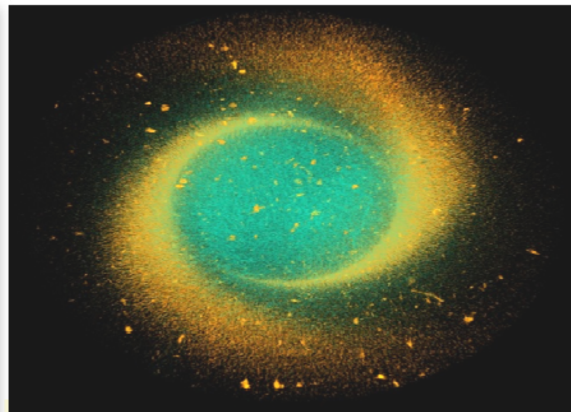
UCSD Jacobs | School of Engineering

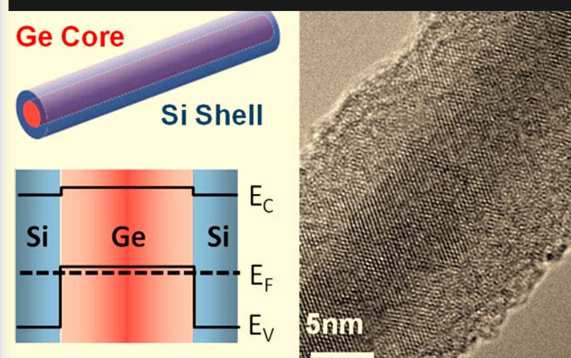
Fall 2013

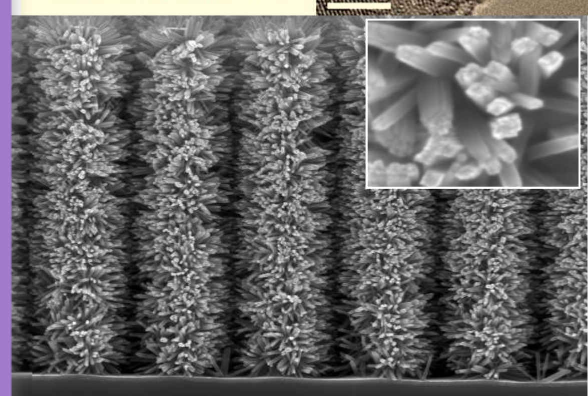
MATERIALS NEWS

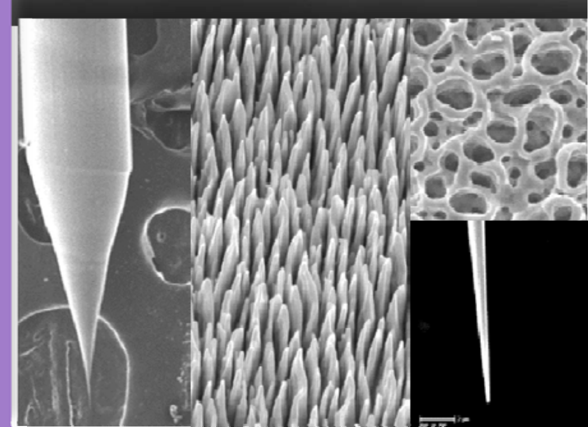
UCSD Materials Science & Engineering Newsletter



IN THIS ISSUE







CONTENTS

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LETTER FROM THE DIRECTOR

This is the YR 2013 newsletter describing UC San Diego's Materials Science & Engineering (MSE) Program, and I hope you enjoy reading about education and research activities in our program. The MSE Program at UC San Diego is a university-wide, highly interdisciplinary program with more than 85 participating UCSD faculty members. The professors and students in our program come from various divisions of UCSD, including the Jacobs School of Engineering (Departments of Electrical and Computer Engineering, Mechanical and Aerospace Engineering, Structural Engineering, Bioengineering, Nanoengineering), Division of Physical Sciences (Department of Physics, Department of Chemistry & Biochemistry), Division of Biological Sciences, the School of Medicine, and the School of Pharmacy.

Our MSE faculty members are mostly outstanding in their research and education career, with the faculty now including 8 National Academy of Engineering, 5 National Academy of Sciences, 3 Institute of Medicine members, and the prestigious National Medal of Science Awards in recent years to Prof. Shu Chien and Prof. Marye Anne Fox who are also our MSE members. Having such an excellent quality of faculty, combined with one of the highest per faculty research grants in the nation, provides a stimulating environment for our graduate students working toward their MS and PhD degrees.

The total number of our graduate students in Materials Science and Engineering is now ~150 with ~130 of them in PhD program. UCSD's Materials Science & Engineering (MSE) is ranked 14th among all Materials Science doctoral programs in the United States by the prestigious National Research Council (NRC) data-based assessment. I am always proud of our faculty and graduate students in the MSE program for their enthusiasm toward high quality education and research. With future newsletters, we will continue to share the latest information on academic, research, and career progress of our faculty, students, postdocs, and alumni from our MSE Program.

Sungho Jin
Director, UCSD Materials Science & Engineering Program
Distinguished Professor of Materials Science

Nanotree Structures For Efficient Hydrogen Fuel Production

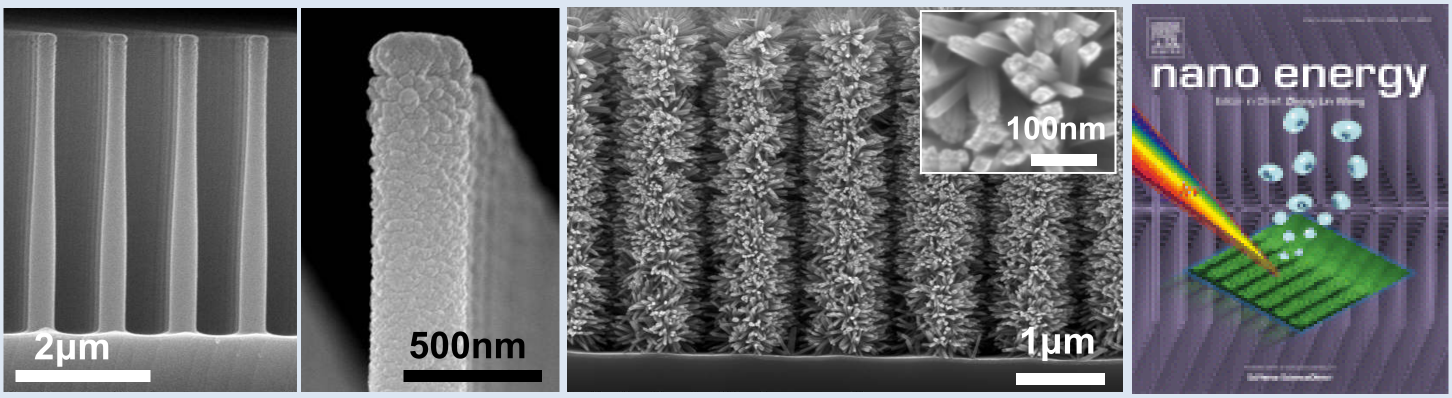


Fig. 1 **SEM images of Si, TiO2 coated Si, branched TiO2/Si nanowire arrays, and cover image of Nano Energy, the journal which includes this research article.**

Hydrogen fuel is considered a clean fuel because it doesn't generate carbon emissions. However, the conventional method of producing hydrogen gas relies on energy from fossil fuels to separate the atoms from other molecules like water. Wang group at UCSD has developed a forest of nanowire trees to cleanly harvest more solar energyto generate hydrogen fuel efficiently by a process called photoelectrochemical (PEC) water-splitting, without using fossil fuels. A successful fabrication of hierarchical three-dimensionally branched TiO2/Si nanowire arrays was reported in the journal, Nano Energy (Figure 1).

The branched TiO_2/Si nanowire arrays improved the PEC performance compared to TiO_2 thin film coated Si nanowire arrays because of the substantially increased surface area for electrochemical reactions and enhanced charge transfer kinetics. The working mechanism based on recombination at this heterogeneous n–n junction was proposed (Figure 2). This study provides insights on the fundamental understanding and potential optimizations of nanoscale hierarchical 3D structured devices for renewable energy applications.

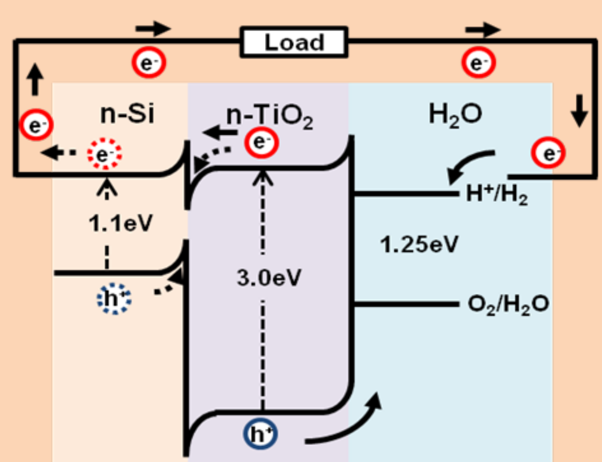


Fig. 2 **Schematic of band energies and charge transfer.**

The research team undertaking this effort includes Materials Science graduate student Sun Young Noh, and Professors Deli Wang and Sungho Jin.

Anti-biofouling, Low-Impedance Neural Electrodes

Neural electrodes are critical components for electrical stimulation as well as neural signal recording in human body. The human neural system essentially controls all body functions including the sensing/hearing of the outside stimulus to human body and needed body response with actuation or movement, as well as triggering of automatic impulse such as breathing. Disorders in the neural system often arise due to the damaged connections within the network of neurons. In order to mitigate these problems, it is desirable to develop advanced technologies to control/modulate human neural function. As the basis of neural function is to send and receive electrical signals, a reliable and sensitive interfacing via robust electrodes is essential.

The graduate students in Prof. Sungho Jin's lab have designed extremely sharp metallic, low-impedance electrodes from biocompatible alloy wires such as MP35N and Pt-Ir by introducing nanostructures with very high surface area. (Fig. 1 and Fig. 2) Anti-biofouling coating that can minimize tissue encapsulation problem while maintaining the low impedance has also been developed. The researchers involved include Jirapon Khamwannah, Calvin Gardener, Laura Connelly, Prof. Sungho Jin, in collaboration with Prof. Patrick Mercier's group (in Electrical and Computer Eng Dept).

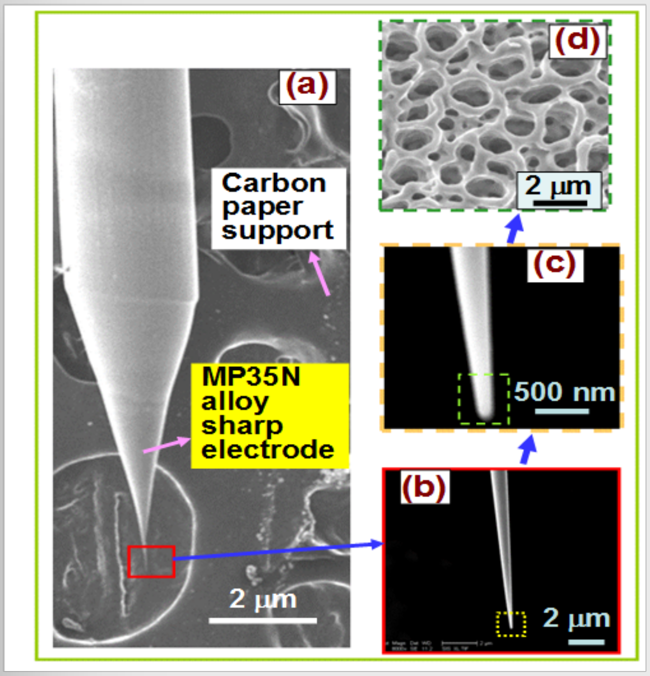


Fig. 1. Sharp-tip neural electrode (~100 nm tip radius) for cell penetration, having a large-surface-area nanostructure for reduced impedance and drug deliverable porous tip

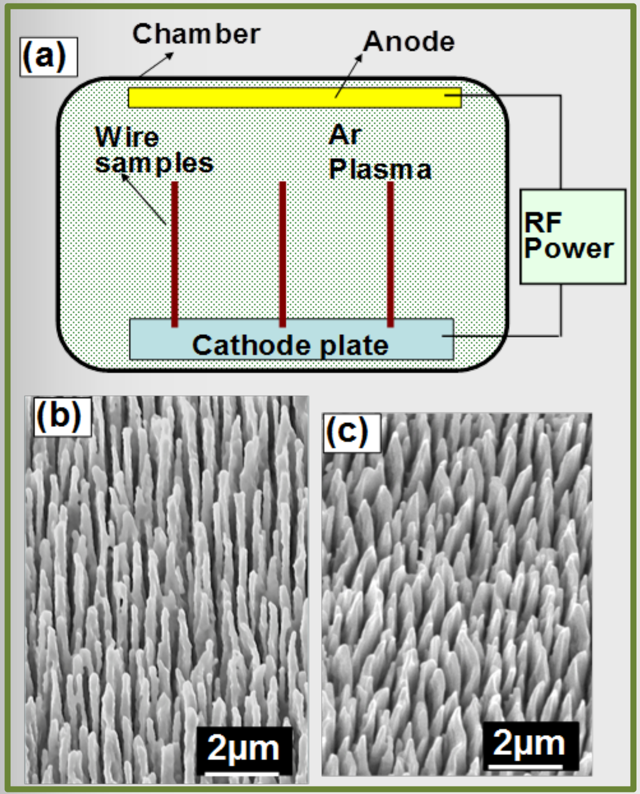


Fig. 2. (a) RF plasma processing to grow metallic nanowire array. (b) SEM micrographs of MP35N (Co-Ni-Cr-Mo alloy) coronary stent alloy electrode surface with high-aspect-ratio vertical nanowires, (c) Pt-10%Ir pacemaker alloy electrode with surface nanowires

Magnetic Freeze Casting for Novel Micro/Nano Biomimetic Structures

Natural materials, such as wood, bone, and seashells, exhibit exceptional mechanical properties due to a hierarchy of structural organization across multiple length scales. Magnetic freeze casting is a new materials processing method, developed by Michael Porter, a graduate researcher led by Profs. Joanna McKittrick and Marc Meyers, to fabricate bioinspired composites that mimic such properties. The technique expands on conventional freeze casting - a popular method in which a colloidal suspension, typically composed of ceramic particles and water, is directionally frozen, then sublimated to remove the frozen solvent, and sintered to partially densify and strengthen the porous constructs. During solidification, the particles are pushed between and trapped within growing ice crystals, leading to pore channels that are direct replicas of the frozen solvent. Although many freeze cast materials exhibit high strengths and toughness, these properties are generally limited to a single direction (parallel to the direction of ice growth).

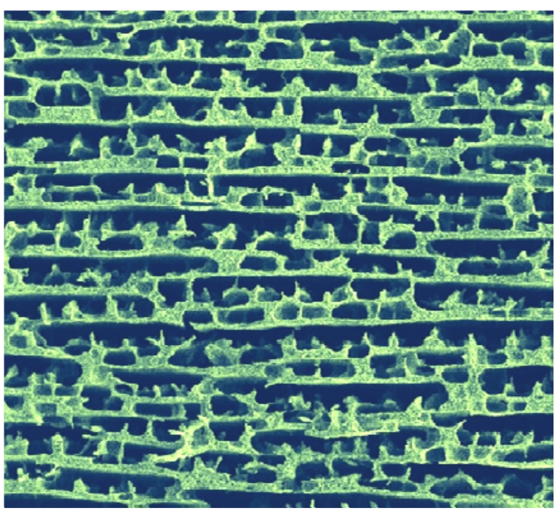


IMAGE 1. Scanning electron micrograph of a composite scaffold with aligned micro-channels, freeze cast with a static magnetic field propagating perpendicular to the solidification direction (out of the page). The micro-channels are ~10 μm wide.

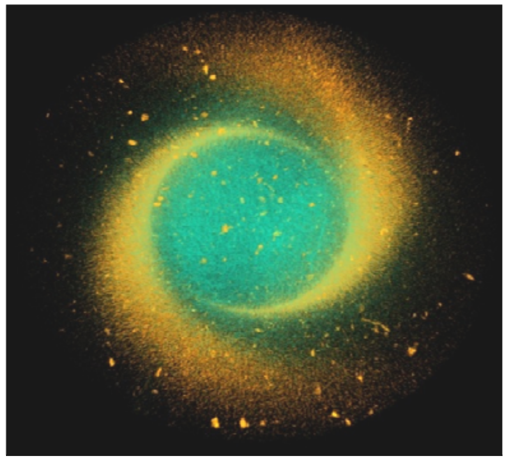
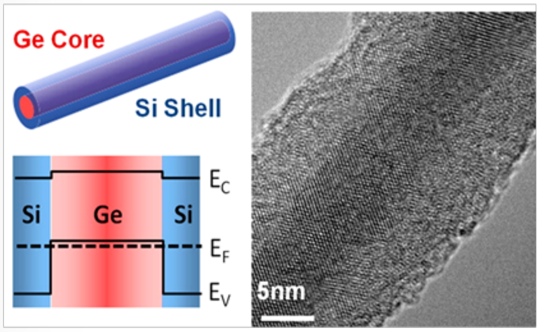


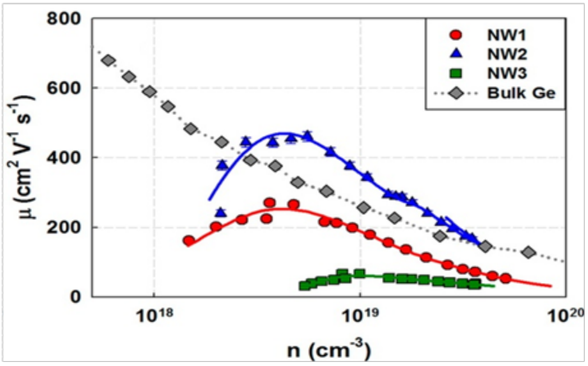
IMAGE 2. Micro-computed tomography image of a composite scaffold with spiral-reinforcement, freeze cast with a magnetic field rotating about the axis of the solidification direction (out of the page). The cylindrical scaffold is ~20 mm in diameter.

Magnetic freeze casting allows for the manipulation of magnetic nanoparticles during solidification. Researchers at UCSD have shown that materials freeze cast with magnetic fields propagating perpendicular to the solidification direction display a hierarchy of structural alignment in multiple directions (i.e., the ice growth and magnetic field directions). The images below illustrate two levels of architectural alignment: i) micro-channels aligned parallel to a static magnetic field; ii) spiral-reinforcements aligned to a rotating magnetic field. These tailored architectures have led to composite materials with enhanced compressive properties (image 1) and torsional rigidity (image 2). Michael Porter is currently developing an analytical theory to describe the process, which combines theories from solidification, magnetism, and colloid sciences. The potential of magnetic freeze casting is extensive and vastly unexplored - with a variety of promising applications, ranging from bone implants to lightweight armor.

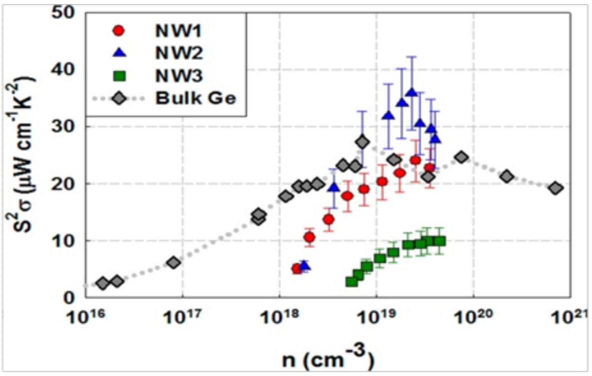
See related articles; Michael Porter, Joanna McKittrick, Marc Meyers, "Biomimetic materials by freeze casting." *JOM*. 65(6), 720 (2013). http://dx.doi.org/10.1007/s11837-013-0606-3 . Also see M. M. Porter et al, "Magnetic freeze casting inspired by nature." *Materials Science and Engineering: A*. 556, 741 (2012).

Core-Shell Heterostructured Ge-Si Nanowires for Enhanced Thermoelectric Properties





(up) Schematic of the band diagram in Ge–Si core–shell nanowires and representative high-resolution TEM image of the Ge–Si core–shell NWs. (right) mobility vs. hole concentration and thermoelectric power factor vs. hole concentration.



Thermoelectrics could be used to convert waste heat energy to electric energy if the efficiency can be improved. For best energy conversion efficiency, high electrical conductivity and thermopower are required, along with low thermal conductivity. However, this combination has been challenging due to the interdependency between the three parameters in bulk materials. Nanostructured materials have been considered as promising thermoelectric materials, and one of unique systems on this front is Ge-Si core-shell heterostructure nanowire.

A collaborative team led by Prof. Jie Xiang (ECE and MSE) and Prof. Renkun Chen (MAE and MSE) has been studying the unique thermoelectric behaviors in Ge-Si core shell nanowires. The band offset between Ge and Si leads to hole accumulation in undoped Ge cores. This doping mechanism avoids the degradation of carrier mobility due to ionized impurity scattering, as usually encountered in bulk thermoelectric materials. They experimentally studied thermoelectric power factor of this heterostructured nanowire system with Ge core wire diameter down to ~10 nm. Field effect devices were fabricated to conveniently modulate the hole concentration within a wide range of carrier concentration for a better understanding of the thermoelectric transport behavior. They found that the power factor is correlated with the carrier mobility, which is higher than that of bulk Ge in some of the core–shell nanowires because of the suppressed ionized impurity. This study shows that the core-shell heterostructure system is very promising for thermoelectric applications.

The investigators involved in the project include Prof. Renkun Chen of MAE department, Prof. Jie Xiang of ECE department, Graduate students Jaeyun Moon, Ji Hun Kim, and Zack Chen. The study was published in: “Gate-Modulated Thermoelectric Power Factor of Hole Gas in Ge–Si Core–Shell Nanowires” J. Moon, J. Kim, Z.C.Y.Chen, J. Xiang, and R. Chen Nano Letters, 13, 1196 (2013).

Novel Electrode Materials for Rechargeable Na-Ion Batteries with High Energy and Low Cost

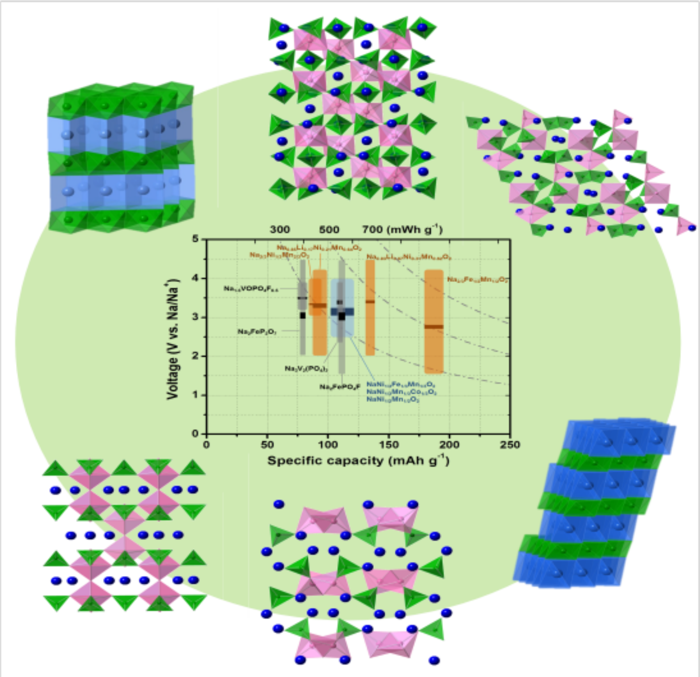


Figure 1. A summary of specific capacity, operating voltage range and energy density of the intercalation cathode materials for Na-ion batteries. (Center bar indicates average voltage).

The pressing needs for better energy storage technologies in large-scale applications that are economically feasible and environmentally benign are strong drivers for fundamental research in new materials discovery. Li-ion batteries offer the highest energy density among all secondary battery technologies, have dominated the portable electronics market and have been chosen to power the next generation of electric vehicles and plug-in electric vehicles. Nevertheless, the concerns regarding the size of the lithium reserves and the cost associated with Li-ion technology have driven the researchers to search more sustainable alternative energy storage solutions. In this light, Na-ion batteries have made a major comeback because of the natural abundance of sodium.

Materials Science & Engineering graduate student, Jing Xu and her teammates in Prof. Shirley Meng's group (NanoEngineering Dept) have performed a comprehensive research on the novel electrode materials for Na-ion battery by combining First Principles calculations and advanced characterization techniques. In the layered Na transition metal (TM) oxides, $Na_x[Li_yNi_zMn_{1-y-z}]O_2$ (0<x, y, z<1), the intercalation in the transition metal (TM) slabs and 2-D transportation of Na-ions occur concomitant with TM redox change during cycling. By identifying the interplay among structural evolution, electronic transition, and electrochemical reactions, the optimized composition is designed and significant improvement in battery performance is achieved. In addition to the cathode study, they also work on $Na_2Ti_3O_7$ as anode in Na-ion batteries, since it is able to provide 177 mAh/g specific capacity at an ultra-low voltage, 0.3 V. New phase is identified upon cycling. A Na-ion full cell with the two electrode materials has been successfully fabricated with high voltage and excellent reversibility, indicating a bright future for Na-ion batteries. A review paper written by this team is selected by editors as the featured article in Functional Materials Letters, and the figure is highlighted as the journal cover image (Figure 1). For more information on this NSF funded work, see the article, "Recent advances in sodium intercalation positive electrode materials for sodium ion batteries", by J. Xu, D. H. Lee, and Y. S. Meng, Functional Materials Letters 6, 1 (2013).

Combustion Synthesis of Boride Compounds

Prof. Graeve was recently awarded a patent on the hexaboride work her group has been working on for several years (O.A. Graeve, R. Kanakala, and G. Rojas-George, "Combustion synthesis method and boron-containing materials produced therefrom," US Patent number 8,557,208 issued on October 15, 2013). This patent is in reference to her activities exploring the scalable manufacturing and fundamental behavior of nanoscale boride materials for applications in several industrially relevant technologies, with special emphasis on energy generation and gas storage capabilities

Boride compounds, especially nanoscale materials, exhibit interesting electronic, mechanical, thermal and other physical properties. However, the synthesis of boride materials is not always easy. Researchers in Prof. Olivia Grave's group have explored the scalable manufacturing and fundamental behavior of nanoscale boride materials for applications in several industrially relevant technologies, with special emphasis on energy generation and gas storage capabilities. Her NSF-funded program led to patented results on two novel and complementary processing techniques for the continuous and scaled nanomanufacturing of boride materials (solution combustion synthesis for production of the boride powders and spark plasma sintering for consolidation of the powders). The research also involved fundamental studies that will eliminate critical roadblocks during scale-up. The morphologies of the newly synthesized boride powders obtained are illustrated in Fig. 1 , which show quite unique cube-related geometry. This is a particular effort of James T. Cahill, Materials Science PhD student, who has been working on this project since his arrival at UCSD in January, 2013

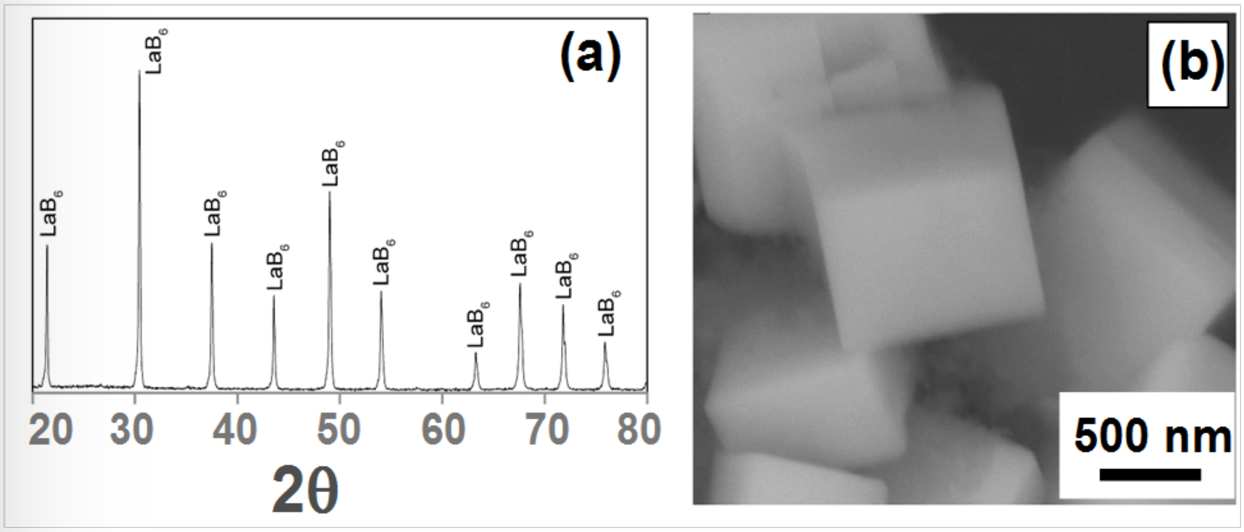


Fig. 1. (a) X-ray diffraction pattern and (b) scanning electron microscope image of the LaB_6 powders obtained in Prof. Graeve's laboratory.

Control and manipulation of conductive heat flux in multilayered thermal metamaterials: Applications in thermal lenses, cloaks, and concentrators

One of the biggest sources of energy loss is through the generation of heat. The control of heat flux through the rational design and arrangement of materials could then form the basis for the creation of elements aimed at channeling thermal energy. Devices based on such elements could find widespread use in applications incorporating portable electronics and microprocessors, heat recovery from exhaust gas, integrated micro-combustion systems, battery devices, heat sinking modules in electronic devices, enhanced efficiencies for solar thermal energy utilization, among others.

Krishna Vemuri, a graduate student and Professor Prab Bandaru have discovered that adapting fundamental concepts such as (a) the *thermal extremum principle* - where the propagation of heat takes the path of least thermal resistance, together with the use of (b) *coordinate transformation techniques* – for inducing anisotropy in the thermal conductivity, can lead to optimized materials/material configurations (*metamaterials*), which could then direct the heat propagation *in a different direction* than that in which the thermal gradient is applied. As naturally occurring materials are mostly considered to be isotropic, it is desirable to engineer and control the anisotropy through such arrangements – see Figure 1.

Preliminary work (sponsored by the National Science Foundation), through computational simulations as well as proof of concept experiments, has been used to validate the ideas. Vemuri and Bandaru have applied for a patent on the developed techniques and applications and some of the work has been published in *Applied Physics Letters.* Further research in progress, focuses on design and experimental verification of the behavior of new types of thermal elements *vis-à-vis* geometrical effects. Such experiments will yield profound understanding of thermal energy propagation and transmission.

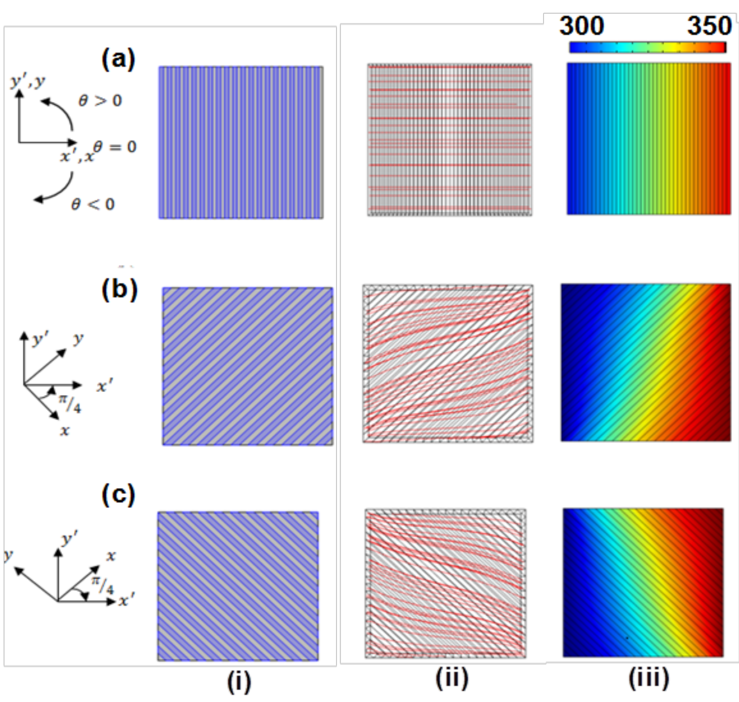


Figure 1 The controlled bending of the heat flux in a multilayered composite(constituted of two materials with isotropic values of thermal conductivity, such as copper and stainless steel) can be used to create thermal lenses, concentrators and cloaks.(a) The reference layer orientation, with $\theta = 0$, indicates linear propagation of the heat flux and corresponding temperature profile variation; (b) when the layers in the composite are rotated by $\theta = \pi/4$, a *downwards* bending of the heat flux is indicated, while when the composite is rotated by (c) $\theta = -\pi/4$, an *upwards* bending of the heat flux is shown.

Student Awards & Honors

Michael M. Porter A third year Materials Science graduate student in Prof. Joanna Mckittrick's group working on biomimetic materials received several honors and recognitions. National Science Foundation I-Corps Award, von Liebig Entrepreneurism Center Award at UCSD (August 2013), Gordon Engineering Leadership Center Award at UCSD (July 2013), Achievement Rewards for College Scientists (ARCS) Award Foundation (July 2013), and Best Student Paper Award, Society of Experimental Mechanics (March 2013). His work research on seahorse-inspired robotics featured in Popular Science, Scientific American, Reuters TV, ABC News, and Discovery News (April 2013).

Gary Johnston A third year graduate student working on orthopaedic implant biomaterials in Prof. Sungho Jin's group received NIH T32 Training Fellowship as a part of Predoctoral Training in Translational Musculoskeletal Research program.

Hasan Faraby A graduate student in Prof. Prab Bandaru's group has received the competitive Qualcomm Faculty Mentor Advisor (FMA) Fellowship for 2013-2014.

Laura Anderson A second year student Prof. Ken Vecchio's group, received the 2012-2013 ASM International (American Society of Materials) Abe Hurlich Award for being an exemplary student in materials science and engineering discipline. Laura's extensive research experience in metallic glasses, academic excellence and community involvement were highlighted. The award consists of a cash scholarship, one-year ASM membership, and a medallion.

Alexander Lieberman, a Materials Science student in Prof. Andrew Kummel's lab received NIH F31 Fellowship award to work on *in vivo* study of silica nanoshells.

MSE New Faculty

Jian Luo (Department of NanoEngineering)
Professor Luo's group is focusing on studies of Interfacial thermodynamics, Surfaces, Grain Boundaries, and Hetero-phase interfaces, Nanoscale interfacial (surficial or intergranular) films, Materials characterization (TEM, HRTEM., XRD etc.), Nanostructured thin films: Spin and dip coating; Nanoclay-based multilayers, Optical materials and fibers, Continuum-level material and optical simulations.

Olivia Graeve (Dept of Mechanical & Aerospace Engineering)
Professor Olivia A. Graeve has gained international recognition in the area of Nanomaterials Manufacturing. Her research expertise connects fundamental principles of materials processing with specific engineering needs, with special emphasis on electromagnetic multifunctional materials for sensors and energy applications

Patrick Mercier (Dept of Electrical and Computer Engineering)
Prof. Mercier's group conducts research on Energy-efficient Microsystems, circuit and system design, Neural recording, Biomedical applications, and Energy harvesting architectures.

Shengqiang Cai (Dept of Mechanical & Aerospace Engineering)
Professor Cai's research focuses on the field of Mechanics of artificial and biological soft materials, Energy harvesting and storage, Micro-fabrication techniques of polymeric structures and soft/stiff hybrid structures, Deformable acoustic and electromagnetic metamaterials.

New Graduate Students 2013

Welcome 42 New Graduate Students who joined our Materials Science & Engineering Program this academic year.

Alvarado, Judith

Cahill, James Timothy

Cai, Wei

Choi, Seongcheol

Estrada, Daniel

Fang, Cheng-Yi

Fang, Yuankan

Grosshandler, Debbie

Hollett, Geoffrey

Hsiao, Yi-Hsuan

Huang, An

Huang, Chih-Cheng

Huang, Wei

Huang, Yuran

Jiang, Yunfeng

Jung, Jae-Young

Kavrik, Mahmut

Kim, Gunwoo

Kim, Tae-Woo

Kwak, Iijo

Li, Yingmin

Li, Zezhou

Lin, Yuh-Chieh

Liu, Hang

Mei, Jiyang

Naleway, Steven

Oh, Kiwon

Qin, Mingde

Quan, Haocheng

Shafer, Devyn

Shih, Wei Yuan

Shin, Sumin

Tanaka, Atsunori

Wang, Joanna

Xie, Sibai

Yang, Ao

Yao, Shi jie

Yavuz, Serdar

Zhanaidarova, Almagul

zhang, Boyao

Zhao, Shiteng

We would love to hear the achievements and milestones from the UC San Diego Materials family that comprises students, alumni, faculty, visiting scientists and staff for inclusion in our next newsletter.

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