

MATERIAL NEWS



University of California San Diego Materials Science & Engineering

Graphene
(FLG)

FLG
layers

Zigzag
Armchair



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Cover Figure courtesy of

Nanoletters, 15, 3067,

(2015)

Letter From the Director



Greetings! What you will find in this newsletter is a glimpse of the happenings in the Materials Science Program at UC, San Diego. Encompassing departments in Engineering (Mechanical and Aerospace, Electrical, Structural, Nanoengineering, and Bioengineering), the Sciences (Physics, Chemistry and Biology), and the School of Medicine, our program is dynamic proof that "Materials are everywhere". More than ninety faculty are associated with the program, which is on a continual upward trajectory of growth and development.

You will find here samples of the work in the program, *e.g.*, the development of structural materials for habitats on Mars, detailed studies on electrically induced light emission, biocompatible silicon nanoparticles for tissue imaging, transparent ceramics for laser gain media, the influence of contacts on compound semiconductors for sub 10 nm transistor technologies, advancing the *More than Moore* paradigm.

We are also very proud of the accomplishments of our students and alumni. We are glad to welcome more than 40 new graduate students with far reaching diversity and scientific and technological range. A seminal award named after a pioneering ex-colleague, the late Prof. Gareth Thomas (who worked at both UC, Berkeley and UC, San Diego), was given to Steve Naleway who discusses his research in biomaterials. Both Dr. Po-Yu Chen, now a Professor in National Tsing Hua University and Dr. Michael Porter, now a Professor in Clemson University, discuss their time spent in the program. We also advertise the CaliBaja Center for Resilient Materials & Systems, part of the Agile Research Centers, recently launched at the Jacobs School of Engineering.

We hope you enjoy reading the newsletter and welcome your feedback, support and good wishes.

Sincerely yours,

A handwritten signature in blue ink that reads "Prab R. Bandaru". The signature is written in a cursive, flowing style.

Prab R. Bandaru

Martian “Bricks”

RESEARCH

Under the supervision of Professor Yu Qiao, Graduate Student Researchers Brian J. Chow and Tzehan “Derek” Chen recently developed martian “bricks”, by using simulants of appropriate martian soils. The martian “bricks” are strong and durable, and contain no terrestrial components. The processing is fast and energy-efficient.



A Mars-1a “brick”; Upper-left corner shows the raw Mars-1a grains. Upper-right corner shows a TEM image.

Manned martian exploration missions are rapidly moving forward. While the first-generation habitats will be produced and transported from the Earth, it is desirable that the maintenance and expansion of martian bases/outposts rely on locally harvestable resources. Martian-soil-based structural materials can be utilized to construct launch landing platforms, foundations, structural parts, etc.

Martian soil simulants may be classified into either basaltics and clays, for primordial and secondary martian soils, respectively. In Professor Qiao’s research, the basaltic simulant was chosen as JSC Mars-1a, based upon its physical characterization and geological background.

The clay simulant was chosen to be montmorillonite, a common clay mineral that has been reported on the surface of the Mars.

The martian soil simulants were vacuum-dried at 600 °C to remove organic contaminants and excess moisture, and immediately compacted, to form strong bonding among the simulant grains, as shown in the attached figure. The compaction can be either quasi-static or dynamic. Three-point bending tests were performed to measure the flexural strength, which was comparable with that of steel reinforced concrete. TEM microscopy reveals that bonding among the Mars-1a grains is achieved through the iron oxides phase.

Professor Qiao’s findings contribute to the promise of allowing economical and self-sustainable production of martian infrastructural materials without periodic supplies from the Earth. The formation of martian “bricks” may be carried out either manually by an astronaut or by a simple machine powered by solar panels.



Professor Qiao’s group focuses on the researches of high-performance structural materials, energy-related materials and systems, smart materials and structures, and failure analysis of engineering materials and structures. Recently, he is also interested in robust and multifunctional battery systems, green building materials, and in-situ utilization of martian and lunar regolith.

(More information: <http://mmrl.ucsd.edu/>)



Hydroxyapatite as a fluorescence probe for medical technologies

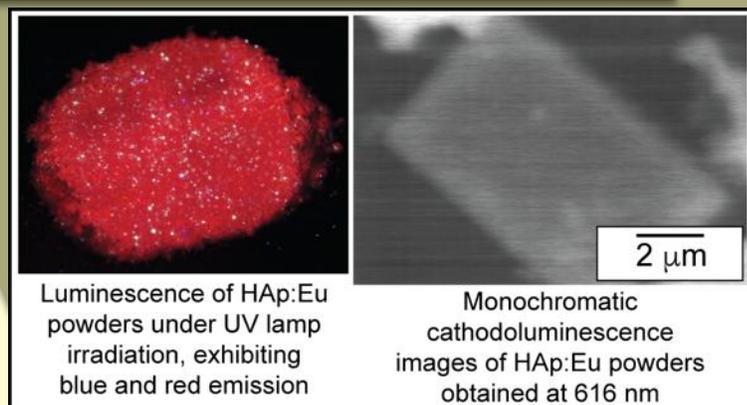
Recently, we completed a cathodoluminescence study of the spatial distribution of Eu^{2+} and Eu^{3+} dopants in hydroxyapatite powders, for investigation of its use in fluorescent probing.

L.A. Zavala-Sanchez, G.A. Hirata, E. Novitskaya, K. Karandikar, M. Herrera, and O.A. Graeve, "Distribution of Eu^{2+} and Eu^{3+} Ions in Hydroxyapatite: A Cathodoluminescence and Raman Study," *ACS Biomaterials Science & Engineering*, 1 [12] 1306-1313 (2015).

Hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, HAp) is well known for potential applications as a drug and gene delivery agent, chromatographic adsorbent, gas sensor, and catalyst. Doped with rare-earth ions, it can also be used to acquire contrast-enhanced images from magnetic resonance, X-ray, and near-infrared reflection imaging, as a fluorescent probe in medical technologies.

The results from Prof. Graeve's group demonstrate that the distribution of europium ions in the hydroxyapatite lattice depends on their valence state. Cathodoluminescence from prismatic powders show that while the Eu^{2+} is distributed homogeneously in the entire powder volume, the Eu^{3+} is present mainly at the powder edges. The luminescence spectrum of the Eu^{2+} ions display a wide and strong blue emission centered at 420 nm, while the luminescence spectrum of the Eu^{3+} ions display several orange-red emissions covering the range from 575 to 725 nm.

The powders were synthesized by the combustion synthesis method, varying the pH of the precursor solutions to modify the concentration ratio of Eu^{2+} with respect to Eu^{3+} . X-ray photoelectron spectroscopy was used to determine the ratio $\text{Eu}^{2+}/\text{Eu}^{3+}$. Thermal treatments, at 873 K in oxygen, resulted in a strong quenching of the Eu^{2+} luminescence due to oxidation of the Eu^{2+} ions into Eu^{3+} , as well as probable elimination of calcium vacancy defects by annealing.



Luminescence of HAp:Eu powders under UV lamp irradiation, exhibiting blue and red emission

Monochromatic cathodoluminescence images of HAp:Eu powders obtained at 616 nm



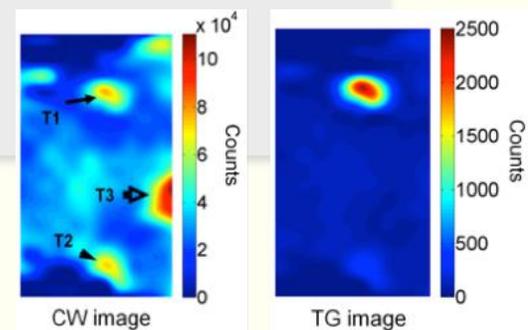
Prof. Graeve's research focuses on fundamental studies of the synthesis and processing of nanostructured materials, including ceramic and metallic nanomaterials and amorphous/nanocrystalline composites for both structural and functional applications, with a special emphasis on electromagnetic multifunctional materials for sensors and energy applications. A particular highlight in her laboratory has been on creating efficient manufacturing technologies that allow the team to obtain new materials and new mixtures of materials in a few minutes or a few hours at most. (More information: <http://graeve.ucsd.edu>)

Fluorescence imaging is one of the most versatile visualization methods in biomedical research, has provided new windows into the function of cells at the molecular level, and may be used as a powerful tool to identify and track diseased tissues such as cancer. A major challenge for the imaging of biological samples is tissue autofluorescence--molecules natively present in cells and tissues that glow under the same conditions being used to detect the tracers. Such background autofluorescence can be so bright in tissues such as the skin, the brain, and the liver that it is typically the limiting factor in obtaining useful information from fluorescence images--in particular when the tracer probe is present at the very low concentrations typically required for translation to human diagnostics.

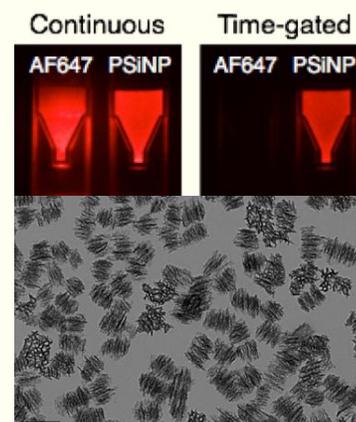
Professor Michael J. Sailor's group has developed a new type of nanoparticle for bioimaging based on silicon quantum dots. Silicon nanoparticles possess a very long-lived excited state, allowing their fluorescence signal to persist 1000 times longer than signals originating from most naturally occurring fluorescent molecules in tissues. By gating their imaging system such that the light used to excite fluorescence is switched off a few hundred nanoseconds before acquiring the image, the signals from tissue autofluorescence can be suppressed, revealing the strong fluorescence from even a very small quantity of silicon nanoparticles.

The biocompatibility and biodegradable characteristics of Sailor's porous silicon nanoparticles overcome the safety issues of cytotoxic or non-biodegradable fluorescent probes commonly employed for *in vivo* imaging, and they have shown that the silicon nanoparticles can be induced to carry therapeutic payloads such as anti-cancer agents or molecules for gene therapy.

For more information, see: "In vivo time-gated fluorescence imaging with biodegradable luminescent porous silicon nanoparticles", L. Gu et al., **Nature Communications**, 4 (2013) 2326, and "Gated Luminescence Imaging of Silicon Nanoparticles", J. Joo et al., **ACS Nano**, 9 (2015) 6233.



Conventional fluorescence image (Left) and the image using Gated Luminescence Imaging of Silicon Nanoparticles (GLISiN)(Right) of a same region in the mouse injected subcutaneously with silicon nanoparticles (T1) and a conventional organic imaging dye (T2). The bright fluorescence of the liver (T3) is typical of fluorescence imaging. Color bar at the left indicates increasing fluorescence intensity.



Cuvettes containing a conventional fluorescent organic dye ("AF647", at left) and porous silicon nanoparticles ("PSiNP", at right). When viewed under continuous UV light, both cuvettes glow with the characteristic red color of the probe. After turning off the UV excitation, light from the silicon probe persists for more than 50 microseconds. Lower image shows a transmission electron microscope image of the porous silicon nanoparticles. Scale bar is 100 nm.



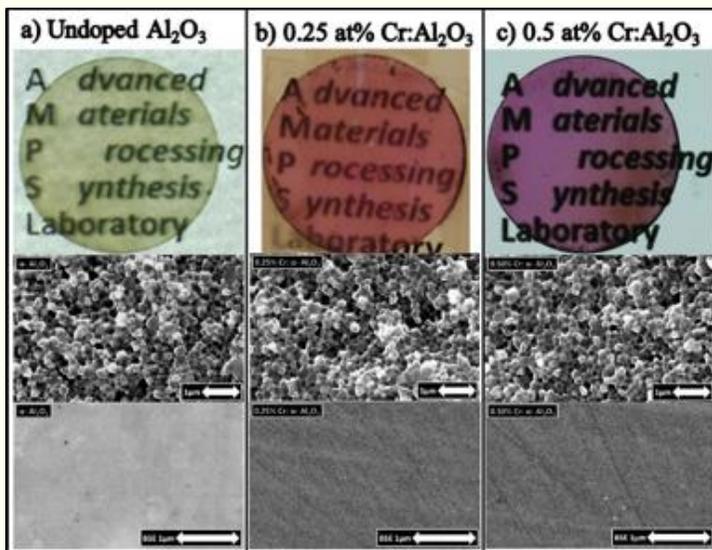
Prof. Sailor's group synthesizes nanomaterials and studies their fundamental chemistry, photochemistry, electrochemistry, optical, and biomaterials properties. Their emphasis is on porous silicon and iron oxide nanostructures. Research topics include drug delivery materials, *in vivo* imaging with luminescent or magnetic nanoparticles, batteries, and chemical or biochemical sensors. (More information: <http://sailorgroup.ucsd.edu/index.html>)



Birefringent polycrystalline ceramics

E. H. Penilla, C. L. Hardin, Y. Kodera, S. A. Basun, D. R. Evans and J. E. Garay.

Journal of Applied Physics 119, 023106 (2016)



Pictures and SEM micrographs a) Undoped Al_2O_3 b) 0.25 at% $\text{Cr}:\text{Al}_2\text{O}_3$ c) 0.5 at% $\text{Cr}:\text{Al}_2\text{O}_3$

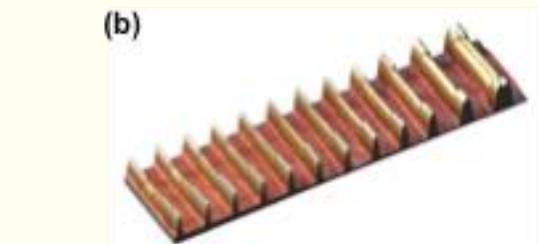
Light scattering due to birefringence has prevented the widespread use of polycrystalline ceramics with anisotropic optical properties in applications such as laser gain media. However, continued development of processing technology has allowed for very low porosity and fine grains, significantly improving transparency. Prof. Garay's group has now developed a method (see E. H. Penilla, C. L. Hardin, Y. Kodera, S. A. Basun, D. R. Evans and J. E. Garay. *Journal of Applied Physics*, 119, 023106, 2016.) for producing highly transparent Cr^{3+} doped Al_2O_3 (ruby) using current activated pressure assisted densification (CAPAD). The one-step doping/densification

process produces fine grained ceramics with well integrated (doped) Cr, resulting in good absorption and emission. The SE and BSE micrographs do not show sign of phase separation, confirming incorporation of Cr atoms into the Al_2O_3 lattice.

In order to explain the light transmission properties, an analytical model based on the Rayleigh-Gans-Debye (RGD) approximation that has been previously used for undoped alumina was extended to include absorption. In addition the measured emission spectra and emission lifetime were found to be similar to single crystals, confirming the high optical quality of the materials.



Professor Garay is the principal investigator of a vibrant experimental laboratory called the Advanced Material Processing and Synthesis (AMPS) Lab. Research in the AMPS Lab focuses on advanced material processing and synthesis with particular emphasis on designing the micro/nanostructure of bulk materials for property optimization. AMPS Lab also has in-house capabilities in property measurements and device design allowing seamless interplay between the design of materials and evaluation of material performance in devices. (More information: <http://jacobsschool.ucsd.edu/faculty/>)



Size dependent kinetics for nickelide contact formation.

Ultra-scaled III-V compound semiconductor devices including InGaAs FinFETs promise alternative high performance low power alternatives for sub-10nm technology nodes. At such length scales, the crystal orientation, size, structural phase, and interfacial properties between metal contacts and InGaAs nanochannels play dominant roles in device performance. The majority of prior efforts on InGaAs channels were conducted on planar structures on InP substrates, which precluded revealing size and orientation effects that will emerge in nanoscale channels.

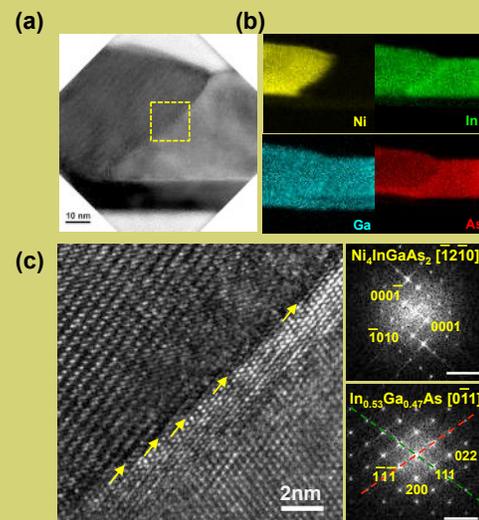
Prof. Shadi Dayeh who directs the Integrated Electronics and Biointerfaces Laboratory (IEBL) and his student Renjie Chen reported in the journal: *NanoLetters* (Original article: DOI: [10.1021/acs.nanolett.5b00327](https://doi.org/10.1021/acs.nanolett.5b00327))

the first study on the influence of size and orientation on reaction kinetics and thermodynamics in Ni-InGaAs *fin structures*, and the detailed investigation of their structural and interfacial characteristics and their implications on device performance.

Building on a novel all-solid-state wafer bonding approach developed at IEBL for the fabrication of the first InGaAs FinFETs on Si, the team prepared *Fin* channels with various widths (30 ~ 500 nm) by e-beam lithography and dry etching which were then subjected to rapid thermal annealing to react Ni with InGaAs Fins.

The team demonstrated unequivocally a size-dependent Ni surface diffusion dominant kinetic process, which gradually departed to volume diffusion as the Fin width increased. Under same reaction time, nickelide segment was longer for smaller Fin channels, and the nickelide length showed a square-root of time dependent elongation, indicative of Ni surface diffusion.

The team also identified the interfacial structure to be $\text{Ni}_4\text{InGaAs}_2$ (0001) || $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ (111) contact interface (Fig. a-c). The resulting in-plane compressive stress lifts the degeneracy of the heavy-hole and light-hole bands, and increases the InGaAs bandgap from 0.75eV to 1.26eV. Such observations are aimed to inspire new processes for engineering contacts that can maximize device performance.



Interfacial structures and strain-induced energy band-edge of InGaAs.



Prof. Dayeh is the director of the Integrated Electronics and Biointerfaces Laboratory (IEBL). IEBL strives to develop an understanding of and control over electronic materials from atomic scale all the way to functional systems by applying fundamental scientific principles to solve pressing engineering problems. Applications include low and high power electronics, neuronal interfaces, solar powered wearable devices, and a wide range of integrated sensors. (More Information: <http://iebl.ucsd.edu/>)

MATSE Alumni INTERVIEWS

Dr. Michael Martin Porter
Assistant Professor, Mechanical Engineering Department
Clemson University



How is your new faculty job? How is it being a professor?

The job is great, although it requires a much different skill set than being a graduate student; needs more of a managerial approach to developing new project ideas and advising new students. My lab. (naturalengineering.org), has five graduate students and four undergraduate students.

How useful was your training in the MATSE program at UCSD?

The program prepared me very well for the interdisciplinary nature of my current research, focused on biomimetics and bioinspired design. The flexibility in coursework and research allowed me to focus on topics that I found interesting and innovative. I also benefited from the Gordon Engineering Leadership Center and the von Liebig Entrepreneurism Center.

Additionally, the access to equipment, faculty, and special facilities that were associated with the program helped. I am especially thankful to my advisors (J. McKittrick and M. Meyers)

What are your suggestions and advice for current MATSE students?

Pay attention to details, be confident, and always make time for your friends and family. Also, don't forget to show appreciation for your advisors and collaborators; without them, it would be very difficult to be successful.

NEW STUDENTS IN 2015

Ahles, Christopher

Cai, Xiaosheng

Chan, Esther

Chen, Hsuan-Yu

Chen, Hsueh-Szu

Chen, Li

Chen, Peng

Chen, Wenjun

Cheung, Carson

Choi, Jong Youn

De Souza, Camila Rita

Dubnov, Tamoz

Fan, Gaochen

Fang, Chengcheng

Fowler-Gerace, Lewis

Gild, Joshua Joseph

Gong, Zhiyu

Gu, Yue

Helstowski, Darren Geoffrey

Hornig, Chris

Hossain, Lorraine Amena

Hu, Hongjie

Hu, Yu-ching

Hu, Ziyang

Huang, Yang

Jiang, Sicong

Jung, Hankyeol

Karshalev, Emil

Kou, Rui



Dr. Po-Yu Chen
Associate Professor, Department of Materials Science
and Engineering
Institute of Biomedical Engineering
National Tsing Hua University

MATSE Alumni INTERVIEWS

How is your new faculty job? How is it being a professor?

I have established the Biological and Bio-inspired Materials Laboratory and supervised 10 graduate students, and work in bio-inspired composites and multi-functional surfaces. Life is quite different and challenging as a professor compared to a graduate student or postdoc. I spend a lot of time and effort on teaching, supervising students, writing proposals/papers, attending meetings, administrative duties, traveling, and discussing with collaborators/sponsors.

How useful was your training in the MATSE program at UCSD?

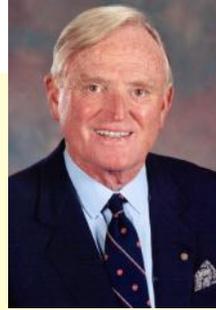
I appreciate the design of comprehensive exam, literature exam, senate exam, and thesis defense in the program. The periodic testing helped strengthen my MATSE related expertise. I think the multi-disciplinary nature of the program really helped my career development.

What are your suggestions and advice for current MATSE students?

As a graduate student, I initiated much collaboration with researchers in different departments, universities and countries. Be enthusiastic, self-motivated, committed to your research. TA is a good opportunity to practice your teaching and communication skills. Be actively involved in professional societies, such as TMS, MRS, etc. Finally, enjoy the nice weather in San Diego. It's quite important to have hobbies!

Lee, Chen-hsun,	Perezjara, Uriel Esaud Ridley,	Yang, Yangyuchen
Lee, Min-han	Robyn Elizabeth	Ybarra, Juan Carlos
Lee, Minjae	Tseng, Chi Yang	Zeng, Yuan
Lee, Seunghyo	Vargas Consuelos, Carlos	Zeng, Yuze
Li, Xiaochen	Ingram	Zhang, Yuchen
Maris, Pavithran	Wang, Jiaying	Zhao, Yizhi
Martinez Pallares, Fabian	Wang, Kaiping	Zheng, Yue
Martin	Wang, Yongjie	Zhong, Ying
Matsushita, Albert Keisuke	Wen, Mingrui	Zhou, Benjamin Hsiaowei
Min, Xin	Wynn, Thomas Andrew	Zhou, Jiayun
Ouyang, Jingyi	Yang, Vincent Bin-chyuen	Zhu, Chaoyi

Gareth Thomas Award



This award is to honor the memory of the late Prof. Gareth Thomas, a pioneer in the use of electron microscopy in Materials Science.

Steven E. Naleway

Winner of Gareth Thomas Award

Please briefly describe your research interests.

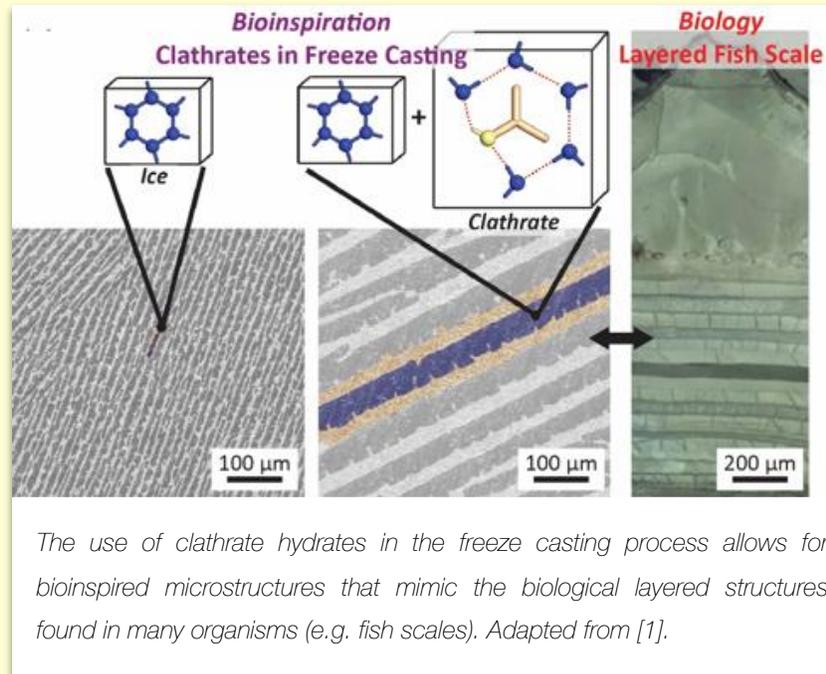
My research focuses upon the interconnected fields of biological materials science and bioinspired design, at the interface between nature and physical science. In the former, I investigated fascinating aspects such as the armored carapace of the boxfish, the impact resistant skull of the woodpecker and the self-sharpening teeth of the sea urchin. Also relevant to engineering is, two phase ductile-brittle composites (e.g. collagen-hydroxyapatite in bone and fish scales, aragonite-chitin in abalone shell), exhibiting a layered hierarchical structure, with numerous interfaces that increase both strength and toughness. I have also developed new biomedical materials through a novel fabrication process, named freeze casting (See Figure), which may be used for control of the geometry and superior mechanical properties.

What have been your experiences in the MATSE program? How has your training in the MATSE program at UC, San Diego helped your growth?

The MATSE program has been incredibly beneficial for my development as a student, researcher and mentor. My co-advisors, Profs. Joanna McKittrick and Marc Meyers, provided me with excellent guidance to do world class research while still allowing me the independence to formulate and undertake my own research ideas and plans. I have also been able to mentor a number of excellent undergraduates. Additionally, the ARCS Scholars program, the Gordon Scholars Engineering Leadership program and the Grad Slam TED Talk competition, have made it possible for me to explore different aspects of research and academia and broaden my view.

Where do you see yourself in the future?

In the future I hope to continue my research into biological materials and bioinspiration as a professor. This would allow me to not only continue doing the research that I enjoy, but also pass along this information through teaching and mentoring.



The use of clathrate hydrates in the freeze casting process allows for bioinspired microstructures that mimic the biological layered structures found in many organisms (e.g. fish scales). Adapted from [1].

[1] Naleway SE, Yu CF, Porter MM, Sengupta A, Iovine PM, Meyers MA, McKittrick J. "Bioinspired composites from freeze casting with clathrate hydrates" *Materials & Design* (2015) **71**, 62-67.



Raymond A. de Callafon

Mechanical and Aerospace Engineering

Simulate, monitor, predict and control a variety of dynamical and electromechanical systems.



David Fenning

Nanoengineering

Develop approaches for controlling impurities and defects for high efficiency photovoltaics and photo/(electro)-catalysis.



James Friend

Mechanical and Aerospace Engineering

Interaction of electromechanical fields at the micro and nano scale for medical technologies.



Javier Garay

Mechanical and Aerospace Engineering

Design and synthesis of advanced materials for optical and magnetic devices and thermal energy storage.



Jesse V. Jokerst

Nanoengineering

Molecular imaging with emphasis on nanoparticle contrast agents and ultrasound imaging.



Jan Kleissl

Mechanical and Aerospace Engineering

Co-Director of the Center for Renewable Resource and Integration, specializing in solar energy meteorology.



Sergei Krasheninnikov

Mechanical and Aerospace Engineering

Plasma turbulence and transport and plasma-material interactions



Vitaliy Lomakin

Electrical and Computer Engineering

Development of numerical electromagnetics with applications to electronic and photonic structures.



Vlado A. Lubarda

Mechanical and Aerospace Engineering

Mechanics of materials, addressing damage mechanics, nano and biomechanics.



Jeffrey Rinehart

Chemistry and Biochemistry

Synthetic and physical techniques of colloidal nanochemistry of high-coercivity magnetic materials.



Gabriel A. Silva

Bioengineering

Pathophysiology of the neural retina and technology to treat degenerative retinal disorders.



Michael Tolley

Mechanical and Aerospace Engineering

Design and fabrication of bioinspired and soft robotic systems.



Sheng Xu

Nanoengineering

Functional soft inorganic materials as building blocks for soft electronics and energy storage.



Kesong Yang

Nanoengineering

Properties of materials using first-principles electronic structure calculations.

Non-oxide ceramic nanomaterial
for aerospace applications

We revolutionize the design, testing and manufacturing of materials and systems for extreme environments

Ultra-high temperatures

Radiation

Extreme deformations

Ultra-low temperatures

Extreme pressures

Acidic conditions

Center Thrust Areas

Materials and devices for extreme environments

We develop and manufacture new materials and devices principally for the aerospace, nuclear and biomedical industries, including advanced materials for jet engines, next-generation nuclear reactors and biomedical devices.

Global scientists and engineers

We produce global scientists and engineers who can connect and communicate across borders. These professionals not only develop new technologies, but are also socially engaged and have the necessary cultural understanding to promote economic growth in the CaliBaja region.

Environmental technologies and systems

We develop new technologies that can provide information, statistics and trends on the environment and climate of CaliBaja.

resilientmaterials.ucsd.edu

100 nm



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Professor, UC San Diego

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