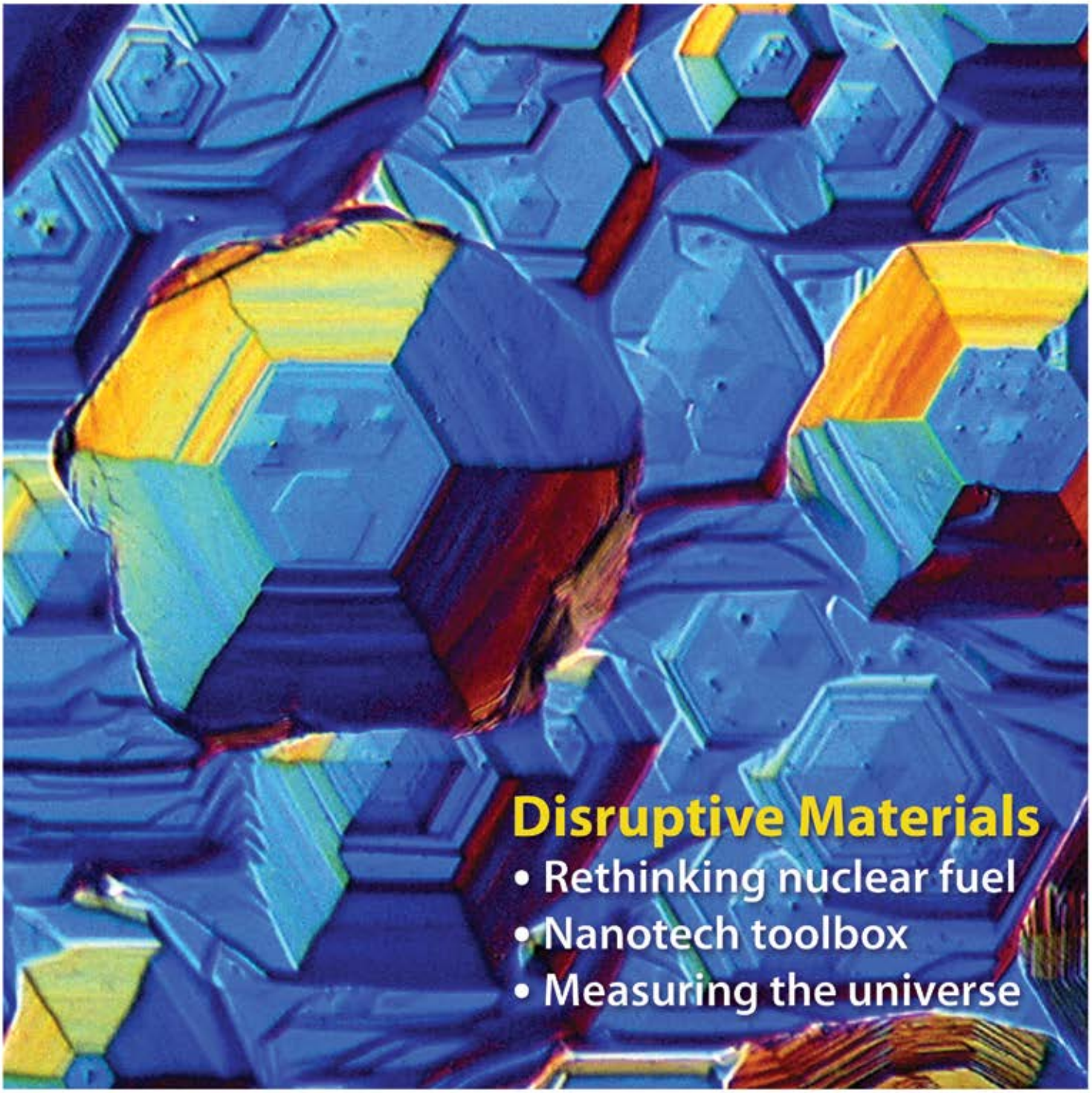
OAK RIDGE NATIONAL LABORATORY

REVIEW

• MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY •

Vol. 46 • No. 1 • 2013
www.ornl.gov/ornlreview



Disruptive Materials

- Rethinking nuclear fuel
- Nanotech toolbox
- Measuring the universe

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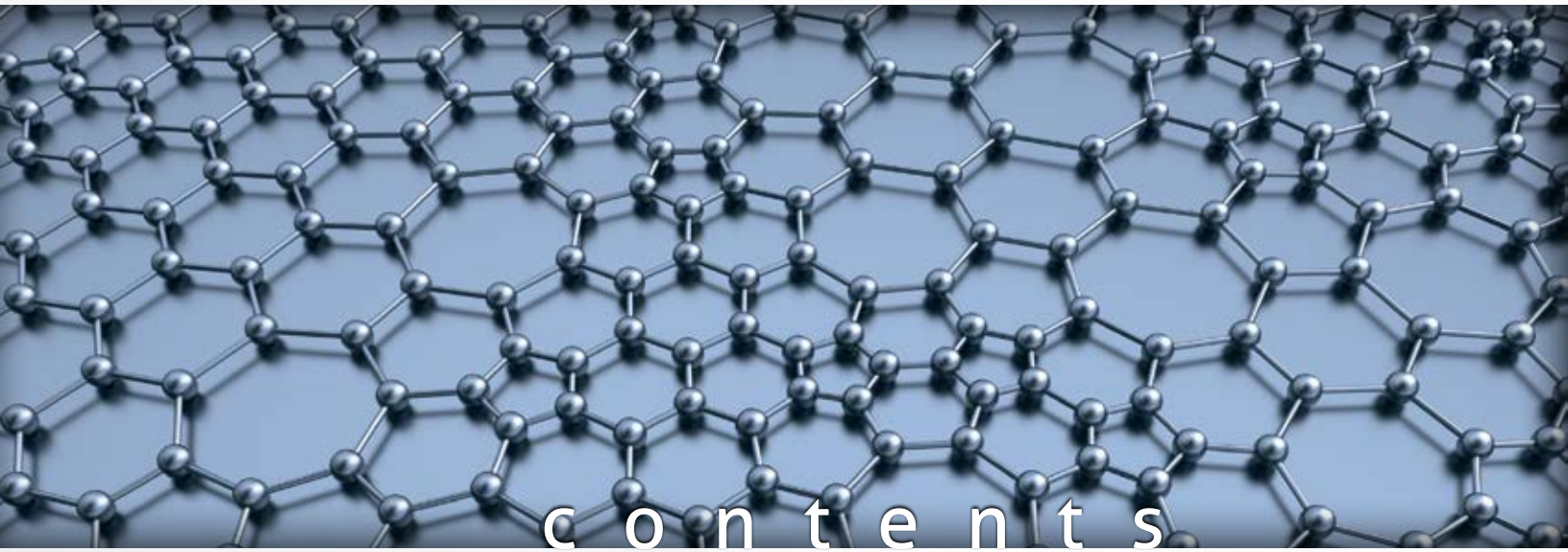

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on the cover

The cover micrograph shows the surface of a single crystal of thermochemically treated zinc oxide. At ORNL, these crystals have been used for a variety of purposes, including studies of hydrogen fuel production, radiation detectors and enhanced electronics. *(Micrograph: Lynn Boatner, Joanne Ramey and James Kolopus)*

DISRUPTIVE MATERIALS

Driving innovation in the 21st Century

It has been more than 100 years since the invention of the solar cell, electric car and rechargeable battery. Fossil plants operate at only two-thirds their optimum efficiency. There is still no consensus on the disposition of spent nuclear fuel. None of these technologies is close to meeting its full potential, not because the underlying physics or chemistry make it impossible, but due to the scarcity of materials that can extend performance to ultimate efficiencies and extreme environments.

Advances in materials have enabled technological revolutions since the beginning of civilization. It's why materials lend their names to Ages. Stone, bronze, iron and steel, nuclear. With each successive Age, a new material disrupted established technology. The Stone Age did not end because we ran out of stones. The Information Age owes its existence to silicon-based microelectronics, not incremental improvements in vacuum tubes. There is a disruptive material behind virtually every technological innovation.

This issue of the Review focuses on disruptive materials research at ORNL. Materials research has always been a distinguishing competency at the Laboratory, broadly underpinning our science and technology work. The importance of materials was recognized early with advances that enabled progress in nuclear reactors, nuclear fuels and isotope production. Materials for chemical separations led to nuclear fuel reprocessing and more recently to the large-scale separation of nuclear waste. Advanced alloys from ORNL can be found in most fossil and nuclear power plants, and new high-temperature and radiation-resistant alloys offer the potential to substantially improve the performance of these plants. Advanced composites developed at ORNL have enabled centrifuge technology used to enrich uranium, and new carbon fiber composites are being applied to the development of lightweight materials for transportation. ORNL advances in nanoscale materials are transforming the development of advanced batteries, membranes, magnets and renewable energy technologies.

Many of these advances—alloys, nuclear fuel reprocessing, isotopes, separations, advanced composites—have already led to technological developments with impacts measured in the billions of dollars. The articles in this Review provide a glimpse of the next wave of disruptive materials research at ORNL. Materials that enable precision measurement of the neutron, fibers that separate uranium from seawater, accident-tolerant nuclear fuels, graphene technology, and new innovations in materials design and development accelerated by nanoscale science and computer simulation.

From the beginning, ORNL recognized and nurtured the transformative potential of materials by co-locating basic and applied materials research and connecting this research to technology outcomes. The result is a large, highly integrated materials enterprise widely acknowledged as one of the best and most impactful in the world. Sustaining leadership in materials research, and taking advantage of ORNL's scientific expertise across multiple disciplines, is a high priority. With new capabilities in nanoscale and neutron science, as well as advanced computing, the future of disruptive materials research at ORNL looks bright.

Jim Roberto

Interim Director for Science and Technology
Oak Ridge National Laboratory

Disruptive materials

Revolutionary advances in performance are needed to boost energy technologies and the economy

A remarkable number of technologies are driven by advances in materials science. Breakthroughs in energy, computing, transportation and communication products often are rooted in improvements in the materials from which they are made. The more scientists know about the basic structure of materials, the more easily they can tailor those properties to specific needs.

Stronger materials, for example, result in safer cars. Photoelectric materials can boost the efficiency of solar panels, and lightweight materials improve the fuel efficiency of all kinds of vehicles.

"I think one of the laboratory's biggest challenges for the future is to develop what we call *disruptive* materials," ORNL Associate Laboratory Director Michelle Buchanan says. "I'm not talking about incremental changes; we're looking for quantum changes in the performance of materials that will help us greatly improve energy efficiency and achieve energy independence."

Focusing on disruptive materials is a natural evolution for ORNL, which not only supports one of the largest materials science programs in the world but also has a tradition of pairing basic and applied materials research that reaches back to the lab's World War II origins. Former lab director and Manhattan Project scientist Alvin Weinberg is generally credited with institutionalizing the coupling of "bench" science and practical applications at the laboratory. "Applied research done in a basic atmosphere has a sophistication that is hard to duplicate in a less scientific environment," Weinberg observed, "and ... basic research done in an applied atmosphere has a kind of no-nonsense aggressiveness that is hard to duplicate when basic research is done entirely by itself."

Says Buchanan, "Emphasizing this scientifically inclusive approach to materials science is unique to Oak Ridge among all the other laboratories. It's one of the defining characteristics of our program."

Hidden potential

The ability to unlock the hidden potential of materials is one of the keys to developing game-changing applications. Some of the biggest opportunities for this exist in the areas outlined below.

"We are beginning to understand the 'why' part," Buchanan says. "We are using computational tools and our experimental expertise to analyze existing materials and understand how defects cause them to fail, as well as how to create new materials with fewer defects."

Increased storage capacity would be a huge plus not only for electric vehicle batteries, but also for storing power on the grid. One of the reasons wind and solar power generation aren't more widespread is that they can provide power only when the wind is blowing or the sun is shining. These systems need a way to store large amounts of electricity when it's still and dark. Buchanan envisions new battery technology providing better storage options for individual homes or even neighborhoods.

"Nobody wants to fill their basement with batteries," she says. "If we expect people to store power at home, we need to develop batteries the size of heat pumps that can sit outside their houses—reliable batteries that could be charged over and over for many years. We also envision larger batteries powering entire neighborhoods."

We're looking for quantum changes in the performance of materials

Ultrastrong materials—Among the main attractions of developing stronger materials are their fringe benefits. For instance, if some of the steel parts in your car were replaced by a much stronger material, your car likely would be safer as a result of the sheer strength of the material. It also might be more durable because the stronger parts would last longer, and it almost certainly would be lighter because less material would be needed to produce the new parts. Finally, if your car were lighter, it would be more fuel efficient because less energy is needed to move a lighter vehicle.

Another attraction of pursuing ultrastrong materials is that there's plenty of room for improvement in material strength. Because of tiny defects throughout their structure, most materials used in manufacturing today only possess about 10 percent of their theoretical strength. Research at ORNL's Center for Defect Physics is gradually uncovering the reasons for this disparity and devising ways to take advantage of the 90 percent of the strength that seems to be unnecessarily lost.

Energy storage—Another area ripe for disruption is the effort to increase the energy storage capacity of batteries. The electric and hybrid vehicle industries have great interest in storing more energy in smaller packages, since batteries account for 20 to 25 percent of each vehicle's weight. Laboratory researchers are exploring new ways to get battery electrodes to store more ions—the more ions, the more electricity. One way to squeeze more ions onto the electrodes is to make the electrodes out of a material that has lots of texture at the nanoscale.

"We have been experimenting with materials with small holes, called nanopores, on their surfaces," Buchanan says. "These holes are only a few thousandths of an inch in diameter, but because they are three-dimensional, rather than flat, they increase the surface area from which ions can come and go and greatly improve the battery's ability to store energy. We're in the early stages of this research, but if we can get these materials to perform as well as we think they can, it would be revolutionary."

Separating materials—Chelators are specialized molecules designed to chemically grab and separate very specific materials from a liquid mixture. This makes them handy for tasks such as environmental cleanup. A good example of chelation in action is an ORNL-developed system for separating radioactive cesium, a common environmental contaminant, from other

waste products—a process that makes the remaining waste safer to handle. This process has been tested extensively and will be part of a $1.7 billion waste processing facility being built at the Department of Energy's Savannah River Site.

The success of the cesium-targeting chelator led its developers to apply the same kind of technology to the task of separating uranium from seawater for use as nuclear fuel. This development could have profound long-term impacts because there is much more uranium dissolved in seawater than there is on land.

Researchers have figured out how to attach a uranium-seeking chelator to points along the length of feather-like polymer fibers. They are planning to assemble these fibers into weighted nets and lower them into the ocean where the chelators will react with the uranium dissolved in seawater as it flows past. When the fibers are ready to harvest, workers just haul the net up and recover the uranium through a simple chemical process.

"The disruptive aspect of this technology is that it is much cheaper to extract uranium from seawater than it is to mine uranium," Buchanan explains. "There's only so much material you can mine easily and cheaply, and then you still have to worry about the environmental impact. Extracting uranium from the sea using chelation would avoid mining altogether."

Similar applications of this separation technology are being investigated for recycling materials that are vital to our nation's economy and come from discarded electronics, solar cells and magnets. These so-called "critical materials" include elements that possess unique magnetic, catalytic and luminescent properties needed to manufacture clean energy products, such as wind turbines, solar panels, electric vehicles and energy-efficient light fixtures.

"When it comes to critical materials," Buchanan says, "we have the ability to make every step of their lifecycle, from the mine to the recycling bin, more efficient. The Department of Energy's national laboratories, particularly those partnering in the new Critical Materials Institute, have all the components needed to make a lot of progress in this area. We have the expertise and the facilities, and we can apply computational tools to help us project what materials we should look at first."

Making an impact

"I think the laboratory is always going to be a leader in coming up with technologies that use basic science to solve practical energy-related problems," Buchanan observes. "Our goal is to meet the nation's future energy needs and spur economic growth. That's just what we have to do. Some of our technologies will be spun off into defense programs and health and all sorts of things, but we need to keep our eye on the ball. We want to serve the nation's needs in energy in general and its materials needs in particular."

Over the next few years, Buchanan expects the lab's materials science R&D program to have its biggest impacts in the area of extreme materials—structural elements that can hold their own under high levels of stress, strain and radiation better than conventional materials; functional materials like those found in batteries and solar cells; thermoelectrics—materials that turn waste heat into power; and polymer science—where ORNL's neutron science capabilities are spurring research in areas ranging from drug delivery to lightweight composite materials to carbon dioxide remediation.

"I think Alvin Weinberg would be very pleased with our progress," Buchanan says, "particularly with the way our basic and applied research programs support one another. We use the same philosophy in our unique user facilities like the Nanoscience Center, the ShaRE microscopy program and the Spallation Neutron Source. These facilities are making our scientific capabilities available to the entire scientific community and are helping to teach the next generation of scientists the skills of our trade." ® — *Jim Pearce*

Nanotech toolbox

Self-assembling molecules lend a helping hand

Nanotechnology is about building new materials and even simple machines out of microscopic bits and pieces. By manipulating molecules and atoms, scientists have made huge strides in improving their ability to understand what causes materials to have specific physical properties, such as strength, flexibility or heat resistance, and to tailor new materials to meet specific needs.

One of the most remarkable aspects of this super-small-scale world is that, under the right conditions, bits and pieces of materials will put themselves together—a natural phenomenon known as self-assembly. For example, polymer molecules, like the ones used to make plastic bags, organize themselves into a variety of structures based on what's going on in their environment.

"You don't have to engineer these molecules, and you don't have to manipulate them; they just assemble themselves," says Bobby Sumpter, a chemical physicist who works at ORNL's Center for Nanophase Materials Sciences.

Sumpter and his CNMS colleagues have spent a lot of time developing an array of techniques calculated to harness this natural behavior to enhance energy technologies.

"We can influence how polymers and other materials self-assemble by changing the conditions around them—changing the temperature, adding chemicals or chemical groups to encourage formation of targeted structures or reactions. That's good news for the prospect of discovering both new materials and new applications for existing materials."

Transformational potential

The transformational potential of this technology is amplified by the wide-ranging capabilities of research centers such as CNMS. The center's scientists not only can analyze new materials with computer models before they are even created but also can make the materials in the laboratory, then double-check the results of the original computer model using state-of-the-art neutron analysis and electron microscopy facilities.

"We're fortunate to have some of the country's best materials scientists here at ORNL," Sumpter says. "Beyond that, we have the computational and characterization infrastructure needed to turn good ideas into reality."

The concept of manipulating nanoscale materials has been around since at least the late 1990s; however researchers didn't have the technical ability to apply those ideas until relatively recently. In the '90s, nanotech was mostly limited to linking polymer molecules together in a line. Today, scientists have uncovered ways of persuading polymers to self-assemble into all kinds of exotic arrangements, creating a range of shapes and mechanical properties in the process. The number of possible combinations generated by these new capabilities is so large that making and testing each one is out of the question.

That's where the laboratory's advanced computing capabilities come into play. Even low-resolution models of these complex materials have to be run on ORNL's Titan supercomputer, the most powerful computer in the world.

Materials scientist Jamie Messman uses a Tesla coil to test the vacuum of a polymer synthesis apparatus. (Photo: Jason Richards)

"We can model 25 million to 100 million atoms, which is big enough to tell us what we need to know," Sumpter says. "Modeling just nanoseconds' worth of self-assembly is computationally intensive. The process is the same whether we're working with materials for batteries, biomaterials or solar cells. The ability to simulate materials in a digital environment enables researchers to evaluate huge numbers of configurations without having to create them—which would take years. It really accelerates the R&D process."

Energy impact

Sumpter's research group is pursuing a number of nanotech projects, including those described below, that involve various self-assembling materials—all with potential applications in the energy field:

Smaller, lighter batteries—Improving the capacity and durability of batteries is particularly important for electric vehicles and grid storage applications. Nanotech researchers at the laboratory are experimenting with batteries that use solid polymer electrolytes rather than typical liquid electrolytes. This reduces the size of batteries by eliminating the need for separation of liquid electrolytes on the positive and negative sides of the battery. The use of solid electrolytes also addresses a number of problems related to deterioration of the battery's electrodes over time.

"Solid electrolytes reduce both the size and weight of batteries," Sumpter says, "and we have been able to design polymers that conduct ions as well as traditional electrolytes."

When researchers use computer simulation to develop materials such as solid electrolytes, it's an iterative process. If a simulation shows promising properties, researchers make the material and study its characteristics using neutron analysis and electron microscopy. If the results of these studies match the simulation, the material is likely to be explored further, and the accuracy of the computer model will have been validated, increasing its usefulness for modeling similar materials.

Cleaner water—ORNL scientists have looked into the possibility of using durable, flexible polymer membranes for separating liquids, including water filtration applications that remove brine and other impurities.

"The current technology for water filtration is very energy-intensive," Sumpter says. "Water is possibly the most important commodity in the world, so there is a huge demand for energy-efficient ways to purify it. A breakthrough in this area could be transformational. We're investigating physical and chemical filtration processes. Both techniques involve membranes that are activated by the presence of impurities. So far materials like this haven't made the jump to industrial applications, but they offer a lot of promising possibilities."

Smart materials—An oft-cited goal of nanotech research is the development of materials that are "stimuli-responsive," meaning they respond to environmental conditions such as temperature or mechanical strain by displaying new structures or properties.

Smart materials usually have either the ability to sense "problems" within themselves, such as strains or defects that could eventually cause the material to fail, or self-healing capabilities—such as the capacity to self-repair chemical bonds that have been broken by mechanical stress.

"Our group is working on materials that can sense problems," Sumpter says. "Energy science-wise, it would be an advantage if one could prevent or predict catastrophic materials failures, which are rather costly both in terms of energy and, more importantly, life."

His group and their collaborators have been investigating the possibility of creating such materials using carbon nanostructures that look like stacks of ice cream cones. When the stacks are straight, their electrical resistance is high. When they bend in response to an outside force, their resistance drops to near zero.

The interesting thing about these stacks is that the cones are not chemically bonded; they're just slipped inside one another. The ability of this arrangement to vary conductivity in response to strain lends itself to building sensors into the fabric of, perhaps, critical structural components of transportation vehicles (such as airplane wings) and similar structures where measuring stress is important.

Light-related properties—A number of energy technologies would benefit from materials with enhanced light-related properties. Toward this end, CNMS scientists have been experimenting with enhancing polymers to improve their potential for use in light emitting diodes or to respond to changes in light for use in solar cells.

Sumpter notes that one of the challenges of working with bulk quantities of self-assembling materials is that sometimes they don't self-assemble into structures of optimal size. Additionally the structures that these self-assembling materials create may contain defects.

"Defects usually have a negative effect on the properties of the material, and it's hard to get rid of them," Sumpter says. "A single defect, for example, can have a profound effect on a material's ability to conduct electricity or light."

Eliminating defects generally involves investigating why they occur and finding ways to avoid them. One of the most successful workarounds has been the practice of using a defect-free crystalline surface such as copper, gold or silver as a pattern or template for self-assembling molecules. As it turns out, structures that self-assemble on top of this type of template tend to be defect-free as well.

"We learn a lot from developing solutions to these kinds of problems," Sumpter says. "We attempt to tease them apart from the bottom up. It's a step toward understanding what's important in nanoscale systems and what's not."

Point, counterpoint, solution

It's fair to say that pairing experimentation with computation in areas such as polymer self-assembly could shave years off the process of developing new materials and is transforming the field of nanotechnology.

Sumpter, who has worked in the field since its earliest days, says the biggest difference between now and 15 years ago is that today researchers have a lot more confidence in the results of computer simulations.

Our ability to model materials, make them and then measure their properties is what makes us unique

"Computation is a good counterpoint to intuition," he says. "We've had a number of situations where intuition was leading us in one direction, and our computational models were leading us in another. Now we trust the models enough to believe them when they say Option A is better than Option B. Having the computing power needed to create highly detailed material models has reduced the time required for problem-solving by a huge amount, so now the idea of using theory to guide experiment is actually practical."

The potential for groundbreaking research to be conducted at CNMS is enhanced by scientists' access to all the resources necessary to exploit the technology.

"We can handle the full spectrum of R&D activities at the laboratory," Sumpter says. "Our ability to model materials, make them and then measure their properties is what makes ORNL and the Center for Nanophase Materials Sciences unique—and kind of neat, I think." ® — *Jim Pearce*

Materials for measuring the universe

Did wobbly neutrons give us a starry sky?

Most people have heard of the "butterfly effect," a phrase coined by mathematician and meteorologist Edward Lorenz to describe how tiny changes can have profound effects over time. Lorenz was talking about the vagaries of weather prediction, suggesting that a butterfly flapping its wings in one part of the world could affect whether a tornado forms in another.

Physicists have their own version of the butterfly effect that makes the meteorological consequences of a few wing flaps pale by comparison. Their scenario hinges on extremely precise measurements of one of the basic building blocks of the universe—the neutron.

We're all familiar with atoms from stylized images in grade school science books—a swarm of tiny electrons orbiting a big nucleus made of neutrons and protons.

For decades, physicists have been trying to accurately measure the "roundness" of the neutron—partly because of the implications of the measurement for the accuracy of models of the early universe. This measurement, also known as the neutron "electric dipole moment," was first made at ORNL's Graphite Reactor.

ORNL physicist Vince Cianciolo explains that the best measurements of the EDM to date indicate that the neutron is round—within the limits of the accuracy of those measurement techniques. However, he and his research partners at ORNL and other institutions are working to put together an experiment that would enable them to measure the EDM one hundred times more accurately—to within one quadrillionth (0.000000000000001) of the neutron's diameter.

So why all this fuss about something so small it can barely be measured?

Physicist Hussein Hijazi loads a sample of clear plastic into ORNL's Multicharged Ion Research Facility. Researchers are using the MIRF to implant metal ions in the surface of the plastic, enabling it to conduct electricity.
(Photo: Jason Richards)

The most widely accepted model of the early universe suggests that as the universe expanded immediately after the "big bang," there were equal amounts of matter and antimatter. When matter and antimatter meet, they annihilate each other—both cease to exist. So by rights, all the material in the universe should have been gone long ago. The fact that you're sitting here reading this, physicists theorize, suggests there was a vanishingly small imbalance in the early universe favoring the preservation of matter. That imbalance, they suggest, may be related to the EDM.

"We know that the ratio of protons and neutrons to photons in the universe today is about one part in a billion," Cianciolo explains, "This tells us that about one billionth of the matter that originally existed in the early universe escaped annihilation. In a rather complicated way, the question of why this matter was left behind is tied to the roundness, or lack thereof, of the neutron. If it's not perfectly round, that could account for the preservation of matter. If it appears to be round at that degree of accuracy, that would be a very interesting result as well."

A knotty problem

Researchers measure the EDM by polarizing a group of neutrons so they're all spinning in the same direction (a neutron spins on its axis, like the Earth), putting them in a magnetic field, and then applying an electric field—first in the same direction as the magnetic field, then in the opposite direction. If there's a difference in how fast the neutrons spin when the electric field is reversed, that's evidence the neutrons aren't perfectly round. The bigger the difference, the greater the irregularity in the neutrons' shape.

Cianciolo and his colleagues are in early stages of a years-long effort to develop an instrument called nEDM (Neutron Electric Dipole Moment) that is designed to measure the EDM with unprecedented accuracy. The nEDM will eventually be installed at ORNL's Spallation Neutron Source.

At the heart of this instrument is a particularly knotty materials science problem waiting to be solved.

The nEDM will feed neutrons into a measurement cell filled with ultra-cold liquid helium where, thanks to the super-low temperature, they can be stored while their spins are being measured. The measurement cell is surrounded by a magnetic field and high-voltage electrodes. The cell is made of clear acrylic, which is particularly good at transmitting the small bursts of light created during the measurement process and carried through the wall of the cell to a light sensor. The electrodes connected to the cells also have to be made of acrylic because the instrument will operate at a half degree above absolute zero; using different materials for the cell and electrodes would cause the instrument to fall apart as it cools and warms. Making electrodes out of clear plastic is where the materials challenge comes in.

"Obviously acrylic doesn't conduct electricity," Cianciolo explains, "so to turn it into an electrode, we have to find a way to modify its surface to make it conducting. Also, to prevent interfering with the rest of the experiment, the surface cannot be magnetic or superconducting. It can't become radioactive when it interacts with neutrons, and it has to be tough enough to endure extreme temperatures and the occasional spark."

Cianciolo's collaborators—atomic physicist Fred Meyer and polymer chemist Mark Dadmun—are leading the development of two approaches to solving this problem: implanting metal ions in the surface of the polymer or creating a carbon nanoparticle polymer composite material—an acrylic that has been seeded with conducting nanoparticles. Materials scientist Harry Meyer is providing expertise in analyzing the performance of the modified polymers.

"There are a lot of possible combinations of materials to evaluate in both of those scenarios," Cianciolo says. "Right now we're considering all of the material requirements—not magnetic, not superconducting, etc.—and trying to match them up with the properties of the materials we're able to synthesize to determine what sort of new material might meet our needs. There is some computer simulation involved in this process, but our studies are conducted primarily through experimentation. I suppose there might be an analogy for this kind of work in Thomas Edison's search for a light bulb filament. He tested 1,000 different types before he found one that worked the way he wanted it to. We're trying to gain a similar understanding of how to make an acrylic-based material that conducts electricity."

Tweaking the standard model?

So once nEDM is up and running, what do researchers hope to learn? It all boils down to whether the results support or contradict the "standard model"—the overarching model that physicists use to explain how objects interact in the physical world. The model predicts an EDM much smaller than current measurement techniques could detect. Cianciolo finds that feature of the nEDM experiment particularly attractive.

"Because the standard model prediction is immeasurably small, any experiment that detects a non-zero EDM is exploring physics that lies beyond the standard model," he says.

Generally speaking, physicists know the standard model is incomplete, and various theories make predictions that go beyond the model. Most of those predict a measureable, non-zero EDM.

"We expect that either our experiment will see something that is not predicted by the standard model, or it will suggest that something is wrong with all of these extensions to the standard model," Cianciolo says. "Any result from this experiment will have an impact on a number of theories.

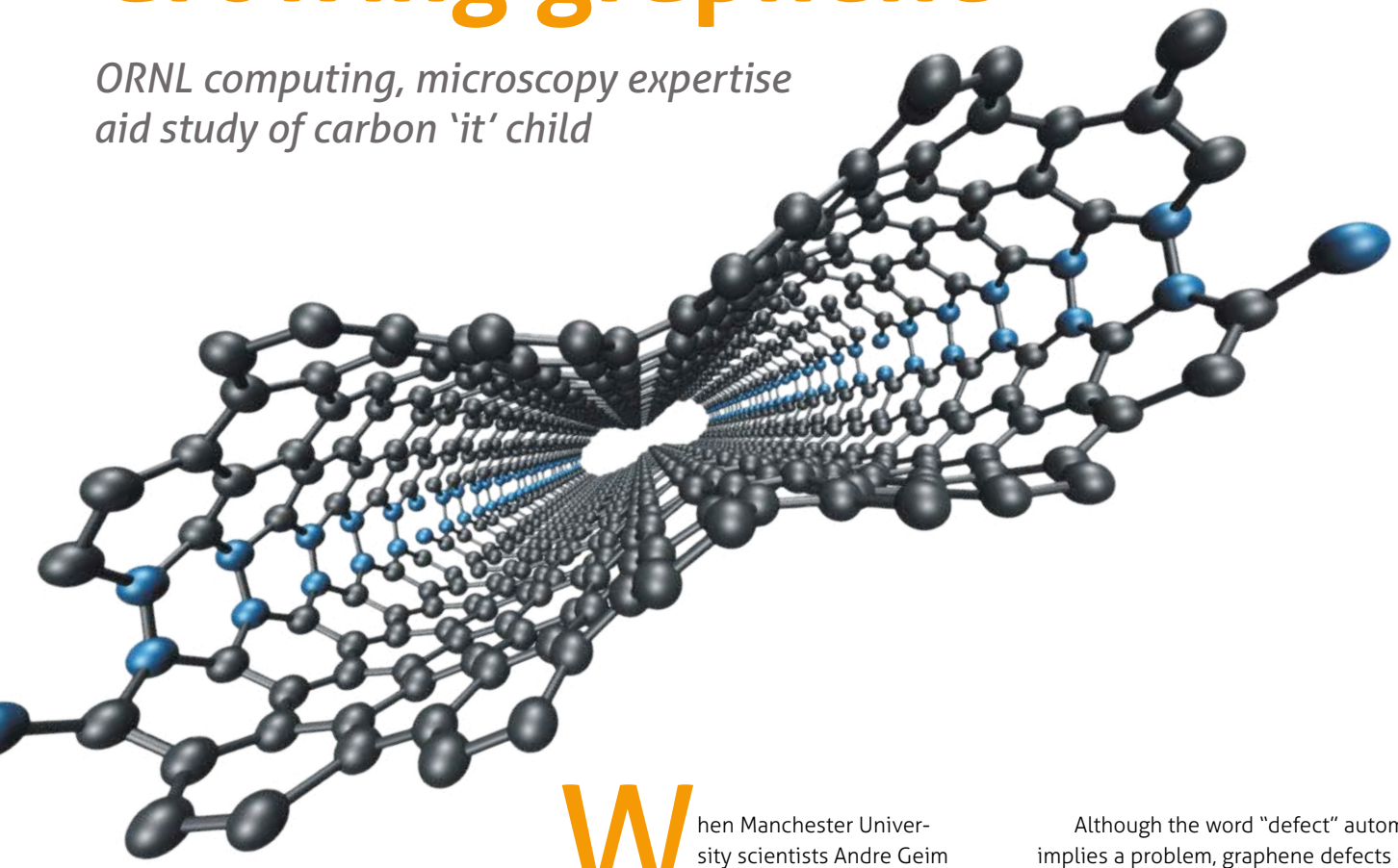
"The effort complements the work being done at the Large Hadron Collider, the world's premiere high-energy physics facility. At the LHC, which straddles the border between France and Switzerland outside Geneva, scientists are using high-energy collisions to directly produce particles that aren't explained by the standard model and are measuring their decay.

"We're trying to take the opposite approach by making a measurement that's so precise that we can see the very tiny signatures of physics that go beyond the standard model, even at the low energies we're working with," Cianciolo says.

Any results from the nEDM experiment are sure to provoke as many questions as answers. An immeasurably small EDM would leave questions about the creation of matter in the early universe unanswered. A measurable EDM would suggest that a miniscule wobble in the shape of the neutron spelled the difference between a starry sky and an empty cosmos. Either way, the universe as we know it was balanced on a knife's edge from the beginning. ® — *Jim Pearce*

Growing graphene

ORNL computing, microscopy expertise aid study of carbon 'it' child



When Manchester University scientists Andre Geim and Konstantin Novoselov famously used cellophane tape and a pencil to create a one-atom-thick layer of carbon in 2003, they gave birth to the scientific wunderkind of the past decade—graphene.

The seemingly simple material, made of a single sheet of carbon atoms in a chicken-wire-like lattice, landed the scientists the 2010 Nobel Prize for Physics and spawned a flurry of research into its amazing properties. Graphene's high strength, light weight, optical transparency and ability to conduct electrons make for potentially exciting applications in flexible electronics, sensors and fuel cells, among others. But, like a lot of children, graphene has some growing up to do.

Current manufacturing methods can produce graphene in bulk but often result in defects or impurities that are by-products of the growth process. Defects can include other kinds of atoms such as silicon that sneak into the otherwise purely carbon lattice. Carbon itself can be an impurity, forming uneven lumps on graphene's two-dimensional surface.

Although the word "defect" automatically implies a problem, graphene defects are not necessarily undesirable. They may even be beneficial for certain applications. But their very existence means a lack of control over the production process, so scientists are trying to learn how defects form and how to control them for different applications.

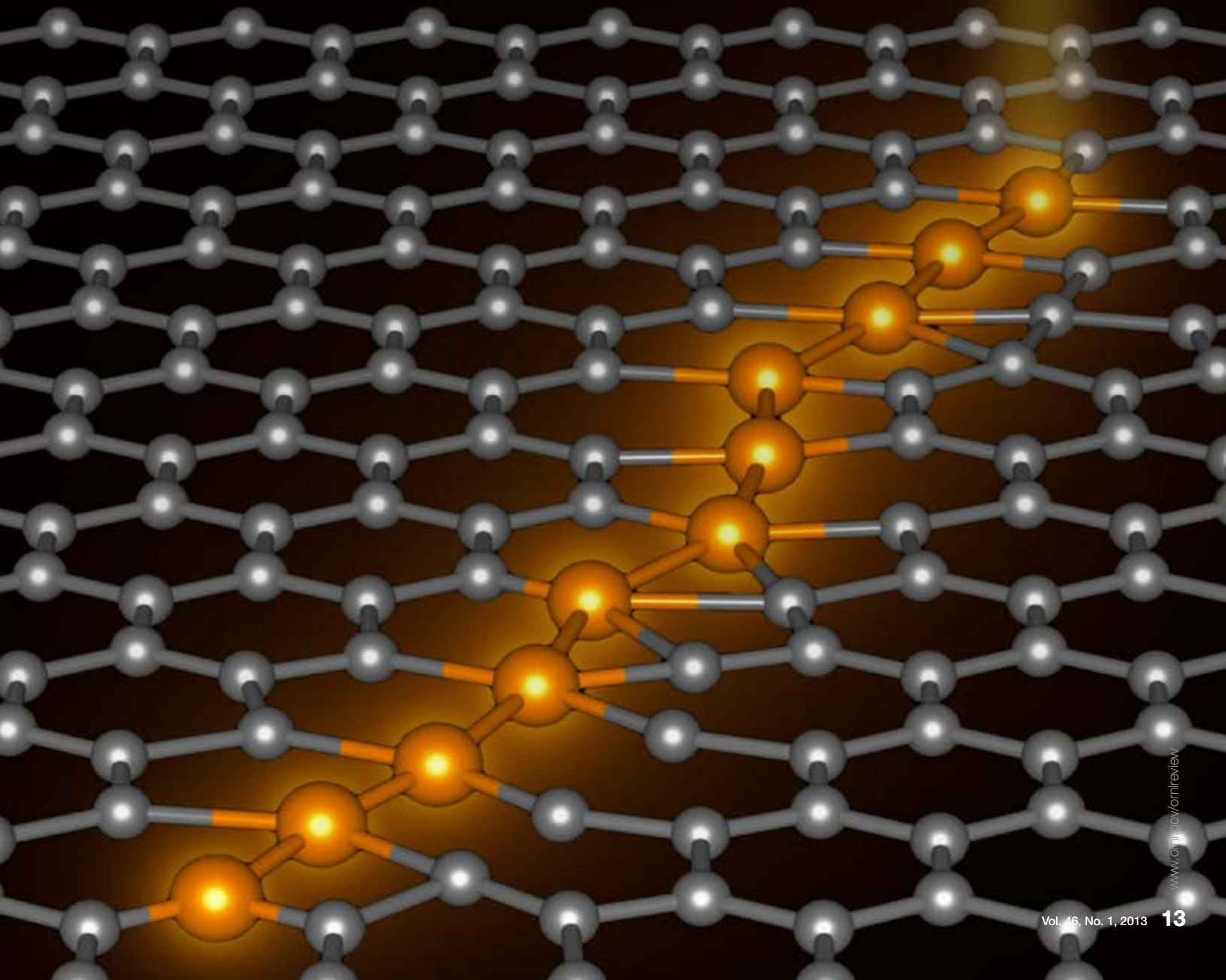
"It's still difficult to fabricate a sheet of graphene without defects," said Bobby Sumpter, a staff scientist at ORNL's Center for Nanophase Materials Sciences. "Defects are nature's way, and you have to either develop a good understanding of what they do to the material or figure out a way to minimize them."

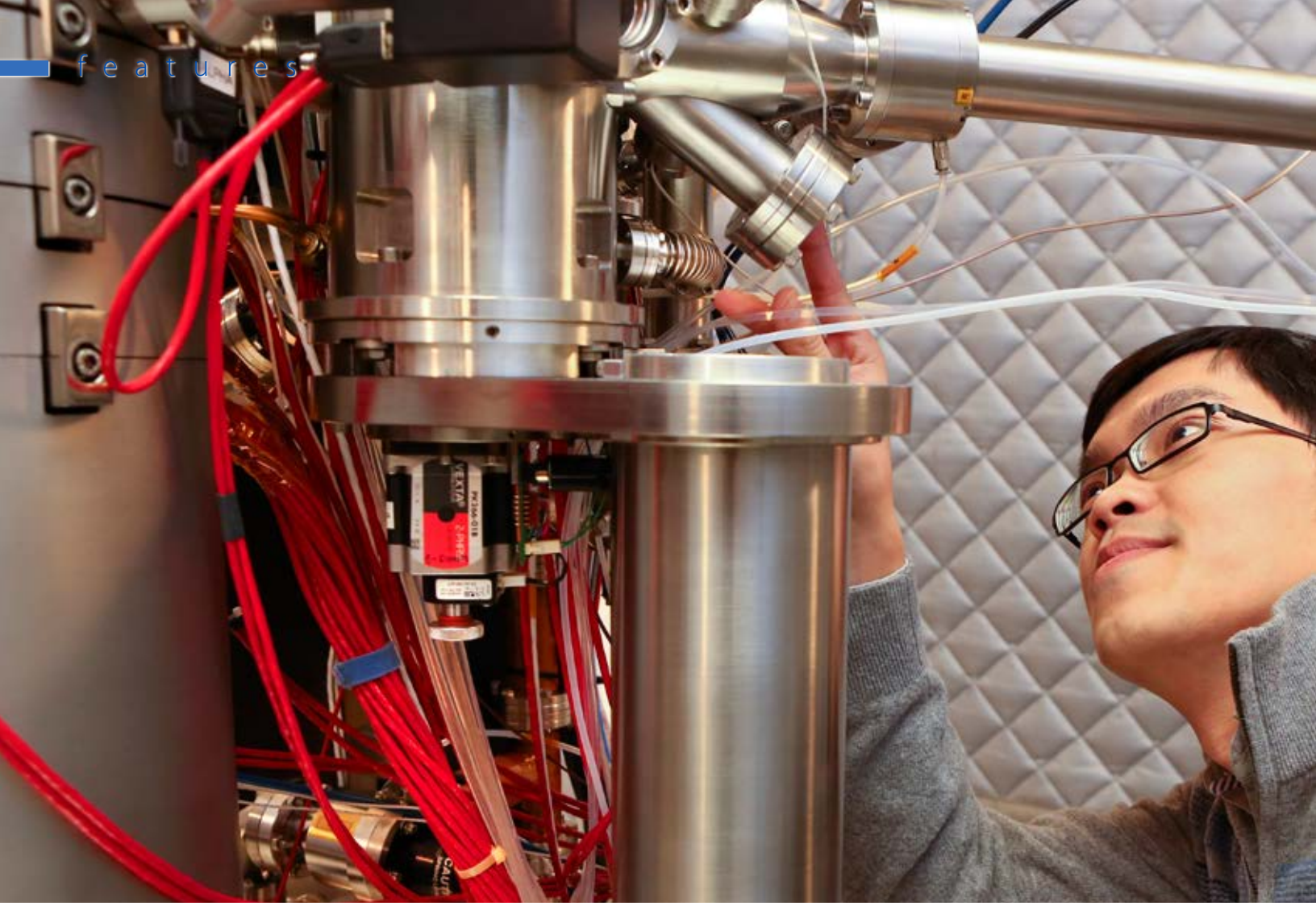
Calculating behavior

For Sumpter, getting to know a material such as graphene and its defects comes down to a mathematical equation. "The equations we solve are the same.

Computer simulations of graphene help scientists understand and control factors that influence the material's structure (above and facing page).

Defects are not always undesirable; they may even be beneficial for some applications





Wigner Fellow Wu Zhou uses an electron microscope to study materials atom-by-atom. (Photo: Jason Richards)

It doesn't matter if it's graphene or copper or gold or a hybrid," Sumpter said. "There are specific sets of equations we need to solve; it's just not always easy. Oak Ridge has a core capability in mathematics and the infrastructure in high-performance computing. That allows us to solve a number of those equations very accurately."

Sumpter uses computational simulation, in collaboration with experimental researchers, to explain and ultimately predict how materials such as graphene behave in different circumstances. One recent study focused on developing a new way to make graphene nanoribbons, where the material is constrained in width. Controlling the width of a graphene piece is important for electronic applications because the width determines graphene's semiconducting properties.

The research team realized multiwalled carbon nanotubes, or carbon cylinders rolled up inside one another, could be unzipped to form graphene nanoribbons with reasonably clean edges, another critical property. The researchers first filled the nanotubes with liquid nitrogen and then dumped boiling water on top to turn the liquid nitrogen into a gas. The resulting high pressure caused the nanotubes to rip apart along a neat line and form graphene nanoribbons. The team's simulations helped explain the mechanics behind the process.

"It's like taking a hot dog and putting it in boiling water," Sumpter said. "It always splits down the middle along a seam. Here we have a 'nano hot dog'!"

Another study took advantage of graphene's defects. Sumpter and his collaborators made a graphene-based supercapacitor, a device that can store electrical energy. In this case defects can be a benefit because they may serve as local reaction sites that contribute to the supercapacitor's energy storage capability.

"For lightweight, strong materials, you don't necessarily need defect-free graphene," Sumpter said. "As a matter of fact, it could be better to have some defects for certain applications because that's where stronger interactions between one material and another material typically happen—at the interface. A plane of graphene is inert and fairly stable, so the defects are where things go to oxidize or functionalize."

Under the microscope

While Sumpter studies graphene with equations and simulations, fellow lab researchers are using complementary experimental techniques to examine the material in real time. With the help of some of the most powerful microscopes in the world, ORNL's Juan-Carlos Idrobo and his colleagues are looking at graphene at a scale that has never been reached—down to the level of individual atoms.

"Our goal is to poke around in materials to see if we can find new physical phenomena or understand, for instance, why specific defects behave in the way they do or

how they change the material properties on a larger scale," Idrobo said. "Defects are the way you control the performance of a material and therefore the device."

The electron microscopes available at ORNL through DOE's Shared Equipment Research User Facility and the lab's Scanning Transmission Electron Microscopy group are ideal for studying defects in two-dimensional materials such as graphene. Scientists can use the microscopes to precisely pinpoint individual atoms and understand how those atoms bond to the surrounding structure. Such information is useful for predicting or improving different material properties and performance.

Aberration-corrected scanning transmission electron microscopy, which ORNL researchers have helped perfect in recent years, is well suited for imaging carbon-based materials such as graphene because of the technique's unique ability to maintain high spatial resolution at low voltages.

"To study these materials, you need two things: you need a very good resolution, but you also need to have the microscope working at low voltages," Idrobo said. "The problem is that when you work at low voltages, your spatial resolution decrease. Aberration correction allows you to go to lower voltages without losing spatial resolution. There is nothing comparable to these microscopes, if you want to study materials on the atomic scale."

In a proof-of-concept experiment published in *Nature Nanotechnology*, Idrobo and his coauthors used the high-powered microscopes to show how silicon defects in graphene could potentially transfer data at the atomic level.

"We showed that a tiny wire made up of a pair of single silicon atoms in graphene, in principle, can be used to convert light into an electronic signal, transmit the signal and then convert it back into light," Idrobo said.

The team's imaging analysis found that the silicon atoms act like atomic-sized antennae, enhancing the optical-like signals of graphene and creating what's known as a plasmonic device.

The basic research done at ORNL is helping carbon materials come of age

"The idea with plasmonic devices is that they can convert optical signals into electronic signals," Idrobo said. "So you could make really tiny wires, put light in one side of the wire, and that signal will be transformed into collective electron excitations known as plasmons. The plasmons will transmit the signal through the wire, come out the other side and be converted back to light."

In an ongoing project, Idrobo and his colleagues are putting ORNL's powerful microscopes to work to understand what happens at the atomic level when current is applied to a sheet of graphene. "We can heat the material up under the microscope and see how the atoms move," he said. "Because our microscopes have the best atomic resolution and sensitivity, we will be able to see what nobody else can."

Graphene combos

As they continue to study graphene and its defects, Sumpter and Idrobo are also interested in combining graphene with other two-dimensional materials to make hybrids that could yield even more interesting characteristics.

"Graphene has all these wonderful properties that make it suitable for applications in a number of areas ranging from simple electronics to photonics to energy storage to arrays for solar energy," Sumpter said. "The problem is going from the little bitty thing up to something that's macroscopic and then to the device scale. That's not easy, and that's where composites come into play."

Idrobo added that graphene has to overcome substantial barriers to entry into today's electronics industry, which has invested billions of dollars and decades of research in silicon-based devices.

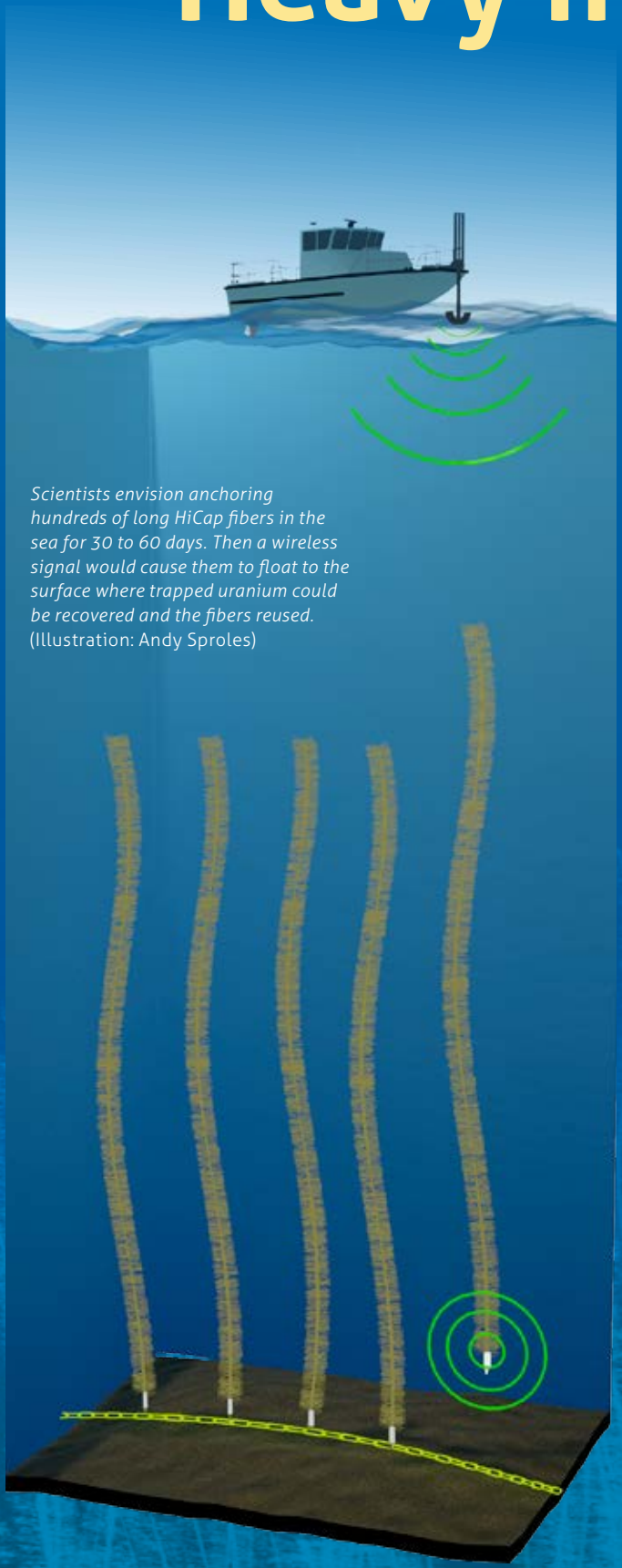
"Graphene by itself is not going to replace silicon in the electronics industry," Idrobo said. "But the combination of graphene with other materials is something that could be used to make novel devices. In theory you could make a flexible cellphone by imprinting a whole electronic circuit into a graphene substrate.

"Developing the quality that the electronics industry requires for mass production is not going to happen over night," Idrobo added. "You need to understand the material's surface, chemistry, physics and more. That's what we're working to understand."

It may take a while before graphene, by itself or in a composite, matures into technologies like bendable iPhones or automotive fuel cells, but the basic research done by Sumpter, Idrobo and others at ORNL is helping the material come of age, one baby step at a time. ® — *Morgan McCorkle*

Heavy metal fishing

New technology at ORNL may secure nuclear energy for hundreds of years



Scientists envision anchoring hundreds of long HiCap fibers in the sea for 30 to 60 days. Then a wireless signal would cause them to float to the surface where trapped uranium could be recovered and the fibers reused. (Illustration: Andy Sproles)

For decades, researchers have searched for a way to extract the oceans' estimated 4 to 5 billion tons of uranium. The element rolls in the waves, crashes on the beaches and tickles the toes of beachgoers everywhere, but it could never be captured cheaply enough or in sufficient quantities for energy or defense applications.

With the help of surface-area-enhancing techniques developed and patented by Florida-based Hills Inc., Oak Ridge National Laboratory researchers are creeping closer to unlocking the limitless energy stores buried in the waves.

The Department of Energy is interested in ensuring the United States continues to have uranium for nuclear power and national security. With nuclear power providing more than 20 percent of the nation's energy supply, running out of uranium is simply not an option.

"Scientists have forecast that eventually there will be a tremendous shortage in nuclear fuel if we continue to mine it only on land," said Sheng Dai, technical lead on the ORNL project.

Mining uranium on land involves either physically removing or chemically dissolving the element from a limited number of ore sources. Removing uranium from seawater is safer and recovers the same elemental form of uranium found on land.

"If we could recover uranium from seawater, we could provide enough nuclear energy to supply the whole world for hundreds of years," Dai said.

The goal of extracting uranium from the oceans began with research and development projects in the 1960s, with Japan conducting the majority of the work. DOE became a major player in this research area in 2010, when Hills and ORNL began tinkering with the surface areas of plastic fibers. The adsorbent fiber the team developed was designed to recognize and selectively trap dissolved uranium.

Hills, an innovator in the field of fiber technologies, helped ORNL researchers increase the surface area of the adsorbents by incorporating complex ridges and folding patterns into the plastic material. These modifications and other processing improvements resulted in HiCap Adsorbents, a 2012 R&D 100 Award winner and patent-pending technology. HiCap harvests uranium seven times faster than its competitors—and reduces the initial $1,230 cost of removing one kilogram of uranium from seawater by up to 50 percent.

ORNL's new technology is made from polyethylene fibers—the same material used to make grocery bags and milk cartons. Researchers can melt, spin and braid these plastic fibers. Afterward, they can zap it with an electron beam to open grafting sites and chemically add metal-catchers called amidoxime groups. These modifications turn this everyday plastic into "a fancy heavy-metal fisherman," said Yatsandra Oyola, a member of ORNL's research team.

Despite recent progress, researchers acknowledge additional work is needed to make the technology commercially viable. Fishing for uranium is still five times more expensive than mining it on land, but as land reserves are depleted and uranium prices rise, the technology will become more attractive. The notable cost reduction provided by HiCap suggests that, with additional tweaks, the product could be the key to ensuring nuclear energy security for generations. The ability to extract uranium from seawater, no matter the expense, will allow the government to make decisions about the future of nuclear power with the confidence that the material will be available in the long term.

"The government often funds projects that are developing technologies like HiCap that won't be commercialized immediately," said Erich Schneider, a project collaborator from the University of Texas at Austin. "They are trying to develop it to the point that, if in the future we run out of uranium on land, a company can take the adsorbents off the shelf and quickly commercialize them."

Laboratory tests have shown that collecting uranium is as easy as submerging the product in water for minutes or several days, said Chris Janke, one of HiCap's inventors and a member of ORNL's research team. Scientists envision dropping many metal chains tied to hundreds of 60-meter-long adsorbent fibers into the sea—packing the seabed with row upon row of HiCap Adsorbent fibers and creating something resembling an underwater cornfield. The HiCap field could extend for thousands of square miles along the sea floor, covering an area comparable to two Rhode Islands.

Uranium would be harvested after 30 to 60 days. Ships would float over the submerged fibers and wirelessly detach them from the chains by sending a signal from a handheld device, allowing the fibers to float to the surface. At that point the fibers and any trapped uranium could easily be scooped up and shipped back to labs. Chemists could then extract the uranium from the fibers and regenerate the adsorbents so the fibers could be reused.

Researchers from seven universities and a variety of national laboratories are collaborating with ORNL's team to improve the uranium extraction process. They are focusing their efforts on using carbon-based materials instead of polyethylene fibers, alternative chemical coatings to amidoxime and less harsh chemical treatments for stripping metals. Other researchers are determining HiCap's potential environmental impacts and performing economic analyses.

"We are just scratching the surface on what this product is capable of," Janke said. "The product design will have to be a compromise among binding capacity, durability, amount of chemical groups and price."

In the meantime the adsorbents originally created to catch uranium from seawater can take center stage in environmental cleanup efforts and the recovery of precious metals.

Because HiCap's adsorbents are selective for heavy metals other than just uranium, the technology can be used to extract toxic or valuable dissolved metals from a variety of water sources worldwide. Nets fashioned from HiCap adsorbents and placed throughout contaminated streams could selectively remove other heavy metals, improving water quality and rehabilitating aquatic ecosystems.

"It's a very competitive product for certain types of environmental remediation and metal recovery applications because it's not that expensive to make," Janke said.

Researchers believe the heavy metal waste collected can be recycled, potentially allowing HiCap adsorbents to start paying for themselves.

No matter the need, HiCap—or an improved version of the technology—can change the game for a wide variety of applications.

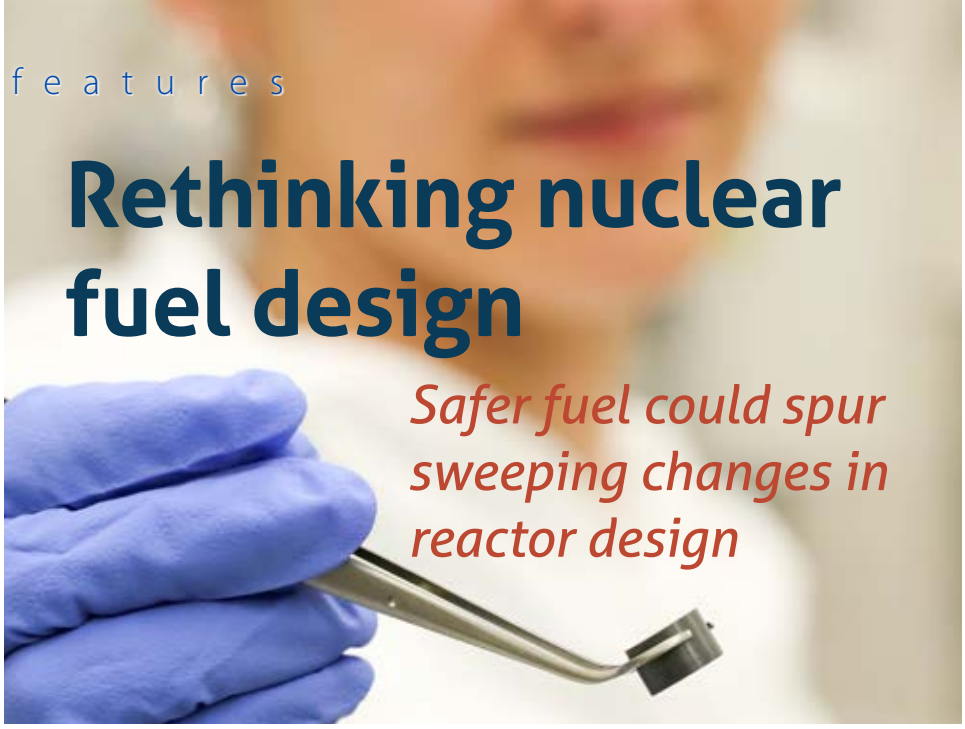
"We have a material that we know can work," Janke said. "Now we just need to figure out the best places to use it and make sure that it's deployed effectively." ®

— *Jennifer Brouner*

Chemist Yatsandra Oyola prepares a braid of polyethelene fibers for use in HiCap research. (Photo: Jason Richards)

Rethinking nuclear fuel design

Safer fuel could spur sweeping changes in reactor design



Scientists differ on what actions might have prevented the near destruction of three of the Fukushima Daiichi nuclear plant's six reactors in the wake of the tsunami that struck Japan in March 2011. They agree, however, that the design of the reactors' fuel elements contributed to both the hydrogen explosions that heavily damaged the facilities as well as to the subsequent contamination of land and water near the facility.

The design of the fuel used in the Fukushima reactors, like that used in most commercial reactors, hasn't changed much in 60 years. Its lineage can be traced directly to the reactor designs favored by Admiral Hyman Rickover to power the first nuclear submarines in the 1950s. These systems were, in turn, scaled up for use in commercial power plants.

"Today's nuclear reactors are designed around the strengths and weaknesses of their fuel," says Kurt Terrani, a nuclear engineer in ORNL's Nuclear Fuels Materials group. "The current fuel is extremely reliable under normal circumstances, and it has enjoyed 60 years of development and improvement. However, under extreme accident scenarios, it becomes a reactor's Achilles' heel."

A safer alternative

But what if someone developed a fuel that didn't have this Achilles' heel? How would that affect the US nuclear industry?

"An inherently safe fuel would fundamentally change reactor design and the cost of reactors," says scientist and Materials Science and Technology Division Associate Director Lance Snead. "In current reactors, a lot of expensive systems are dedicated to ensuring that the fission products from burned fuel do not escape from the plant under any circumstances. As a result, nuclear power plants can't compete with natural gas plants in terms of cost. Until we develop a less expensive fuel technology, the nuclear industry will lag behind other energy alternatives, and we will continue to burn fossil fuels."

So what would an inherently safe nuclear fuel look like? Snead suggests that it would have a lot in common with the tristructural-isotropic (TRISO) fuels ORNL has spent the last decade pushing to record levels of performance.

Originally developed for use in rocket engines, TRISO fuel designs have been around for 50 years. They are made up of microspheres of fuel coated with layers of carbon and a radiation-resistant shell of silicon carbide. Each millimeter-wide sphere is basically its own small pressure vessel that traps the radioactive byproducts of nuclear fission, such as xenon and cesium.

Interest in TRISO technology has waxed and waned over the years. However, in 2002, Gary Bell's research group at ORNL was tasked with applying TRISO technology to the development of small cylindrical containers of fuel, called "compacts"—first for testing in Idaho National Laboratory's Advanced Test Reactor and eventually for use in a proposed high-temperature gas cooled reactor.

"When this fuel was placed in the Advanced Test Reactor for three years," Snead says, "the compacts made by John Hunn and his colleagues in our fuels group performed flawlessly. I think that established our TRISO as the new gold standard. It doubled the burn-up, or fuel efficiency, of previous fuels."

Rethinking fuel design

In 2010, an ORNL research team investigating advanced fuels for light water reactors began looking for other ways to apply TRISO technology. One proposal was to encapsulate the long-lived components of commercial nuclear waste in TRISO spheres and then burn them as fuel in commercial reactors. The group calculated that this recycling process would decrease the waste volume by 80 percent, enabling waste repositories to last five times longer.

"While we were developing this variation on TRISO fuel, it was always clear that this kind of fuel design could also be used to replace traditional reactor fuel," Snead explains. "However, because the fuel would have been considerably more expensive, there was little motivation to explore that possibility."

The events at Fukushima in the following year and the obvious shift in research emphasis toward safer, accident-tolerant nuclear fuels caused Snead's group to switch its focus.

One key advantage of TRISO fuels in Fukushima-like accident scenarios is that they completely enclose both the fuel kernel and its waste products in two layers of protection. The fuel itself is wrapped in a SiC sphere, which is then contained within a dense, impermeable SiC matrix. The fuel cladding, which historically has been the primary barrier to release, provides a third barrier.

Another shortcoming of conventional fuel is that its zirconium-based cladding can actually burn under extreme conditions. In fact, the explosions that happened at Fukushima resulted from hydrogen released by steam interacting with burning cladding.

Snead explains that steam attacks SiC exceedingly slowly when compared to its effects on zirconium-based cladding. "If TRISO fuel were subjected to conditions like those at Fukushima, after burning through the cladding, the steam would have to penetrate both the SiC matrix and the TRISO

spheres to reach the harmful fission products. It would take dozens or hundreds of hours for that to happen."

Safer for this generation and the next

Bell, leader of the lab's Nuclear Fuel Materials Group, notes that a key consideration in developing a new fuel for use in existing commercial power plants is to design something that looks and performs like the fuel they're already using. That's what motivated Snead and ORNL materials scientist Yutai Katoh to develop a new type of TRISO fuel called FCM (fully ceramic microencapsulated fuel), which is designed to replace the fuel in any fission reactor.

Of course, added safety comes at a price. "FCM production is a multi-step process and requires uranium enrichment of about 19 percent—about four times the level of standard fuel. This would increase the fuel costs for existing reactors, although it could also enable savings in reactors using next-generation designs," Snead says.

"Our goal with FCM is to show that TRISO fuel is safer and more efficient for both current-generation reactors and next-generation designs."

Part of the difficulty of introducing a new fuel to the nuclear industry is the extent to which every aspect of reactor operation is tied to the behavior of the current fuel.

"In the 1970s, prior to Three Mile Island, the nuclear energy community hypothesized accident scenarios," Terrani says. "Then they defined design criteria to manage those scenarios. Their philosophy is defense in-depth. Reactors have multiple barriers, multiple systems and multiple levels of safety—all designed to respond when anything goes wrong within the reactor.

"When we talk about using TRISO fuel, or something similar, for the next generation of reactors, we are talking about an opportunity to redefine reactor design based on what we expect to happen under scenarios involving the new fuel."

TRISO is also a potential game-changer for waste disposal. When today's fuel is removed from a reactor, it has turned into a sandy substance called "rubble" that has to be to be processed before it can be disposed of permanently. On the other hand, silicon carbide-based FCM fuel comes out of the reactor essentially "repository-ready" and looking exactly as it did when it went in—at least that has been the case with the surrogate fuel pellets that have been tested so far.

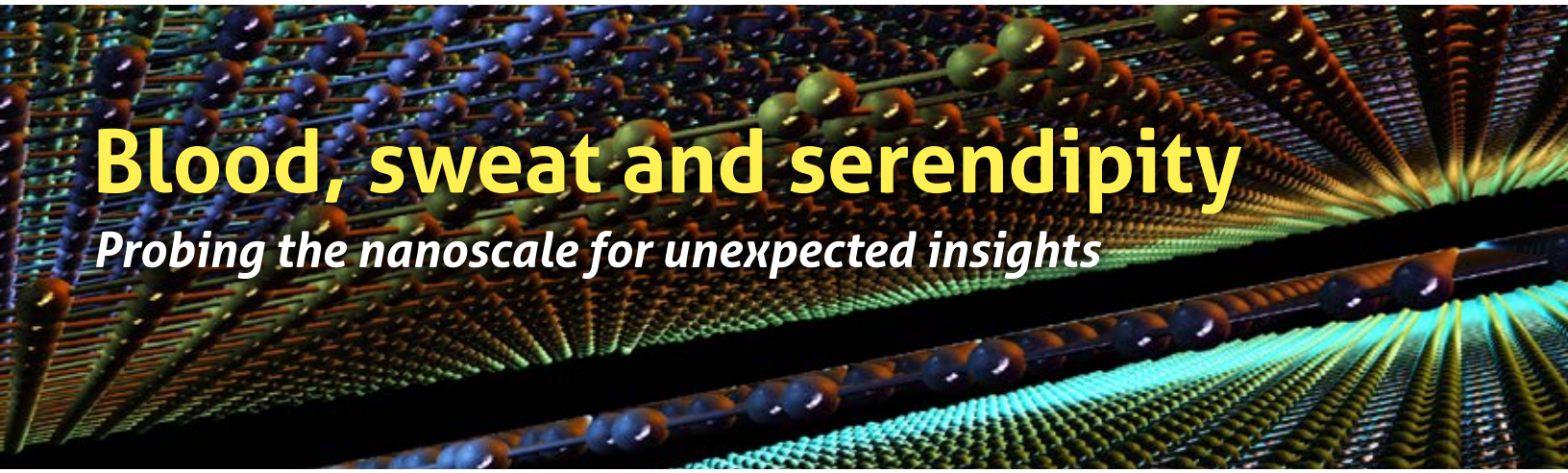
Historic opportunity

The development of a safer, more efficient alternative to traditional nuclear fuel could bring sweeping changes to the safety, design and operation of commercial nuclear reactors.

"I think in the very near term we will be able to clearly demonstrate that we can manufacture stable FCM fuel," Snead says. "People in the nuclear industry are interested in testing this fuel in a commercial reactor, but the industry is also very cautious. Inserting the FCM fuel into a commercial reactor for the purpose of eventually licensing it would be historic, but it also would be just the start of a very long road to implementing the technology. However, once this fuel or one like it is proven in the current generation of reactors, it will give designers of next-generation reactors a fuel option that doesn't exist today."

That new fuel option, his team believes, will give the nuclear industry the opportunity to rethink reactor design from the ground up for the first time since the very early days of nuclear power. ® — *Jim Pearce*

Nuclear engineer Kurt Terrani and lab technician Stephanie Curlin at the controls of an ion-beam milling machine used to prepare samples of both new and irradiated TRISO fuel for study. (Photo: Jason Richards)



Blood, sweat and serendipity

Probing the nanoscale for unexpected insights

Discovering how electrons move through materials tells scientists a lot about their physical qualities. Are they good insulators? Good conductors? Can they be polarized? The nuances of "electron transport" account for phenomena as exotic as the northern lights and as commonplace as the information stored on the memory chip in your phone.

Physicists normally handle measurements of this process with kid gloves, taking care not to change the materials through the act of measuring them. By this standard, the analytical methods used by ORNL materials scientist Peter Maksymovych and his colleagues—blasting materials with high-energy electrons and subjecting them to intense electric fields—seem a bit iconoclastic.

Experience and perspective

"Most people think that if you stimulate a material with a strong electric field or inject high-energy electrons into it, that will significantly alter the material, or simply destroy it, and you will not learn anything," says ORNL materials scientist Peter Maksymovych. "Our research team disagrees profoundly."

Maksymovych's skepticism is based both on experience and perspective. While many scientists in the field work with relatively large material samples, at the laboratory's Center for Nanophase Materials Sciences, Maksymovych and his team probe materials at the nanoscale—at the level of single molecules.

"Because we use scanning probe microscopy to examine materials," he says, "we have a unique perspective. We can see phenomena at the nanoscale that aren't apparent in larger samples."

Maksymovych and his team are currently trying to find evidence of new behaviors, new phenomena and new materials by exposing ferroelectric materials, such as those used to make memory chips and other electronic devices, to very large electric fields and high electron currents.

One of the issues they have been studying is related to the production of ferroelectric-based memory chips, or FE-RAM—a specialized type of memory chip that is faster and requires less energy than many other forms of digital memory. Data is recorded on FE-RAM by creating very small polarized and non-polarized regions on the material. This is read as 1s and 0s by the computer, just like any other binary memory medium. Unfortunately, polarization-based FE-RAM memory requires a lot of space—relatively speaking—and can't be scaled down beyond a certain point.

"The challenge with FE-RAM has been scalability," Maksymovych explains. "The FE-RAM uses a layer of ferroelectric film to store information. Making a bit (the smallest unit of information) smaller than 100–200 nanometers across (about as much as a fingernail grows in two minutes) and still read it has proven to be fundamentally difficult. That's because reading FE-RAM depends on detecting a charge on the surface of the material. There's a limit to our ability to measure that. As a result, while we could use conventional techniques to write data to a smaller area of ferroelectric film, we couldn't read it."

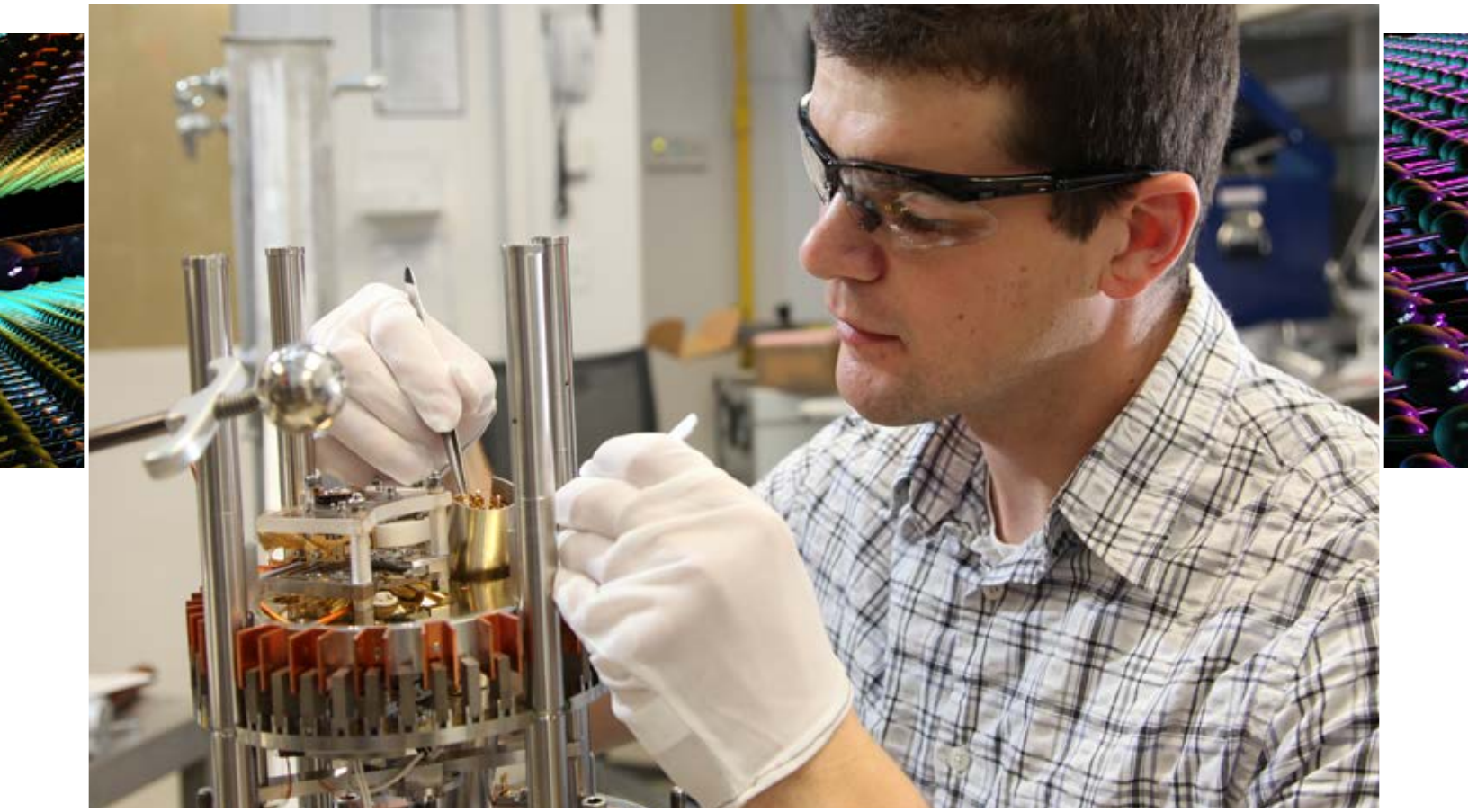
Serendipity steps in

Just as the research team was coming up empty in its search for a way around this "reading" problem, Maksymovych says serendipity took over. They found that, contrary to conventional wisdom, when they applied a large electric field to a tiny area of the ferroelectric film, which is normally an insulator, the area became electrically conductive.

This behavior not only opens up the potential for writing, reading and erasing much smaller "bits" of information (down to at least 10 nanometers), suggesting a way around the scalability problem, but it also hints at possibilities for new electronic applications for ferroelectric materials.

The discovery is also of interest to researchers because of the type of conductivity it uncovered. The team found that applying an electric field to the otherwise insulating material had turned on metallic conductance. This is significant because, unlike many other conducting materials, metallic conductors work at all temperatures—opening them up to a much broader range of potential applications.

"If you take the material down to very low temperatures where the ability of semiconducting materials to conduct electricity would nearly die out," Maksymovych explains, "the difference in conductance is seven to eight orders of magnitude. In addition, the amount of current being conducted is easily two to four orders of magnitude higher when ferroelectric materials become metallic. This phenomenon is particularly attractive because it has these colossal magnitudes tied to it."



Scanning probe microscopy enables materials scientist Peter Maksymovych and his colleagues to see nanoscale phenomena that aren't apparent in larger samples. (Photo: Jason Richards)

Also attractive to scientists is the prospect of being able to create conductive "nanodomains" within an otherwise insulating material. Maksymovych suggests that this behavior alone opens up a new realm of nanotechnology which he refers to as "topological nanostructure."

"Instead of depositing a material here or changing the composition of a material there," he says, "all we have to do is apply electric fields to the ferroelectric material and we can control conductance. By doing this we were able to observe phenomena that had been hypothesized, but certainly not observed."

A beautiful playground

Shrink the size of the probed region by another order of magnitude, and you enter the world of molecules. Maksymovych suggests that the ability to control molecules using electric fields is a compelling platform for understanding physics in general.

"Today there are still many mysteries surrounding molecular physics," he says. "Even though we can develop complex simulations, we still don't know everything we want to know. Ideally, we would like to apply what we have learned so far to developing a better understanding of organic molecules."

Maksymovych envisions devising a way to inject high-energy electrons into molecules and then applying the knowledge his team has accumulated and the analytical techniques they have devised to the task of understanding how electrons interact within organic molecules and how molecules interact with each other "on a whole new level." One specific area of interest is the role electron transport plays in conductivity at the molecular level, including materials like "Mott insulators" that can be either insulators or conductors—depending on the conditions—and inorganic superconductors.

"Some people will say that we already understand electron behavior in molecular conductors pretty well," he observes, "but the simplicity of a lattice of organic molecules (like the molecules in a sugar crystal) has the potential to give us more insight, particularly at the nanoscale. We can count the number of molecules, count the number of defects, create new defects, and sometimes even count the number of electrons. We cannot do that in inorganic materials yet. This kind of research would move us in that direction."

Scientists normally look for the simplest possible setting in which to study a phenomenon, and Maksymovych and his research team believe molecular assemblies are an elegantly simple platform for studying the nature of materials.

"Often these kinds of studies are done using individual atoms at extremely low temperatures—the so called cold atom lattices," he says, "but there are lots of things a single atom can't tell you. Molecules, or lattices of molecules, give us the opportunity to study a much wider range of phenomena."

Maksymovych is betting that observing how electrons enable molecules to "communicate" with one another will have multiple benefits: providing us with a better understanding of their structure, affording insight into elusive phenomena such as superconductivity and uncovering more unanticipated properties of everyday materials.

"If we use molecules in this way, I believe we can build a new and beautiful playground for the study of electron physics," he says. ® — *Jim Pearce*

Something new under the sun

Laying the foundation for the next generation of materials

Metals have been at the heart of technological advancement for 4,000 years—since people moved from tools of stone, bone and wood to copper, bronze and, eventually, iron and steel. The rise of metallurgy—the ability to extract, refine and mix metals—also coincides with the development of writing and the rise of the first cities. Since then metals have been intertwined with virtually every aspect of civilization, from pots and pans to geopolitics, from manufacturing to macroeconomics.

While this millennia-long fascination with metals has had obvious benefits, it actually presents something of a challenge to scientists trying to modify materials atom by atom to give them radically different physical properties—in this case, ultrastrong steels for nuclear energy systems and other extreme environments.

"People have been working with metals for thousands of years—and very assiduously for the last couple hundred," says materials scientist Malcolm Stocks, director of ORNL's Center for Defect Physics. "So we have a lot to choose from, and they have all been refined to fit very particular purposes. That's why coming up with something that has properties outside of these accepted boundaries—disruptively outside of these boundaries—is a very difficult task."

The goal of the CDP and other research being conducted at ORNL with the support of the US Department of Energy's Office of Basic Sciences is to use advanced synthesis, analytical and computational tools to better understand how materials work at very small scales and under extreme conditions. This knowledge will then be used to make more quantitative connections between the relevant aspects of materials' structure and properties such as strength and radiation resistance.

"We're really looking at two different, but related, definitions of 'extreme,'" Stocks says. "In the case of the CDP, we are trying to develop materials that can resist damage from high levels of external radiation."

"On the other hand, our other work for the Office of Basic Energy Sciences, as well as for applied DOE programs, some of which evolved from our BES work, tends to focus on the intrinsic properties of materials," explains ORNL materials scientist Easo George. Those investigations explore extremes of a somewhat different kind and address questions that deal with how to more closely approach and function effectively near the intrinsic limits of materials, such as their melting points or theoretical strengths.

Metal has been at the heart of technological advancement for 4,000 years

The knowledge gained by this research will be incorporated into computer models designed to accelerate the development of materials for use in applications such as next-generation nuclear energy systems, where radiation damage is a concern, or turbine blades, where heat-resistant materials play a critical role.

Failure is not an option

The need for accurate descriptions of material behavior is particularly acute in the realm of structural materials, where expectations of performance are particularly high. For example, if you were driving across a bridge and a streetlight went out, you probably wouldn't be too upset; however, if the bridge collapsed, that would be a different story.

"We think of structural materials differently than other materials," says George. "A new consumer electronic device can take over the market in the relative blink of an eye, but it takes a long time for new structural materials to get into service and become useful. Structural materials have to go through a lot of testing—sometimes over long periods of time, depending on their expected length of service—to be sure they are going to work all the time."

Detailed models of material structure validated by experiments like those the center is developing will eventually reduce the time required for testing by identifying the structural characteristics that a material must have in order to achieve desired properties. If you wanted a material with improved radiation resistance, for example, this type of model would identify certain characteristics these materials would need to have and eliminate materials that didn't have them.

The need for advanced modeling capabilities becomes even more acute when you consider that most structural materials have to meet a number of requirements simultaneously.

"There are very few structural applications where only one property is important," George says. "It's almost always a combination of properties. You need strength, you need toughness, you need corrosion resistance, and you need the ability to manufacture and form the material. It's not hard to make a superstrong material that has no other desirable properties. For example, a material can be very strong and very brittle at the same time. However, getting the right combination of properties takes a lot of work. That's a big part of what our research is about."

"Model" materials first

The strength of a material is determined by its defects, so to gauge a structure's strength, researchers need precise knowl-

edge of what kinds of defects are present in the material and how those defects are distributed. Generally speaking, the fewer defects there are in a material, the stronger it is. Similarly, if a composite material contains two different materials, the composite's properties generally lie somewhere between the two.

For example, George and his colleagues are studying a composite material that consists largely of a standard nickel-aluminum alloy, but it is reinforced with ultra-strong, defect-free fibers made of either molybdenum or chromium that are five to ten times stronger than their normal dislocation-containing counterparts. Although the fibers represent only a small fraction of the composite's total volume, their contribution to its high-temperature strength is tremendous relative to their size. For example, the composite's ability to resist deformation at high temperatures is a million or more times greater than that of the nickel-aluminum alloy.

Developing the ability to produce defect-free crystalline fibers like these from a range of metals may eventually enable scientists to design materials that combine traits, such as strength and ductility, or strength at extreme temperatures.

"The composites currently being investigated are relatively simple 'model' materials," George explains. "Before we move on to more complex systems, we need to understand how each phenomenon is related to the structure of the material."

Certainty and flexibility

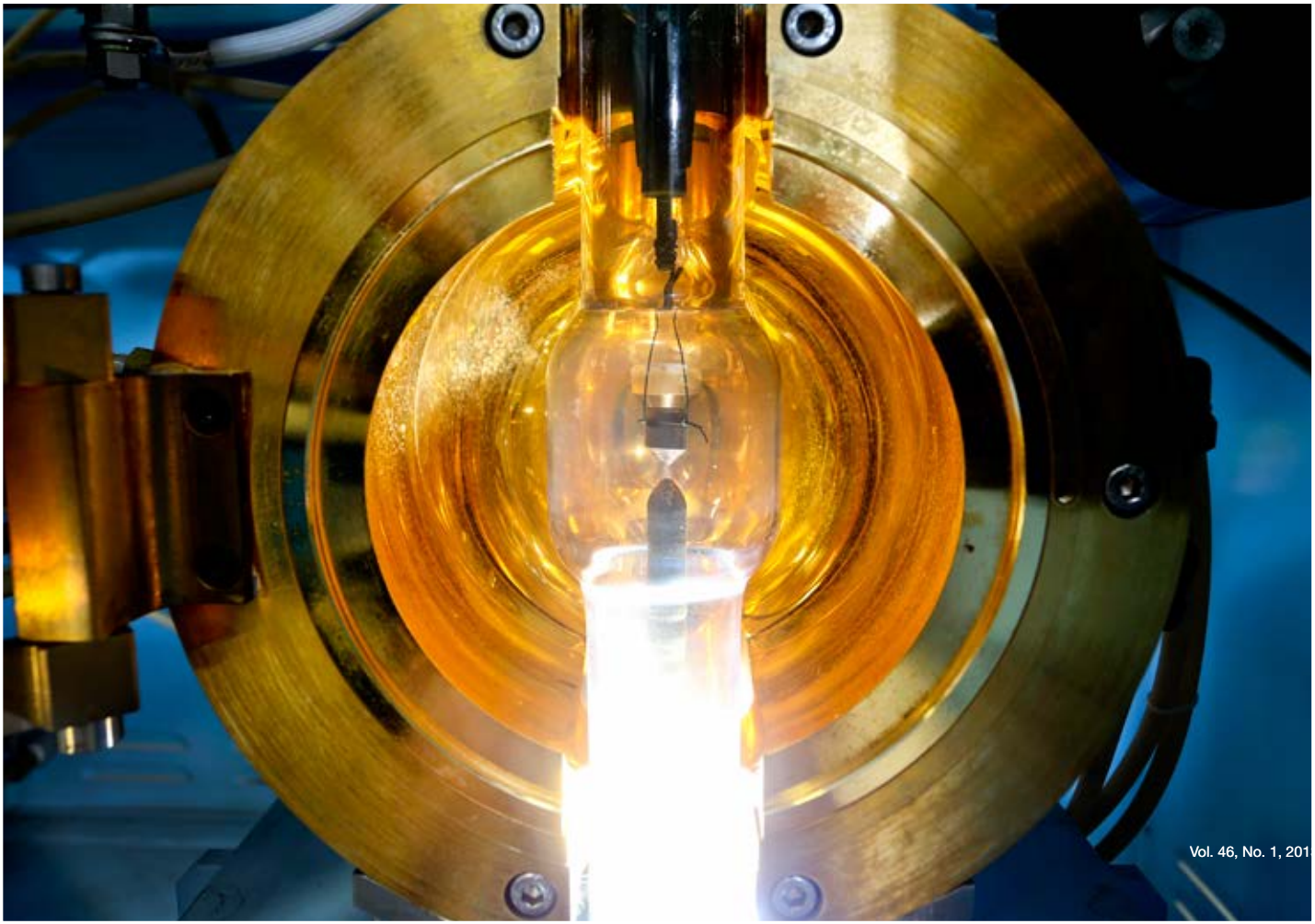
While scientists have known for a long time that understanding defects is the key to controlling other aspects of material behavior, they haven't had a good understanding of precisely how defects work at the small scales Stocks, George and their colleagues are investigating.

"We know that defects that appear at very small scales ultimately control the properties of materials at the macro scale," Stocks says. "The point of our research is to make the link between these scales increasingly quantitative. If we can do that, we think we can overcome many of the conventional limitations of material behavior. If we can incorporate an understanding of the defects at this fundamental scale into our computer models, this will allow engineers greater latitude and enable them to use materials closer to their extremes."

Traditionally, engineers have had to work within the narrow confines of materials whose properties and performance characteristics had been established explicitly through experimentation. ORNL's materials researchers are trying to broaden those parameters by providing the next generation of engineers with the modeling tools needed to identify materials that meet specific requirements or even guide the development of entirely new materials.

"Our goal is to increase the engineer's certainty as well as flexibility," Stocks says. "The ability to predict very precisely how a particular material will behave under a specific set of circumstances is invaluable." ® — *Jim Pearce*

A xenon-arc-lamp floating-zone furnace is used to make single crystals and composite materials with well-aligned nanoscale microstructures. These model systems are used to study the fundamentals of materials at extremes. (Photo: Jason Richards)



Kinga Unocic

Before coming to work at ORNL, materials scientist Kinga Unocic completed her doctoral and master's degrees in materials science and engineering at The Ohio State University. She also obtained her master's degree in metallurgical engineering at AGH University of Science and Technology in her native Poland. Although she finished the research for her AGH degree at Lehigh University in Pennsylvania, Unocic says she didn't originally have plans to stay in the US.

"I wanted to finish my research, improve my English language skills, then return to Poland to start my career," she says. "Having a second language is very important in Poland in the business and scientific fields. However, while I was at Lehigh, I became accustomed to the US lifestyle. More importantly I found a sense of purpose regarding my research interests. I also met my husband at Lehigh, which also changed my plans."

Transplanting her professional life across the Atlantic turned out to be a good move for Unocic. "I came to the US with two suitcases, $500 in my pocket and a dream. In retrospect I'm very happy with the way things worked out," she says. "At ORNL I've had the opportunity to work among the leading scientists in my field on cutting-edge research projects that challenge me as a scientist. It is also important that the research that I am conducting has a direct impact on society. I probably would not have had the same range of opportunities at other institutions."

We asked Unocic what led her to a career in materials science and how she sees advances in the field affecting our daily lives.

You're often held up as an example of the "next generation" of materials researchers. What distinguishes your generation of scientists from previous generations?

Previous generations of scientists laid the scientific groundwork for our fundamental knowledge of materials science and engineering. The current technological revolution allows us to apply that knowledge to developing new materials for specific applications. Recent advances in technology enable us to make scientific progress at a much faster pace than previous generations of researchers could have ever imagined. We also benefit from improvements in analytical equipment that enable us to characterize material properties all the way down to the atomic scale.

What made you want to pursue a career in materials science?

I wanted to be a part of something bigger than myself, something that would make a difference in people's lives. At first I wanted to be a medical doctor, but in high school I found that I excelled at courses in math and physics rather than biology and chemistry. Materials science seemed like a career choice that matched my interests and would allow me to work on interesting materials-specific problems.

What qualities would you say are most important for being a successful researcher?

I would say dedication, passion, being a team player, collaboration—and most importantly having fun. Recently one of my very accomplished colleagues said to me, "It's important to have fun while you are doing research." I think he is exactly right. If you enjoy what you are doing, then you'll be a more effective researcher, and you'll be able to make the scientific advances that can change people's lives.

You work in the lab's ShaRE microscopy user facility. What does ShaRE do?

ShaRE stands for Shared Research Equipment. It's a US Department of Energy, Office of Science user facility that provides researchers from universities, industry and other national laboratories with the opportunity to conduct their research using an array of state-of-the-art electron microscopes. They also collaborate with our staff scientists who are all experts in their fields. Most of the research done at ShaRE involves investigating energy-related issues in the areas of materials science, chemistry and physics.

Where can we see the results of the kind of R&D being done at ShaRE in our daily lives?

The world is dependent upon energy, and there is a constant demand for increased energy efficiency and environmentally friendly alternative energy sources. Developing these technologies often requires new materials. Power plants, for example, can increase their efficiency by operating at higher temperatures. However, higher temperatures place an increased demand on the mechanical properties and long-term stability of materials. ORNL has a long history of alloy development for such high-temperature applications. One of the projects I worked on recently involved analyzing a new alloy after it had been exposed inside the boiler of a biomass- and waste-fired power plant. Understanding how new alloys perform in these aggressive, high-temperature environments will help us direct our research toward developing materials that will make new and more efficient power-generation technologies a reality.

Five years from now, what sort of research problems do you expect to be investigating? How will they be different from what you're working on today?

Well, that's difficult to say. Currently the use of natural gas is increasing in the US, so in five years we may be looking at technologies to improve the efficiency and reliability of natural gas power plants. We may also be helping to develop new materials and coatings for use in more efficient, high-temperature gas-fired turbines. There might even be a demand for automotive gas turbines with ultra-low emissions and the ability to burn natural gas, diesel or biodiesel—depending on the price of fuel.

I also work closely with ORNL's Corrosion Science & Technology Group. A lot of my work involves understanding how extreme conditions affect the performance and reliability of materials. One of my current projects involves studying the durability of lightweight magnesium alloys. These alloys could have a significant impact on the efficiency of cars and planes, so the research is very timely.

Our ability to develop new materials often provides a pathway to improving the efficiency of existing technologies or developing entirely new technologies. I expect the field of materials science will always provide exciting problems for me to investigate and solve. ®

'Zoomable' map of poplar proteins offers new view of bioenergy crop

Researchers seeking to improve production of ethanol from woody crops have a new resource in the form of an extensive molecular map of poplar tree proteins, published by a team from ORNL.

Populus, a fast-growing perennial tree, holds potential as a bioenergy crop due to its ability to produce large amounts of biomass on non-agricultural land. Now, a study by laboratory scientists with the Department of Energy's BioEnergy Science Center has provided the most comprehensive look to date at poplar's proteome, the suite of proteins produced by a plant's cells. The study was featured on the cover of January's *Molecular and Cellular Proteomics*.

"The ability to comprehensively measure genes and proteins helps us understand the range of molecular machinery that a plant uses to do its life functions," says ORNL's Robert Hettich. "This can provide the information necessary to modify a metabolic process to do something specific, such as altering the lignin content of a tree to make it better suited for biofuel production."

The ORNL research team measured more than 11,000 proteins in different parts of poplar, including mature leaves, young leaves, roots and stems. This systematic approach yielded a so-called proteome atlas, which maps out the proteins present in the various tissue types at a given point in time. Lead coauthors Paul Abraham and Richard Giannone describe how the atlas offers a broad overview of the poplar proteome and also the ability to zoom in on specific biological features, such as pathways and individual proteins.

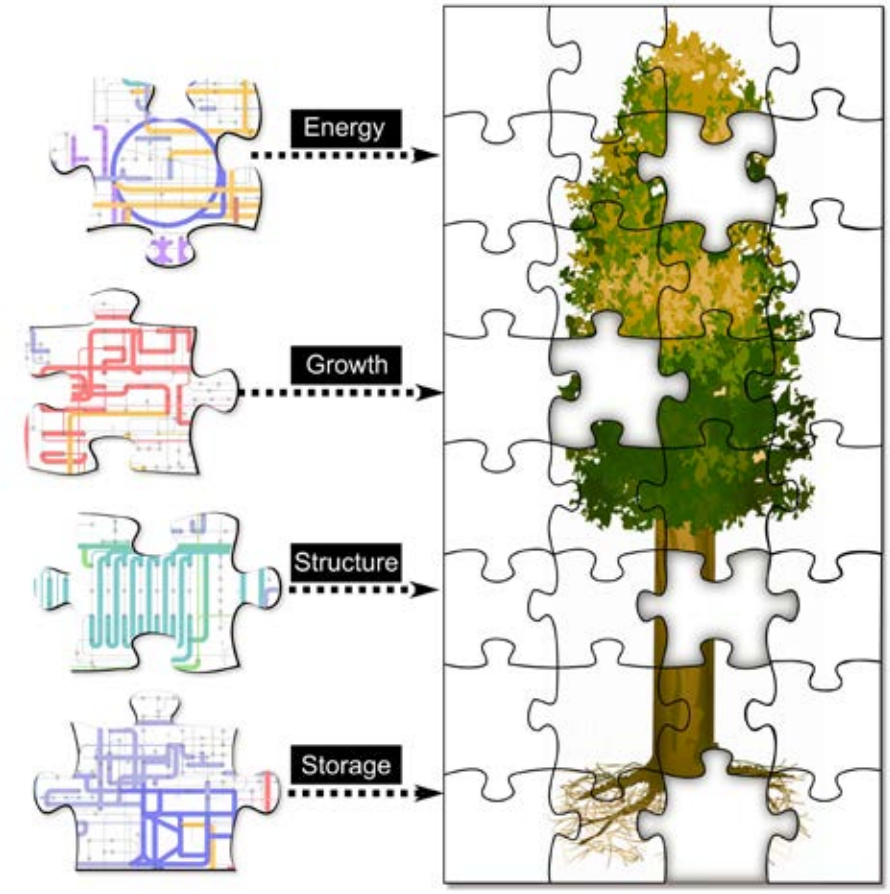
"We tried to provide a zoomable view, like Google maps, so you can look at the system from various perspectives," Abraham says. "By having these different viewpoints, it makes it easier to mine out the relevant biological information."

Obtaining and analyzing information about plant proteomes is especially tricky, considering a plant such as poplar can potentially manufacture more than 40,000 different proteins. Unlike an organism's genome, which is the same for every cell and remains constant, the proteome varies from cell to cell and changes over time as the plant adapts to different environmental conditions.

"The analytical techniques we've demonstrated allow us to measure the range of proteins very deeply and specifically, so we can start to figure out, for instance, how the protein machinery in a leaf differs from the ones in the trunk," Hettich says. "Or we can look at a tree that's very young versus one that's very old, enabling us to understand how all these proteins are changing as a function of the tree growing older."

Knowing how plants change and adapt to environmental surroundings by altering their proteins could help bioenergy researchers develop poplar trees better suited to biofuel production.

"It's the proteins that directly alter the morphology, anatomy and function of a plant cell," Abraham says. "If we can identify the proteins that create a favorable trait such as fast growth, then we can incorporate that protein or modify it to develop a superior plant with all favorable traits through transgenics." — *Morgan McCorkle*



An extensive molecular map of poplar tree proteins offers new insight into the plant's biological processes. Knowing how poplar trees alter their proteins to change and adapt to environmental surroundings could help bioenergy researchers develop plants that are better suited to biofuel production. The study is featured on the cover of January's Molecular and Cellular Proteomics. (Illustration: Paul Abraham)

ORNL scientists solve mercury mystery

By identifying two genes required for transforming inorganic into organic mercury, which is far more toxic, scientists have taken a significant step toward protecting human health.

The question of how methylmercury, an organic form of mercury, is produced by natural processes in the environment has stumped scientists for decades, but a team led by ORNL researchers has solved the puzzle. Results of the study, published in the journal *Science*, provide the genetic basis for this process, known as microbial mercury methylation, and have far-reaching implications.

"Until now, we did not know how the bacteria convert mercury from natural and industrial processes into methylmercury," says ORNL's Liyuan Liang, a co-author and leader of a large Department of Energy-funded mercury research program that includes researchers from the University of Missouri–Columbia and University of Tennessee.

"This newly gained knowledge will allow scientists to study proteins responsible for the conversion process and learn what controls the activity," says Liang, adding that it may lead to ways of limiting methylmercury production in the environment.

For some 40 years, scientists have known that when mercury is released into the environment, certain bacteria can transform it into highly toxic methylmercury. Exactly how bacteria make this happen has eluded scientists. The challenge was to find proteins that can transfer a certain type of methyl group and to identify the genes responsible for their production.

Ultimately, by combining chemical principles and genome sequences, the team identified two genes, which they named hgcA and hgcB. Researchers experimentally deleted these genes one at a time from two strains of bacteria, which caused the resulting mutants to lose the ability to produce methylmercury. Reinserting these genes restored that capability, verifying the discovery.

The researchers found that this two-gene cluster is present in all known mercury-methylating bacteria, and they predicted that more than 50 other microorganisms may methylate mercury because they have a pair of similar genes.

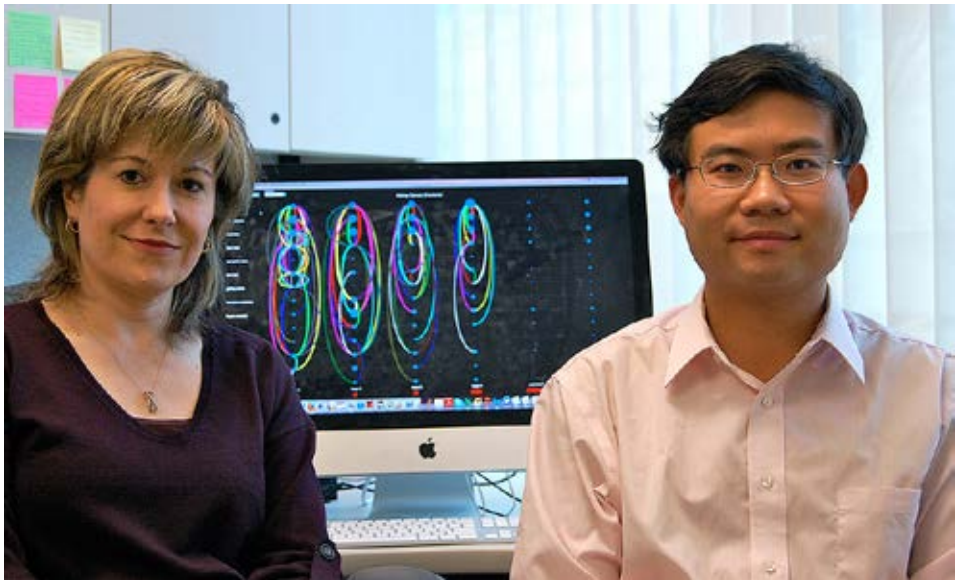
Another key to the development was the collection of talent assembled to work on the problem.

"This discovery was made possible by our diverse team, which includes scientists with expertise in chemistry, computational biology, microbiology, neutron science, biochemistry and bacterial genetics," says Liang, who rated this paper as one of the most satisfying of her career.

Mercury is a toxin that spreads around the globe mainly through the burning of coal, industrial use and natural processes such as volcanic eruptions. The chemical element bioaccumulates in aquatic food chains, especially in large fish. Various forms of mercury are widely found in sediments and water.

In a report recently released by the United Nations Environmental Programme, Achiim Steiner, United Nations under-secretary general and executive director of UNEP, notes that "mercury remains a major global, regional and national challenge in terms of threats to human health and the environment." ® — *Ron Walli*

Researchers from ORNL, the University of Missouri and University of Tennessee have identified the genes required for bacterial mercury methylation. (Image: Thomas Splettstoesser, info@scistyle.com)



Georgia Tourassi and Songhua Xu use information found on social networks to study the cancer risks associated with migration. (Photo: Jennifer Brouner)

Mobility and risk

Social networks may play a role in understanding relationship between population migration, cancer

Public forums on social media may enable ORNL researchers to study environmental cancer risks virtually, bringing the scientific community closer to understanding the impacts of modern population migration patterns on cancer risk.

Over the next four years, Georgia Tourassi and Songhua Xu in ORNL's Biomedical Science and Engineering Center will use such information to try to answer a question that has puzzled experts for decades: What environmental factors change the risk of various cancers when people move from one geographic region to another?

The ORNL researchers hope the endless supply of case studies available online and in newspapers will enable them to develop a framework that will help epidemiologists narrow future studies.

"There is a general movement to see how we can use social networks to not only help epidemiologists discover and monitor the spread of infectious diseases, but also answer a large range of epidemiological questions specifically related to cancer," Tourassi says. "Plenty of studies strongly suggest that many answers we get through expensive clinical trials are similar to those we get quickly by mining online media. If we demonstrate that social media can be used to answer epidemiological questions, we will have set the stage for this line of research in the cancer scientific community."

Epidemiology studies and clinical trials on cancer are typically time consuming, expensive and complex, and major breakthroughs have been stalled for the past few years. This lull has prompted the National Institutes of Health to fund 38 research teams who proposed high-risk creative projects that aim to answer 24 of the most provocative questions in cancer research.

The ORNL research duo's four-year grant is worth more than $1.6 million and will allow them to design cyber informatics tools that can search for, read through, and translate large amounts of online information.

Xu, an expert on web intelligence and online contents mining, will tailor the programs to identify reliable stories on breast and lung cancer — creating a tool that acts like an army of computer analysts constantly collecting and processing information. Linking these stories with publicly available environmental data and mining them using artificial intelligence will allow the ORNL team to search for associations between changes of migration-influenced environmental factors and cancer risk. Each phase of the project will be reviewed by the Oak Ridge Institutional Review Board to assure proper protections are in place for information that is mined and used in their research.

Collaboration with clinical specialists, cancer environmentalists and biostatisticians from Brown University and the University of North Texas will help ORNL researchers interpret the associations they discover.

"ORNL will have a very critical role to play when it comes to this type of research because of its unique computing resources and scientific capabilities," Tourassi says. "This research fits perfectly with DOE's mission of scientific discovery from big data, ensuring that its resources are put to use to advance the public good."

NIH's Provocative Questions initiative aims to engage a diverse range of scientists in an exercise that will define and solve perplexing questions in cancer research. For fiscal year 2012, $18 million was distributed to research teams. ® — *Jennifer Brouner*

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Spanning disciplines to find solutions

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OAK RIDGE NATIONAL LABORATORY REVIEW
P.O. Box 2008, Oak Ridge, Tennessee 37831-6266

ORNL *Review*

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Oak Ridge National Laboratory is managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract DE-AC05-00OR22725

ISSN 0048-1262

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