased by 100% compared to pristine carbon nanotubes which is indication of covalent functionalization of the AEP. The proton nuclear magnetic resonance of the growing AEP showed 99.8% conversion from monomer to polymer in 69.30 hours. The scanning electron microscopy of nanoresin films fabricated on mixed ester cellulose (MCE) membrane for performance testing showed a smooth morphology of

mesh of SWCNTs with conformal polymer coating. The step height of the fabricated film determined under atomic force microscopy was 142.31 nm. The measured membrane resistance of the thickest nanoresin film was determined to be $\kappa_m = 2.1 \times 10^{11} \text{ m}^{-1}$ which is smaller than typical ultrafiltration membranes with $\kappa_m = 2 \times 10^{12} \text{ m}^{-1}$.

We demonstrate the removal of several types of pharmaceuticals (*viz.*, tetracycline hydrochloride and carbenicillin disodium), pesticides (*viz.*, bentazon, terbacil, and bromacil), DPBs (*viz.*, bromoacetic acid and chloroacetic acid) and PFAS (*viz.*, perfluorooctanoic acid (PFOA) and perfluorooctanesulfonate (PFOS)), from water via adsorption capacity measurements. The percentage removal of PFOA and PFOS, for a starting concentration between 2-4 mg/L of contaminant, was 92.67% and 95.8%, respectively. The regeneration studies performed upto 20 cycles, showed a slope of $-0.23 \pm 0.18\%$ per cycle which demonstrates that the nanoresin could be regenerated. The green synthesis of nanoresin, the ability to remove different classes of pervasive contaminants & the regeneration capacity corroborate an effective & sustainable solution to water purification & enhancement of water quality.

NM04.12.19

Microbial Platinum/Carbon Based Anode for Wastewater Treatment [Andres F. Gonzalez](#), Myreisa Morales-Cruz and Carlos R. Cabrera; University of Puerto Rico, Rio Piedras Campus, San Juan, Puerto Rico.

The recycling of human urine has become a main research area in wastewater treatment due to the increased demand of water. Urine is composed of 95% of water and 2% of urea and the rest are organic and inorganic salts. Urea is a toxic molecule that may cause renal failure and gastrointestinal bleeding. It is difficult to remove urea by common methods since it is a small uncharged molecule. In this work we develop a microbial carbon brush anode for the removal of urea. The bacterium uses urea and generates ammonia as a byproduct, subsequently oxidized by platinum at the carbon fiber surface. To improve the efficiency of the system we prepared carbon brush electrode as the anode material since it has been used to provide high surface areas for bacterial growth and high power densities in microbial fuel cells and modified with platinum for better catalytic properties. We synthesized platinum nanoparticles in our laboratory and attached it to the carbon fiber brush surface by impregnation. We tested unsupported and supported with Vulcan platinum nanoparticles synthesized in our laboratory and commercial platinum black and platinum nanoparticles in order to compare the catalytic activity for ammonia oxidation. The Pt-based catalysts were characterized by cyclic voltammetry and SEM to compare their capability and adhesion to the carbon fibers. We obtained better ammonium oxidation currents using the synthesized Pt nanoparticles than by using commercial platinum. Also we did a series of modification experiments with the bacteria in the anode surface to find the best modification conditions among temperature, voltage and time. These results were characterized by SEM imaging to observe the amount of carbon fiber surface covered by the bacteria. In our results the modifications of the carbon with bacteria were best when we didn't use any voltage at 37°C.

NM04.12.20

A Scalable Approach for Manufacturing Nanoporous Silicon Membranes for Unconventional Separations [Rahul Ramakrishnan](#), Brendan D. Smith and Jeffrey C. Grossman; Department of Materials Science and Engineering, Massachusetts Institute of Technology (MIT), Cambridge, Massachusetts, United States.

Thermal separations are extremely energy-intensive processes integral to many industries worldwide, and are responsible for 12% of all energy use in the United States. By switching from thermal to membrane separations, over 70 TWh could be conserved. Traditional polymer membranes, which are commonly used for filtration, possess high chemical sensitivity as well as an inability to withstand temperatures above 40 °C. Ceramics are a second class of membrane materials which offer chemical and thermal resilience. Their high cost, however, deters their popular use. Nanoporous silicon (NPSi) membranes have recently been shown to provide excellent performance and enhanced chemical and thermal stability, but have only been produced on the millimeter scale.

Here, we present a scalable method for the production of NPSi membranes via a modified metal-assisted chemical etching (MACE) process that allows for catalyst-dependent control over pore morphology. Through a simple three-step process involving selective chemical thinning of standard silicon, sputter-deposition of metal catalysts, and MACE of ultrahigh aspect ratio nanopores, a novel membrane is produced using common commercial materials and processes.

The core advancement of metal catalyst sputter-deposition allows for greatly improved avoidance of nanoscale catalyst aggregation and sintering on the surface prior to MACE, translating to well-dispersed individual nanopores which can exceed aspect ratios of 1000:1.

SEM and TEM images reveal pore diameters of less than 5 nm and surface porosities greater than 5%. In terms of membrane performance, we also demonstrate that the NPSi produced via our method is suitable for water filtration, achieving 92% rejection of 2 nm gold nanoparticles while exhibiting minimal permeability loss with respect to pure water as measured by UV-Vis spectroscopy and flow rates. These results suggest that NPSi membranes produced via this process can remove bacteria, viruses, emulsified oils, and even heavy metals from water in one step. We demonstrate that even after harsh chemical and thermal treatment via immersion in nitric acid (pH < 0) and high temperature environments (over 200 °C), NPSi membranes created via our method remain able to conduct filtrations with the same rejections and permeabilities. Our simple and innovative approach can also be modified for health care applications such as hemodialysis, as well as numerous other applications in the food and beverage and biopharmaceutical spaces, among others.

NM04.12.21

High Performance Capacitive Deionization via Manganese Oxide-Coated, Vertically Aligned Carbon Nanotubes [Wenbo Shi](#)¹, [Xuechen Zhou](#)¹, [Jinyang Li](#)², [Eric R. Meshot](#)³, [André Taylor](#)⁴, [Shu Hu](#)¹, [Jaehong Kim](#)¹, [Menachem Elimelech](#)¹ and [Desiree Plata](#)¹; ¹Department of Chemical and Environmental Engineering, Yale University, New Haven, Connecticut, United States; ²School of Materials Science and Engineering, Southwest Jiaotong University, Chengdu, China; ³Physical and Life Sciences Directorate, Lawrence Livermore National Laboratory, Livermore, California, United States; ⁴Department of Chemical and Biomolecular Engineering, New York University, Brooklyn, New York, United States.

The growing population and corresponding rise in clean water scarcity create appeal for transformative and sustainable desalination technology development and innovations. The capacitive deionization (CDI) desalination, where salt is removed by an electrochemical method, have emerged to tackle the limitations of poor energy efficiency, complex infrastructure, and high cost of other well-developed desalination technologies. Discovering electrode materials with exceptional capacitance, an indicator of the ability of a material to hold charge, is critical for CDI device development. Manganese oxides (MnO_x) have shown promise, but exhibit a trade-off where higher active MnO_x loading comes at a cost of lower conductivity. To address this challenge and achieve high salt adsorption, we designed and fabricated carbon nanotube (CNT)-MnO_x core-shell vertically aligned array electrodes using atomic layer deposition (ALD) to coat thin films of MnO_x onto vertically aligned CNTs (VACNTs). The hierarchical, anisotropic, 3D macroporous structure of VACNT-MnO_x and the unique tunable coating hallmark of ALD enabled the co-optimization of the hybrid material's specific capacitance in dimensions of mass and geometric area, with an exhibited optimized mass-specific and geometric area-specific capacitance at $215 \pm 7 \text{ F/g}$ and $1.1 \pm 0.1 \text{ F/cm}^2$, respectively. This co-optimized, outstanding capacitance not only positions them as candidate materials for traditional usage as energy storage devices, but

also exhibits promise with a remarkable salt adsorption capacity (29 ± 1 mg NaCl /g material; two-fold higher than pristine VACNTs) to enable water desalination *via* CDI.

NM04.12.22

Cellular Responses of Hyaluronic Acid-Coated Chitosan Nanoparticles Abdulaziz Almalik^{1, 2}, Ibrahim A. Alradwan¹, Majed Majrashi¹ and Ali H. Alhasan^{2, 1}; ¹National Center for Pharmaceutical Technologies, King Abdulaziz City for Science and Technology, Riyadh, Saudi Arabia; ²KACST-BWH/Harvard Center of Excellence for Biomedicine, King Abdulaziz City for Science and Technology, RIYADH, Saudi Arabia.

In recent years, nanotechnology has been proven to offer promising biomedical applications for in vivo diagnostics and drug delivery, stressing the importance of thoroughly investigating the biocompatibility of potentially translatable nanoparticles (NPs). Herein, we report the cellular responses of uncoated chitosan NPs (CS NPs) and hyaluronic acid-coated chitosan NPs (HA-CS NPs) when introduced into Chinese hamster ovary cells (CHO-K1) in a dose-dependent manner (2.5, 0.25, 0.025, 0.0025, and 0.00025 mg mL⁻¹) at two time points (24 and 48 h). MTS assay, cell proliferation, showed a decrease in the viability of cells when treated with high doses of CS NPs (0.25 and 2.5 mg mL⁻¹). When exposed to high doses of CS NPs, the lactate dehydrogenase (LDH) enzyme started to leak out of the cells and the cellular levels of mitochondrial potentials were significantly reduced accompanied by a high production of intracellular reactive oxygen species (ROS). Our study provides molecular evidence of the biocompatibility offered by HA-CS NPs, through ROS scavenging capabilities rescuing cells from the oxidative stress, showing no observed cellular stress and thereby revealing the promising effect of anionic hyaluronic acid to significantly reduce the cytotoxicity of CS NPs. Our findings are important to accelerate the translation and utilization of HA-CS NPs in drug delivery, demonstrating the pronounced effect of surface modifications on modulating the biological responses.

NM04.12.23

Formation of Metal Nanoparticles Directly from Bulk Sources Using Ultrasound and Application to E-Waste Upcycling John Watt¹, Mariah J. Austin², Simocko K. Chester³, Doug Pete¹, Jon Chavez¹, Lauren Ammerman¹ and Dale Huber¹; ¹Sandia National Laboratories, Albuquerque, New Mexico, United States; ²The University of Texas at Austin, Austin, Texas, United States; ³San Jose State University, San Jose, California, United States.

We present a method for creating nanoparticles directly from bulk metal sources using ultrasound, therefore bypassing high energy and potentially toxic intermediates and increasing atom efficiency. Nanoparticle formation occurs in water, in the presence of a bilayer forming surfactant system. Implosive collapse of cavitation bubbles occurs asymmetrically near the bulk metal surface, which generates powerful microjets leading to material ejection. This liberated material is captured by the surfactant bilayer and stabilized in the form of nanoparticles. The method is first characterized in detail using gold, but is also demonstrated on other metals and alloys, and is generally applicable. We show that nanoparticles can be produced from a number of different bulk metal form factors, as long as there is a sufficiently large planar surface to induce asymmetric bubble collapse. We then extend the method to an environmentally important problem, the reclamation of gold from an electronic waste stream.

This work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525. The views expressed in the article do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

NM04.12.24

Highly Efficient Oil/Water Separation by Superhydrophobic/Superoleophilic Sponges Based Oil Skimmer Ziai Liu, Xuyue Wang and Jinlong Song; Dalian University of Technology, Dalian, China.

Functional materials inspired from lotus leaves possess outstanding water repellency and oil affinity simultaneously, which refers to superhydrophobicity and superoleophilicity, respectively. By utilizing the contrary extreme wettability to water and oil, such bio-inspired functional materials can be used for oil/water separation. In recent years, oil/water separation has received extensive attention owing to the growing oil pollution problem caused by oil spills, domestic sewages and industrial effluents. Therefore, the fabrication of functional materials for oil/water separation has been a research hotspot. However, most of the methods to fabricate the extreme wettability materials involve the use of toxic chemical reagents and complex processes. Herein, a simple and efficient immersion method is presented to prepare superhydrophobic/superoleophilic sponges for sustained separation of oil/water mixtures. The sponge with super-wettability is fabricated by dipping common polyurethane sponge in cupric stearate solution. The introduced micro/nanostructures and long-chain alkyl group of cupric stearate enable the sponge to be superhydrophobic and superoleophilic in air. Water droplets can be supported as spheres with contact angles above 158° and can easily roll off from the surface, while oils can spread completely on the sponges. The prepared sponge can maintain its superhydrophobicity after being fixed under water for more than 4 hours, showing good durability and stability. By employing the as-prepared superhydrophobic/superoleophilic sponges, a large-scale oil skimmer is designed to collect oil spills with a wide range of kinematic viscosities (0.42~74.4 cSt at 40 °C). Results show that the floating oils can be successfully separated from the mixtures with separation efficiencies above 90% for different oils. Additionally, no water is observed in the separated oils, demonstrating high purity of the collected oils. This facile, environmental friendly and efficient method could offer a new perspective on practically solving pollution caused by oily industrial/domestic wastewater and oil spills.

NM04.12.25

Aldehyde Gas Detection Based on Cellulose Colorimetric Films Dongjin Han, Gyugeob Oh and Byung Yang Lee; Korea University, Seoul, Korea (the Republic of).

By detecting gases, we can take early measures in keeping the safety and freshness of our life. Here, we introduce a biomimetic colorimetric film that can be utilized for the detection of aldehyde gases from food deterioration, especially the rancidity of fat. The film is fabricated by cellulose and nanocellulose fibers on a reflectant metal surface such as Au or Ag. By simple dip and pulling method, cellulose-based films with diverse colors from dark blue to yellow are formed. The color range can be controlled by changing the layer thickness from 46 nm to 165 nm with the pulling speed (from 1 mm/min to 10 mm/min) and drying conditions (from 58 to 60% relative humidity) during the self-assembly of cellulose fibers. Afterwards, the films are functionalized with amine groups to make them sensitive to aldehyde gases. When the film is exposed to the target gas, this functionalization intensifies structural color change and makes it possible to detect aldehyde gas down to several ppm. We demonstrate that sensing data analysis with a phone camera and discriminant analysis algorithms can tell apart the different gases to which the sensor is exposed. We expect that our results will be utilized in providing a low-cost and low-power systems for the monitoring of environmental gases.

NM04.12.26

CdTe/CdS Core/Shell Quantum Dots Cocatalyzed by Sulfur Tolerant [Mo₃S₁₃]²⁻ Nanoclusters for Efficient Visible-Light-Driven Hydrogen Evolution Dongting Yue and Yixin Zhao; Shanghai Jiao Tong University, Shanghai, China.

CdTe quantum dots (QDs) have an extended absorbance region compared to that of CdSe or CdS QDs for solar utilization, however, their low activities, especially the chemical stability, limit their applications in photocatalytic hydrogen evolution. We report on enhanced visible-light-driven hydrogen evolution based on CdTe QDs via forming CdTe/CdS core/shell and using sulfur tolerant catalysts of the $[\text{Mo}_3\text{S}_{13}]^{2-}$ nanocluster. The aqueous synthesized CdTe/CdS QDs exhibit much better photocorrosion resistance than regular CdTe QDs for photocatalytic hydrogen generation. The sulfur compound covered CdTe/CdS QDs are facilely decorated with the low cost sulfur tolerant $[\text{Mo}_3\text{S}_{13}]^{2-}$ nanoclusters to exhibit enhanced visible-light photocatalytic H_2 generation than the CdTe QDs catalyzed with classical cocatalysts of Pt. In all, the combination of sulfur tolerant $[\text{Mo}_3\text{S}_{13}]^{2-}$ nanoclusters and CdTe/CdS core/shell structure significantly enhance the activity and stability of CdTe QDs for visible-light photocatalytic hydrogen evolution.

NM04.12.27

Detection of Environmental Imidacloprid Using a Molecularly Imprinted Polymer Sensor [Alyson G. Michael](#) and Joseph J. BelBruno; Dartmouth College, Hanover, New Hampshire, United States.

A sensor for the environmental detection of the neonicotinoid pesticide imidacloprid has been designed by leveraging the selectivity of molecular imprinting and the sensitivity of conductive polyaniline nanowires. Imidacloprid is a widely used pesticide that has been linked to declines in bee populations. Imidacloprid from solution hydrogen bonds with imprinted PMMA-co-PMAA, and de-dopes the surrounding polyaniline nanowires, thereby increasing the resistivity of the system. The success of the system is justified by LCMS, FTIR spectroscopy, and resistance measurements. The sensor permits straightforward monitoring of the presence of imidacloprid in the environment and the assessment of sustainable bee keeping practices.