Visualizing Materials
The beauty beneath the data
Message from the Director

Penn State has a wide spectrum of strengths in materials, but underpinning those strengths is the ability to characterize the composition and structure of materials and devices. In this issue, we will look at a variety of analytical methods with a special focus on visualization of the data.

We are all familiar with scientific images that provide both information and aesthetics. Astronomical images of galaxies and nebulae evoke our sense of wonder using visible light, X-rays, or radio telescopes while probing the origins of black holes and dark matter to answer fundamental questions in astrophysics. Less widely known are the images that reach into the opposite dimension and show the structure of matter at the molecular and atomic level. The questions these images can answer tell us something as simple as why a microscopic component fails, to something as profound as how new material properties can arise through atomic-scale strain or engineered control of defects.

Each year, MRI and the Department of Materials Science and Engineering at Penn State hold the Materials Visualization Contest. The contest offers prizes for the best images in the categories of scientific and visual. Some of the most recent entries are showcased in this issue. For the judges, it is often difficult to tell in which category the entry belongs. While it is not literally the case that “beauty is truth, truth beauty,” the scientific imaging of nature can be both beautiful and informative.

Materials Day is fast approaching, and I invite you to mark your calendars for October 7 and 8. Along with a number of interesting and informative talks, you will have the opportunity to interact with many bright and talented graduate researchers at both our “meet the graduates” reception and our interactive poster session. In addition, we are expecting Materials Day to be the first opportunity to introduce our new MRI director, as I will step down from this position to resume full-time teaching and research.

So I will also take this opportunity to say that it has been a privilege and an honor for me to lead the MRI for almost 17 years. I believe the MRI is making a positive difference for Penn State students and faculty in their pursuit of excellence in research. This required significant change and investment, and could not have succeeded without the support and encouragement of the Penn State administration and the commitment and hard work of the faculty and staff. It has been rewarding for me and I thank you all.

Sincerely,

Carlo Pantano

Distinguished Professor of Materials Science and Engineering
and Director of the Materials Research Institute

To access the materials expertise at Penn State, please visit our Materials Research Institute website at [www.mri.psu.edu](http://www.mri.psu.edu) or the Office of Technology Management website at [http://www.research.psu.edu/offices/otm](http://www.research.psu.edu/offices/otm)
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Snapshots are brief summaries of significant materials-related breakthroughs by MRI researchers. More information is available by visiting the links at the end of each summary.

CONDUCTING POLYMERS FOR BIOSENSING AND TISSUE ENGINEERING

Researchers in biomedical engineering are making patterned films of conducting polymers using a variety of differently shaped hydrogel stamps. Their purpose is to study excitable cells, such as neurons or muscle cells. The ultimate goal is to create a substrate for growth and manipulation of cells, according to Sheereen Majd, assistant professor of biomedical engineering at Penn State.

By varying the types of biomolecules and manipulating the cells using electrical and chemical signals, the researchers can carry out multiple experiments at the same time. Also working on this project were SooHyun Park and Guang Yang, graduate students in bioengineering; Nrutya Madduri, visiting scholar; and Mohammad Reza Abidian, assistant professor of bioengineering. The Charles E. Kaufman Foundation at the Pittsburgh Foundation provided partial support for this work. Contact Prof. Majd at sum30@psu.edu.

To read the complete story by Andrea Elyse Messer, visit the MRI News page at http://www.mri.psu.edu/news/.
Researchers at Penn State are developing genetics-based algorithms to design manmade (meta) materials for a variety of optical and broadband devices. Recent work by Jeremy Bossard, a postdoctoral fellow in the lab of Douglas Werner, McCain Chair Professor of Electrical Engineering, developed a design for a broadband absorber in the infrared.

“Other screens have been developed for a narrow bandwidth, but this is the first that can cover a super-octave bandwidth in the infrared spectrum,” Bossard said.

The researchers looked at silver, gold and palladium as the metamaterials system, but found that palladium provided better bandwidth coverage. This new metamaterial is actually made of layers on a silicon substrate or base. The first layer is palladium, followed by a polyimide layer. On top of this plastic layer is a palladium screen layer. The screen has elaborate, complicated cutouts – sub-wavelength geometry – that serve to block the various wavelengths. A polyimide layer caps the whole absorber. Collaborators in the Mayer group in electrical engineering and the Penn State Nanofabrication Laboratory fabricated the complicated absorber pattern.

“Genetic algorithms are used in electromagnetics, but we are at the forefront of using this method to design metamaterials,” said Bossard.

Douglas Werner can be contacted at dhw@psu.edu. For the rest of the story by Andrea Messer at http://www.mri.psu.edu/news/.

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A team of Penn State mechanical engineers led by Donghai Wang has reported a new method for making porous silicon with nanoscale pores. Because of the reactivity of silicon to sunlight and the large surface area created by the pores, the material can act as a strong catalyst to break the molecular bonds of water when exposed to sunlight.
Vanadium dioxide (VO₂) is called a “wacky oxide” because it transitions from a conducting metal to an insulating semiconductor and vice versa with the addition of a small amount of heat or electrical current. A device created by electrical engineers at Penn State uses a thin film of VO₂ on a titanium dioxide substrate to create an oscillating switch.

When Ph.D. student Nikhil Shukla added a second similar oscillating system, he discovered that over time the two devices would begin to oscillate in unison. This coupled system could provide the basis for non-Boolean computing similar to the way the brain functions. The results were reported in the May 14 online issue of Nature Publishing Group’s Scientific Reports.

“‘We wanted to use it for a different kind of computing called associative processing, which is an analog rather than digital way to compute,’” said Shukla’s adviser, Suman Datta, professor of electrical engineering.

An array of oscillators can store patterns, for instance, the color of someone’s hair, their height and skin texture. If a second area of oscillators has the same pattern, they will begin to synchronize, and the degree of match can be read out. “They are doing this sort of thing already digitally, but it consumes tons of energy and lots of transistors,” Datta said.

The research was primarily supported by Office of Naval Research through award N00014-11-1-0665 entitled Basic Research Challenge (BRC) on “Novel Electronic Devices Based on Coupled Phase Transition.” Additional funding was provided by the National Science Foundation’s Expeditions in Computing Award – 1317560.

Contact Suman Datta at sdatta@engr.psu.edu.
Advantech US, Inc. is a Pittsburgh-based technology company that uses a green additive manufacturing shadow mask process to build electronics and fine-line conductors by deposition of vaporized bulk materials – such as metals – onto various rigid and flexible substrates. By building up components layer by layer, Advantech is able to create complex devices with features in the size range of 3–50 micrometers, filling an important size gap between nanoscale lithography and printed circuit board manufacturing, with significant cost benefits, broad design flexibility, simpler processing steps, and reduced material use. Their products include active matrix display backplanes for ePaper and OLED displays.

In Penn State’s Nanofabrication Laboratory, etch and deposition lead Guy Lavallee, working with research and development engineer Chad Eichfeld and lithography process engineer Michael Labella, successfully fabricated a prototype mask of silicon etched with the required micrometer-scale features. A second prototype with fine alignment features is being developed.

Advantech’s evaporation process can deposit metals, dielectrics, and semiconductors using the miniLine™, an in-line multi-chamber vacuum deposition system. At times, however, unexpected particle contamination affects the performance of the deposited micrometer-sized electronic devices. Vince Bojan and Julie Anderson in the Materials Characterization Laboratory are using the scanning electron microscope with an Auger spectroscopy attachment to identify the chemical elements in the contaminants and thus pinpoint the source of such yield-limiting defects. Together, the two labs are helping a Pennsylvania company expand into the highly competitive microelectronic devices and circuitry market with a simpler, more economical process.

Advantech Senior Scientist Volker Heydemann had this to say about working with MRI:

“It’s extremely helpful to identify the chemistry of the contaminants on our products. Vince Bojan and Julie Anderson in the Materials Characterization Lab had useful results in just a couple of days. They are real experts in electron microscopy and spectroscopy. The opportunity to apply Nanofab’s processing capabilities with MCL’s advanced materials characterization techniques and expertise provides insights in our process beyond the capabilities of our in-house suite of test and quality assurance tools. Our project with Penn State helped identify and improve critical steps in our manufacturing process.”
A FESEM image of conducting polymer nanostructured around microflattened biodegradable polymer to improve electrical properties of electrodes
Pouria Fattahi, graduate student, Chemical Engineering

B TEM image of GaAs nanowires on a Au growth “seed”
Kofi Adu, faculty, Penn State Altoona

C SEM image of tin sulfide is incredibly sensitive to growth conditions, forming various unique structures
Rona Banai, graduate student, Materials Science and Engineering

D FESEM image of tetrathiafulvalene-Au nanostructures which looks like flowers and leaves
Mangquan Lu, graduate student, Engineering Science and Mechanics

E SEM image of the clumping of Bi2Se3-coated silicon nanowires
Joseph Brom, graduate student, Materials Science and Engineering
“This is the missing piece,” says materials scientist and transmission electron microscopy expert Nasim Alem, speaking about the new transmission electron microscope from FEI. “We have had the capability to probe very small features, but never at this scale.”
The Titan is an aberration corrected microscope that can image down to the atomic scale. You can do spectroscopy and understand the material’s atomic bonding and valence. You can see what happens at the junction of two different materials. We can see things clearly that we were not able to see before.”

Alem arrived at Penn State in May 2013 from a post-doctoral position in the Physics Department at UC Berkeley, where she was affiliated with the Lawrence Berkeley National Lab’s National Center for Electron Microscopy. NCEM is a national user facility supported by the U.S. Department of Energy. She chose Penn State to begin her independent research career because of the facilities available and the collaborative nature of the faculty across disciplines, which makes for better science, she believes.

Her collaborations developed quickly. Alem is part of the new Center for 2D and Layered Materials, where she works closely with Mauricio Terrones on catalytic materials, in particular transition metal chalcogenides, a class of materials with interesting semiconducting, optical, magnetic, thermoelectric, and catalytic properties. When strain is applied to these materials at the atomic scale, new properties may emerge. She also looks at the atomic structure and the defects to see how they change the catalytic response. “Are they good defects or bad defects?” she asks, meaning do they contribute to the desired properties or do they detract from them?

Alem also collaborates with several faculty members in the Penn State Center for Nanoscale Science, in particular, Venkat Gopalan, John Badding, Vin Crespi, Jun Zhu, Tom Mallouk, and Josh Robinson, professors in materials science, physics, and chemistry. With this group she is using transmission electron microscopy to look at complex oxide superlattices, nanostructures, and 2D crystals. Alem is using her expertise in microscopy to see what is happening at the interfaces of these materials and how stacking and strain affect atomic structures. “We’ve also been working to try to understand the oxygen cage rotation in these materials,” she adds, referring to crystals with oxygen atoms at their center that will rotate in order to find their lowest energy level. This behavior is one mechanism the researchers are using to try to couple electricity to magnetism at room temperature in materials that could be used, for instance, for fast, stable, low energy memory storage.

Alem works with the new FEI Titan scanning/transmission electron microscope (S/TEM) recently installed in the Millennium Science Complex’s underground quiet labs, which are designed specifically to house this type of advanced microscope. Aberration-corrected microscopy has been described as like adding a pair of glasses to clear up fuzziness at smaller scales, making it possible to clearly see things at scales never seen before. Because this instrument’s electron beam has different capabilities, it can be used as a spectroscope to understand a material’s band structure, electrical structure, and optical bandgap. “We can see grain boundaries and defects, and see how the defects can introduce new properties in the material,” she says.

“The work I’m doing is collaborative,” she continues, “but my ultimate goal is to understand how defects at atomic scales and at the nanoscale change the properties of the material.”

**The future of electron microscopy**

Ten years from now it will be routine to be able to manipulate materials inside the microscope, Alem says. This has already begun, with many universities making specialized holders to shine lasers onto the material or introduce and purge gases, add liquids, manipulate with photons, and heat or cool the material. This will teach us new physics and chemistry that is happening all the way down at the scale of the atoms. Because materials are used in many different environments, researchers will have a sense of how the material will perform in the field. That is the direction the field is heading today, she believes. The advanced training and skills she brings from the National Center for Electron Microscopy will be a boon for her colleagues at Penn State.

**Nasim Alem is an assistant professor of materials science and engineering. She received her B.S. degree in Metallurgical Engineering from Sharif University of Technology, Tehran, Iran, and her M.S. degree in Materials Science and Engineering from Worcester Polytechnic Institute in Worcester, MA. She performed her Ph.D. work in the Materials Science Department at Northwestern University, graduating in 2008. After her post-doctoral work in the Physics Department at UC Berkeley, she joined Penn State’s Materials Science and Engineering Department in 2013. She can be contacted at nua10@psu.edu.**
In many fields, the right instrument can move the field quickly. In astronomy, for instance, radio, X-ray, infrared, and gamma-ray telescopes have far expanded the understanding of the cosmos beyond the limits of visible light. In materials science, the ability to see beyond the diffraction limit of light has advanced science into the quantum realm. Electron microscopes, using electron beams with wavelengths 100,000 times shorter than visible light, can resolve features orders of magnitude smaller than ordinary light microscopes.

MCL staff scientist Trevor Clark shows the new Titan TEM to former Penn State President Rodney Erickson during installation. Credit: Patrick Mansell, Penn State
“The basic premise of scanning electron microscopy has been around more than 75 years,” according to Trevor Clark, staff scientist and electron microscopy manager in MRI’s Materials Characterization Laboratory. “It’s a way of getting around the diffraction limit of light. Any item smaller than 1/2 the wavelength of light is too small to see with most light microscopes.”

A focused electron beam is scanned across a sample and generates electrons whose intensity varies with the structure of the surface. Those electrons are collected and a magnified map is created that shows the structure of the surface. Additional information about the composition of the material can be gathered in many scanning electron microscopes (SEMs) via elemental analysis.

MRI has seven SEMs, including the two state-of-the-art SEMs by FEI (the Helios NanoLab 660 focused ion beam (FIB)/SEM) and Zeiss (the Gemini Merlin SEM for the Nanofabrication Laboratory’s Cleanroom). The Helios combines a FIB column with a high resolution scanning electron microscope. “With the Zeiss and the FEI, we now have both top-of-the-line FESEMs here,” says Clark.

**Why is the new FIB/FESEM useful?**

Current SEMs have limitations that are overcome with the new Helios FIB/SEM. “The question comes up in multiple ways,” Clark explains, “but the spirit is the same. ‘Trevor, I’ve made this device that is on an insulating substrate and I need to be able to image its true structure.’ Since the electrons that hit the insulator had no way to get to ground, we would coat these specimens with a thin layer of a conductor like gold.”

But gold could mask the true structure of something with features on the order of nanometers. The new SEM is capable of imaging uncoated insulators with high spatial resolution.

A second limitation the new Helios will overcome is making thin slices of a device or material to be imaged in the higher resolution transmission electron microscope. To do that the sample has to be thinner than 50 nm, which is around 250 atoms. In the TEM, electrons pass through the thin slice rather than scattering off of it as in the SEM. The interaction of the electron beam with the sample can be captured by an imaging screen. Clark compares the TEM to shining a powerful flashlight through the partially transparent flesh of your hand through which you can make out shadows of tendons and bone structure.

With the newly acquired Helios FIB/SEM, they will be able to pull out a slice only 25 atoms thick. The thinner the sample, the more information the TEM will reveal about the nanoscale structures. Prior FIBs damaged the samples to a depth of around 5 nm on each side of the slice. This meant that the TEM was unable to resolve individual atoms at interfaces. With the new FIB, they will be able to use a lower energy ion beam to polish off that damage.

Another important feature of the new dual FIB/SEM is that the complementary SEM column has such high resolution that many samples can be polished and imaged without removing the sample to the TEM. This will allow MCL users to get results much faster, says Clark.

**The Titan S/TEM solves one researcher’s decade-old problem**

A list of new characterization equipment in MCL would include the new FIB/SEM for uncoated samples and biologicals, a 3D optical surface profiler, an atomic force microscope, and new X-ray diffraction capability. But the most anticipated addition has to be the FEI Titan3 scanning transmission electron microscope, a double aberration corrected S/TEM that came online in summer 2014.

The Titan is one of the most powerful commercial electron microscopes on the planet, the result of a research collaboration funded by the Department of Energy between three national laboratories, two companies - FEI and CEOS - and the University of Illinois at Urbana–Champaign. The Titan has sub angstrom resolution and the capability of imaging atoms and columns of atoms and obtaining crystal structure and chemical information.

The Titan will finally make it possible for one of the researchers Trevor Clark has been
working with for the better part of a decade to see if his drug delivery scheme is working the way he envisions. Jim Adair, professor of materials science and engineering, has developed nanoparticles made of biocompatible materials that he wants to load with anticancer drugs for targeted delivery to tumors.

“Trevor Clark, working with me for the better part of a decade, told me that he has been here almost nine years, and that we must have a way to help Adair see his nanoparticles. He said, ‘Trevor, I want to embed drugs inside these particles, but the drug cannot go on the outside. Can you put them in the TEM, because I can’t see them with any other technique?’

Clark put Adair’s particles into the TEM, but the electron beam was too strong and damaged the particles. He tried using a lower electron dose, but the particles were still damaged. He also tried to cool the particles down, which helps with some samples. Not this time. Adair had to continue the development of his drug delivery system without visual confirmation.

“We have not been able to image those particles until we got the Titan. With a cryo (cooling) stage, in scanning mode, and with the ability to use lower doses of electrons at higher energy, we are finally able to answer the question we were stumped by for nine years,” Clark concludes.

Contact staff scientist and electron microscopy manager Trevor Clark, Ph.D., at trevor@psu.edu or 1-814-865-8476.
Bernd Kabius has an intimate knowledge of the new transmission electron microscope recently acquired by Penn State’s Materials Research Institute. He helped create it. More specifically, he was part of the team that developed the double aberration corrected TEM, an instrument similar to the new FEI Titan housed in a quiet lab in the Millennium Science Complex. As a member of that team, his task was to come up with applications and design the science experiments that would showcase the possibilities of aberration correction on the high-powered instrument.

It is the nature of both optical and electron microscopes to focus their beams using curved lenses. One of Kabius’ former colleagues described the quality of electromagnetic lenses used for electron microscopes as being like the bottom of a wine bottle. “It magnifies a little bit, but the imaging quality is
terrible,” says Kabius. “The physics sets limits that you cannot get around. So these lenses can only be built to a certain level, and that level is bad.”

Kabius worked on the two types of aberration correction incorporated into the Titan, first spherical aberration correction at the European Molecular Biology Laboratory in Heidelberg, Germany, and in the next decade chromatic aberration correction at the Electron Microscopy Center at Argonne National Laboratory. Like adding two sets of eyeglasses to the lenses, these components focused the electron beam to minimize information delocalization by a factor of 10. In addition, current density is greatly enhanced, which improves sensitivity, he says. The new Helios focused ion beam system in the Materials Characterization Laboratory will make better samples for even higher quality imaging in the Titan.

With a resolution capability of 0.5 angstrom, about twice the radius of the smallest atom, TEM has reached its foreseeable limit, Kabius believes. “There are no projects ongoing to try to improve that. It would cost $30 million to get to 0.3, and nobody knows for what.”

That doesn’t mean that TEM development is at an end. In the last two decades there has been a flurry of innovations in new components that can be placed inside the instrument to allow for new science experiments to be performed and observed in place. “With these components, I believe the mainstream for the next decade will be in situ experimentation,” he predicts.

One immediate benefit of this approach could be observing a catalytic reaction under the electron beam as it is occurring and in a controlled environment. “You cannot get the information to improve the reaction if you look at it after it has happened and not in its environment,” he states. “In situ chemical reactions are a big topic in science.” The new capabilities available with in situ TEM will benefit researchers in chemistry, physics, electrical engineering, mechanical science, and materials, Kabius says.

However, only a few small companies are making these experimental components, called stages, for in situ experimentation. Kabius sees this as an opportunity to partner with these companies and Penn State’s Nanofabrication Laboratory to build new stages that don’t currently exist. This is an area in which Penn State could create a unique capability, he believes.

“When we first got these incredible instruments, we only wanted to look at images,” Kabius recalls. “But now we want to get more quantitative information. Penn State has the qualities required to move this field ahead: great scientists with great ideas, a great microscope, and people with expertise in theory to match our experiments.”

Kabius will begin work at Penn State on July 1 as a senior scientist in the Materials Research Institute. He comes from the Environmental Molecular Sciences Laboratory, a part of Pacific Northwest National Laboratory, where he was lead microscopist. Contact Bernd Kabius at bck13@psu.edu.
When you think of CT scans, you probably imagine lying in a claustrophobic closed box while an X-ray machine clanks around you taking images of your body. In Penn State’s Center for Quantitative X-ray Imaging (CQI), the closed box is actually a large, lined room and the CT scanner is industrial size.

2D CT image of the human distal tibia (at the ankle), a 3D surface reconstruction of a portion of the bone with the cortical and trabecular bone segmented separately, and a 3D volume of trabecular bone with local thickness mapped onto a skeletonized representation of the structure. Credit: Tim Ryan, Penn State

High resolution microCT data is used to reconstruct a Eulemur skull. Credit: Tim Ryan, Penn State
“Our scanner is mostly used to look at rocks and bones,” says center co-director Zuleima Karpyn, an associate professor of petroleum and natural gas engineering, “but the common denominator is that everything we are looking at is a material – natural materials, synthetic materials, fabricated materials.”

For many hard and soft materials, X-ray CT makes it possible to see what internal structures look like in three dimensions, nondestructively, and over time. Karpyn uses it primarily to look at the flow of liquids and gases through rock pores, and how that changes under varying environmental conditions, such as temperature and pressure. Her work has applications in oil and gas extraction technologies, as well as in Co₂ sequestration.

“If you can detect density you can map structures,” she continues. “You can also detect compositional features – one part is material A and another part is material B.”

The open layout of the system makes it possible to have a variety of peripheral equipment, such as high pressure pumps and heaters, to provide environmental conditions that mimic geological conditions, such as the flooding of porous materials. The same techniques have been used to study the effects of water saturation in a PEM fuel cell. “Being able to connect your sample to peripheral equipment is one of the biggest advantages of this particular instrument,” she says.

Because it is an open user facilities, outside companies have made use of the instrument and expertise of faculty and staff to inspect and measure a variety of materials and products, including batteries and catalysts, and even the distribution of air bubbles in chocolate and how that relates to texture.

From fuel cells to chocolate to bones, the uses of the instrument are only limited by the researcher’s imagination, Karpyn suggests. The X-ray CT works using an X-ray source that is directed through a sample to a detector that is similar to the panel on a camera. The detector has 1024 pixels in both the x and y direction. The diameter of the sample determines the resolution, so if the sample is an inch across, the resolution will be 1/1024 of an inch. The resolution limit of the current instrument is around five microns. The largest sample they can scan is about four inches in diameter.
“What you get from the scanner is a grid of numbers,” Karpyn explains. The numbers indicate X-ray attenuation, which relates to density. The numbers translate via software into a gray scale ranging from black to white, with white being the most dense and black the least. Depending upon the application, this information can tell a lot about the internal structure of a sample. The sample is rotated through 360 degrees and thousands of 2D images are created and then spliced together by the software to make three dimensional displays. Individual slices can be selected from the 3D image for further study. Or all of the images with certain qualities, densities of particular interest can be pulled out and studied. Then, images can be taken at different time periods under changing conditions to see how environmental factors affect the sample. “You are creating a digital replica of what you are scanning,” Karpyn sums up.

The current scanner is 13 years old and parts are growing harder to find. So, co-director Tim Ryan and Karpyn, along with a number of other faculty across campus, have submitted proposals to add a new microCT scanner as well as a nanoCT, both of which utilize X-rays.

In regard to CO$_2$ sequestration, Karpyn has projects in which she is creating models for how long CO$_2$ will remain trapped underground and how the chemistry of the rock will affect the gas. “There is a lot of physical analysis from the point of view of fluid flow and interactions,” she says. To add to the detail and complexity of her models, her group will create synthetic samples, such as packs of sand or beads. By building the experiment and imaging various stages in 3D, and then adding the 4th dimension of time, they can build more accurate simulations. The same holds true for experiments in other fields. The more the researcher knows about the chemistry and structure of their materials, the better they can calibrate their models. “With more computational capabilities, there is more and more that you can image and map and feed into models,” says Karpyn.

In the CQI lab in room 204 of the Academic Activities Building on the University Park campus, Karpyn explains the workings of the X-ray CT scanner and points out the heavy shielding in the walls that keeps X-rays from escaping into the environment. The Universal HD-600 was purchased with a NSF Major Research Instrumentation grant and is available to researchers across campus, from industry, or from other academic institutions. Cost depends on image acquisition time and complexity of the analysis. An example of a typical cost projection is available on the CQI website, http://www.cqi.psu.edu/index.html.

An Anthropologist Uses X-Ray CT to Look at Microstructure in Bone

Karpyn’s co-director in the CQI lab, Tim Ryan, an associate professor of anthropology, uses the system extensively to study the internal formation of bones that can indicate types of locomotion in animals. Bone is a material and can be studied in ways that are familiar to many researchers in the materials community, he says. He has recruited several faculty in the Materials Research Institute to collaborate on the proposal to NSF for the state-of-the-art nanoCT scanner.

Many of the questions he wants to answer about the evolution of primates and humans overlap with what materials scientists want to learn about the fine structure of the materials they process and measure. A nondestructive way to look at the microstructure and internal structure of bone...
fossils has helped Ryan understand how early human or pre-human primates moved. “In anthropology, it’s a powerful approach, because museums are reluctant to destroy their fossils,” he points out.

In his own research, the nanoCT and a new microCT available in Fall 2015 will enable him to reconstruct dietary and behavioral shifts in the evolutionary history of our primate ancestors from 3.5 million years ago. In a more recent timescale, higher resolution imaging data will enable him to investigate osteoporotic bone loss in the aging population.

The Zeiss nanoCT, if acquired, will be housed in the Materials Characterization Lab in the Millennium Science Complex. As part of the core user facilities, the nanoCT will be available campus-wide, and open to researchers from national labs, other universities, and private industry.

Its capabilities include synchrotron-level spatial resolution in a laboratory setting, with spatial resolution of 50 nm and 150 nm, phase-contrast scanning modes for imaging of soft, low-z materials and low contrast materials with structural/compositional variation, visualization of time-dependent processes, and low X-ray energies for higher contrast and better image quality.

**Potential users cross multiple disciplines**

For their proposal to the National Science Foundation, principal investigators Tim Ryan, Zuleima Karpyn, and Theresa Mayer enlisted the input of a wide swath of the research community at Penn State. Their X-ray CT projects will look at the 3D microstructure of plant lignocellulose for agricultural and biological engineering purposes that include cellulose-based biofuels, building materials, paper, and textiles; examine the fine internal details of new types of materials for infrastructure, such as recycled cement and nanofiber strengtheners, as well as infrastructure damage monitoring and testing; study coral growth behavior under environmental stress; and map small pore networks in soil for ecosystem health.

Steven Schiff in engineering science and mechanics would like to use the tool to help create computational models of microfluidic flow in brain interstitial spaces and to understand the multiscale nature of brain anatomy. Theresa Mayer in electrical engineering would like to collect the first direct 3D tomographic images of optical nanocomposites that manipulate light in unprecedented ways. New methods of imaging can have a broad impact across many fields of physical and life sciences and engineering.

Tim Ryan is associate professor of anthropology and information sciences and technology. He can be contacted at tmr21@psu.edu.

Zuleima Karpyn is associate professor of petroleum and natural gas engineering and interim director of the Penn State Energy Institute. Contact her at ZKarpyn@psu.edu.
While discussing imaging techniques with MCL’s Trevor Clark, he suggested I find out something about the capabilities of the Huck Institutes’ microscopy facilities, located down the hall from MCL’s underground laboratories. Materials researchers have been using some of the specialized instruments and equipment since moving into the Millennium Science Complex. I contacted Greg Ning, the scientist in charge of Huck’s shared Microscopy and Cytometry Facility, and he invited me to stop by.
Ning’s background includes both an MD degree from China Medical University, and a Ph.D. in physiology and anatomy from Kyoto University in Japan. Ning has managed Huck’s microscopy facilities for 11 years. When his microscopy lab was moved to the MSC in fall 2011, it was merged with two other labs, which comprise four clusters of instruments: the flow cytometry lab, where particles, mainly cells, are analyzed for their physical, biological, and biochemical characteristics; the histology section, where the samples are prepared for optical microscopy; the optical microscopy lab, with traditional light microscopes and high-end research microscopes such as fluorescent, confocal, polarized, differential interference contrast, and phase contrast; and the electron microscopy lab, which includes two transmission electron microscopes (TEMs) specifically designed for analysis of biological specimens, and a variable pressure field emission scanning electron microscope from Zeiss, which is not yet online.

“Our TEMs are in constant use, day and night, and on the weekends,” Ning remarked as he toured me through his labs. “We really like the Technai BioTwin, which we got from FEI at the same time you got your Titan TEM in the Materials Characterization Lab. People especially like the cryoEM, which is used for studying hydrated samples, such as single particle work, viruses and protein particles, nanoparticles, and even liposomes. Materials people come in to use it, too, especially polymer researchers.”

Ning is looking forward to the arrival of the new Zeiss scanning electron microscope. Its adjustable pressure facilitates high resolution imaging of non-conductive samples by reducing the surface charging on the sample, which Ning compares to looking down from an airplane through clouds. With the surface charging eliminated, the clouds clear away and the surface is clearly visible. The Materials Characterization Lab has a similar instrument, but Ning says theirs will be complementary and configured to biological purposes.

One of the additions to the Zeiss SEM is called the 3View, which is a device that allows the user to make extremely thin slices of the sample block inside the microscope chamber, image block surface after each slice, and then digitally reconstruct the images for a 3D view. This is an improvement on the traditional practice of slicing samples on a microtome outside the instrument, and then trying to orient the slices one at a time in the microscope. “Daniel Cosgrove’s group wants to use this to look at plant lignocellulose and some materials people want to use it, too, for instance to look at hydrogels in 3D,” Ning said. There are a number of researchers from the Penn State College of Medicine and Hershey Medical Center who are interested in using the Zeiss, he added.

I asked Dr. Ning if there was competition between the materials and life sciences facilities. He gave a thoughtful reply. “Potentially there is some competition to grab users,” he said. “But for me, I would say it is more complementary. We want to have equipment that materials science doesn’t have on their side. We don’t want to pursue things they already have, but for example, we have the critical point dryer and we have a carbon coater, neither of which MCL has. We have a major piece of equipment, the cryoEM, but materials people can use that, too.” The cryoEM is a transmission electron microscope that examines samples at
ultralow temperatures. “I don’t think duplicating that kind of functionality is wise,” he continued. “Like the Titan (MCL’s high-end electron microscope), if you put something from the cryo into the column, it can potentially contaminate it, and then the Titan will be down for some time while they clean it. Our samples are usually hydrated and in plastic that can outgas.”

Some researchers who sit on the materials side of the building are frequent users of Huck’s facilities, especially those working at the materials/bio interface. Tony Huang is a professor of engineering science and mechanics whose ultrasound devices are used to capture individual and groups of living cells in microfluidic devices. Siyang Zheng is an assistant professor of bioengineering, who constructs a number of microdevices to count blood cells and capture circulating cancer cells. Jim Adair is a professor of materials science and engineering and bioengineering who invented nanotechnologies for targeted cancer drug delivery. All are frequent visitors to the life sciences labs.

Ning cites the weekly Millennium Café talks held in the third floor commons for encouraging collaborations between the building’s materials and life sciences wings. “It’s good to have materials people and biology people get to know each other better,” he told me. “We have been working well so far, and we will continue to walk in that direction.”

Dr. Gang (Greg) Ning can be contacted at gxn7@psu.edu.
Tim Tighe is a staff scientist in the Materials Characterization Lab (MCL) with responsibility for atomic force microscopy (AFM). AFM is a scanning mode technique that uses a tip, like the stylus on a record player, to measure various forces between the tip and the surface of the material being scanned.
The AFM covers the size regime between SEM and TEM and differs from scanning electron microscopy and transmission electron microscopy in that SEM and TEM measure the contrast in a sample, while AFM measures the topography, giving a kind of contour map of the sample. The current AFM in the basement of the Millennium Science Complex can measure with sub-angstrom height resolution (z) and angstrom resolution on the lateral (x-y) plane, Tighe explained recently.

“Our Bruker AFM is new to us in 2011,” he said. “That upgrade was big, since our previous AFM was a 2000 model, and in the 11 years between the two a lot of nice upgrades were made in electronics and data acquisition.”

One of the upgrades in the new AFM is the ability to do Peak Force Tapping, a technique that was only developed in 2010, the year prior to MCL’s acquisition of the AFM. The technique is so new that articles are only now appearing in journals about its use. In Peak Force Tapping, the stylus is raised and lowered on the sample either 1,000 or 2,000 times a second. A laser measures the deflection of the tip as it encounters the sample and converts that into an electrical signal that gives a line of data as the tip traverses the sample. This line of data is turned into a topographical image, which can be colorized based on height.

Tighe notes that numerous groups are getting atomic scale images on the AFM in the MCL. “Groups are
looking at very thin films made by molecular beam epitaxy and atomic layer deposition, and they can see how the films are nucleating and forming. With sub-angstrom resolution, we can easily measure atomic step heights, which is important in emerging nanoelectronics. Other groups come down to measure the piezoelectric responses of their materials. Anybody who is doing depositions will use the AFM to measure the roughness of their material.”

There are three basic modes of operation with atomic force microscopy: continuous contact mode and two tapping modes. In contact mode the tip is kept in contact with the sample and dragged across the surface. In tapping mode, the cantilever is vibrated at its oscillation frequency and the oscillating tip is lowered to near the surface. In tapping mode, the amplitude of the oscillation is measured to provide information. In peak force mode, as with contact mode, the amount of bend in the cantilever is measured.

“If Peak Force Tapping is so good, people wonder, why do we need those other techniques?” Tighe asked. His answer is that those three basic techniques allow for many other ways to gather information about a sample. For instance, Piezoresponse Force Microscopy is a contact mode technique used to study ferroelectric materials and devices at the sub-angstrom scale; while Electrostatic Force Microscopy and Magnetic Force Microscopy are tapping mode techniques in which the oscillating cantilever does not make contact with the sample. “We can do pretty much all of the different techniques by adding the appropriate module to our AFM,” Tighe remarked.

AFM is versatile in other ways. Paul Painter’s group at Penn State has used AFM to study adhesion forces. Painter is looking at ways to separate oil from tar sands or to clean beaches polluted by oil spills. He uses a liquid to slip between the sand and the tar and measures changing adhesion of silicon on bitumen as the composition of the fluid changes. For industry, AFM can help understand what is happening when one run turns out differently from the prior run – for, instance why does one polymer run come out brittle while the next comes out flexible? Or what size pore diameters are being formed when aluminum is anodized.

**A biological approach**

Bruker, the equipment maker, had an interesting project in which they modified their tip to determine why a class of bacteria was developing drug resistance to a type of contact dependent drug. They functionalized the probe with a coating of the drug and probed a normal bacterium and found high adhesion to many active sites on the cell membrane. On the drug resistant bacterium there was very low adhesion. They discovered that the bacteria were changing the amino acid sequence so that active sites terminated differently. The drug manufacturers needed to design their drug differently in order to stick to that particular type of bacteria.

Recently, Tighe has begun working with biological cells in the AFM, studying the physical properties of the cell membranes in liquid with the Esther Gomez group. Peak Force Tapping makes imaging in fluids easier than ever, he said. With biological samples, the researchers match the probe to the hardness range of the material to avoid damaging the sample. With cells they will use dull, soft probes. With polymers, the probes can range from soft to stiffer and stiffer tips. By controlling the force in Peak Force Tapping mode, the tip life can be extended and there is less likelihood of picking up surface contaminants.

“My lift height is higher and my forces are softer, so I’m more likely to image contamination than I am to pick it up, which avoids a large problem with both contact mode and tapping mode. Peak Force Tapping has eliminated a lot of the problem with dirty samples,” Tighe concluded. “It’s a great instrument, and Peak Force has been a very nice addition.”

For more information about using the AFM, staff scientist Timothy Tighe can be contacted at tbt1@psu.edu or 1 814 863-8408.
The SNIPE Project: Building a Better Microscope

A one-of-a-kind scanning probe microscope (SPM) is under development that will live in the basement of Osmond Building on the University Park campus. Funded by a National Science Foundation Major Research Instrument grant, the 3-year project will be a milestone in atomic scale surface characterization of materials and devices.

Day-to-day operations of the instrument development is guided by post-doctoral researcher Ivan Skachko, a physicist who for purposes of the SNIPE project has retrained himself as an engineer. Overseeing the project are principal investigator Eric Hudson, and co-PI Moses Chan, both professors of physics with extensive experience in scanning tunneling and atomic force microscope construction and cryogenic systems respectively. Skachko, who is mentoring one of Hudson’s graduate students on the project, expects to have the instrument and accompanying external systems completed and ready for testing in summer of 2015.
In its various parts, the SNIPE (which stands for scanning nanoscale interface probe ensemble) does not require any breakthrough science, although there will be plenty of technical challenges to overcome. Something of a Frankenstein monster, with parts taken from commercial microscopy systems and homemade components, it will in its combination of capabilities and techniques open up a unique set of measurement capabilities for atomic scale devices and device physics. A long list of faculty from the Physics, Materials Science, Electrical Engineering and Chemistry departments are eager to get their hands on it.

The instrument revolves around a new precision scanning head from equipment maker SPECS, a partner on the project, that makes it possible to rapidly change to any type electrical sensor – scanning tunneling mode, various atomic force modes – while avoiding the tedious process of precisely relocating the nanoscale location to be measured. It will also be possible to swap out samples, for instance for calibration purposes, while returning to the original sample location.

Many researchers will benefit from a scanning tunneling microscope with sub-picometer resolution and the capability of mapping local electron density of states, a quantum mechanical description of the freedom of electrons to move which can be related to the topography of materials at small scales, for instance nanotubes, nanowires, and nanoscale devices. The addition of a dilution refrigerator system increases sensitivity of the STM tremendously. Environmental controls will allow the refrigeration system to operate in the high vacuum measurement chamber at temperatures ranging from 50 mK (approaching absolute zero) to room temperature. At the lowest temperatures, experiments with superconductivity can be performed and observed.

Most refrigeration systems paired to STMs use liquid helium to achieve low temperatures. By using a cryocooler in conjunction with a dilution refrigerator,
the skyrocketing expense of liquid helium (currently around $30,000 per year) can be avoided. This system, from partner company Janis Research, will also eliminate the need for helium transfers, which cause lengthy interruptions to experiments. Only a few SPMs in the world, and none at Penn State, operate at cryogenic temperatures.

Once tested and in operation, the SNIPE will be available to users in core facilities. The investigators on this project expect the scope of techniques available in this multi-instrument package to have broad impacts in understanding new materials systems using multiple approaches. The impact will be felt, they believe, in increased interdisciplinary collaborations and in the training of a generation of students in the interpretation of the interconnected data this approach will create.

For more information on the SNIPE project, visit the Hudson group website at http://www.personal.psu.edu/ewh10/.

Contact Ivan Skachko at izs2@psu.edu
Adding Holography to Spectroscopy for Better 3D Images

Zhiwen Liu in the Ultrafast and Nonlinear Optics Lab
Credit: MRI
When a beam of light hits an object, a part of the light will be deflected at a longer wavelength depending on the characteristic vibration of molecules in the object. This is the Raman effect discovered by C.V. Raman, an Indian physicist, in 1928. The Raman effect led to the development of Raman spectroscopy, which uses a laser beam to produce the very feeble signal of the Raman scattered light in order to identify the chemical makeup of objects.

CARS (coherent anti-Stokes Raman spectroscopy) is a type of coherent Raman spectroscopy technique with more sensitivity than standard Raman. In CARS, two lasers are focused on a sample and the difference in frequency between them can be tuned to coherently drive the oscillations of chemical bonds. The resulting emitted light will be at the new blue-shifted frequency, called the anti-Stokes beam. The CARS technique has been especially important in the study of biological fatty acids, the lipid bilayer that forms the cell membrane.

The principles of holography have been known since the 1940s, but it took the invention of the laser to make the three-dimensional imaging technique practical. Now, researchers at Penn State have combined the holography with an advanced Raman spectroscopy technique to make rapid 3D images and chemical characterization of both inorganic and biological materials.

Zhiwen Liu, an electrical engineer and expert in ultrafast and nonlinear optics, and his group have developed new techniques that combine the chemical specificity of CARS with the 3D imaging capability of holography at the time scale of a laser pulse.

“Usually, when you talk about holography, you shine a laser beam on some object and you get a scattering...
signal,” Liu explains. “That scattering signal interferes with a reference wave, and it gives you a hologram. What’s unique here is it’s not conventional holography. It’s spectroscopic holography.”

One of the difficulties with standard Raman spectroscopy is the very low signal level. CARS enhances the Raman signal by orders of magnitude and when combined with holography is fast enough to capture motion at the microscale in vivo using a pulsed laser. By integrating CARS with holography, it is possible to probe the molecular vibration, which gives the chemical fingerprint of the material, while imaging the spatial distribution of the molecules via holography. Penn State has filed a patent on the CARS holography technique.

**Imaging cells with CARS**

Cellular imaging typically requires staining the cells with a contrast agent, which can damage or change the cell in some way. But CARS uses molecular vibration as the contrast mechanism so that the cell can be imaged in its native state. Sunney Xie’s group at Harvard has been a pioneer in developing CARS to study the lipid bilayer. Other groups in the U.S., and in Asia and Europe, are active in this field.

Liu’s group at Penn State has used the CARS holography technique to image HeLa cells, an immortal cell line used in scientific research and made famous in Rebecca Skloot’s bestseller *The Immortal Life of Henrietta Lacks.*

The benefit of using Liu’s CARS holography technique is that CARS on its own requires scanning to capture a 3D image. Scanning limits CARS’ ability to image quickly changing chemical reactions or biological specimens in motion. With CARS holography, a 3D image can be captured at laser pulse duration time limited speed (e.g., a few nanoseconds). This is done by capturing both the amplitude (measure of the distance from peak to trough of a wave) and the phase (the position of the wave in its vibration cycle) and computationally reconstructing the hologram image. If the sample is transparent, the technique can digitally focus at different layers within the sample, for example, to image the sub-cellular components in live HeLa cells without the necessity of staining by toxic materials.

**Proposed Near-field Spectroscopic Holography Microscope**

Zhiwen Liu has submitted a proposal to the National Science Foundation for funding to develop a unique Near-Field Spectroscopic Holography Microscope that will provide critical information, such as molecular composition and the phase of the spectroscopic signal, on the nanometer scale. Current spectroscopic holography is limited by the diffraction limit of light to around 1 micrometer. By capturing the near-field region of the optical field close to the sample using a near-field scanning optical microscopy probe, the instrument can increase resolution down to around 50 nm or better.

If funded, the proposed instrument will be housed in the Millennium Science Complex as a shared-use instrument available to researchers within and outside of the university. Faculty in the Center for Nanoscale Science and the Center for 2D and Layered Materials are interested in this type of instrument to study polar, magnetic, and structural phases in complex oxides, and 3D domain wall structures. The instrument will also enable the study of fundamental properties of two-dimensional materials on the nanoscale. Professors Douglas Werner and Theresa Mayer will use the instrument to study the optical characteristics of manmade structures called metamaterials as they are designed by Werner’s group and built by Mayer’s group in the Penn State Nanofabrication Laboratory. (In the past, Liu’s group has used a technique called spectral holography to measure the optical properties of their metamaterials.) Seong Kim, professor of Chemical Engineering, will use the instrument to study promising biopolymers as alternative biofuels. Altogether, around 20 senior investigators across 10 departments are expected to be major users once the instrument is developed.

**Winning Vodafone project leads to start-up company**

In 2013, Liu and two of his students, Perry Edwards
and Chuan Yang, entered the Vodafone Americas Foundation Wireless Innovation Project with an entry they called the G-Fresnel Cell-phone Spectrometer. The purpose of the contest is to “promote innovation and increase the development of mobile and wireless technology for a better world,” according to their website.

Their invention is a high performance optical spectrometer integrated with a cell phone for applications such as health monitoring. A second application is optical color analysis for chemical analysis and color matching, for instance for people with color blindness. Their third place finish, out of around 100 entries, netted them a $100,000 prize to help develop their technology. Last year, Liu and Edwards formed a start-up company, called Atoptix (http://www.atoptix.com), with additional funding and business support from Ben Franklin Technology Partners/ Central and Northern Pennsylvania.

“We have a prototype, but it’s crude,” Liu says. “Hopefully, in the next several months we can make a more advanced commercial product.”

Liu came to Penn State in 2003 after earning a Ph.D. and doing post-doctoral work, both at the California Institute of Technology. His B.S. and M.S., in radio electronics, are from Peking University. He is a professor of electrical engineering. He can be contacted at zzl1@psu.edu.
MRI Labs Help Pittsburgh Company Enter Printed Electronics Market

When Pittsburgh-based Advantech US wanted to expand their shadow mask additive manufacturing process into the printed electronics market, they turned to Penn State’s Nanofabrication Laboratory. And when they needed advanced analytical capabilities to solve a problem on their assembly line, they called on Penn State’s Materials Characterization Laboratory.

Two problems, two labs, one solution – MRI

The Materials Research Institute at Penn State

For the full story, see page 7

Auger Spectrometer Images

An Auger spectrometer is used to identify the chemical elements in the contaminants and thus pinpoint the source of defects. Photo credit: Vince Bojan, Materials Characterization Lab at MRI
The opportunity to apply Nanofab’s processing capabilities with MCL’s advanced materials characterization techniques and expertise provides insights in our process beyond the capabilities of our in-house suite of test and quality assurance tools. Our project with Penn State helped identify and improve critical steps in our manufacturing process.

Volker Heydemann, Advantech Senior Scientist
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Event Details: [www.mri.psu.edu/materials-day](http://www.mri.psu.edu/materials-day)

In the Next Issue: **SMART MATERIALS**