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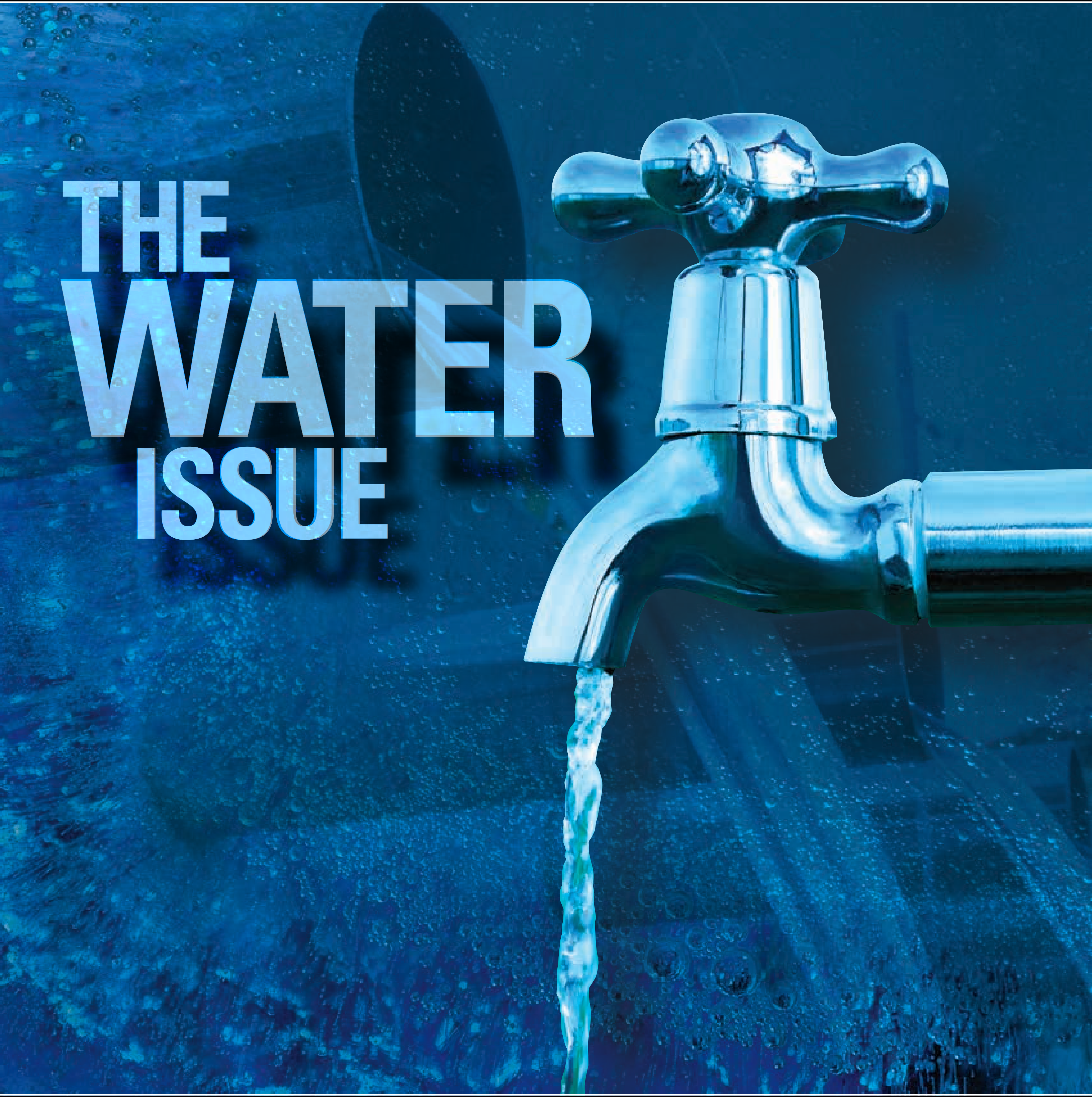
FOCUS on MATERIALS

MATERIALS RESEARCH INSTITUTE BULLETIN FALL 2016

THE WATER ISSUE



MATERIALS RESEARCH INSTITUTE

Focus on Materials is a bulletin of the Materials Research Institute at Penn State University. Visit our web site at **www.mri.psu.edu**

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Message from the Director

Clive Randall

Our society, and indeed our existence, depend on water for survival. As civilization developed, communities built close to rivers where there was a ready supply of clean drinking water. As our population increases, and along with it our agriculture and manufacturing, the stewardship of water is critical for health, security, and the continued development of our society.

The fragility of the water supply is always apparent and shouldn't be taken for granted. In countries with poor infrastructure and drought, women and children can spend five hours a day walking to secure water. After earthquakes, getting clean water to affected regions is always a priority. Here in the USA, according to the EPA, 41 states have unsafe levels of lead in the water supply. We frequently hear of the results of poor infrastructure investment and bad management, such as was exposed in Flint, Michigan. Drought has challenged water supplies in states from California to Connecticut. Casey Dinges, senior managing director of the American Society of Civil Engineers, points to the financial cost of poor water infrastructure, risking GDP of $400 billion and 700,000 jobs by 2020.

Our Penn State faculty are engaged with many of these global challenges. In this issue of *Focus on Materials*, we highlight a number of examples of faculty addressing water-cleaning solutions through materials. These can range from fracking water remediation to nuclear and chemical water contamination to oil spill cleanup, as well as new nature-inspired filtration approaches.

Stewardship of our natural resources is an important part of the Penn State strategic plan. MRI partners with other stakeholders in the University to maximize impact in this area, and without a doubt, our faculty have many creative approaches to address the management and supply of clean water in the modern world.

The tragedy of a time where there is "Water, water, everywhere, nor any drop to drink" must not be accepted for anyone, anywhere on the globe, today or in the future. This is a goal that is achievable and worthy of our commitment both for our students and our faculty, and indeed, for all of society.

Sincerely,

Clive Randall

Director of the Materials Research Institute
and professor of materials science and engineering

To access the materials expertise at Penn State, please visit our Materials Research Institute website at **www.mri.psu.edu** or the Office of Technology Management website at **http://www.research.psu.edu/offices/otm**

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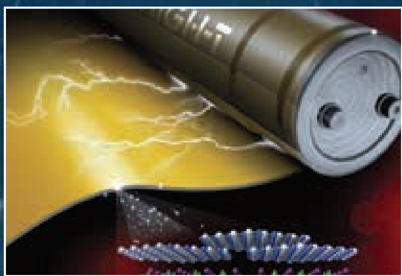

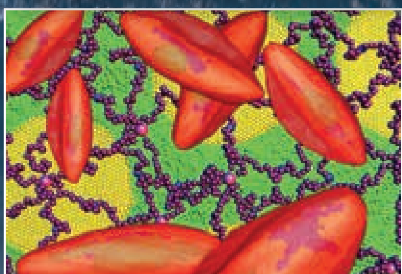

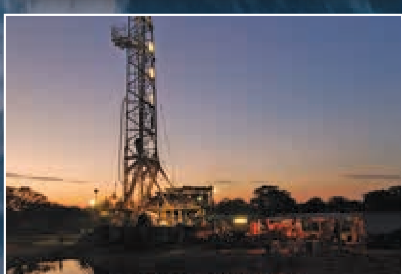

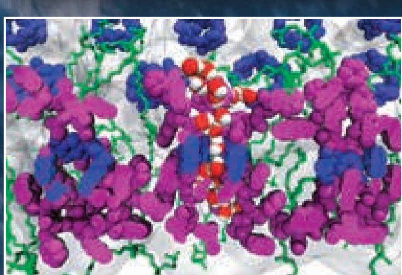

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THE WATER ISSUE

Cover images: Bigstock

Snapshots are brief summaries of significant materials-related breakthroughs by MRI researchers.

3D PRINTING OF PATTERNED MEMBRANES OPENS DOOR TO RAPID ADVANCES IN MEMBRANE TECHNOLOGY

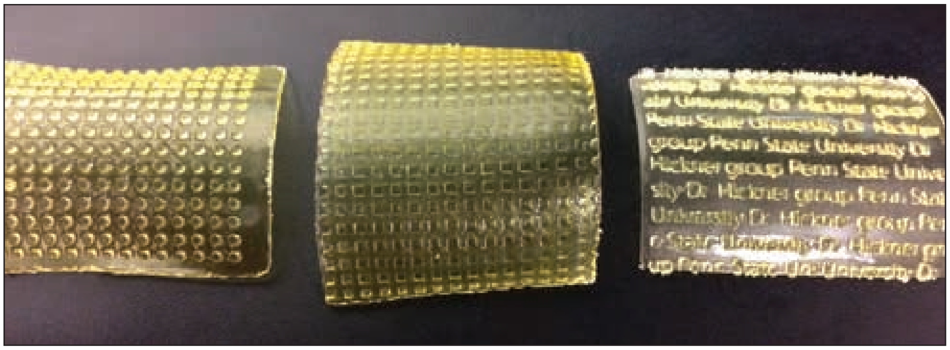
A new type of 3D printing developed by researchers at Penn State will make it possible for the first time to rapidly prototype and test polymer membranes that are patterned for improved performance.

Ion exchange membranes are used in many types of energy applications, such as fuel cells and certain batteries, as well as in water purification, desalination, removal of heavy metals and food processing. Most ion exchange membranes are thin, flat sheets similar to the plastic wrap in your kitchen drawer. However, recent work has shown that by creating 3D patterns on top of the 2D membrane surface, interesting hydrodynamic properties emerge that can improve ion transport or mitigate fouling, a serious problem in many membrane applications.

Currently, making these patterned membranes, also called profiled membranes, involves a laborious process of etching a silicon mold with the desired pattern, pouring in the polymer and waiting until it hardens. The process is both time-consuming and expensive, and results in a single pattern type.

“We thought if we could use 3D printing to fabricate our custom-synthesized ion exchange membranes, we could make any sort of pattern and we could make it quickly,” says Michael Hickner, associate professor of materials science and engineering at Penn State.

In a paper published online today in the American Chemical Society’s journal *ACS Applied Materials and Interfaces*, Hickner’s team describes the development of a custom 3D photolithographic printing process



Patterned membranes created by 3D printing • Image credit: Hickner Group/Penn State

A simple parallel resistance model describes the effect of the pattern on lowering the resistance of these new membranes. This insight gives us a design tool to continue to innovate and create new patterns for further improvements along with changing the intrinsic chemistry of the material."

similar in concept to a current 3D process called stereolithography. The team developed a photocurable mixture of ionic polymers and exposed the mixture under a light projector to harden the base layer. They then added more polymer to the base layer and projected a pattern on the new material to selectively harden the surface. The surface pattern increases the conductivity of the membrane by as much as a factor of two or three.

"Membranes act like a resistor in a battery or fuel cell," says Hickner. "If you can lower the resistance by a factor of two or three, you've really got something useful."

Lead author and a Ph.D. candidate in materials science and engineering, Jiho Seo, added, "While surface patterned membranes have been studied previously, this is the first 3D printed example of these structures and the first model that really explains the resistance decrease in a quantitative way.

The team will continue to optimize the geometry and chemistry of the membranes they print, as well as learn to print new materials, both for membranes and beyond, that have never been printed heretofore.

"We want to bridge the fundamental chemistry and materials science that we do with the engineering and rapid design iterations that the 3D printing industry is really good at," Hickner concludes.

In addition to Seo and Hickner, Douglas Kushner, Ph.D. student in materials science and engineering, contributed to the paper titled "3D Printing of Micro-patterned Anion Exchange Membranes."

Support for the photolithography system was provided by Penn State Department of Materials Science and Engineering. The Materials Research Institute and The Institutes of Energy and the Environment provided infrastructure support.

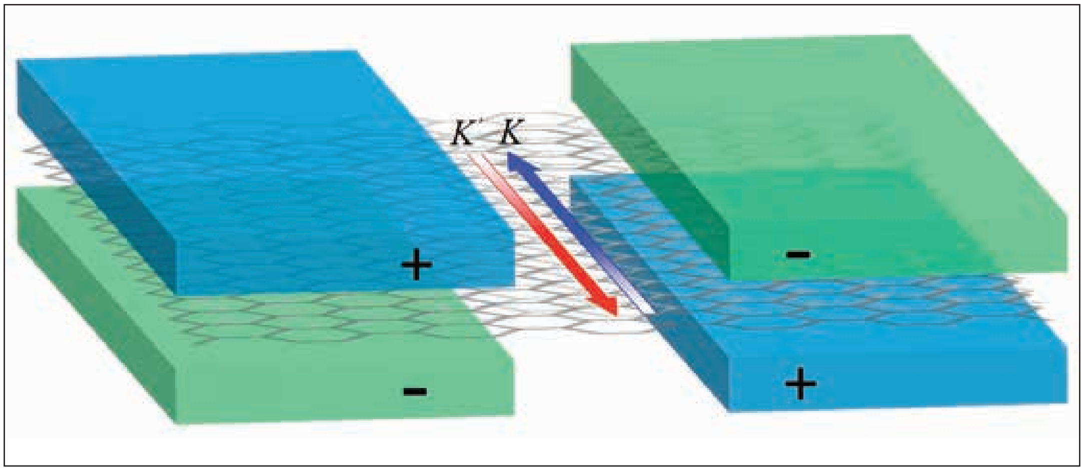
Contact Michael Hickner at mah49@psu.edu.

A DEVICE TO CONTROL "COLOR" OF ELECTRONS IN GRAPHENE PROVIDES PATH TO FUTURE ELECTRONICS

A device made of bilayer graphene, an atomically thin hexagonal arrangement of carbon atoms, provides experimental proof of the ability to control the momentum of electrons and offers a path to electronics that could require less energy and give off less heat than standard CMOS transistors. It is one step forward in a new field of physics called valleytronics.

"Current silicon-based transistor devices rely on the charge of electrons to turn the device on or off, but many labs are looking at new ways to manipulate electrons based on other variables, called degrees of freedom," said Jun Zhu, associate professor of physics at Penn State, who directed the research. "Charge is one degree of freedom. Electron spin is another, and the ability to build transistors based on spin, called spintronics, is still in the development stage. A third electronic degree of freedom is the valley state of electrons, which is based on their energy in relation to their momentum."

wires, that are color-coded freeways for electrons. The red cars travel in one direction and the blue cars travel in the opposite direction. In theory, colored electrons could travel unhindered along the wires for a long distance with very little resistance. Smaller resistance means power consumption is lower in electronic devices and less heat is generated. Both power consumption and thermal management are challenges in current miniaturized devices.



One-dimensional wires created in bilayer graphene gated by two pairs of split gates above and below the sheet. Wires traveling in opposite directions carry electrons of different valley states labeled as K and K' in the figure. • Image credit: Jun Zhu/Penn State

"Our experiments show that the metallic wires can be created," Li said. "Although we are still a long way from applications."

Zhu added, "It's quite remarkable that such states can be created in the interior of an insulating bilayer graphene sheet, using just a few gates. They are not yet resistance-free, and we are doing more experiments to understand where resistance might come from. We are also trying to build valves that control the electron flow based on the color of the electrons. That's a new concept of electronics called valleytronics."

Think of electrons as cars and the valley states as blue and red colors, Zhu suggested, just as a way to differentiate them. Inside a sheet of bilayer graphene, electrons will normally occupy both red and blue valley states and travel in all directions. The device her Ph.D. student, Jing Li, has been working on can make the red cars go in one direction and the blue cars in the opposite direction.

"The system that Jing created puts a pair of gates above and below a bilayer graphene sheet. Then he adds an electric field perpendicular to the plane," Zhu said.

"By applying a positive voltage on one side and a negative voltage on the other, a bandgap opens in bilayer graphene, which it doesn't normally have. In the middle, between the two sides, we leave a physical gap of about 70 nanometers," Li explained.

Inside this gap lives one-dimensional metallic states, or

Li worked closely with the technical staff of Penn State's nanofabrication facility to turn the theoretical framework into a working device.

"The alignment of the top and bottom gates was crucial and not a trivial challenge. The state of the art electron beam lithography capabilities at the Penn State Nanofabrication Laboratory allowed Jing to create this novel device with nanoscale features," says Chad Eichfeld, Nanolithography Engineer.

Their paper, titled "Gate-controlled topological conducting channels in bilayer graphene," appears online today, August 29, in the journal *Nature*

Nanotechnology. Additional authors include Ke Wang and Yafei Ren and their advisor Zenhua Qiao of University of Science and Technology of China, who performed numerical studies to model the behavior of the wires. The high-quality hexagonal Boron Nitride crystals used in the experiment came from Kenji Watanabe and Takashi Taniguchi of National Institute for Material Science, Japan. Two undergraduate students, Kenton McFaul and Zachary Zern, contributed to the research.

Funding was provided by the U.S. Office of Naval Research, the National Science Foundation and funding agencies in China and Japan. Kenton McFaul, a visiting student from Grove City College, was supported by a Research Experience for Undergraduates grant from the NSF NNIN.
Jun Zhu is a member of the Center for 2-Dimensional and Layered Materials in Penn State's Materials Research Institute.

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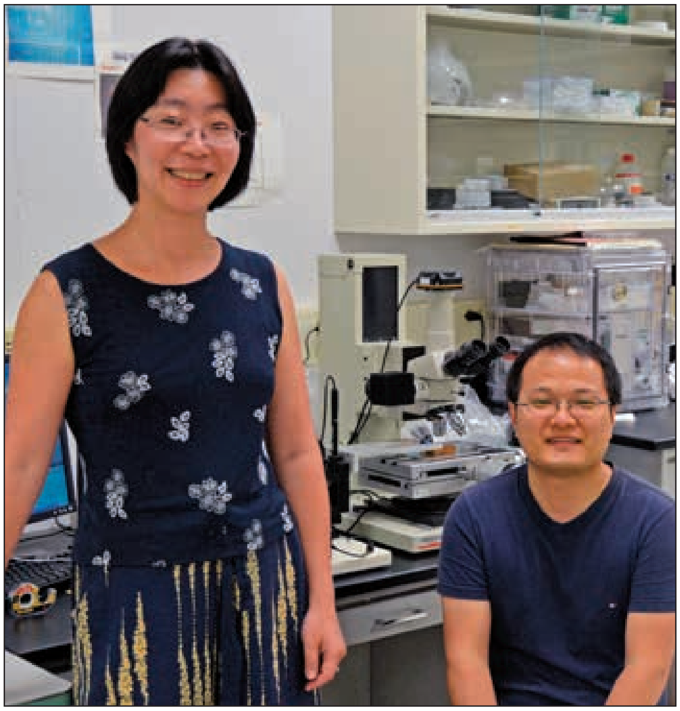
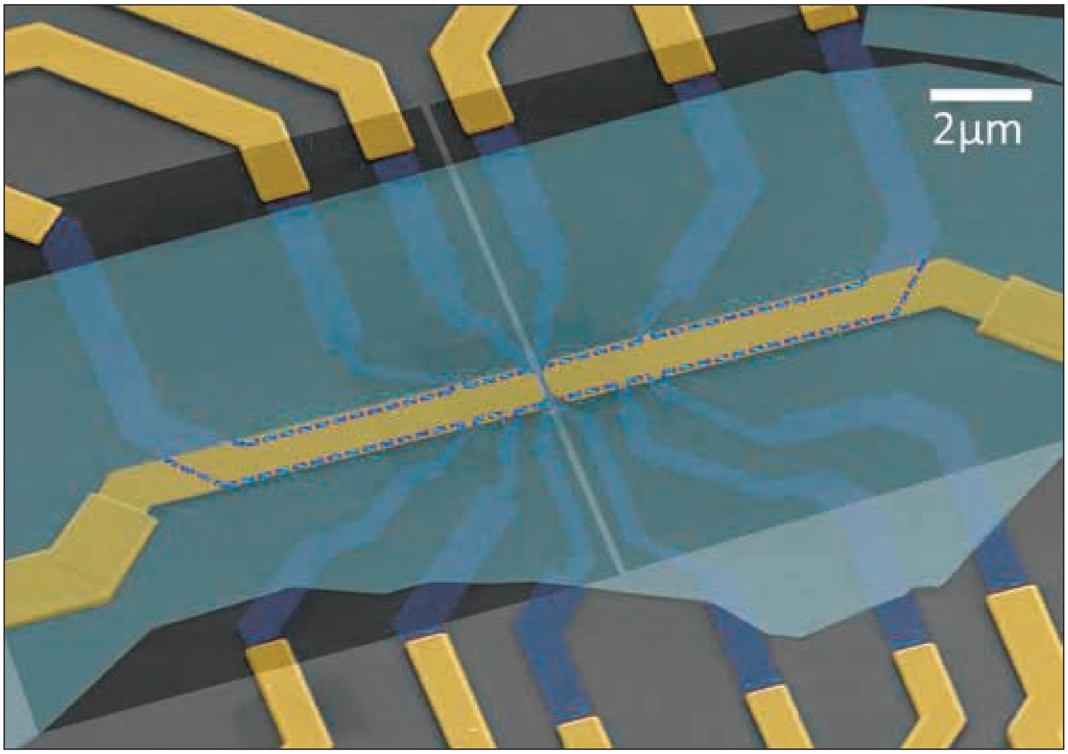


Jun Zhu, associate professor of physics, and her Ph.D. student Jing Li. • Photo credit: MRI/Penn State



A scanned electron micrograph of a device used in this experiment. Thin sheets of graphene and hexagonal Boron Nitride are stacked and shaped by electron beam lithography to create this device. The purple layer is the bilayer graphene sheet. The bottom pair of split gates (dark squares) are made of multi-layer graphene. The top pair of split gates (gold bars) are made of gold. The one-dimensional wires live in the gap created by the split gates.

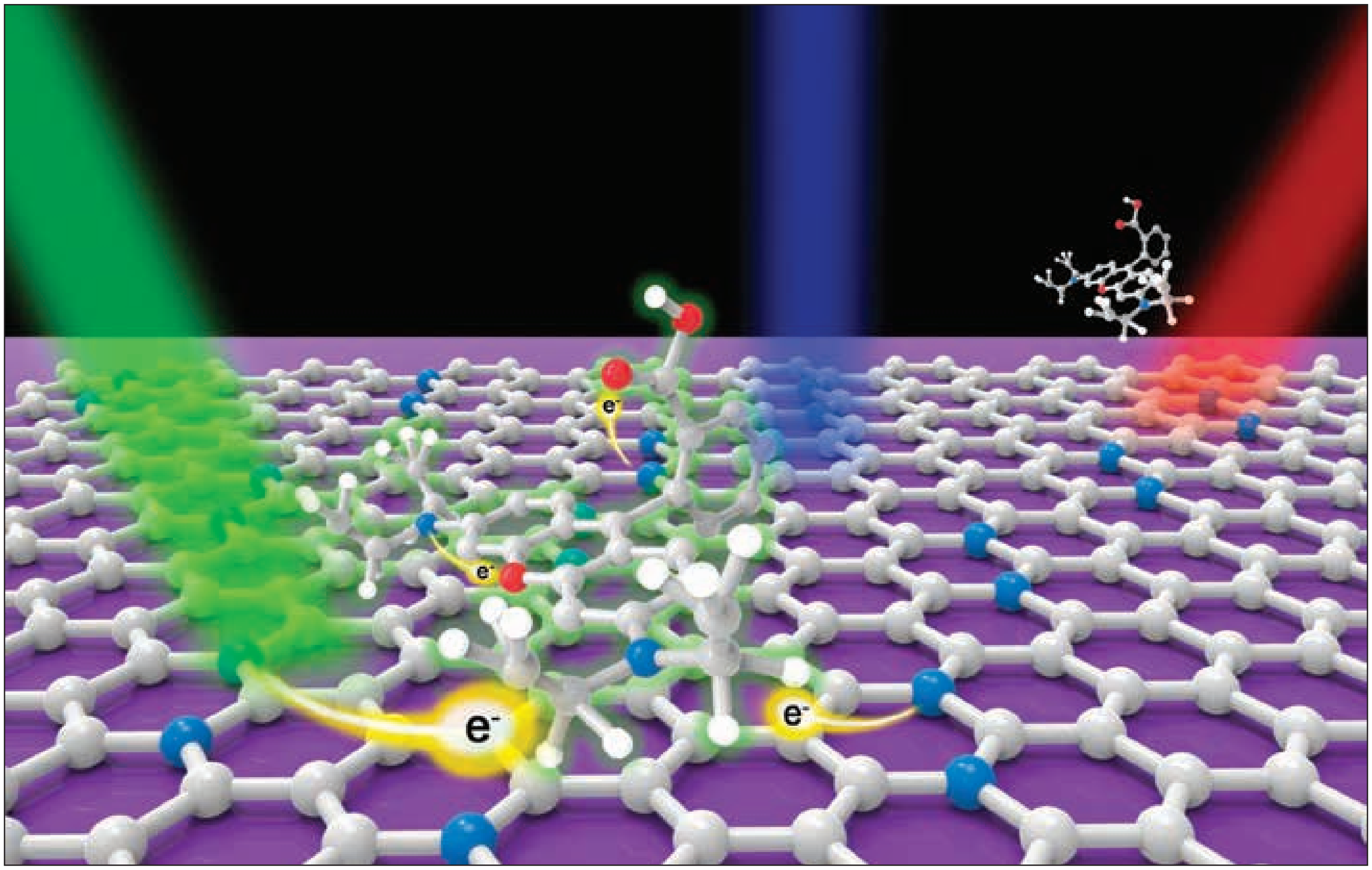
Image credit: Jing Li/Penn State

ULTRASENSITIVE SENSOR USING N-DOPED GRAPHENE

A highly sensitive chemical sensor based on Raman spectroscopy and using nitrogen-doped graphene as a substrate was developed by an international team of researchers working at Penn State. In this case, doping refers to introducing nitrogen atoms into the carbon structure of graphene. This technique can detect trace amounts of molecules in a solution at very low concentrations, some 10,000 times more diluted than can be seen by the naked eye.

Raman spectroscopy is a widely adopted identification technique used in chemistry, materials science, and the pharmaceutical industry to detect the unique internal vibrations of various molecules. When a laser light irradiates crystals or molecules, it scatters and shifts colors. That scattered light can be detected in the form of a Raman spectrum, which constitutes a fingerprint for every Raman-active irradiated system.

"Basically, different colors in the visible spectrum will be associated to different energies," says Mauricio Terrones, professor of physics, chemistry, and materials science at Penn State, who led the research. "Imagine each molecule has a particular light color emission, sometimes yellow, sometimes green. That color is associated with a discrete energy."



A model showing the charge transfer (e-) mechanism of Rhodamine B molecules (top) interacting with N-doped graphene (bottom sheet) when excited with different laser lines, which leads to ultrasensitive molecular sensor with N doped graphene. The white, blue and red balls represent carbon, nitrogen and oxygen atom respectively.
Image credit: Terrones Lab, Penn State

The team choose three types of fluorescent dye molecules for their experiments. Fluorescent dyes, which are frequently used as markers in biological experiments, are particularly hard to detect in Raman spectroscopy because the fluorescence tends to wash out the signal. However, when the dye is added to the graphene or N-doped graphene substrate, the photoluminescence – fluorescence – is quenched.

On its own, the Raman signal is so weak that many methods have been used to enhance the signal. A recently developed enhancement technique uses pristine graphene as a substrate, which can enhance the Raman signal by several orders of magnitude. In a paper published in the journal *Science Advances*, Terrones and colleagues reveal that adding nitrogen atoms to the pristine graphene further enhances sensitivity and, importantly, they give a theoretical explanation for how graphene and N-doped graphene cause the enhancement.

"By controlling nitrogen doping we can shift the energy gap of the graphene, and the shift creates a resonance effect that significantly enhances the molecule's vibrational Raman modes," says lead author Simin Feng, a graduate student in Terrones' group.

"This is foundational research," says Ana Laura Elias, a coauthor and research associate in Terrones' lab. "It is hard to quantify the enhancement because it will be different for every material and color of light. But in some cases we are going from zero to something we can detect for the first time. You can see a lot of features and study a lot of physics then. To me the most important aspect of this work is our understanding of the phenomenon. That will lead to improvements in the technique. "

Terrones adds, "We carried out extensive theoretical and experimental work. We came up with an explanation of why nitrogen-doped graphene works much better than regular graphene. I think it's a breakthrough, because in our paper we explain the mechanism of detecting certain molecules."

Because of graphene's chemical inertness and biocompatibility, the team expects that the new technique will be effective in detecting trace amounts of organic molecules. Elias is excited about the prospect of combing the technique with available portable Raman spectrometers that can be taken to remote places to detect, for instance, dangerous viruses. The fluorescent dyes they studied will make it fast and easy to see the presence of compounds inside biological cells. Because the technique is simple-- just dip the graphene substrate into a solution for a short amount of time – it should be feasible to create an entire library of the Raman spectrum of specific molecules, Terrones says.

Researchers from Brazil, China, and Japan contributed to this work while visiting the Terrones Lab at Penn State. The paper is titled "Ultrasensitive Molecular Sensor Using N-doped Graphene through Enhanced Raman Scattering."

Other coauthors include Maria Cristina dos Santos, Brazil; Bruno R. Carvalho, Brazil; Ruitao Lv, China; Qing Li, China; Kazunori Fujisawa, Penn State; Yu Lei, Penn State; Nestor Perea-López, Penn State; Morinobu Endo, Japan; Minghu Pan, China; and Marcos A. Pimenta, Brazil.

Funding was provided by MURI grants from the U.S. Army Research Office and the U.S. Air Force Office of Scientific Research. Agencies within their home countries provided support for the visiting faculty and students.

Mauricio Terrones is director of the Center for Two-Dimensional and Layered Materials (2DLM) at Penn State. Contact him at mutt11@psu.edu.

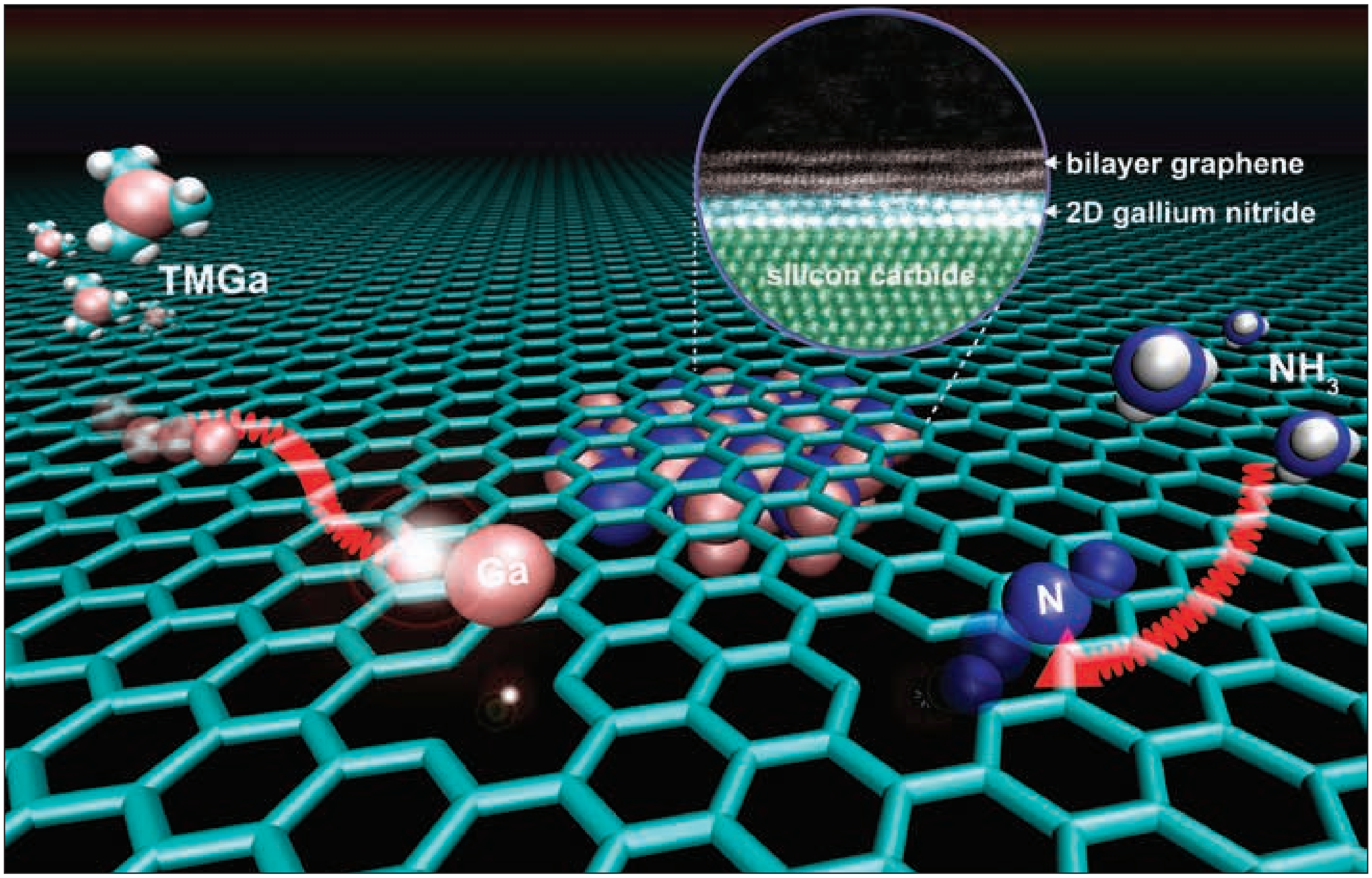
GRAPHENE KEY TO GROWING TWO-DIMENSIONAL SEMICONDUCTOR WITH EXTRAORDINARY PROPERTIES

A newly discovered method for making two-dimensional materials could lead to new and extraordinary properties, particularly in a class of materials called nitrides, say the Penn State materials scientists who discovered the process. This first-ever growth of two-dimensional gallium nitride using graphene encapsulation could lead to applications in deep ultraviolet lasers, next-generation electronics and sensors.

"These experimental results open up new avenues of research in 2D materials," says Joshua Robinson, associate professor of materials science and engineering. "This work focuses on making 2D gallium nitride, which has never been done before."

An illustration of the Migration Enhanced Encapsulated Growth (MEEG) process to stabilize novel wide-bandgap two-dimensional nitride semiconductors that are not naturally occurring. MEEG is facilitated by defects in the graphene lattice that act as pathways for intercalation. When the gallium and nitrogen atoms meet at the graphene/SiC interface, they chemically react to form two-dimensional gallium nitride.

Image credit: Z. Al Balushi and Stephen Weitzner, Penn State Materials Science and Engineering



Gallium nitride in its three-dimensional form is known to be a wide-bandgap semiconductor. Wide-bandgap semiconductors are important for high frequency, high power applications. When grown in its two-dimensional form, gallium nitride transforms from a wide-bandgap material to an ultrawide-bandgap material, effectively tripling the energy spectrum can operate in, including the whole ultraviolet, visible and infrared spectrum. This work will have a particular impact on electro-optic devices that manipulate and transmit light.

Graphene is key

"This is a new way of thinking about synthesizing 2D materials," said Zak Al Balushi, a Ph.D. candidate coadvised by Robinson and Joan Redwing, professor of materials science and engineering and electrical engineering. Al Balushi is lead author on a paper appearing online today, Aug.29, in the journal *Nature Materials* titled "Two-Dimensional Gallium Nitride Realized via Graphene Encapsulation."

"We have this palette of naturally occurring 2D materials," he continued. "But to expand beyond this, we have to synthesize materials that do not exist in nature. Typically, new material systems are highly unstable. But our growth method, called Migration Enhanced Encapsulated Growth (MEEG), uses a layer of graphene to assist the growth and stabilize a robust structure of 2D gallium nitride."

The graphene is grown on a substrate of silicon carbide, which is a technologically important substrate used widely in industry for LEDs, radar and telecommunications. When heated, the silicon on the surface decomposes and leaves a carbon-rich surface that can reconstruct into graphene. The advantage of producing the graphene in this way is that the interface where the two materials meet is perfectly smooth.

Robinson believes that in the case of two-dimensional gallium nitride, the addition of a layer of graphene makes all the difference. Graphene, a one-atom-thick layer of carbon atoms, is known for its remarkable electronic properties and strength.

"It's the key," Robinson says. "If you try to grow these materials the traditional way, on silicon carbide, you normally just form islands. It doesn't grow in nice layers on the silicon carbide."

When gallium atoms are added to the mix, they migrate through the graphene and form the middle layer of a sandwich, with graphene floating on top. When nitrogen atoms are added, a chemical reaction takes place that turns the gallium and nitrogen into gallium nitride.

Adds Redwing, "The MEEG process not only produces ultra-thin sheets of gallium nitride but also changes the crystal structure of the material, which may lead to entirely new applications in electronics and optoelectronics."

Additional coauthors include Ke Wang, Rafael Vila, Sarah Eichfield, Yu-Chuan Lin and Shruti Subramanian of Penn State, Ram Krishna Ghosh and Suman Datta of Notre Dame, Joshua Caldwell, U.S. Naval Research Laboratory, Xiaoye Qin and Robert Wallace The University of Texas at Dallas and Dennis Paul, Physical Electronics USA.

Funding was provided by Asahi Glass Co., Ltd, Japan, and the U.S. National Science Foundation. Funding for Al Balushi was provided by the NSF Materials Science and Engineering Center at Penn State. Other funding was provided by the Alfred P. Sloan Foundation, the Penn State Materials Characterization Laboratory and the Center for Low Energy Systems Technology (LEAST), funded by the Semiconductor Research Corporation and DARPA.

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"IDEAL" ENERGY STORAGE MATERIAL FOR ELECTRIC VEHICLES DEVELOPED

The goal of a polymer dielectric material with high energy density, high power density and excellent charge-discharge efficiency for electric and hybrid vehicle use has been achieved by a team of Penn State materials scientists. The key is a unique three-dimensional sandwich-like structure that protects the dense electric field in the polymer/ceramic composite from dielectric breakdown. Their results are published today (8/22/16) in the Proceedings of the National Academy of Sciences (PNAS).

"Polymers are ideal for energy storage for transportation due to their light weight, scalability and high dielectric strength," says Qing Wang, professor of materials science and engineering and the team leader. "However, the existing commercial polymer used in hybrid and electric vehicles, called BOPP, cannot stand up to the high operating temperatures without considerable additional cooling equipment. This adds to the weight and expense of the vehicles."

The researchers had to overcome two problems to achieve their goal. In normal two-dimensional polymer films such as BOPP, increasing the dielectric constant, the strength of the electric field, is in conflict with stability and charge-discharge efficiency. The stronger the field, the more likely a material is to leak energy in the form of heat. The Penn State researchers originally attacked this problem by mixing different materials while trying to balance competing properties in a two-dimensional form. While this increased the energy capacity, they found that the film broke down at high temperatures when electrons escaped the electrodes and were injected into the polymer, which caused an electric current to form.

"That's why we developed this sandwich structure," Wang says. "We have the top and bottom layers that block charge injection from the electrodes. Then in the central layer we can put all of the high dielectric constant ceramic/polymer filler material that improves the energy and power density."

The outer layers, composed of boron nitride nanosheets in a polymer matrix, are excellent insulators, while the central layer is a high dielectric constant material called barium titanate.

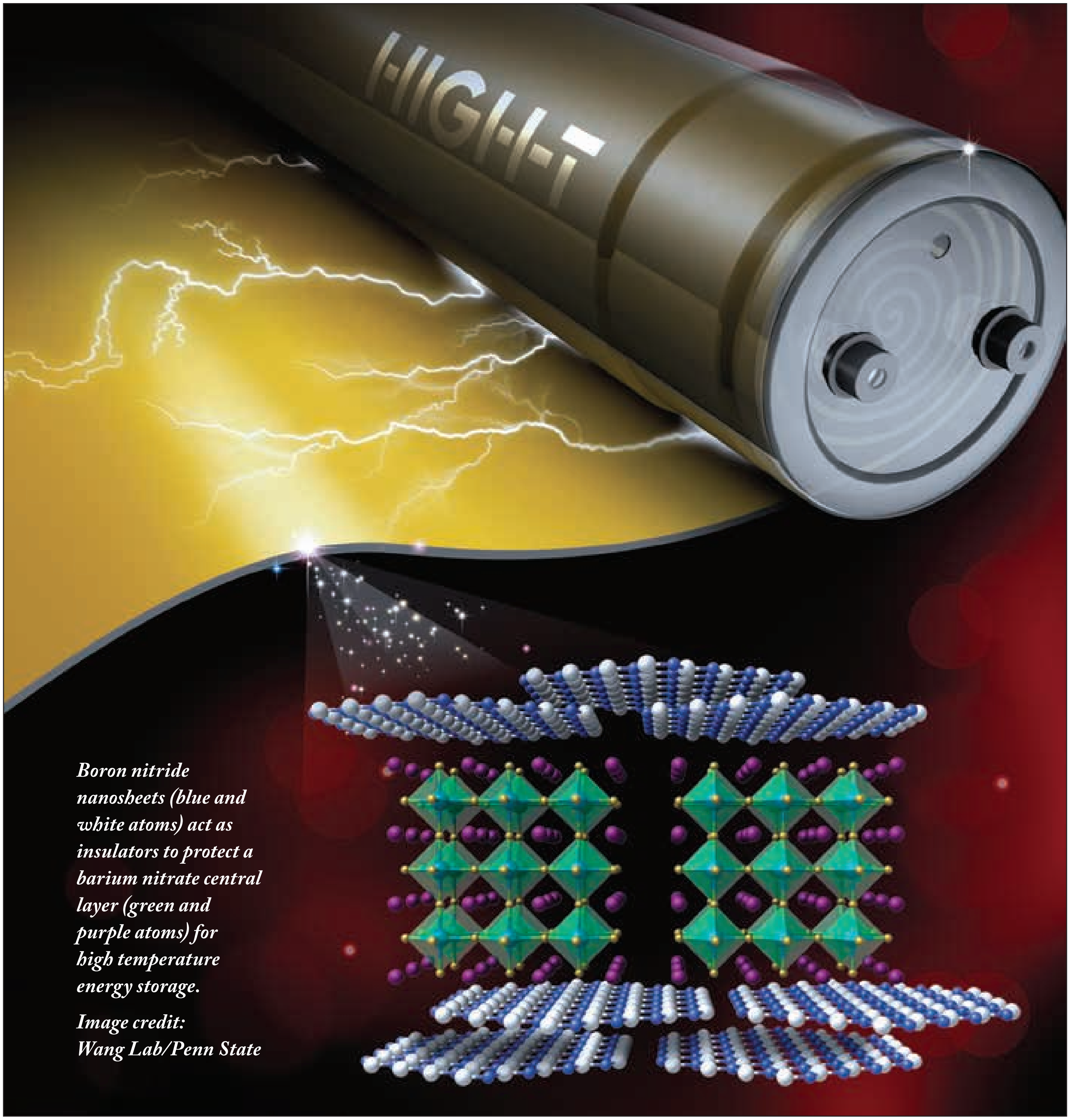
"We show that we can operate this material at high temperature for 24 hours straight over more than 30,000 cycles and it shows no degradation," Wang says.

Comparison to BOPP

A comparison of BOPP and the sandwich structure nanocomposite, termed SSN-x, in which the x refers to the percentage of barium titanate nanocomposites in the central layer, shows that at 150 degrees C, SSN-x has essentially the same charge-discharge energy as BOPP at it typical operating temperature of 70 degrees C. However, SSN-x has several times the energy density of BOPP, which makes SSN-x highly preferable for electric vehicle and aerospace applications as an energy storage device due to the ability to reduce the size and weight of the electronics significantly while improving system performance and stability. The elimination of bulky and expensive cooling equipment required for BOPP is an additional bonus.

"Our next step is to work with a company or with more resources to do processability studies to see if the material can be produced at a larger scale at a reasonable cost," Wang says. "We have demonstrated the materials performance in the lab. We are developing a number of state-of-the-art materials working with our theory colleague Long-Qing Chen in our department. Because we are dealing with a three-dimensional space, it is not just selecting the materials, but how we organize the multiple nanosized materials in specific locations. Theory helps us design materials in a rational fashion."

In addition to Professors Wang and Chen, contributors to the paper, titled "Sandwich-Structured Polymer Nanocomposites with High Energy Density and Great Charge-Discharge Efficiency at Elevated Temperatures," include first author and post-doctoral



Boron nitride nanosheets (blue and white atoms) act as insulators to protect a barium nitrate central layer (green and purple atoms) for high temperature energy storage.

Image credit: Wang Lab/Penn State

scholar Qi Li, Ph.D. student Feihua Liu, Matthew Gadinski, a former Ph.D. student now at DOW Chemical, Guangzu Zhang, a post-doctoral scholar, all in Wang's lab, and Tiannan Yang, a graduate student in Chen's group.

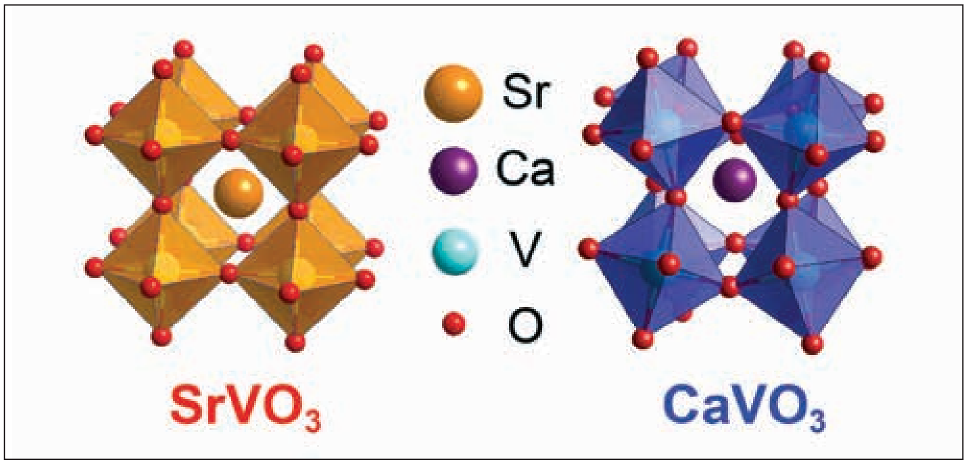
This work was supported by the U.S. Office of Naval Research.

Contact: Qing Wang, wang@matse.psu.edu

TRANSPARENT METAL FILMS FOR SMARTPHONE, TABLET AND TV DISPLAYS

A new material that is both highly transparent and electrically conductive could make large screen displays, smart windows and even touch screens and solar cells more affordable and efficient, according to materials scientists and engineers at Penn State who have discovered just such a material.

Indium tin oxide (ITO), the transparent conductor that is now used for more than 90 percent of the display market, has been the dominant material for the past 60 years. But in the last decade, the price of indium has increased dramatically. Displays and touchscreen modules have become a main cost driver in mobile devices, such as smartphones and tablets, making up close to 40 percent of the cost. While memory chips and processors get cheaper, following Moore's Law, smartphone and tablet displays get more expensive from generation to generation. Manufacturers have searched for a possible ITO replacement, but until now, nothing has matched ITO's combination of optical transparency, electrical conductivity and ease of fabrication.



A figure showing the crystal structure of strontium vanadate (orange) and calcium vanadate (blue). The red dots are oxygen atoms arranged in 8 octohedra surrounding a single strontium or calcium atom. Vanadium atoms can be seen inside each octahedron. Credit: Lei Zhang/Penn State

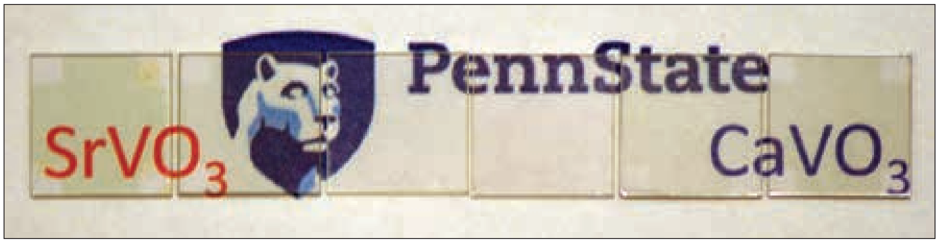
In a paper appearing Dec 15, 2015 online in *Nature Materials*, Roman Engel-Herbert, assistant professor of materials science and engineering, and his team report a new design strategy that approaches the problem from a different angle. The researchers use thin (10 nanometer) films of an unusual class of materials – called correlated metals – in which the electrons flow like a liquid. While in most conventional metals, such as copper, gold, aluminum or silver, electrons flow like a gas, in correlated metals, such as strontium vanadate and calcium vanadate, they move like a liquid. In this paper, the authors explain why these correlated metals show a high optical transparency despite their high, metal-like conductivity.

"We are trying to make metals transparent by changing the effective mass of their electrons," Engel-Herbert says. "We are doing this by choosing materials in which the electrostatic interaction between negatively charged electrons is very large compared to their kinetic energy. As a result of this strong electron correlation effect, electrons 'feel' each other and behave like a liquid rather than a gas of non-interacting particles. This electron liquid is still highly conductive, but when you shine light on it, it becomes less reflective, thus much more transparent."

To better understand how they achieved this fine balance between transparency and conductivity, they turned to a materials theory expert, Professor Karin Rabe of Rutgers University.

"We realized that we needed her help to put a number on how 'liquid' this electron liquid in strontium vanadate is," Engel-Herbert says.

Rabe helped the Penn State team put together all the theoretical and mathematical puzzle pieces they needed to build transparent conductors in the form



Samples of the correlated metals strontium vanadate (two squares on left) and calcium vanadate (two squares on right) with two uncoated squares in center. The film thickness is 12 nanometers and 4 nanometers on the coated squares. Image credit: MRI/Penn State

of a correlated metal. Now that they understand the essential mechanism behind their discovery, the Penn State researchers are confident they will find many other correlated metals that behave like strontium vanadate and calcium vanadate.

Lei Zhang, lead author on the *Nature Materials* paper and a graduate student in Engel-Herbert's group, was the first to recognize what they had discovered.

"I came from Silicon Valley where I worked for two years as an engineer before I joined the group. I was aware that there were many companies trying hard to optimize those ITO materials and looking for other possible replacements, but they had been studied for many decades and there just wasn't much room for improvement," says Zhang. "When we made the electrical measurements on our correlated metals, I knew we had something that looked really good compared to standard ITO."

Currently indium costs around $750 per kilogram, whereas strontium vanadate and calcium vanadate are made from elements with orders of magnitude higher abundance in the earth's crust. Vanadium sells for around $25 a kilogram, less than 5 percent of the cost of indium, while strontium is even cheaper than vanadium.

"Our correlated metals work really well compared to ITO. Now, the question is how to implement these new materials into a large scale manufacturing process. From what we understand right now, there is no reason that strontium vanadate could not replace ITO in the same equipment currently used in industry," says Engel-Herbert.

Along with display technologies, Engel-Herbert and his group are excited about combining their new materials with a very promising type of solar cell that uses a class of materials called organic perovskites. Developed only within the last half dozen years, these materials outperform commercial silicon solar cells but require an inexpensive transparent conductor. Strontium vanadate, also a perovskite, has a compatible structure that makes this an interesting possibility for future inexpensive, high-efficiency solar cells.

Engel-Herbert and Zhang have applied for a patent on their technology.

Along with Zhang and Engel-Herbert, coauthors on the paper titled "Correlated metals as transparent conductors" are Hai-Tian Zhang, Craig Eaton, Yuanxia Zheng and Matthew Brahlek, all students and postdoctoral Fellows in Engel-Herbert's group. Others from Penn State and the Materials Research Institute include Moses Chan, Evan Pugh professor of physics, and his postdoctoral Fellow Weiwei Zhao, and Venkatraman Gopalan, professor of materials science and engineering and his student Lu Guo. Rabe and her student Yuanjun Zhou, Rutgers University, and Anna Barnes, Hamna Haneef and associate professor Nikolas Podraza, University of Toledo also contributed on this project.

The U.S. Office of Naval Research, the National Science Foundation and the Department of Energy funded this work. Fabrication of the correlated metals was performed at the Materials Research Institute in the laboratory facilities of Penn State's Millennium Science Complex.

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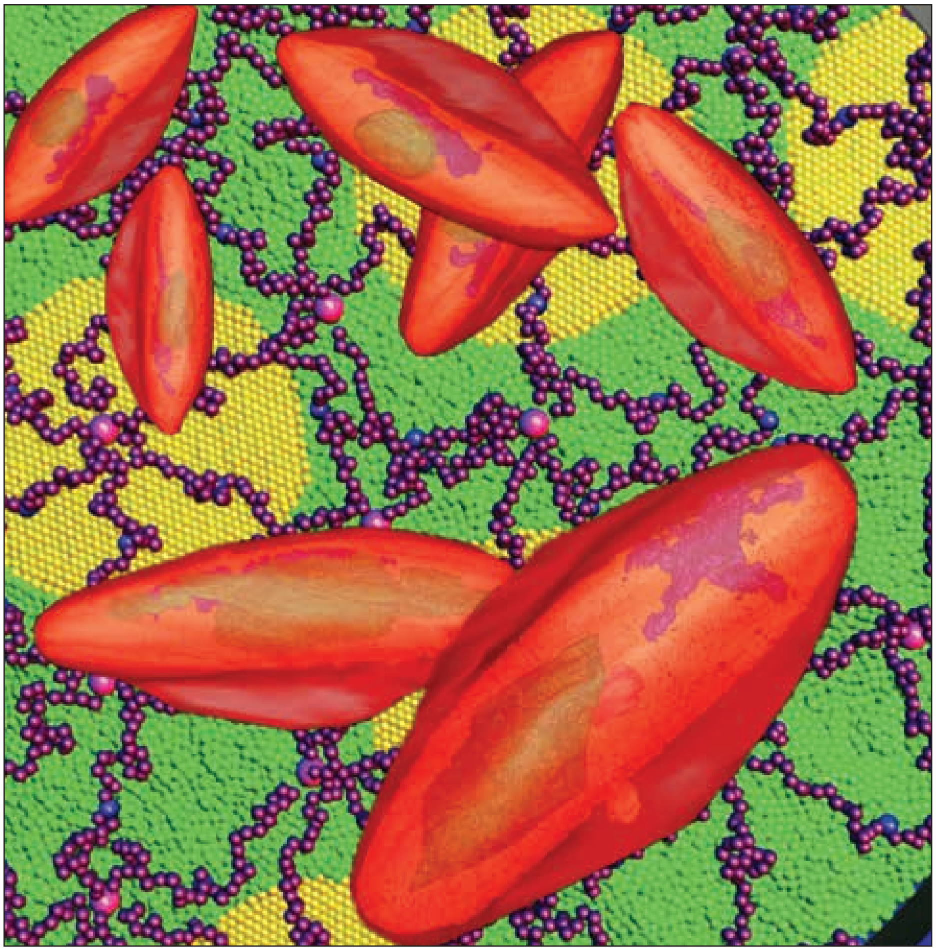
CRACKING THE CODE OF THE MALARIA PARASITE MAY HELP STOP TRANSMISSION

The most dangerous malaria parasite, Plasmodium falciparum, is responsible for nearly half a million deaths annually across Africa and Southeast Asia. Of increasing concern, this parasite is now developing resistance to common antimalarial drugs. Gaining a better understanding of the parasite's development in the body is urgently required. Now, a multi-university team, which includes Penn State, has broken the code that may lead to new defenses against the deadly parasite.

To get a clear picture of how the parasite manipulates its host – the human red blood cell – an international, multidisciplinary team of life scientists, mathematicians and engineers, including Sulin Zhang, associate professor of engineering science and mechanics and biomedical engineering at Penn State, has used advanced imaging technology coupled with computationally efficient coarse-grained modelling to understand how the sexual blood stage of the parasite transforms its own structure and then the structure of the red blood cell to hide from the body's normal defenses and later re-enter the bloodstream for transmission via mosquito bite. With this understanding, methods to inhibit the blood cell's transformation may be possible.



Electron micrographs of malaria gametocytes • Image credit: Boyin Liu and Eric Hanssen, University of Melbourne, and Yao Zhang and Peng Zhao, Penn State

"Once you understand the molecular mechanisms, it becomes easier to find drugs to target them," says Zhang, who developed the computational methods the group used to understand the remarkable physical transformations in the infected red blood cells that allow them to avoid removal in the spleen and later prepare to be transmitted to a mosquito host.

Healthy red blood cells are able to squeeze through small slits in the spleen, whereas damaged and aging red blood cells cannot and are filtered out and removed from the circulation. To avoid this fate, the sexual stage malaria parasite first makes the red blood cell rigid and hides out in deep tissue, then when it is mature, the infected red blood cells become flexible and elastic, ready to be picked up by a mosquito for disease transmission. Malaria scientists have long wondered how it achieves this remarkable transformation.

To understand these changes, biologists prepared samples of parasites at each stage and studied the changing microstructure using atomic force microscopy. This revealed changes in the organization of a meshwork of tiny spring-like proteins in the blood cell membrane. When the parasite is ready for transmission, it reverses the structural changes.

The team, which included professors Leann Tilley and Matthew Dixon, University of Melbourne and Rajesh Chandramohanadas, Singapore University of Technology and Design, then turned to Zhang, who developed a molecularly faithful and computationally efficient model to explain how subtle changes to the molecular structure of the spring-like proteins of the red blood cell were sufficient to make the cell either rigid or flexible.

Their work was reported in an early online edition of the *Proceedings of the National Academy of Sciences* (PNAS) April 12 in an article titled "Reversible host cell remodeling underpins deformability changes in malaria parasite sexual blood stages."

The team is continuing to use Zhang's model to simulate the overall shapes and the flow dynamics of infected red blood cells in the bloodstream, providing further understanding to researchers looking to find ways to inhibit the malaria parasite's spread.

Funding was provided by the Australian Research Council and National Health and Medical Research Council; Singapore University of Technology and Design; and the National Science Foundation.

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SINGLE MOLECULE DETECTION OF CONTAMINANTS, EXPLOSIVES OR DISEASES NOW POSSIBLE

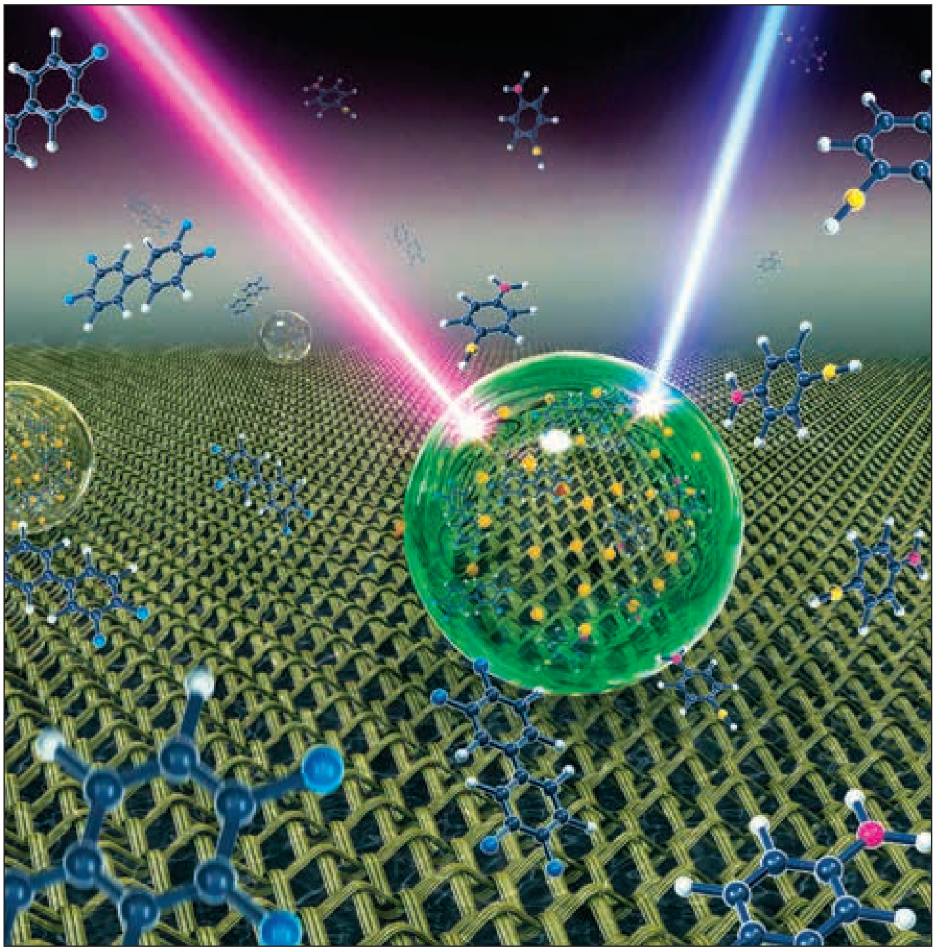
A technique to combine the ultrasensitivity of surface enhanced Raman scattering (SERS) with a slippery surface invented by Penn State researchers will make it feasible to detect single molecules of a number of chemical and biological species from gaseous, liquid or solid samples. This combination of slippery surface and laser-based spectroscopy will open new applications in analytical chemistry, molecular diagnostics, environmental monitoring and national security.

The researchers, led by Tak-Sing Wong, assistant professor of mechanical engineering and the Wormley Family Early Career Professor in Engineering, call there invention SLIPSERS, which is a combination of Wong's slippery liquid-infused porous surfaces (SLIPS), which is a biologically inspired surface based on the Asian pitcher plant, and SERS.

"We have been trying to develop a sensor platform that allows us to detect chemicals or biomolecules at a single molecule level whether they are dispersed in air, liquid phase, or bound to a solid," Wong said. "Being able to identify a single molecule is already pretty difficult. Being able to detect those molecules in all three phases, that is really challenging."

Wong needed the help of postdoctoral fellow Shikuan Yang to combine SERS and SLIPS into a single process. Yang was trained in Raman spectroscopy in the characterization laboratory of Penn State's Materials Research Institute. His expertise in the SERS technique and Wong's knowledge of SLIPS enabled them to develop the SLIPSERS technology. Their work appeared online the week of December 28,2015 in the Proceedings of the National Academy of Sciences, USA (PNAS).

Raman spectroscopy is a well-known method of analyzing materials in a liquid form using a laser to interact with the vibrating molecules in the sample. The molecule's unique vibration shifts the frequency of the photons in the laser light beam up or down in a way that is characteristic of only that type of molecule. Typically, the Raman signal is very weak and has to be enhanced in some way for detection. In the 1970s, researchers found that chemically roughening the surface of a silver substrate concentrated the Raman signal of the material adsorbed on the silver, and SERS was born.



Artistic illustration showing an ultrasensitive detection platform termed slippery liquid infused porous surface-enhanced Raman scattering (SLIPSERS). In this platform, an aqueous or oil droplet containing gold nanoparticles and captured analytes is allowed to evaporate on a slippery substrate, leading to the formation of a highly compact nanoparticle aggregate for surface enhanced Raman scattering (SERS) detection. • Image credit: Shikuan Yang, Birgitt Boschitsch Stogin, and Tak-Sing Wong/Penn State

Wong developed SLIPS as a post-doctoral researcher at Harvard University. SLIPS is composed of a surface coated with regular arrays of nanoscale posts infused with a liquid lubricant that does not mix with other liquids. The small spacing of the nanoposts traps the liquid between the posts and the result is a slippery surface that nothing adheres to.

"The problem," Wong said, "is that trying to find a few molecules in a liquid medium is like trying to find a needle in a haystack. But if we can develop a process to gradually shrink the size of this liquid volume, we can get a better signal. To do that we need a surface that allows the liquid to evaporate uniformly until it gets to the micro or nanoscale. Other surfaces can't do that, and that is where SLIPS comes in."

If a droplet of liquid is placed on any normal surface, it will begin to shrink from the top down. When the liquid evaporates, the target molecules are left in random configurations with weak signals. But if all the molecules can be clustered among the gold nanoparticles, they will produce a very strong Raman signal.

Shikuan Yang explained: "First we need to use conductive nanoparticles, like gold. And then we have to assemble them so they make nanoscale gaps between the particles, called hot spots. The molecules bind to the gaps and a very strong electromagnetic field forms. If we have a laser with the right wavelength, the electrons will oscillate and a strong magnetic field will form in the gap area. This gives us a very strong signal."

Although there are other techniques that allow researchers to concentrate molecules on a surface, those techniques mostly work with water as the medium. SLIPS can be used with any organic liquid.

"Our technique opens up larger possibilities for people to use other types of solvents to do single molecule SERS detection, such as environmental detection in soil samples. If you can only use water, that is very limiting," Yang said. "In biology, researchers might want to detect a single base pair mismatch in DNA. Our platform will give them that sensitivity."

One of the next steps will be to detect biomarkers in blood for disease diagnosis at the very early stages of cancer when the disease is more easily treatable.

"We have detected a common protein, but haven't detected cancer yet," Yang said.

Although the SLIPS technology is patented and licensed, the team has not sought patent protection on their SLIPSERS work.

"We believe that offering this technology to the public will get it developed at a much faster pace," said Professor Wong. "This is a powerful platform that we think many people will benefit from."

In addition to Yang and Wong, postdoctoral Fellow Xianming Dai, and graduate student Birgitt Boschitsch Stogin contributed to the work, which was performed in the Materials Characterization Laboratory's state-of-the-art Raman spectroscopy lab, a part of Penn State's Materials Research Institute.

The research was funded by the National Science Foundation.

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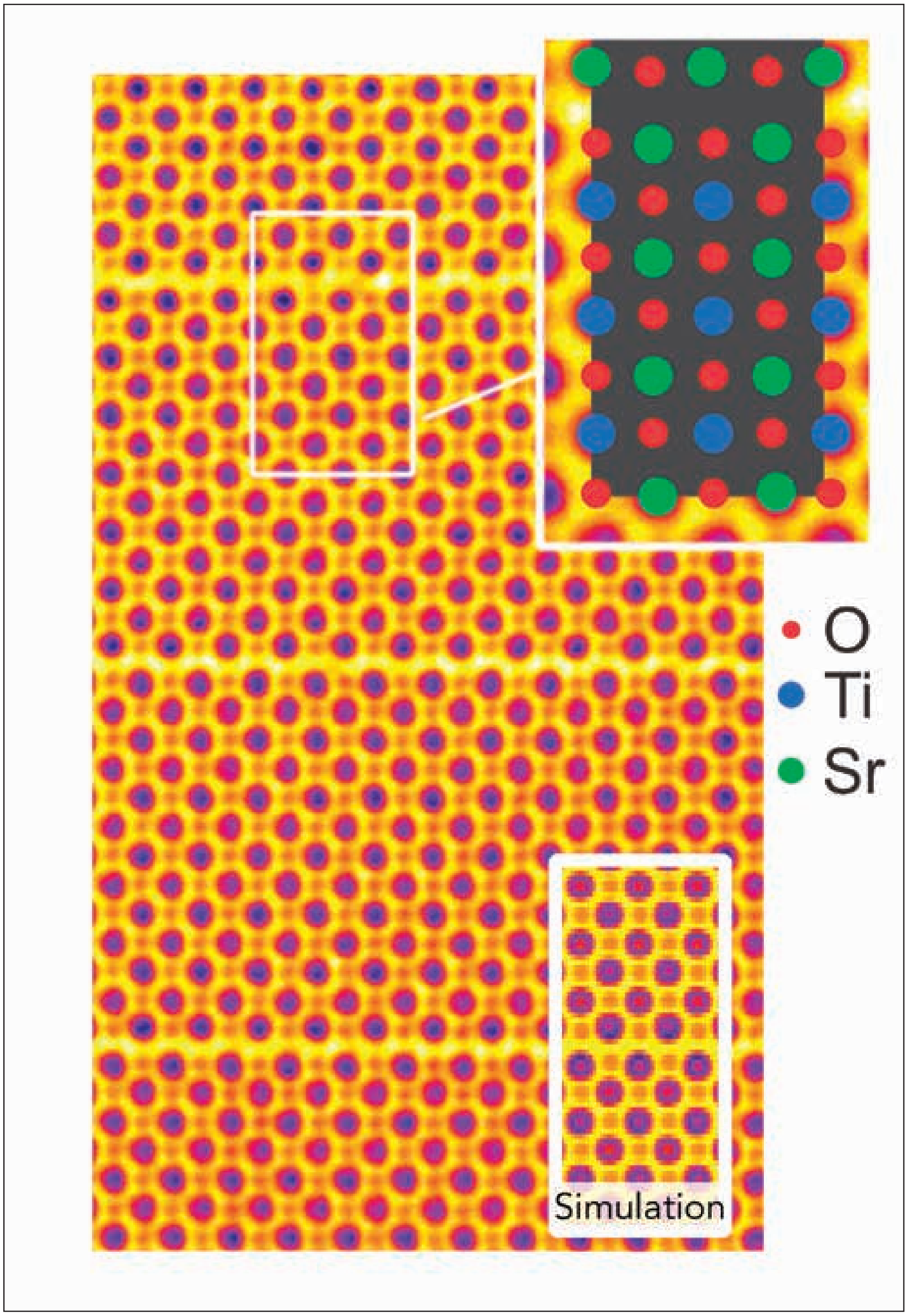
SUBATOMIC MICROSCOPY KEY TO BUILDING NEW CLASSES OF MATERIALS

Researchers at Penn State and the Molecular Foundry at Lawrence Berkeley National Laboratory are pushing the limits of electron microscopy into the tens of picometer scale, a fraction of the size of a hydrogen atom. The ability to see at this subatomic level is crucial in designing new materials with unprecedented properties, such as materials that transition from metals to semiconductors or that exhibit superconductivity. Their work describing the first atomic scale evidence for strain induced ferroelectricity in a layered oxide appeared online August 31, in the journal *Nature Communications*.



Colorized sub-Angstrom scanning transmission electron microscope image clearly shows individual atomic columns of strontium (green), titanium (blue), and oxygen (red). A simulated image is overlaid showing close agreement between theory and experiment. The brick and mortar structure is visible. • Image credit: Greg Stone/Penn State

"This paper is important because it highlights our ability to design new classes of materials that can be tuned, one atomic layer at a time, to get interesting new properties such as high frequency tunable dielectrics, which are of interest to the semiconductor industry," says first author Greg Stone, a former Penn State post-doctoral scholar now at the U.S. Army Research, Development, and Engineering Center.

Designing new materials with potentially useful properties requires the close collaboration of theory, to build mathematical models, synthesis, to create the material in the lab, and characterization, to visualize and measure the material's properties and provide feedback to tweak theories and improve synthesis.

This study builds on previous theoretical work by coauthors Turan Birol and Craig Fennie of Cornell University and experimental work by coauthors Venkatraman Gopalan of Penn State and Darrell Schlom, formerly at Penn State now at Cornell, and their students. Gopalan and Nasim Alem, professors of materials science and engineering at Penn State, led the current study.

Gopalan says, “The material we are looking at is a form of strontium titanate called a layered oxide. This study brings together electron microscopy and density functional theory on a 5-10 picometer length scale to show why these materials are such good tunable dielectrics. The key is phase competition, and for the first time, we show that many polar phases with similar energies compete in this material on the atomic scale, just as theory predicted, which gives it large tunability under a voltage.”

Complex oxides are materials that are formed by the negatively charged oxygen and two other positively charged ions. In this instance, the team examined strontium titanate with a structure called Ruddlesden-Popper (RP), after the two scientists who discovered it. The structure looks like a brick and mortar wall, with the bricks made of the strontium titanate and the thin mortar between the bricks made up of strontium oxide. When the bricks are layered in this fashion, new properties emerge that would not appear in a single brick.

“In the case of RP-strontium titanate, the emergent property is ferroelectricity, which means it has a built-in electrical polarization within its structure. But it could be magnetism or metal-insulator transitions or superconductivity, depending on the atoms involved and the layering order of the materials,” Gopalan says.

Because each layer of brick has a weak connection to other layers, the material can have competing states, with one layer polarized in a direction opposite a neighboring layer. These competing states result in a material with a strong response to a small external stimulus, such as an electric or magnetic field or temperature. In the case of strontium titanate, there is a large dielectric response, which is the ability to store large amounts of energy, as in a capacitor.

Cell phones have many dielectric components that are very small and have to hold a charge. As cell phones transition from 4G networks to 5G, which means they are processing at 5 billion cycles per second, better materials that respond at higher frequencies are crucial. RP-strontium titanate is one such material that is definitely superior to current materials.

Colin Ophus of the National Center for Electron Microscopy facility of the Molecular Foundry says, “This work is an excellent example of the materials advances possible when we close the feedback loop between first principles calculations and atomic resolution electron microscopy.”

His colleague Jim Ciston at the Molecular Foundry adds, “The precision of the agreement between theory and experiment is critical to unraveling the subtle differences in structure between competing ferroelectric phases. These images of atomic positions are more than pretty pictures of remarkable precision, but contain an enormous amount of quantifiable information about the minute distortions in atomic positions that can lead to surprising properties.”

Additional coauthors on the paper, titled “Atomic Scale Imaging of Competing Polar States in a Ruddleston-Popper Layered Oxide,” were Nasim Alem, assistant professor of materials science and engineering, Penn State, Turan Birol, Fennie’s Ph.D. student now assistant professor at University of Minnesota, Che-Hui Lee, Schlom’s Ph.D. student at Penn State and Cornell, and Penn State staff scientist Ke Wang.

Support was provided through the Penn State Center for Nanoscale Science, a National Science Foundation Materials Research Science and Engineering Center (MRSEC), the Department of Energy and the Rutgers Center for Materials Theory. Work at the Molecular Factory was supported by the Office of Science, Office of Basic Energy Sciences, of the U. S. Department of Energy. Portions of the work were performed in the Penn State electron microscopy facilities in Penn State’s Materials Research Institute.

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Humanitarian
MATERIALS ENGINEERING
Stories about socially relevant materials engineering

Moringa Seeds and "Sticky Killer Sand" Work Together to Clean Water By Krista Weidner

(left to right) Andrew (Mike) Erdman (Walter L Robb Director of Engineering Leadership Program and Instructor), Stephanie Velegol, (Undergrad program coordinator and instructor), Andrew Maguire (CTO of Pivot Works), Matt Gantz (Director, Asili Oils), Emma Clement (PSU 3rd year student in Civil and Environmental Engineering), Adam Uliana (PSU, 4th year student in Chemical Engineering). All photos provided by Stephanie Velegol.

Lack of access to clean drinking water is a serious health problem in many developing countries, and often, even when methods for removing disease-causing microbes and sediment from drinking water are available, they are too expensive to be practical.

One traditional method for cleaning water in equatorial regions involves using seeds from the Moringa oleifera tree as a natural antimicrobial: When crushed seeds from the Moringa tree are added to water, they remove microbes and make the water safe for drinking. While this is an easy and accessible technique, it's not ideal because the water can become tainted again while in storage.

The Moringa seed cleans water by releasing a positively charged protein that dissolves in the water and removes pathogens. "The problem is the seed also contains oil and other organic matter that microorganisms in the water can use as food," explains Stephanie Butler Velegol, instructor in civil and environmental engineering. "So after it's been stored, water treated with Moringa seed is no longer safe to drink."

Several years ago, Velegol and her colleagues found that when they add sand, which has a negative charge, to water, the positively charged Moringa protein binds to the sand. When the Moringa protein and the sand bind together, the surface charge of the sand

images/bigstock

Moringa seed cake contains protein necessary for "killer sand."

Rwandan company Pivot Works turns fecal sludge into fuel.

reverses to positive. Pathogens and sediment then stick to this "f sand" (which stands for functionalized sand). "When we rinse the f sand, we are left with 'sticky killer sand' that we can use as a sustainable filter," Velegol says.

Now Velegol and her research group are taking their findings a step further, after receiving the Material Research Institute's inaugural Humanitarian Materials Initiative Award. Created last fall, the award is part of an initiative to support ongoing research aimed at providing long-term and sustainable solutions to problems in under-resourced regions of the world.

The team of scientists is using the $15,000 prize to fund four students, undergraduate and graduate, to do research toward improving the Moringa-coated sand filter.

One student's work in the lab resulted in making the sand/water/Moringa mixture more efficiently—

A "stick test" determines if the sand is charged.

reducing mix time from more than two hours to just ten minutes. "Our process for creating the sand filter involved mixing for two and a half hours, but that's way too long for someone doing this on the ground," Velegol says. "Knowing that we can reduce mix time to just ten minutes, and get the same result, is one important step toward making this technique much more practical."

She also discovered a simple field test for the reliability of the sand filter: the "stick test." When a Moringa

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Stephanie Velegol, (Undergrad program coordinator and instructor)

mixture is put into a plastic water bottle and the bottle is turned sideways and rotated, if the sand sticks to the side of the bottle that means the filter is working. "The sand sticks because the plastic has a positive charge," Velegol explains. "On the ground, the stick test is a quick way to confirm that a particular filter works. And in the lab, we confirmed that every time the sand has a positive charge, the stick test works." Although the stick test shows promise, Velegol emphasizes that more research is needed to ensure that lab results continue to match field results.

Two students are working this summer on creating a mathematical model to predict the filter efficiency and longevity. This will allow the filter to be reproduced under different conditions (e.g. sand type and size, quality of water) around the world.

The research team also used award funding to travel to Rwanda this past spring to extend their Moringa research focus beyond drinking water. They are collaborating with Pivot Works (http://pivotworks.co), a company working in Rwanda that turns fecal sludge into fuel. This sustainable process currently uses a cationic polymer to flocculate the sludge. The team worked with Chief Technology Officer Andrew Maguire to explore the possibility of replacing the polymer with local Moringa seeds to create the fuel much less expensively.

In searching for local growers of Moringa trees, Maguire discovered Asili Natural Oils (http://asilioils.com/), a company that grows the trees and sells the seed oil to personal care companies. "Of course, this company didn't want to compete with Pivot Works for Moringa seeds," Velegol says. "But we realized that when you squeeze the seeds to get the oil out, you end up with a byproduct–a seed cake–which is what contains the Moringa protein we need. It was great news that Pivot Works only needs the seed cake for their process. So if Pivot Works can buy the byproduct from Asili Natural Oils, it's a win all around. The students were so excited about this project and where it led us during our time in Rwanda."

Velegol is optimistic about the future of research on the Moringa seed. "We are linking hardcore science with humanitarian work," she says, "working on strengthening that link between lab research and people on the ground. So many of our undergraduate students have a passion for humanitarian work, and we need to get the message across that engineering helps make the world a better place. Our students want to make a difference–let's show them how they can do that using good science."

Stephanie Velegol's research colleagues include Manish Kumar, assistant professor of chemical engineering, Michael Erdman, director of Engineering Leadership Development in the College of Engineering, and Bashir Yusuf of Ahmadu Bello University, Nigeria. The Humanitarian Materials Initiative awards are sponsored by Covestro LLC (formerly Bayer MaterialScience LLC) and the Materials Research Institute.

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Convergence

Closing the loop between engineering and medical science

A Neurosurgeon and an Electrical Engineer Walk into a Lab

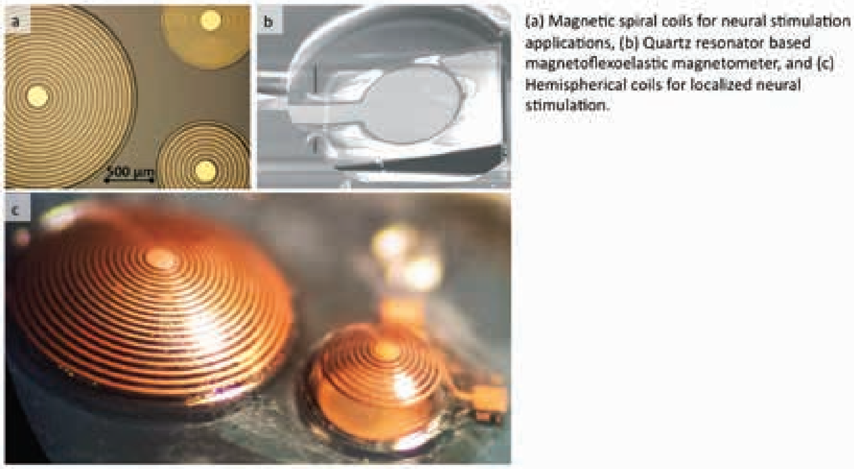
Eugene Freeman, Andrew Whalen and Herve Kadji with a screen image of a magnetic sensing coil. • Credit: MRI/Penn State

In Penn State's newest and most advanced research building, a new program is taking shape that, if successful, will revolutionize the ways in which we interact with the human brain. Led by Srinivas Tadigadapa, an electrical engineer, and Steve Schiff, a neurosurgeon with a background in physics and control engineering, this ambitious project exemplifies the convergence of research fields that are typically separated by distinct disciplinary boundaries.

In 2013, the Obama White House laid out a grand challenge to "accelerate the development and application of new technologies that will enable researchers to produce dynamic pictures of the brain that show how individual brain cells and complex neural circuits interact at the speed of thought." Called the BRAIN Initiative, it is a 12-year plan to fund research into understanding the brain on multiple levels, using a variety of new and developing technologies. With these tools, it is hoped that the many diseases and malfunctions that afflict the brain can be controlled or eliminated. Schiff and Tadigadapa recently won one of Penn State's two exploratory BRAIN awards.

A transdisciplinary team to solve a monumental problem

Steve Schiff has the soothing voice and gentle manner of someone who has spent a large part of his career dealing with children, and frequently, children



Hemispherical coils for localized neural stimulation are about half the size of a grain of salt. • Credit: Eugene Freeman/Penn State

in pain. As a pediatric neurosurgeon, he has lent his skills and bedside manner to treating diseases of the brain in children, but as a researcher he is adding another skill set, one based on his background in engineering and physics, to develop technology to understand and control diseases of the brain.

Schiff is director of the Penn State Center for Neural Engineering, a lab that takes up an entire floor of the Life Sciences wing of the Millennium Science Complex on Penn State's University Park campus. A series of card-swipe controlled laboratories make up the 11,000-square-foot Center, with facilities for the construction of custom electronics, live animal imaging, surgery, and advanced computerized microscopy. His Center colleagues include medical doctors, engineers and biomedical engineers, and the graduate students they are training.

In the Materials wing of the building in a basement micro and nanoscale devices laboratory, Tadigadapa's group is developing microelectromechanical systems (MEMS) that miniaturize device arrays for sensing and actuating, some of which the team hopes will one day be implanted into the human skull in order to explore the brain on a cell-by-cell basis.

Penn State's Millennium Science Complex was built with the concept of integrating the expertise of materials scientists, electrical and mechanical engineers, and nanotechnologists, who occupy the north wing of the building, with medical and biological researchers, who occupy the building's west wing.

"This building we are in reflects this interaction, because we are half materials science and half life sciences," Schiff said. "We will literally build these technologies on one side and walk them up the stairs to our lab where we do experiments on neurons. We will use individual neurons that we will be recording from and stimulating to see how far we can push this technology. We are, to our knowledge, the only center at present that is in a position to manufacture these high density arrays for sensing and stimulation in a nanofabrication facility and then literally transition them to an operating room."

The team also includes, as a consultant, John Wikswo of Vanderbilt University, who is one of the world's leading experts on magnetic fields in neurons. "John provides some of the key physics expertise that no one else in the world has," Schiff said.

In short, Schiff and Tadigadapa, with Wikswo's help, propose to develop a technology capable of measuring the activity of individual cells of the brain and to stimulate those cells at room temperature with a MEMS device capable of being implanted above the inner table of the skull for long-term human use.

Why stimulate the brain?

For the past 70 to 80 years, scientists have been using electrodes on the surface of the brain to measure electrical currents, and, since the 1950s, to stimulate the brain. In recent times, an approach called deep brain stimulation (DBS) was developed as a means to treat the tremors associated with Parkinson's disease. Now, DBS is being studied experimentally as a method to treat major depression, along with a variety of other ailments. In DBS, a pair of electrodes is implanted in the brain and a generator is surgically implanted in the patient's chest wall. A pattern of electrical pulses is used to stimulate portions of the brain. The treatment seems to work for a proportion of patients with major depression, although the exact mechanism is still unknown. Another use of such sensing and stimulation is to run robotics for patients with disabilities. However, bleeding, stroke and infection are potential side effects.

"If I put electrodes into the brain, which I have done a great deal in my career, there is a measurable risk of hemorrhage and damage, and there is always a few percent risk of infection," Schiff said. "If I'm studying a child for epilepsy, I need to take those things out by two weeks, definitely by three weeks, or I have to go in and free them from the scar that's already formed.

"Imagine you are trying to run an artificial hand," posited Schiff. "You want to pick up signals from the hand area of the cortex to give you the intention of the individual to move such a hand. We can only do that now by implanting arrays of electrodes into the hand area of the brain itself."

Because the bone of the skull is a good insulator, electrical signals from neurons in the brain cannot easily pass through it into the outside world. So the skull has to be opened up to place electrodes on the surface or deeper into the brain. This can and often does damage brain tissue and can cause infection in the cerebral fluid, potentially leading to meningitis. Furthermore, electrodes tend to corrode or be scarred over within weeks to a few years, necessitating more surgery.

An engineer steps in

A better choice would be to sense and stimulate the neurons without penetrating the dura, the covering that protects the brain from infection. That's where Tadigadapa steps in. He is exploring magnetic MEMS sensors and actuators that can record and stimulate the brain with non-contact techniques.

The Penn State team will attempt to stimulate single neurons with a magnetic field that creates an electrical current in the individual brain cell. Stimulus is actually easier than recording, according to Tadigadapa. He and his engineering team are creating tiny coils that can deliver a localized stimulation to cells. Eugene Freeman, a Ph.D. candidate in Tadigadapa's lab, is working on the coil approach.

"Usually what people do to stimulate neurons is to have very big coils that go outside the head," said Freeman. "They're not implantable. They're about the size of your fist, so you have to go in to a lab for the treatment, which is called transcranial magnetic stimulation (TMS). These large magnets activate a relatively large part of the brain. You can't get single neuron specificity. We are experimenting and simulating microcoils in different sizes and shapes, the smallest so far being about 500 microns in diameter (about half the size of a grain of salt). We use microglass structures and pattern 3D copper coils on them."

The ability to do three-dimensional fabrication is a recent development, Freeman said. "We are just looking to see if that might be a better way to do it than just a flat coil."

Currently, the only magnetic sensors sensitive enough to detect the magnetic waves of the brain either need to be cooled to liquid helium levels in a device called a SQUID or heated to 180 degrees C to vaporize metals in a device called an atomic magnetometer. Neither technique is suitable for outpatient sensing and stimulation. So, recording of neural activity that is not potentially damaging to the brain either doesn't have cellular resolution, requires shielded rooms, or cannot be performed at safe temperatures. A recently developed third method uses a synthetic diamond material with random nitrogen vacancies to pick up very small magnetic fields, but that requires using microwaves – like the ones in a kitchen microwave – which have a tendency to cook things in the vicinity. Not an optimal solution.

Blocking the Earth's magnetic field

In order to make an implantable sensor to detect magnetic fields in the brain, something has to be done about Earth's magnetic field. Tadigadapa proposes to build active and passive circuits on a CMOS microchip that will cancel out magnetic noise using a simple feedback loop, the same technique used in noise cancelling headphones. The microdevice will generate an on-board magnetic field within the MEMS chip that will compensate for the Earth's magnetic field and other interfering magnetic fields in the nearby environment. Other circuits in the implantable chip will amplify the magnetic signal from the cells.

"The Earth's magnetic field is around 60 microTesla," Tadigadapa said, "and the magnetic field of the human brain is around a picoTesla (around 60 million times weaker). So there is need to block Earth's huge magnetic field. Currently that is done within an isolated room that costs $10 million to build, plus the cost of the SQUID itself and the high cost of liquid helium to cool the device. We hope to be able to do it with an on-chip circuit."

"We have a number of designs that Srinivas is going to be placing on these chips. Unlike in the past, these things can be implanted in the body. They are ambient, which means they assume the temperature of their surroundings, rather than freezing them by being dropped into liquid helium. And when implanted, they will allow us to take this technology out of the laboratory for the use of people in an ambulatory setting," Schiff said.

"It's a good technical challenge," Tadigadapa remarked with patent understatement.

Who benefits from this technology?

"Many of our colleagues in surgery and neurology are very excited that we can do this. At Hershey (Penn State Milton S. Hershey Medical Center), we are working with patients in the ALS clinic. We're keenly interested in improving our ability to let patients communicate as they lose their strength. We are also interested in their ability to control their environment robotically. That's more of an issue of sensing," Schiff said.

"If I have someone like one of our young veterans who has lost an arm, you want him or her to be able to run a prosthetic device for 50 years. You need to be able to maintain the device, not damage them any further (through repeated brain surgeries), and importantly, you need a way to give sensory feedback to the brain. This is a way to interact with the brain and to give it signals reflective of what a prosthetic is sensing as it touches something.

"I've worked in epilepsy for most of my career," Schiff continued. "This is a way to potentially not only sense from a part of the brain that makes seizures, but to modulate the activity to prevent seizures. We've shown that we can stimulate parts of the brain to improve depression and Obsessive-compulsive disorder. One of the major thrusts of the BRAIN Initiative is to get a better understanding of the major cognitive disorders."

The economic impact of very common cognitive disorders, such as depression, which affects 17 percent of the population of the U.S., is tremendous. The technology could also address the communication needs of people with spinal cord injuries, ALS or strokes, and of course, would benefit people who have lost limbs.

When will we have this technology?

Schiff and Tadigadapa hope to make rapid progress. Their recent work on magnetoflexoelastic resonators has demonstrated sensitivity in the tens of nanoTesla and on magnetoelectric magnetometers has achieved ~300 picoTesla sensitivity, all at room temperature. The resources of the Penn State Nanofabrication Laboratory will make it possible to make very thin, high-density arrays of sensors and stimulators. Initial testing will be conducted on rat brain slices in vitro to understand the strength of signals and the magnetic field strength required for stimulation. There are billions of neurons in the brain, not to mention many other types of cells that are also important. They will need to develop mathematical filters that can distinguish one cell from another.

They will also learn whether it is necessary to use single cells or whether they can work with a few cells. A lot of basic science will result from the first couple of years of work.

"The first chips will probably be on the scale of a centimeter for the part of the chip that just does sensing," Schiff said. "For implantation the scale we are targeting is 100 micrometers. We won't be submillimeter for the array the first two years. This is a new technology grant where we've shown we have enough technical advances now that with this support we can go to the next stage of iterating electrical engineering and nanofabrication of devices with experiments."

He expects that the first devices will be placed against the skull, rather than inside, due to the amount of electronics and chip packaging necessary. A wireless transmitter and receiver is also needed. When the electronics packaging issue is solved, Schiff expects to have a biocompatible array that can be placed in a small trough inside the skull where it can be maintained or replaced as needed.

"I think we are looking at a five-year time horizon to the point where we could seriously have the technology ready for application and potential translation testing," Schiff said.

Andrew Whalen, a Ph.D. candidate in mechanical engineering, and post-doc Herve Kadji are working with Schiff to prepare brain slice experiments using the micro-magnetic coils that Eugene Freeman has designed to stimulate neuronal tissue. Through these experiments they hope to understand the fundamental mechanisms of magnetic stimulation on neuronal excitability.

"Magnetic stimulation has some nice advantages over traditional electric stimulation, which has many complications due to the electro-chemical interface between electrode and tissue," Whalen explained. "Magnetic stimulation in theory should bypass these issues with electrical resistance interfering with stimulation transmission and the formation of scar tissue in long term stimulation implants."

"Implantable Brain Microelectromechanical Magnetic Sensing and Stimulation (MEMS-MAGSS)" is a $450K opening grant, funded over two years by the National Institutes of Health to show the feasibility of the technologies, with further possible funding. Peng Li in psychology has the other Penn State BRAIN grant. A patent for this work is pending.

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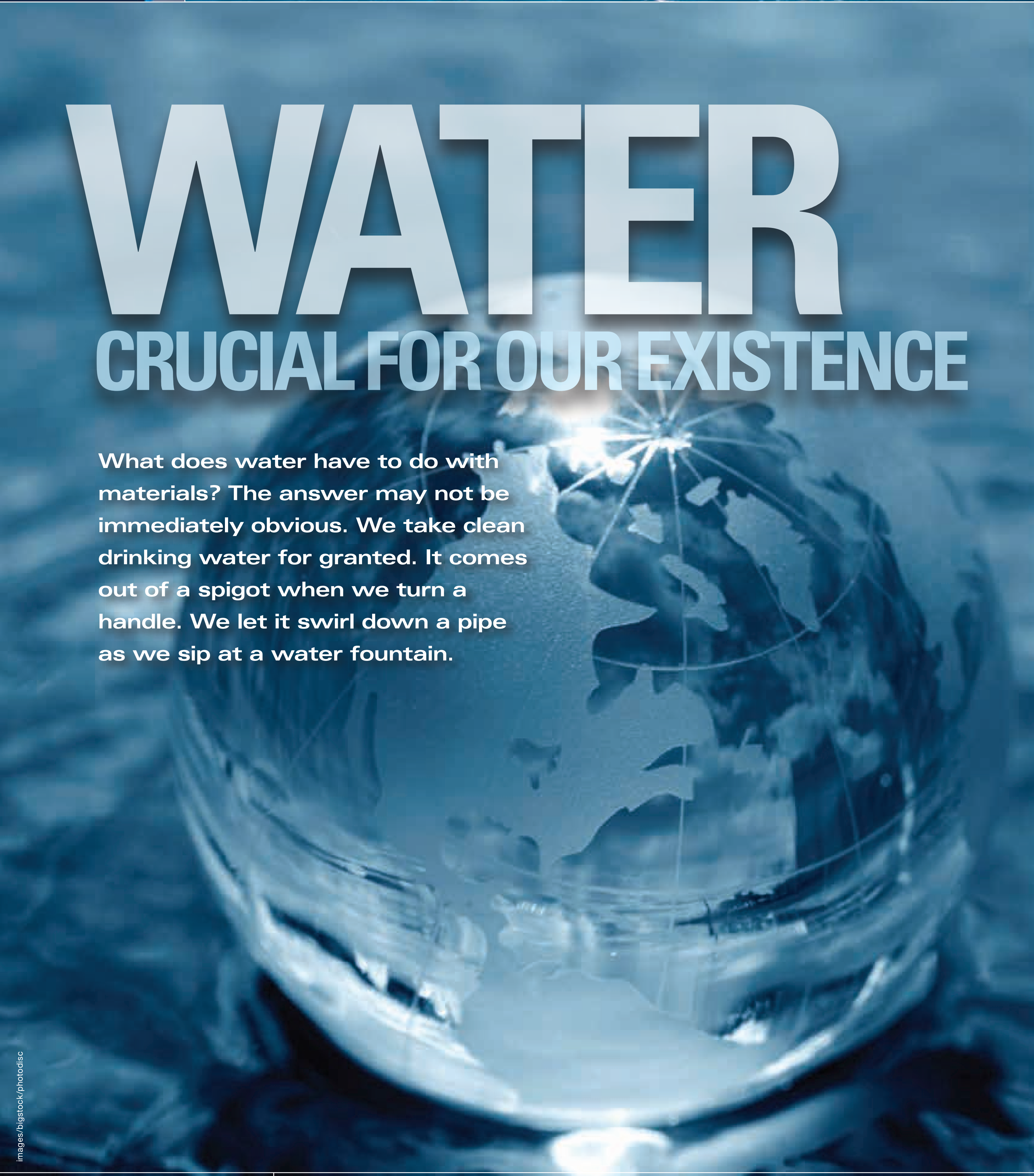
WATER

CRUCIAL FOR OUR EXISTENCE

What does water have to do with materials? The answer may not be immediately obvious. We take clean drinking water for granted. It comes out of a spigot when we turn a handle. We let it swirl down a pipe as we sip at a water fountain.



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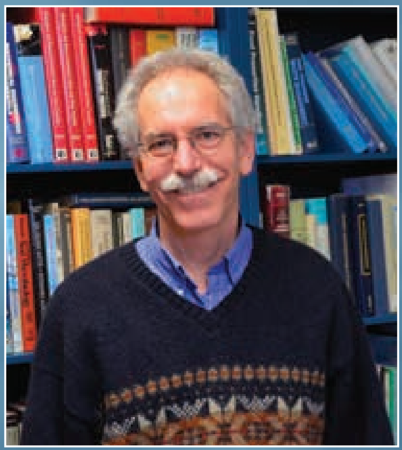
Fresh water is a renewable resource, but not always available where it needs to be. When the demand for water outstrips the supply, the result is water stress. With climate change affecting weather patterns and the growth in demand for readily available clean water as developing nations industrialize, water stress is predicted to seriously impact the warmer regions of the world, including some of the most volatile nations around the globe. The World Resources Institute ranks the most at-risk countries for water stress by the year 2040, and the list includes Palestine, Iraq, and Syria. Water shortages for irrigation in Syria were likely instrumental in destabilizing that country. The U.S. Southwest and areas of China are also predicted to face increased water stress.



Tom Richard
Photo credit: MRI/Penn State

We live on a water planet. All living things have water-based chemistry, making water crucial for our existence. So says Tom Richard, director of the Institute for Energy and the Environment at Penn State and professor of agricultural and biological engineering.

"In our world today, climate change is a major concern, and the way we interface with climate change is almost totally around water," he says.

Rising temperature is important, he continues, but it is also about droughts and floods, about our ability to use irrigation for food, having water for energy. Water cuts across the climate space, the food space, even energy. We don't normally equate water and energy, but we need water to cool all of our power plants: nuclear, coal, gas."

Food-energy-water nexus

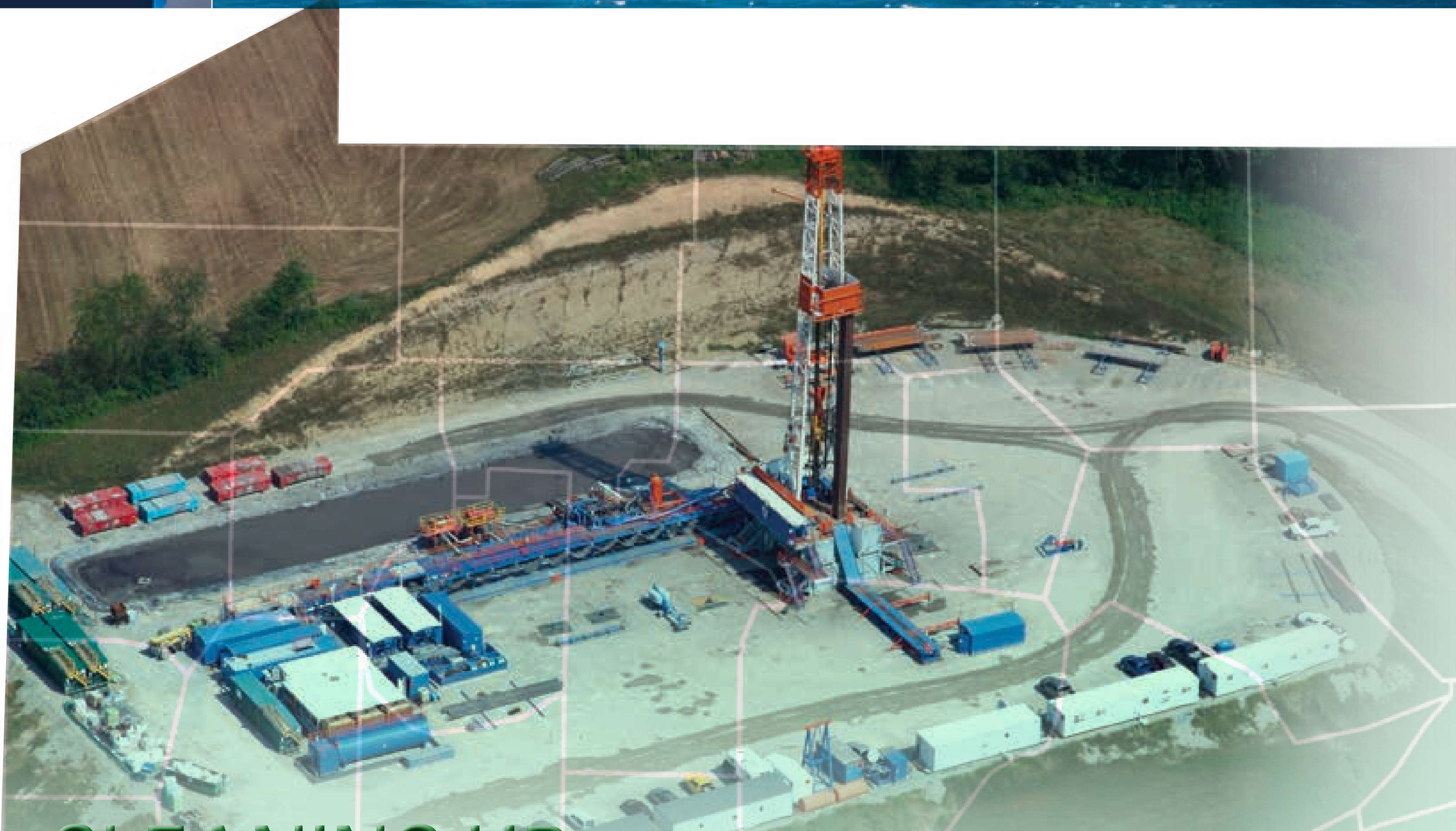
The National Science Foundation has made the food-energy-water connection a major interdisciplinary theme through a $75 million program called INFEWS for Innovations at the Nexus of Food, Energy, and Water Systems. According to NSF, "The overarching goal of INFEWS is to catalyze the well-integrated interdisciplinary research effort to transform scientific understanding of the FEW nexus in order to improve system function and management, address system stress, increase resilience, and ensure sustainability."

Water U.?

While Penn State is currently staking a claim to the title of The Energy University, a strong argument could be made that we are at least as much Water U. Across the university, researchers are deeply immersed in water research, trying to solve the kinds of problems in water management, pollution control or mitigation, climate forecasting, and desalination that affect our nation and world.

Again, according to Tom Richard: "We are in the top 20 universities in terms of our research in water. Among those top 20, our researchers have the highest citation per publication. That's an indication of the quality of our work, because other researchers think it is important enough to cite. In fact it's not even close. Our ratio of citations to publications is 20 percent higher than anybody else in the top 20. It's out of the park quality."

This issue of *Focus on Materials* will highlight a few of the MRI faculty working in materials-related water research.



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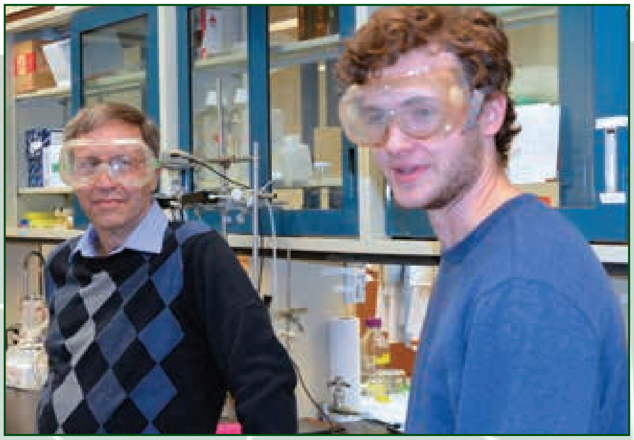
CLEANING UP PENNSYLVANIA'S POLLUTED FRACKING WATER

Forty of Pennsylvania's sixty-seven counties are involved in the production of natural gas through the controversial practice of hydraulic fracking, the process in which a mixture of water and chemicals is driven at high pressure into deep wells to make horizontal fractures in shale rock, releasing trapped gas.

Andrew Zydney is Distinguished Professor of Chemical Engineering and an expert in membrane science, membrane transport phenomena, and membrane technologies for the purification of therapeutic molecules. He is co-PI, with his chemical engineering colleague Manish Kumar, on a project to assess the possibility of using membranes to clean up the water that results from hydraulic fracturing in the natural gas drilling operations in Pennsylvania's Marcellus shale play.

"We're trying to establish if membranes are a feasible solution," Zydney remarked about the fracking wastewater, which is a complex mixture of the chemicals added to the water and the organic and even radioactive material that is brought up from underground. "Could we do this in a way that the membranes last long enough and have enough capacity to filter billions of gallons of fracking wastewater? The reality is that unless regulations are in place, companies are going to take the lowest cost approach, which is



Andrew Zydney in the lab with Neil Butler (Undergrad, Chem. Eng.)

often just trucking the water and disposing of it in deep injection wells."

Each natural gas well uses between 2 billion and 7 billion gallons of water. A portion of that water comes back to the surface, contaminated with high levels of salt, as well as some of the 700 chemicals listed as being used by fracking companies. The first step in cleaning the water is to remove the particulate matter. If the particles are not removed first, they will interfere with subsequent purification processes, for example by fouling the pores of filtering membranes. Zydney's team has been studying the behavior of microfiltration membranes with pores sizes around 200 nanometers as a way to remove much of the particulate matter from frack water.

"We are looking to understand the interactions between the membranes and the different chemicals in fracking wastewater. We are also examining surface modifications of the membrane that might enable them to be less sticky, as well as different geometries and different flow patterns that might let you wash the membranes periodically," he said.

Membranes separate primarily on the basis of the size of their pores. For water treatment, there are multiple stages of filtration using multiple size pores. Membranes with large pores in the 1/10 micron to one micron range are used to remove bacteria such as Giardia from water. To remove viruses, a much smaller pore size is required, on the order of tens of nanometers to a single nanometer. Even smaller pore size membranes can remove small organic molecules and salts.

Why are membranes so expensive?

"There is a lot that goes into making these membranes. They are very thin films and you have to control the pore size very carefully. The base material is a commercial polymer and is not that expensive. But it does require relatively expensive processing," said Zydney.

If the pore sizes are not uniform, the water and whatever is being filtered will tend to migrate through the largest (and least selective) pores. And because the membranes need to be thin in order for large volumes of water to be filtered, they have to be supported mechanically and carefully sealed in a module. All of this adds to their cost.

Membranes for desalination

In the Middle East, much of the water used for drinking and irrigation comes from the desalination of sea water. Even in the U.S., in San Diego, a new $1 billion membrane desalination facility opened in December 2015 to provide a drought-proof supply of drinking water to residents of San Diego County.

But it is expensive to make potable water in this way, 100 to 1,000 times more expensive than the water that comes out of our taps in Pennsylvania. In desalination membranes, the pore sizes are much smaller than the microfiltration pores that Zydney typically studies. Consequently, it requires much more power to push water through these pores, with operating pressures around 500 psi. Pressurizing large quantities of water to 500 psi requires large amounts of energy.

"If you live in an area with insufficient clean water, the cost of desalination is a problem," Zydney said. "If we could make the membranes less expensive, and if the energy costs were more manageable, we could use membrane desalination anywhere in the world."

Because water is generally available in the U.S., we tend to be wasteful. Take the design of a typical water fountain. Only a small fraction of the water is drunk, with most going down the drain. But only around 3 percent of the world's water is drinkable, and a time may come when a growing population and increasing pollution make water too valuable to waste. The water crisis in Flint, Michigan, and other municipalities with lead contamination highlights the crucial importance of clean water.

"We have membranes today that can pull the lead out of the Flint water," Zydney noted. "It just comes down to cost. The cost of water is typically so low that we don't even think of the water we waste."

Zydney's group doesn't make the membranes that they study. Instead they let people in industry supply them and work with those membranes to see if they can improve their performance. He has also begun working with Mike Hickner's group at Penn State, which does make membranes, on the fracking water problem.

Zydney's group also has an emphasis in bio-processing, with a focus on the purification of therapeutic molecules used to treat cancer and many genetic disorders. Drugs that are produced in some type of genetically modified organism have to be purified to incredibly high levels before they can be used safely.

"If there is any foreign protein, bacteria, viruses, any of those impurities, the drug can potentially cause side-effects that are worse than the benefits the therapeutic molecule provides," he said. "A lot of our work is at the interface of membrane science and the application of that technology to the production of high value biological molecules."

What's next?

Zydney will continue working on frack water treatment. They began their work with a tremendous number of unanswered questions about what kinds of pollutants the water contained and which were most important or problematic in terms of treatment. "We began this work only about a year ago with very little information available about what in this mix was important for water treatment," he said. "We wanted a fundamental understanding of what were the characteristics that made this water unique in terms of membrane processing."

A key insight they have developed is that looking at the individual components in membrane filtration is not sufficient. It is essential to look at interactions between the various components in order to truly understand the behavior of the water in the filtration process.

Now, with a reasonable understanding of the complex system, the next step is to use that knowledge to design better membranes and membrane processes that can be used in the field.

"We think we are getting closer to a position where we could say that if we had a membrane with this type of surface properties and this pore size, it would perform better than what is currently being tried," Zydney said.

With some 1.4 billion gallons of wastewater produced in just the Marcellus gas fields, a lot of precious water is simply going down the drain.

Contact: Andrew Zydney, zydney@engr.psu.edu

A worker monitors drilling equipment at a shale gas wellhead.

image/photodisc

A box of transuranic waste is removed from an underground storage trench at the Hanford Site. Photo credit: U.S. Department of Energy

CAN SYNTHETIC CLAYS SAVE A WORLD AWASH IN POLLUTION?

(Or will these potentially life-saving technologies never make it out of the lab?)

Five years after the earthquake and subsequent tsunami that caused the partial meltdown of the Fukushima Daiichi nuclear power plant, more than 10 million bags of contaminated topsoil sit in radioactive pyramids scattered across the landscape. Contaminated water flows through the radioactive ground into the ocean or is captured and stored on the power plant site until some method of disposal can be figured out.

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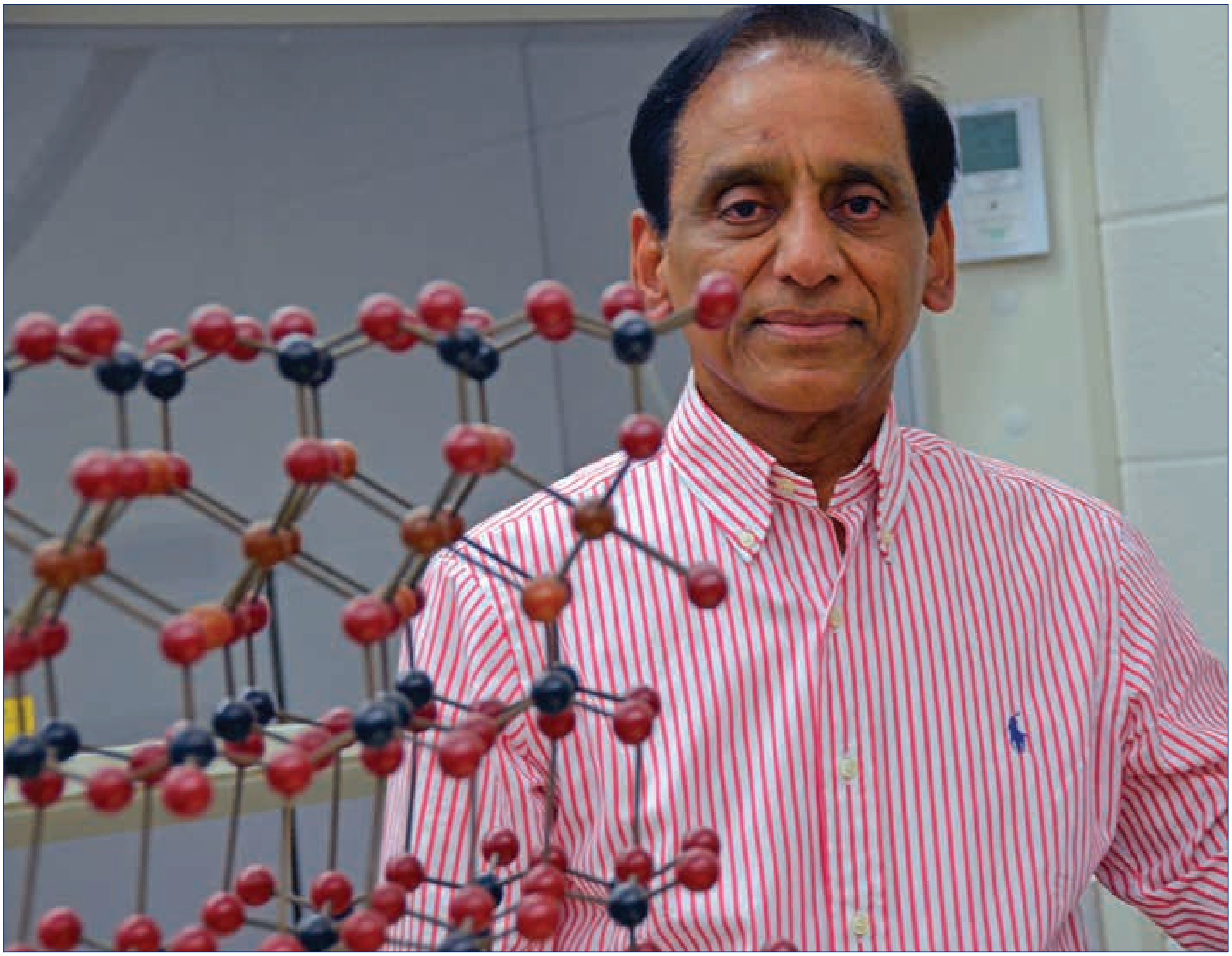


Sridhar Komarneni, materials scientist and Distinguished Professor of Clay Mineralogy
Photo credit: MRI/Penn State

In a series of high profile journal articles published over the past 30 years, Sridhar Komarneni has explored ways to remove radioactivity from the environment. A materials scientist and Distinguished Professor of Clay Mineralogy, Komarneni develops specially structured synthetic clays capable of immobilizing radioactive species by ion exchange.

"When I came to Penn State we had a large program on nuclear waste disposal. Even before that I was at Wisconsin for my Ph.D. working on a Department of Energy program involving selective uptake and fixation of cesium, strontium, and other ions," Komarneni said. "There were many people working in the field, including Rustum Roy."

Roy, a noted Penn State materials scientist who died in 2010, coauthored a 1988 paper in the journal *Science* with Komarneni describing the selective uptake of cesium (137Cs), a radioactive contaminant that was widely dispersed through the environment in the Chernobyl nuclear reactor accident. The material they used to make what they called a cesium ion sieve was a natural mica that they processed though low-temperature leaching to make a structure that was ideal for the exchange and chemical immobilization of cesium at room temperature.

"With nuclear waste solutions, you have so many species, the most dangerous of which are cesium and strontium," said Komarneni. "At that time we mostly worked on cesium. None of the naturally occurring materials were very good at strontium uptake."

Komarneni continued his work on cesium, this time with Della Roy, the wife of Rustum and an expert on cement. The material they studied was tobermorite, a phase that forms when zeolites interact with cement. At that time, there was interest in disposing of radioactive materials by mixing it with clay and depositing it in deep boreholes in the earth, which were then filled in with a mixture of backfill materials and cement. However, when the clays interacted with cement and formed the tobermorite phase, the cesium was released into the environment.

Komarneni and Della Roy developed a synthetic tobermorite in which the silicon atoms were substituted out with aluminum atoms. This material turned out to be a much better cesium exchange material and much more stable in cement. They also published their results in the journal *Science*.

"Then our sights turned to strontium uptake, because that was not yet possible until we began," Komarneni recalled.

Tanneries in Nepal, Bangladesh, and India, where many tanneries are found, dump their industrial wastes directly into rivers where they can leak into soil and groundwater. People also drink and swim in the polluted waterways and use the water for washing and cooking. Some 17 million people are estimated to be at risk.

They based this new research on a novel material called brittle micas discovered by a group in Spain. Komarneni was excited by the Spanish researchers' paper because he realized the special structure of their brittle mica could be used as a potential strontium selective material.

"The material they had made was not very good for exchange applications because they were in large flakes, and that meant diffusion took forever. The flakes were large enough to determine the structure, but too large to be useful," he said.

Their synthesis method also resulted in minute quantities of material.

Komarneni, Rustum Roy, and William Paulus, the latter Komarneni's MS student now at General Motors, developed a synthesis method that could be easily scaled up and that produced small particles of Na-4-mica that selectively exchanged strontium ions and locked them up in holes at room temperature.

"We made the almost perfect material and characterized it thoroughly," Komarneni said. "Then we studied many ions to get clues about the mechanism of ion exchange. We discovered that this material is extremely selective for copper, strontium, barium, and radium. This was the beginning of our work on synthetic clays."

They published their findings in the journal *Nature*.

Radium in drinking water, copper in soil

Many locations in Pennsylvania, and also around the world, have problems with wells and groundwater contaminated with naturally occurring uranium.

"It's the radon problem," said Komarneni. "Wherever there is radon, there is radium. It's a huge problem in some wells and water systems."

In a paper published in *Nature* in 2001 titled "Superselective clay for radium uptake," Komarneni and collaborators Paulus, and Naofumi Kozai of the Japan Atomic Energy Research Institute tested a variety of synthetic micas and natural clays to determine their capacity to exchange radium and fix it for disposal. They tested the materials in a solution containing a million times more sodium than radium and found that their synthetic micas were highly selective for radium. They had the results analyzed using radioactive radium in a Japanese facility by a former student of Komarneni who had returned to Japan. Their materials were by far the best at taking up radium, Komarneni said.

They also proposed their clays for water systems in Wisconsin that had problems with radium, but no one took it up.

The same material was applied to copper-contaminated soils in Chile. Copper, too, is toxic in large quantities, and Chile has the largest copper mines in the world. Heavy metals accumulate in plants, and in animal and human tissue and are known to be carcinogenic. In 2005, Komarneni's student, Jason Stuckey, along with Chilean researcher Alexander Neaman, field tested their clay on contaminated soil near copper mines. They mixed the clay with the copper contaminated soil, and the clay soaked the copper out of the clay and fixed it in place, resulting in soil in which crops could grow without taking up copper and clean ground water.

The big cleanup

A legacy of the nuclear weapons industry in the U.S., the Hanford Nuclear Reservation in Washington State contains 53 million gallons of high-level radioactive waste, 25 million cubic feet of solid radioactive waste, and 200 square miles of contaminated groundwater. In April 2016, a serious leak was discovered in one of the 177 underground tanks containing the waste. Although no waste leaked into the environment, the failure of the tank was alarming, as the Hanford site is near the Columbia River. Already, 1 million gallons of liquid waste has leaked into the ground, threatening fish, wildlife, and Native American habitat.

The Hanford site is in the midst of the largest environmental clean-up in the U.S., a project that has been ongoing for 25 years and is expected to continue for decades more. The same material was tested by Komarneni and colleagues at Hanford with actual well water contaminated with radioactive radium, and they compared the clay with the best commercial materials available at Hanford. Their results showed that Komarneni's clay was superior to existing commercial materials by 4 to 5 times and could be used to help clean up the Hanford site, Komarneni believes.

"After Fukushima, we got interested again in cesium, because the most volatile contaminant in radioactive materials is cesium," he said. "And that spread a couple of hundred kilometers across Japan. Strontium is not so volatile, so it is closer to the accident site."

Recently, Komarneni's group discovered a new material, tin phosphate, which has excellent cesium uptake properties, especially in the highly acidic solutions that were used to extract cesium from contaminated soils of Fukushima. The Japanese government has begun using a commercially available synthetic zeolite-like material called crystalline silico-titanate invented by researchers at Sandia National Lab and Texas A&M University in the '90s and licensed to a division of Honeywell to remediate the site.

Komarneni, Wenyan Huang, a visiting scholar from China, and others tested their tin phosphate material against silico-titanate and found tin phosphate was far better at cesium uptake. Those findings were published just last year in *Chemical Communications*.

"The idea is somebody will have to produce this. We don't have any commercial product. We showed clearly that our material is better. The higher the acidity the better our material performs, because it is stable under highly acidic conditions," Komarneni said.

Pollution in India and China

There are big problems with soil and water pollution around the world, but especially in the developing countries, including India and China. For example, in China there is heavy metal contamination in many locations from unregulated industry. There are some 459 so-called cancer villages spread across almost every province in the country, in which large clusters of cancer deaths occur. Cancer rates overall have increased by 80 percent over the past three decades, attributed to air pollution in cities and the pollution of rivers and lakes in the countryside. In India, heavy metals such as lead, cadmium, and chromium have been found in the groundwater of 113 districts.

"In China, there is also dye pollution in rivers. We are working on all of those things," Komarneni said. "For example, we are working on photocatalytic decomposition. We are developing materials that can be used for destroying these organic chemicals in dyes using only visible light."

Most heavy metals are cations, meaning they have a positive charge. Many materials are available to remove cations, he said, because they are easier to take up through ion exchange. Anions, or negatively charged ions, are much more difficult to deal with. Anions are very mobile in soil, air, and water; many toxic species are anions.

One example of a toxic anion is chromium or its anion chromate. Chromate is a product of leather tanning, where it is used to dilapidate hides, and is commonly used in several other industrial processes. Chromate and chromium poisoning is a wide-spread problem in many developing countries. Tanneries in Nepal, Bangladesh, and India, where many tanneries are found, dump their industrial wastes directly into rivers where they can leak into soil and groundwater. People also drink and swim in the polluted waterways and use the water for washing and cooking. Some 17 million people are estimated to be at risk.

"For chromate, we are developing ion exchange materials for removal from drinking water and waste water," Komarneni said.

They have also developed what they call clay organic nanocomposites that can be used for the removal of anions like chromate, arsenite, arsenate, and especially perchlorate.

Perchlorate in America

Perchlorate is made up of one chlorine atom bonded to four oxygen atoms. Perchlorate affects the thyroid gland, causes endocrine disruption, and is a likely carcinogen. Used in explosive materials and rocket fuel as a propellant, perchlorate pollution has been found in Lake Mead in Nevada and in the Colorado River, the water resources for a large part of the Southwest.

Perchlorate is a major issue in Redlands, CA, where an underground plume of contaminated groundwater has affected the drinking water supply and closed water wells. The soil is contaminated with perchlorates from decades of pollution by a defense contractor making rocket fuel.

"There they are using surfactant-loaded activated carbon to treat drinking water," Komarneni said. "They have columns of activated carbon and they percolate water through them to remove perchlorate."

However, this method has drawbacks, because there is not a strong chemical bond to lock the anions in, and some of the perchlorate can leach out into the water along with the surfactants. Instead of that method, Komarneni is proposing to use clay organic complexes, which can also remove the perchlorate successfully while also locking it up inside the clay structure.

"We are developing these cost effective materials that can also be used for water treatment or wastewater treatment," Komarneni said.

Stuck in the lab

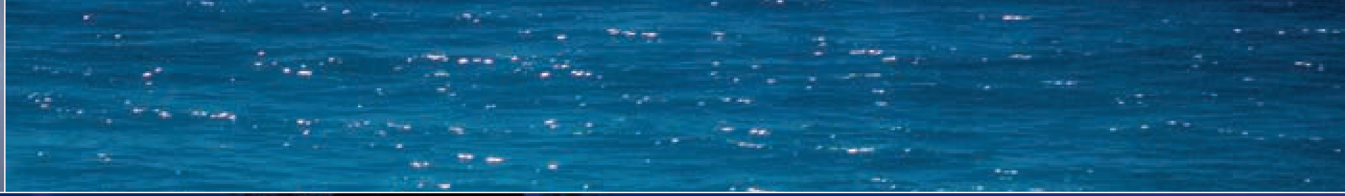
Komarneni is at a loss to understand why his discoveries have not been taken up by the U.S. government, which funded most of his research, or other governments he has tried to interest, including Japan and China.

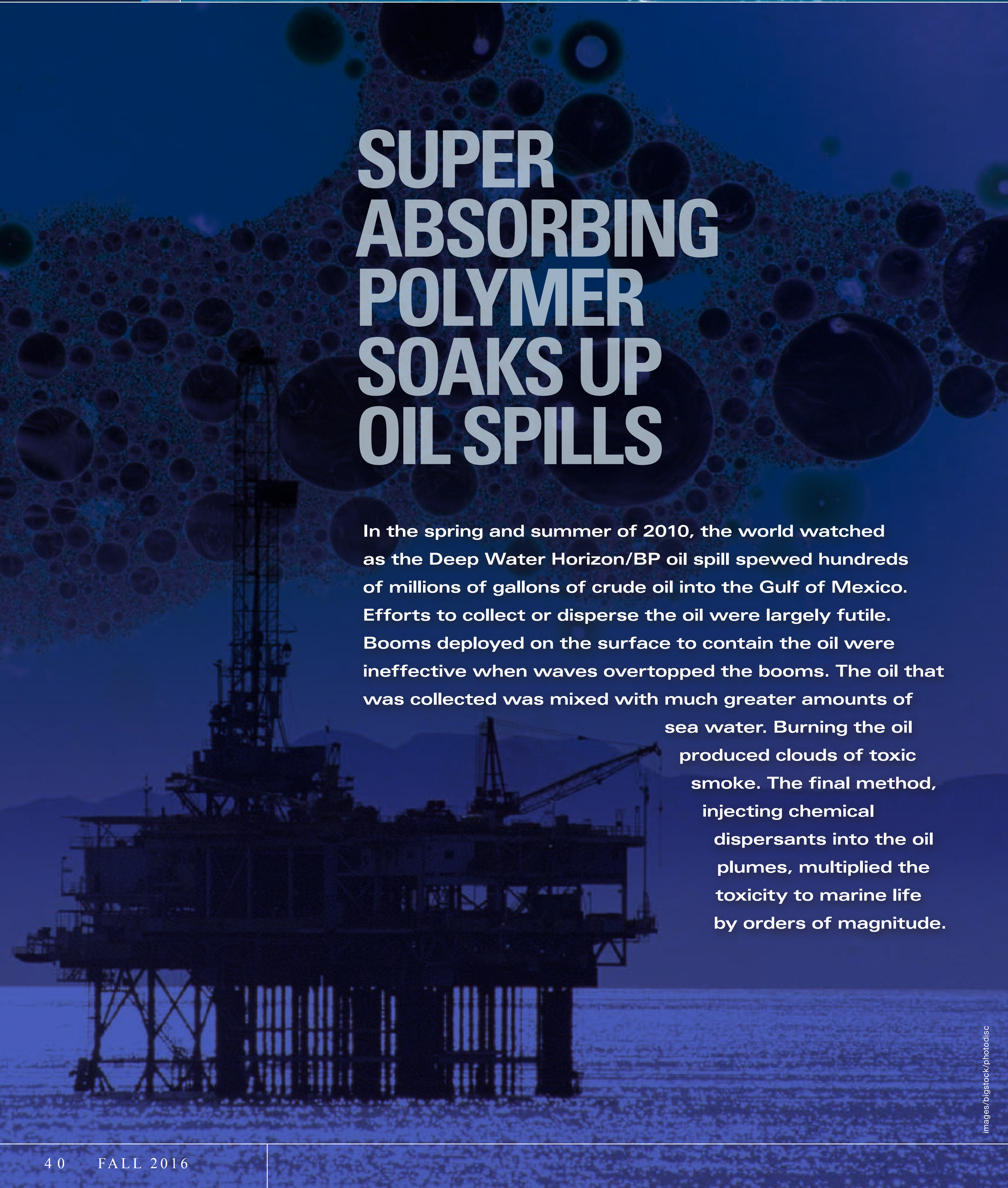
"A government official of Jordan asked me to provide them with a pound or two, but we don't make large amounts. I don't understand why the Japanese didn't take this up. They already make synthetic clays for things like cosmetics. They could do it easily," he said.

Maybe it's because they are too expensive?

"No, it shouldn't be expensive. Natural clays can be used very easily to make synthetic clays," he said. "Unless I start a company myself, I doubt this will ever go out of the lab."

Contact Sridhar Komarneni at sxk7@psu.edu.





SUPER ABSORBING POLYMER SOAKS UP OIL SPILLS

In the spring and summer of 2010, the world watched as the Deep Water Horizon/BP oil spill spewed hundreds of millions of gallons of crude oil into the Gulf of Mexico. Efforts to collect or disperse the oil were largely futile. Booms deployed on the surface to contain the oil were ineffective when waves overtopped the booms. The oil that was collected was mixed with much greater amounts of sea water. Burning the oil produced clouds of toxic smoke. The final method, injecting chemical dispersants into the oil plumes, multiplied the toxicity to marine life by orders of magnitude.

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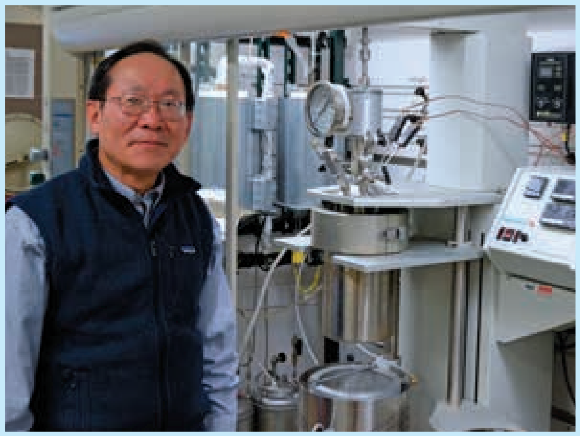
Ohmsett research facilities in Leonardo, New Jersey
Photo credit: U.S. Federal Government



Mike Chung
Photo credit: MRI/Penn State

Mike Chung, a Penn State materials scientist, was as riveted by the unfolding drama as the rest of the world. "It was a disaster," he recalls. "There was no solution."

Chung had worked as a scientist for the Exxon Corporation during the time of an earlier disaster, the grounding of the Exxon Valdez on a reef in Prince William Sound in Alaska in March 1989. The oil ended up coating 1,300 miles of coastline and 11,000 square miles of ocean. Even after almost thirty years, if you dig a few inches into the shore, oil will still seep up out of the sand.

Exxon, too, tried using dispersants, but they were too toxic and eventually, Chung says, they cleaned up what oil they could with the equivalent of paper towels and left the rest. Although the Exxon Valdez oil spill was a major disaster that effected the livelihood of thousands of fishermen, it is ranked as only the 36th largest oil spill on record.

As he watched the BP disaster unfold, Chung asked himself how materials science could help, how *he* could help. In 2010, he and his research group began to work on the problem.

Chung and post-doc Xuefeng Li • Photo credit: MRI/Penn State

The making of Petrogel

Despite advances in so many other fields of modern science, the same largely ineffective methods for cleaning up oil spills are still in use today as at the time of the Exxon Valdez disaster: capturing the oil in booms, burning the oil, or using dispersants to break up the oil to be consumed by microbes. All of these were tried in the Gulf, with mixed success. It is estimated that less than 25 percent of the oil was recovered, and that oil was a mixture that contained 90 percent seawater.

Chung envisioned a synthetic material that could absorb oil while rejecting water. He thought of it as a super absorbing polymer (SAP) similar to hydrogel, the SAP material used in diapers. Only his SAP would be designed to absorb hydrocarbons with different compositions.

"We are polymer chemists," says Chung. "We can use a component from oil – polyolefin – that has a natural affinity for oil."

Petrogel can be made in the form of powder, flakes, or as a film. As it soaks up oil molecules, it turns into a gel. Within two hours, the oil/Petrogel mixture can expand 30 times. Within 24 hours, it will expand 40 times. In comparison, the best oil absorbant material on the market can only absorb 10 times its weight in 24 hours, and it is far more expensive than Petrogel is projected to be, Chung says. In addition, the fast absorption kinetics allows Petrogel to absorb the oil before evaporation.

One pound of Petrogel is expected to cost about $2, but can recover 6-7 gallons of oil. Even at $30 per barrel, Petrogel can collect more than enough reusable oil to pay for itself twice over. Unlike other oil absorbing materials, Petrogel can itself be converted to oil at a temperature of 350 degrees C, well below the 600 degrees C temperature of typical oil refining. Under mass spectroscopy, recovered oil and crude oil look the same, says Chung.

Undergoing testing

The Bureau of Safety and Environmental Enforcement is an agency of the Department of the Interior charged with regulating the safety and overseeing the oil-spill response plans of the off-shore oil industry on the U.S Outer Continental Shelf. The BSEE works closely with sister agencies such as the U.S. Coast Guard and the Environmental Protection Agency to develop technologies and capabilities to enhance oil-spill response.

In fall 2015, BSEE tested Petrogel in small 10x10 foot tanks tank at their Ohmsett research facilities in Leonardo, New Jersey, using Alaskan North Slope crude oil. In the BSEE funded project, two types of Petrogel were studied for viscosity change and basic rheology – how a fluid flows and spreads. This will determine how well the oil/Petrogel mixture will flow in mechanical pumping.

The testing showed that both mixtures of the polymer Petrogel absorbed more than 30-40 times its weight in oil within two hours. Mechanical testing showed that fluid recovery from the water's surface was possible using a skimmer, either with or without a pump attached.

The next step is to do a simulation under arctic conditions. This testing will take place in Ohmsett's mile-long 2.6 million-gallon salt water testing tank in December 2016. In this tank, waves and frigid weather will simulate conditions in the Arctic Ocean. Chung is still working to scale up to the 250 lbs. of Petrogel the testing will require.

Just the beginning

Crude oil from different parts of the world are different from each other. Chung's team designs formulations specific to a particular type of oil. His designs work well with both Alaskan and Gulf oil, but work even better with refined oil. He believes the possibilities for cleanup extend to most any type of hydrocarbon.

"This is just the beginning," he says. "Hydrogel was first developed for disposable diapers. Now it has expanded to many applications. We think Petrogel will be similar."

There are oil spills all of the time, he points out. Pipelines spring leaks, oil or gas spills on the highway or in train derailments, gas stations leak oil. Refineries have dirty water that could be cleaned up using Petrogel, and hydrocarbons leak into streams and rivers from farm runoff.

"The properties are there – they can be used in many ways," he points out.

An unusual application he has been thinking about involves natural gas separation. Natural gas from underground is composed of different types of hydrocarbons – the most important of which is methane (C^1) – that need to be separated through a series of treatments. The current cryogenic method involves lowering the temperature of all components of the gas to minus 150 degrees C. The first gas to boil out is C^1or methane. Lowering to that temperature is a very energy intensive proposition. Chung envisions using pressure combined with gradually lowering temperature to boil off the other gases until at around 0 degrees C, only methane remains. A few early lab experiments seem to indicate this approach might work, possibly saving industry the cost of big cryogenic facilities and the accompanying energy costs.

"It's not enough to just write papers," says Chung. "If you want to have a real societal impact you have to get your ideas into the marketplace."

Chung and Penn State have two patents, one that is pending, on Petrogel, as well as a trademark on the product name. He is seeking the kind of funders who could help him scale up his technology to make Petrogel as common a material as hydrogel, available wherever in the world oil is spilled.

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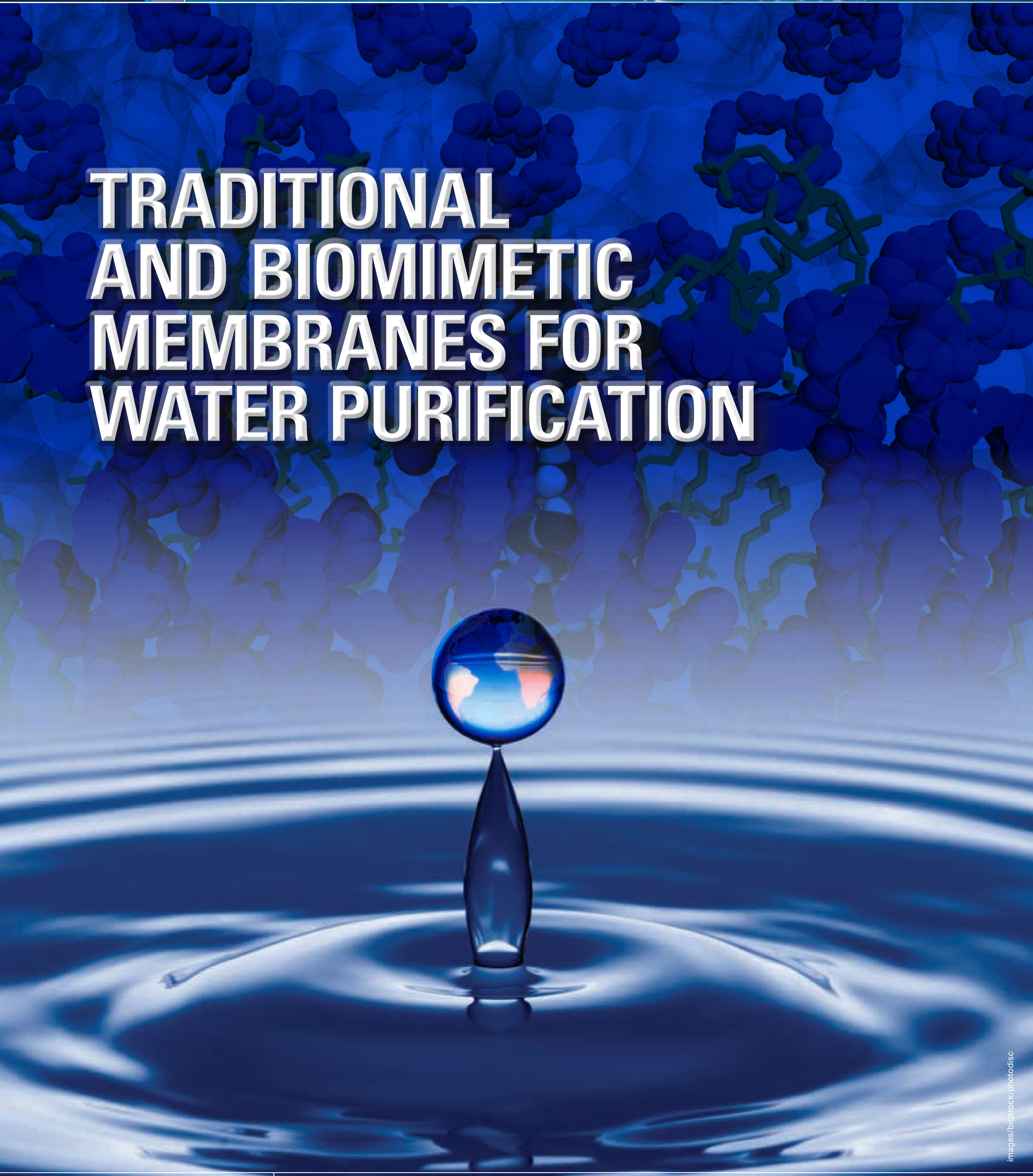
TRADITIONAL AND BIOMIMETIC MEMBRANES FOR WATER PURIFICATION



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Manish Kumar teaches water engineering to middle school campers at Science-U. • Photo provided

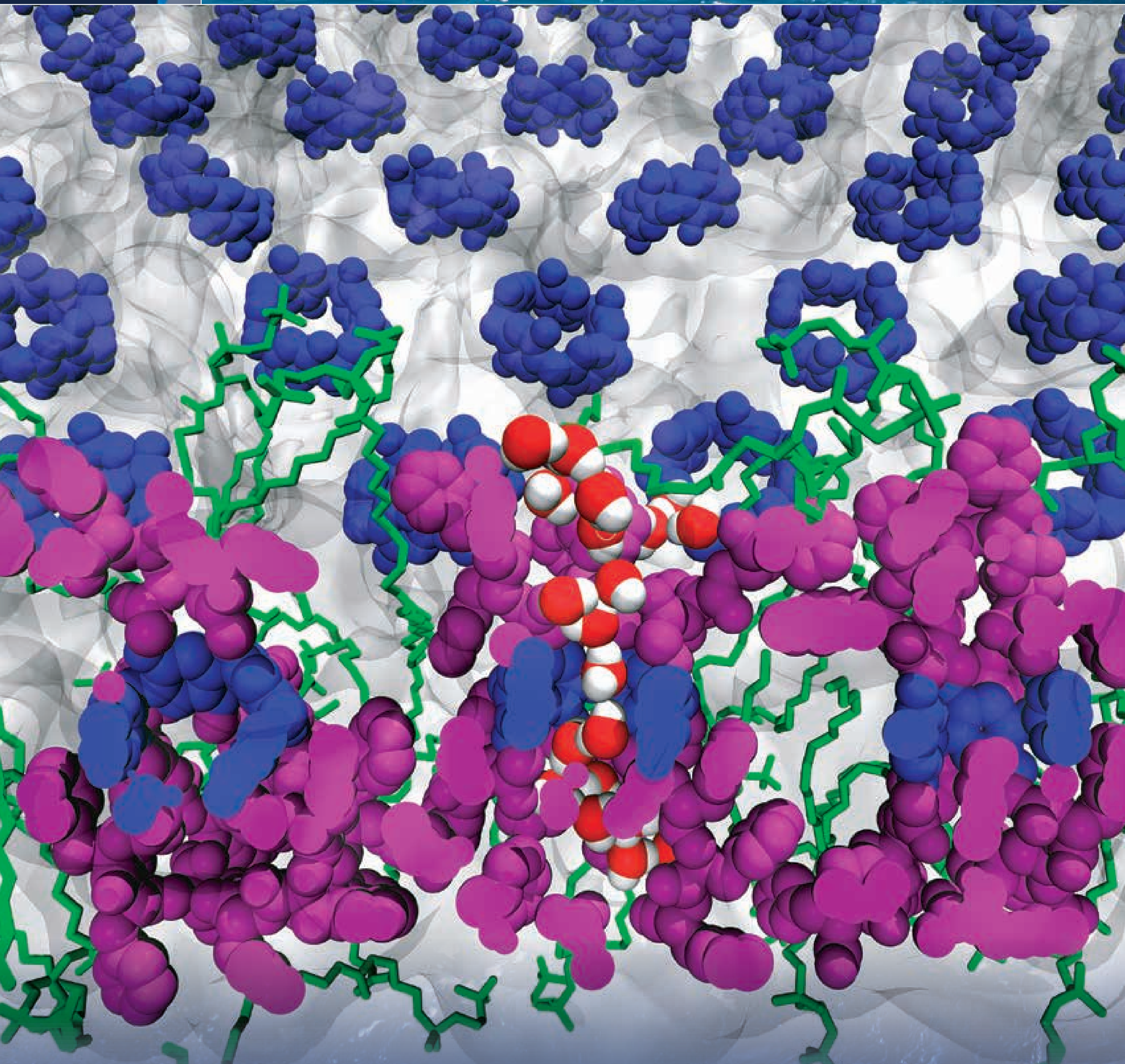
In the current state of water desalination, highly energy intensive sources such as oil or the electric grid are required to push water through a membrane to remove salt. If the membranes that are used in the desalination process could be made more efficient, a less energy rich method, such as solar energy, could be used. This could have a great impact in under-resourced regions of the globe. This is one of the goals that chemical engineering's Manish Kumar has set for himself and his group.

Kumar's group is conducting fundamental research on existing membranes to see how they can be improved, while also working on the next generation of membranes. Their primary focus is trying to make clean water available in a more energy efficient manner to those without access to high-quality water.

"Membrane technologies are already becoming big in developing countries and have been important in developed countries for some time now. It's just that it takes a lot of energy to push water through a desalination membrane," Kumar says. "If we can make the technologies I'm working on cheap enough to be implemented, it could be a very simple way of treating water."

Bioinspired biomimetic membranes

The best membrane for removing minerals from salty water may be the very one that nature has worked on for a billion years or so to protect the cells in our bodies,



Peptide-appended pillararene artificial water channels form highly packed 2D arrays in lipid membranes. They combine the advantages of water channel proteins aquaporins and their synthetic analogs carbon nanotubes, with regard to water conduction efficiency, and improve upon them through simple synthesis and chemical stability. Image credit: Kumar Lab/Penn State

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Kumar says. Nothing engineers have yet developed matches the filtration system of the cellular membrane.

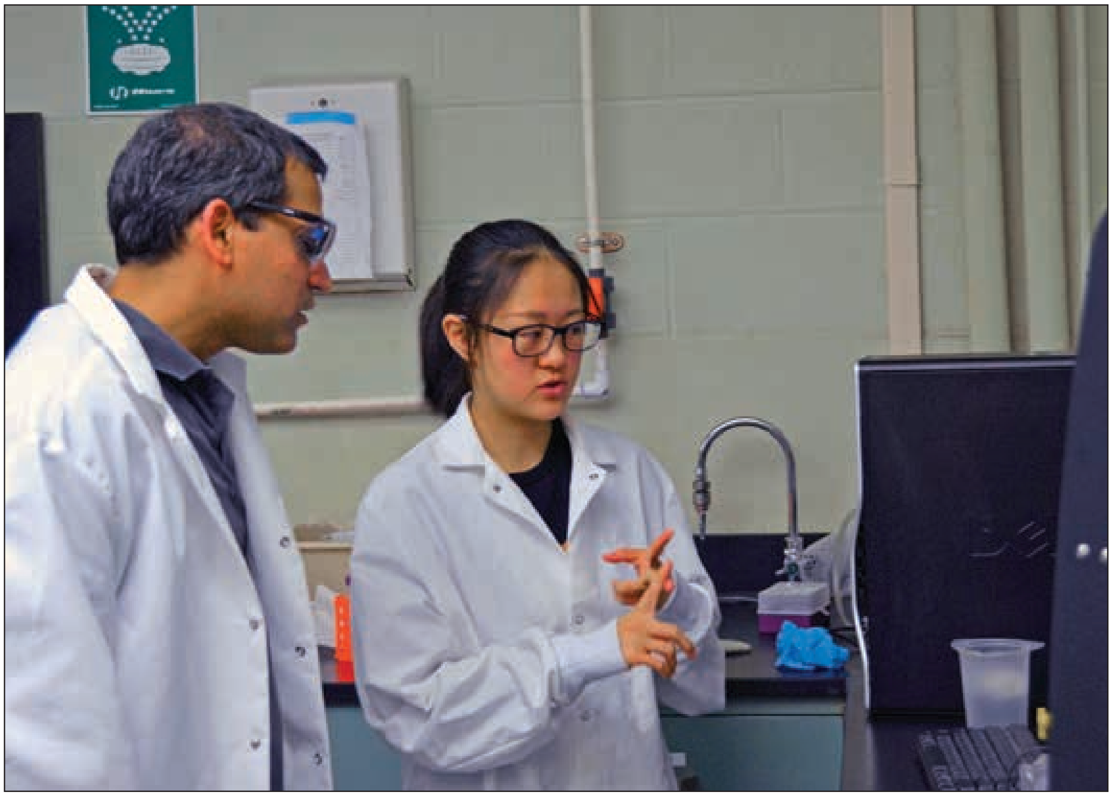
Aquaporins are proteins that transport water through channels in the membranes of biological cells. This protein transports water at about the same rate as one candidate filter, carbon nanotubes. Both aquaporins and carbon nanotubes can transport billions of water molecules per second, but only aquaporins can reject sodium and chloride (salt).

This protein can be taken out of the cell membrane and grown in large numbers in bacteria or yeast. Then they can then be removed from the growth medium and put into a polymer membrane to do filtration that cannot, as yet, be done with synthetic materials.

In 2015, Kumar and colleagues at Penn State and several other university labs synthesized, modeled, and characterized a bioinspired artificial water channel that can self-assemble into arrays in membranes. Based on the structure of the aquaporin protein, this synthetic organic structure has the same high transport rate but not the salt rejection capability that aquaporin has. These next generation synthetic water channels were assembled into highly packed planar membranes as a first step toward developing scalable engineering applications for liquid and gas separation. With modification of the channel pore size, these artificial aquaporin could be functionalized for water desalinization, Kumar believes. Earlier this year, he received a prestigious National Science Foundation CAREER award and five years of research support for this work.

A water engineer

Kumar's background has revolved around water since his undergraduate days in India, where he worked on membranes and ion exchange for water



Kumar and graduate student Tingwei Ren discuss her research in the Kumar Laboratory.

Photo credit: MRI/Penn State

treatment. In graduate school at Illinois, he looked at membrane fouling while earning a master's degree in environmental engineering. From there he moved to industry, working on ways to scale up new membranes to industrial uses and helping to install membranes in utilities.

After nearly seven years in industry, Kumar decided to pursue a Ph.D. in a new area, using ideas from biological cell membranes as water treatment membranes again at Illinois. A post-doc at Harvard Medical School led to the study of a protein that conducts water transport in the eyes – aquaporin 0.

"I consider myself a biomimetic materials engineer, but I tell my kids I'm a water engineer, because I've worked so long in the water industry and feel very connected to this aspect of our work."

Kumar collaborates with a large number of Penn State colleagues on various areas of water treatment and membranes. With chemical engineer Andrew Zydney, he works on frack water treatment. With biochemist Tom Wood, he works on biofilm fouling on membranes. Darrell Velegol, another chemical engineering colleague, and Kumar study how to keep membranes clean from fouling by small colloids and small particles. He also collaborates with Michael Hickner in materials science and engineering on frack water treatment and with Enrique Gomez (Chemical Engineering) on the microstructure of desalination membranes.. A large group of chemists, chemical engineers, and bioengineers at Penn State work in the area of biological and bioinspired membranes. Among them, Kumar collaborates closely with Peter Butler (Biomedical Engineering) and Paul Cremer on membrane protein dynamics in biomimetic membranes.

"If you are talking about membranes, we are really one of the best schools in the country," Kumar says. "There are lots of papers written at Penn State in this area, and a variety of top-of-the-line instrumentation that very few universities have."

Ready, Campers?

Another collaboration is with Chris Gorski, a civil and environmental engineer in Penn State's College of Engineering. Together the two engineers run a water camp each summer at Penn State for middle schoolers in conjunction with Science-U, a program of the Eberly College of Science that immerses thousands of young people in the experience of scientific discovery. Their full-week hands-on water camp teaches students about the whole water system and how it affects them, including water conservation, water treatment, and how water distribution works.

"That's a really fun thing we do with Science-U," he says.

Manish Kumar is assistant professor of chemical engineering.

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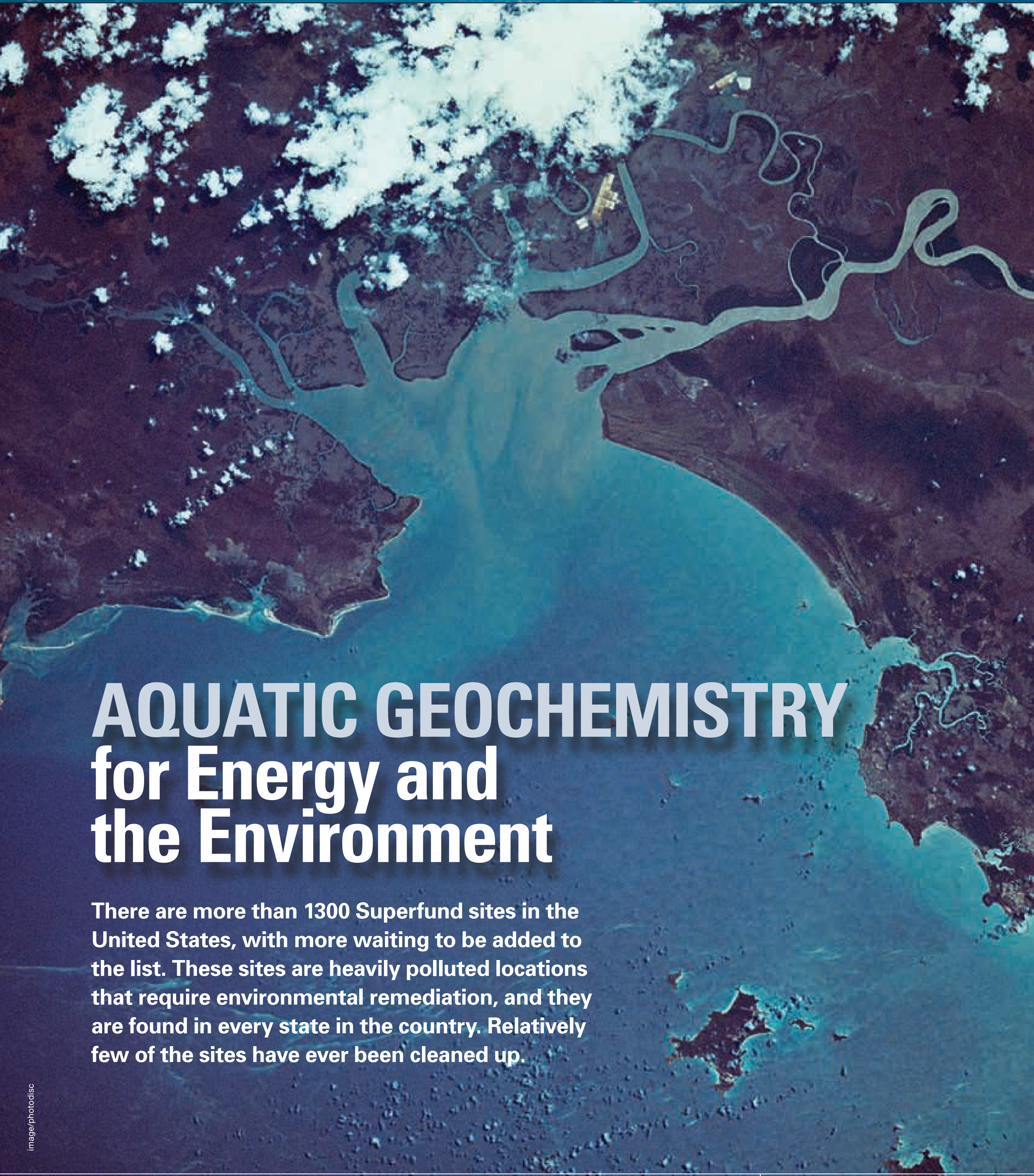
His research website can be accessed at www.kumarresearchgroup.com.



AQUATIC GEOCHEMISTRY for Energy and the Environment

There are more than 1300 Superfund sites in the United States, with more waiting to be added to the list. These sites are heavily polluted locations that require environmental remediation, and they are found in every state in the country. Relatively few of the sites have ever been cleaned up.

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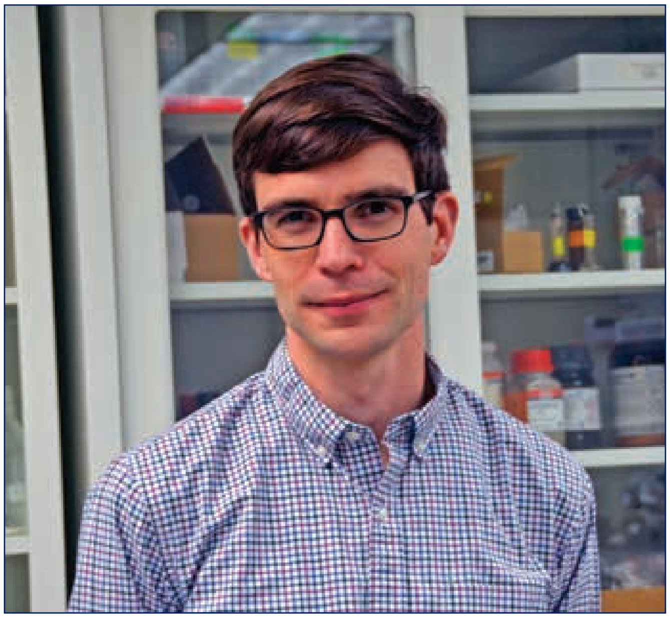

Christopher Gorski, assistant professor of civil and environmental engineering

"It's a huge problem; some say it's an unsolvable problem," remarks Chris Gorski, an assistant professor in the Department of Civil and Environmental Engineering at Penn State, whose group has a number of projects relating to energy and pollution.

"In regard to near-surface groundwater pollution, the classical way to attempt remediation is called pump and treat," he explains. The water is pumped up to the surface, treated to remove contaminates, then pumped back underground. This cycle can go on for decades and is not only expensive, but often unsuccessful.

Many of these sites are polluted with degreasing agents, chlorinated solvents that were allowed to soak into the ground. Some of the solvents will find their way into the water table. Because the solvents are denser than water, they sink to the bottom. Some of the pollutant dissolves and pollutes the water, but much of it sits at the bottom of the water table. When the water is pumped to the surface and cleaned, the solvents seep back into the water and dissolve, re-contaminating the clean water.

"It's a really difficult problem," Gorski says. "People try to inject things directly into the contaminant under the water, but it is difficult to target it. There are, I think, over 150,000 contaminated sites in the U.S., and I worry we are contaminating more and more groundwater."

Gorski and others are now trying to understand and manage these sites rather than clean them up. He attempts to predict, from a chemistry perspective, what happens to contaminants when they enter groundwater. Many of these contaminants can undergo a reaction as they interact with certain bacteria or minerals underground. His group uses electrochemical analyses, spectroscopic analyses, microscopy, and isotope tracers to understand how these reactions can affect pollution in the water table.

Harvesting energy from salinity differences

In the energy-water nexus, Gorski and his colleague Bruce Logan are working on a process called salinity gradient energy, a process that is essentially the opposite of desalination, he says. When fresh water and salt water mix, there is an entropy gain that results in measurable energy production. That energy can be captured using electrochemical systems, similar to a battery.

Many of the world's great cities are located at an energy-water nexus, with fresh water rivers running into salty bays or oceans. The salt water "wants" to mix with the lower salinity water and the resulting increase of entropy can make for a large renewable energy source if captured. To be feasible, this technology would require large, low-cost membranes.

"A lot of what we are working on now is instead of using these natural salinity gradients, we are generating these differences in salinity using heat and salts. We are considering using the low grade waste heat from power plants that would normally just go into the environment, and using it to heat up water to evaporate salts and generate the salinity gradient that way," Gorski says.

In theory, their salinity gradient battery would scale up, Gorski believes. His part of the research involves deciding on the best electrode material to use. That material needs to be cheap, nontoxic, and generate a lot of energy. So far, the most promising electrode material appears to be manganese oxide. Manganese is the 10th most common element in the Earth's crust. Gorski and Logan were recently awarded NSF funding in support of this work.

More efficient hydraulic fracking

Although hydraulic fracturing has opened up the Marcellus Shale region to vast quantities of natural gas, only a small percentage (5-10 percent) of gas is recovered for each well drilled. Gorski is collaborating with Penn State's Darrell Velegol, in chemical engineering, on chemical methods to get much more of the gas out of the surrounding low-permeability rock, while limiting the environmental damage.

"What we're looking at is using different chemical additives in the water used in hydraulic fracking to increase the generation of porosity or to help inject proppants into the rock fracture to keep them open," Gorski explains. The technique involves replacing one mineral phase with another phase while retaining the original shape and texture.

The activity in natural gas extraction is in a lull at the present time with the plunge in gas prices. However, the project's funder, Haliburton, is taking the long view and investing in research and development to be ready for the return of profitable drilling.

"They've taken an interesting approach," Gorski comments.

The research is still at laboratory scale, as field trials are too expensive until more results are in.

For more information on the Gorski group's research, visit their website at http://www.engr.psu.edu/ce/enve/gorski/# or contact Christopher Gorski at gorski@psu.edu.

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