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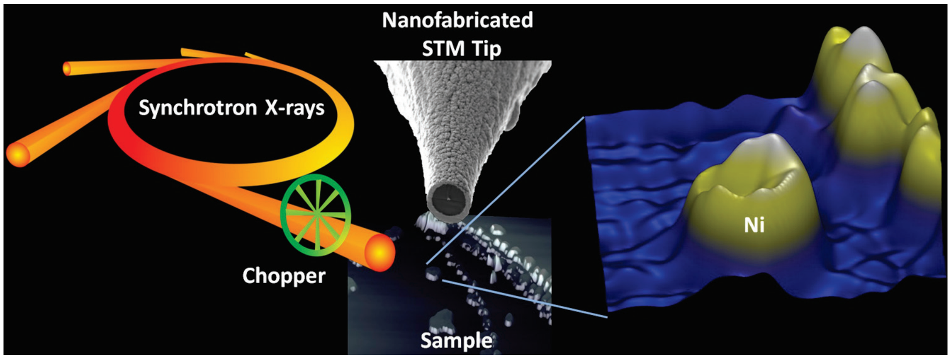
Technique Identifies 'Fingerprints' at Atomic Level



Using synchrotron X-rays as a probe and a nanofabricated smart tip of a tunneling microscope as a detector, researchers were able to identify the atomic fingerprint of nickel atoms on a copper substrate.

Using the most powerful microscope, scientists can image the surface of a single atom. But they can't tell what it is.

Copper? Silver? Gold? To identify elements, scientists bombard atoms with X-rays to reveal their inner atomic fingerprints. But this doesn't work at the level of a single atom. It's too small to see.

So why not combine the two technologies, right? Blast a single layer of atoms with X-rays while viewing them under a scanning tunneling microscope, or STM.

It's simple in concept, but like so much in science, actually doing it has proven incredibly difficult. Saw Hla, a physics and astronomy professor at Ohio University and NQPI member, believes he's solved the problem. Hla divides his time between OU and the Argonne National Laboratory outside Chicago, where he and Volker Rose from Advanced Photon Source led a research team, including OU graduate physics students Heath Kersell and Yang Li, that worked on this project. Their findings were published last November in Nano Letters.

To appreciate the challenge scientists working on this problem face, it helps to understand just how an STM works. Unlike a traditional microscope, it doesn't use optical lenses to magnify objects. Instead, it uses a tiny needle to map the surface. It's like car-

See ***Elements***, *page 4*

Team Finds More Potent Derivative of Anti-Inflammatory Drug

When an army of white blood cells descends on some foreign invader, the area becomes inflamed. In most cases, this inflammation is a natural byproduct of the healing process. It is a sign the body's defense system is working properly.

But sometimes the system goes haywire. The white blood cells cluster where there's no threat. This results in what's called pathological inflammation, causing discomfort and pain for no good reason.

A research team at Ohio University led by Douglas Goetz, a professor of chemical and biomolecular engineering and NQPI member, experimented with a set of small organic compounds that tackle this problem by preventing white blood cells from going to battle against some phantom menace. Other members of the team included Anuja Alapati, Stephen Bergmeier, Kelly McCall and Frank Schwartz. A paper detailing their findings was published in the March issue of the European Journal of Pharmacology.

To understand how the anti-inflammatory compounds work, it helps to understand how the body's immune system mobilizes. When a problem is detected along the wall of a blood vessel, such as tissue damage or an infection, an alarm goes out, Goetz said. This alarm causes the endothelial cells lining the blood vessels to produce VCAM-1, short for vascular cell adhesion molecule-1. The VCAM-1 allows white blood cells to bind to the vessel wall and attack the intruder.

Sometimes the endothelial cells crank out VCAM-1 in the absence of any threat — a false alarm, so to speak.

A drug called methimazole has been found to suppress VCAM-1 production, Goetz said. The drug is used to treat people with an autoimmune condition called Graves' disease wherein the thyroid gland is overstimulated. Methimazole suppresses thyroid production activity. Blood tests of Graves' disease patients revealed that when taking methimazole, their VCAM-1 production goes down as well.

The team found that a derivative of methimazole called C10 is significantly more effective at lowering VCAM-1 production. Goetz and his team experimented with derivatives of C10 to see if they could find an even more potent compound. They found that making a small alteration to the structure of C10 doubled the potency. C10, and each of the derivatives tested, significantly reduced white blood cell adhesion in a laboratory model of pathological inflammation.

A NEW MODEL
Research bridges theoretical and experimental physics
Page 2

COAL POWER
Scientist aims to lower cost of hydrogen extraction
Page 3

TRAFFIC STOP
Experiment corrals electrons on graphene superhighway
Page 4

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Director's Corner

Dear Colleagues,

Greetings! I am happy to welcome you to the 13th edition of the newsletter and to update you on the exciting events taking place within the institute!

I would first like to congratulate NQPI members Alexander Govorov and David Ingram, who recently were honored by Ohio University. Govorov, a professor of physics and astronomy, was selected by the College of Arts and Sciences to receive the Outstanding Faculty Research and Scholarship Award in Natural Sciences. This award recognizes Govorov's recent major contributions in the area of plasmonics.

Ingram, chair of the Physics and Astronomy Department, was selected for the 2014-15 Arts and Sciences Outstanding Faculty Leadership and Service Award for his efforts on behalf of the department, college, university and community at large. We are quite proud of our members!

In this newsletter you will also find examples of work being done by NQPI members covering such diverse topics as drug research, graphene, single atom chemical characterization, a nanoscale "detective story" and more. These exciting results continue to demonstrate the strength and diversity of our NQPI membership.

I would also like to call your attention to two events being organized by NQPI members. Gang Chen has been busy over the semester organizing an upcoming conference on glass and optical materials, while Saw-Wai Hla is organizing a summer conference on spintronics. NQPI was delighted to help support these conferences and to provide a platform to promote open discussions and collaborations on both the national and international level.

We also want to thank our graduate students for completing another year of "Nanoforums," biweekly research presentations that are usually followed by lively discussions. These are open to all interested parties and usually attended by NQPI professors, graduate students, and undergraduate students as well.

I wish you a productive and refreshing summer.

Eric Stinaff, NQPI Director

NanoBytes

- Gerardine Botte, Russ professor of chemical and biomolecular engineering, was named Ohio University's Distinguished Professor for 2015. Botte is the third woman to receive the award, the university's highest academic honor, and is the first female recipient from the sciences.

- The International Workshop on Spintronics 60 will be held in Cancun, Mexico, August 8-9. Ohio University physics and astronomy professor Saw Hla is organizing the conference to honor the 60th birthday of fellow OU physics and astronomy professor Sergio Ulloa.

- Ohio University physics and astronomy professor Alexander Govorov is helping coordinate the Nanoscale Assemblies of Semiconductor Nanocrystals, Metal Nanoparticles and Single Molecules workshop, which will be held in Dresden, Germany, August 24-28. The workshop's focus is on the physical and chemical properties of assemblies composed of nanocrystals, molecules, biomolecules and polymers.

Model bridges gap between theoretical, experimental physics

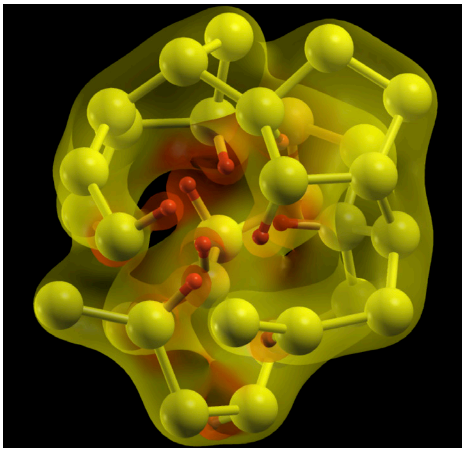
For years David Drabold had been feeding complex code into powerful computers to generate atomic models of materials.

This is what theoretical physicists like Drabold do. One of his specialities is hydrogenated amorphous silicon, a common material with many applications.

But for all the brain and processing power that went into this modeling, the models themselves were not quite realistic.

Like most theorists, Drabold, distinguished professor of physics and astronomy at Ohio University and an NQPI member, constructed his models based on math, paying little attention to data from the physical observations of the experimental physicists. The two camps tend to operate in their own spheres. As a result, the theoretical models don't always conform with what experimental data reveal about the structure of materials.

Drabold tended to brush aside these differences. Then one day he and two other physicists — one from the University of Southern Mississippi, the other from the University of Texas — set out to build a model of hydrogenated amorphous silicon incorporating data from the experimental side. The results were published in December in the Journal of Applied Physics.



A three-dimensional computer model shows nine hydrogen atoms (red) in a spherical complex of hydrogenated amorphous silicon.

Using the experimental data allowed Drabold to more accurately map a peculiar feature of hydrogenated amorphous silicon. The landscape of its molecular structure is dotted with voids. In the theoretical models, Drabold would plug in the voids based on certain assumptions about their distribution.

But using data from nuclear magnetic resonance spectroscopy, he was able to more accurately map the size and location of these voids. And this more precise modeling may be of value to those on the experimental side. One of the uses of hydrogenated amorphous silicon is in photovoltaic cells. Hydrogen atoms are attracted to the voids, which may be associated with a loss of photovoltaic efficiency, Drabold said. So better mapping could aid in the design of more efficient solar panels.

Drabold's research fits within a larger push to bring experimental and theoretical scientists together in the interest of creating materials with certain optimal characteristics that will be of use to government and industry.

The goal, Drabold said, is to create a feedback loop in which theorists use experimental data to guide the design of more accurate computer models, which in turn will shape the creation of materials with the desired properties.

Research Eyes Cheaper Hydrogen Harvest From Coal

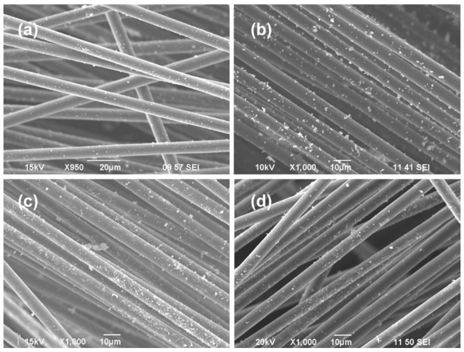
Coal has a dirty reputation. But trapped inside a lump of the Industrial Age fuel is a lot of clean-burning hydrogen that could power a much greener future.

The challenge is extracting the hydrogen in a way that makes it economically feasible for use as an alternative fuel source.

Gerardine Botte, Russ professor of chemical and biomolecular engineering at Ohio University and an NQPI member, is trying to solve this problem. An article published in January in the Journal of Power Sources detailed an experiment in which she found a way to help bring down the cost of harvesting hydrogen from coal.

The process she studied is called coal electrolysis. Coal is ground into powder and mixed with sulfuric acid, and this slurry is charged with electricity flowing through metal electrodes. The current busts apart molecular bonds in the coal, releasing some of the hydrogen and other elements that reside within.

The electrodes typically are coated with platinum, which has proved a very effective catalyst in this molecular demolition. Platinum is also very expensive. Botte experimented with a coating of platinum mixed with iron, a much cheaper element, and found she could get the same performance using less platinum.



Above: Scanning electron micrographs of electrocatalysts with various compositions supported on carbon fibers. (a) Pt, (b) Pt-Fe (7:3), (c) Pt-Fe (1:1), (d) Pt-Fe (3:7). Right: Gerardine Botte.

Botte is also looking at ways to extract hydrogen from coal using less energy to help bring the cost down. It takes a lot of electricity to fracture those coal molecules, so to make the hydrogen extraction economically more attractive, methods must be found to do it with less energy.

While platinum is an excellent catalyst for coal electrolysis, it isn't very targeted, Botte said. Some molecular bonds within coal are harder to break than others, requiring much more energy relative to the payoff in hydrogen released.

The platinum catalyst is indiscriminate when it comes to fracturing coal molecules. But it may be possible, through experimentation with different combinations of elements, to create an anode coating that is more targeted at molecules that are easier to break apart.

If the cost and energy required to harvest hydrogen from coal can be brought down enough, Botte envisions that down the road homes and businesses could be powered by coal fuel cells that use sunlight as the energy source for electrolysis to produce hydrogen. Another challenge along the way will be figuring out what to do with all the leftover coal, mostly carbon, after the hydrogen has been extracted.

Atomic Sleuthing Converts Calibration Mystery Into Discovery

Something was wrong, or so it seemed at first.

The image from the microscope displayed hundreds of tiny bright dots randomly spread across the surface of the thin sample under the needle tip.

This was a surprise.

And so what began as a routine calibration of a new, high-powered microscope revealed a mystery that ended with a scientific discovery for Ohio University physics and astronomy professor and NQPI member Arthur Smith. He and two of his graduate students, Khan Alam and Andrew Foley, published their findings in Nano Letters in February.

Smith and his team were calibrating their cryogenic temperature scanning tunneling microscope using a postage stamp-sized sample of gallium nitride, which has a repeating surface pattern that makes it ideal for calibration purposes. The procedure was being performed at low temperature, with the sample chilled to just a few degrees above zero Kelvin.

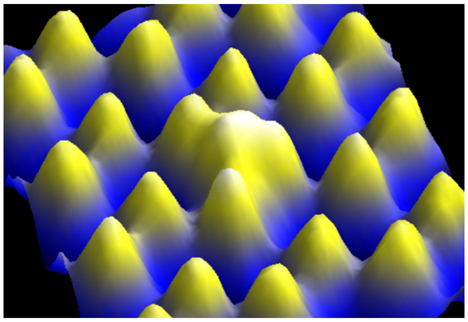
That's when the tiny bright dots appeared, trillions of them per square centimeter.

At first they considered the possibility that the microscope had become contaminated, Smith said. But after running several tests they ruled this out.

Could it be the sample itself? The samples are built in atomic layers by evaporating atoms of gallium and nitrogen. The ideal ratio is not an equal mixture: More gallium atoms are added than nitrogen. The excess gallium atoms gather into sizeable clusters, which are visible under a lesser-powered microscope.

What Smith and his team discovered with their STM, however, is that some gallium atoms continue to roam free. Billions of them, in fact. At room temperature, these atoms are zipping about, joining clusters, leaving clusters. It's like a microscopic pinball machine with billions of balls bouncing around.

At room temperature, these free-ranging, fast-moving atoms are not detected by the microscope, which uses a tiny needle to map the contours of the surface of the material being examined. But when the sample is supercooled, these atoms are essentially frozen in their tracks, Smith said, and show up as tiny bright dots.



A 3-D rendered STM image showing the atomic structure of an L in the middle. A peak at the center of the L can be seen clearly.

The team tested their hypothesis by creating samples with different ratios of gallium and nitrogen atoms. The samples with a higher percentage of gallium produced more bright dots, and vice versa.

There still remained one more mystery to solve. The free-ranging gallium atoms should ideally appear spherical in shape, Smith said. But they looked like the letter 'L' under the microscope. The reason, the team discovered, is because when the gallium atoms "freeze" in place, they're actually dropping into the sample's periodic surface structure and creating a localized lattice distortion.

Stopping Traffic on Graphene Highway

Electrons skim across the surface of graphene with amazing speed and ease, behaving as if they have no mass.

The trick is getting them to stop.

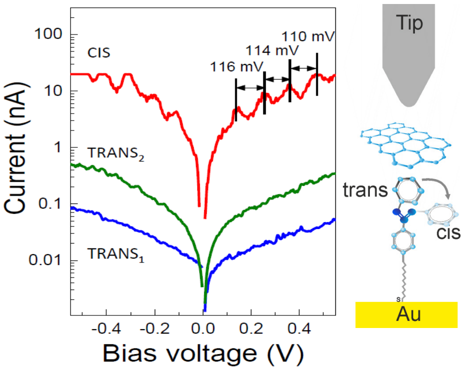
Researchers at the Technical University in Munich and at Ohio University recently published a paper on a process that corrals a tiny cluster of electrons in the midst of this graphene highway, causing them to pause for just a moment.

The experiment in Munich was analyzed theoretically in Ohio by NQPI member Sergio Ulloa, a physics and astronomy professor, and Mahmoud Asmar, a physics graduate student, and featured in the December issue of Nano Letters.

Graphene is a layer of pure carbon one atom thick — the thinnest known substance in the universe. Its two-dimensional, ultra-flat, ultra-smooth surface allows electrons to flow with virtually no obstruction. This highly conductive character is part of what makes graphene such a promising material.

The Munich experiment begins with a microscopically thin layer of gold. Unlike the graphene, this layer is not a continuous strip of gold, but rather lots of little clusters of the precious metal. Molecules of azobenzene are pinned to the gold clusters using sulfur as a binder. The azobenzene molecules stand upright like fibers in a shag carpet. A layer of graphene is then laid on top.

This molecular sandwich is exposed to bursts of ultraviolet light, and probed using an atomic force microscope. The ultraviolet light causes the upright azobenzene molecules to bend over on cue, resulting in a stronger interaction between the azobenzene molecules and the graphene.



Current-voltage curves show switching between high and low current (left) depending on the azobenzene configuration being cis or trans (right).

What these scientists discovered is that the stronger interaction causes a cluster of electrons in the targeted location to linger for a moment, as if they've been corralled by a ring of azobenzene. This corralling gives rise to a series of sharp resonances that reveals the size of the corral.

The experiment proves that it is possible to optically define corrals that affect the flow of electron traffic on the graphene superhighway. Graphene is seen as a possible replacement for silicon in the manufacture of ever-faster computer chips but one of the challenges is figuring out how to control the electrical flow so that it can be switched on and off as in a semiconductor.

Physics Graduate Wins Outstanding Dissertation Award

Zhiyuan Fan has been interested in physics since he was a 10-year-old boy growing up in China. A favorite pastime as a child was reading scientific magazines to learn about faraway galaxies and things a bit closer to home such as rockets and space shuttles.

Zhiyuan Fan

Fan, a former graduate student of physics and astronomy professor and NQPI member Alexander Govorov, has won the third annual NQPI Outstanding Dissertation Award. The award is given to recognize exceptional work performed by a doctoral student and to encourage the highest levels of scholarship, research and writing.

Fan's research and dissertation while at Ohio University focused on optical properties of chiral nanomaterials, which are created by linking metal or semiconductor nanoparticles and biomolecules. Fan, 32, is now a postdoctoral fellow researching metal metasurfaces and graphene plasmonics at the University of Texas at Austin.

Elements: Trick Was Avoiding Image Distortion From X-Ray Blasts

Continued from page 1

tography at the nano level. The tip of the needle is the size of a single atom, allowing it to map the contours of a single layer of atoms.

The image generated from the needle's tracing is like a topographical map. But it only maps the surface of the atoms. It does not reveal the atomic fingerprint that identifies the element.

The elements on the periodic table each have a unique number of electrons (and an equal number of protons). This is what distinguishes lithium, with three electrons, from cobalt, which has 27. When an atom is bombarded with X-rays, the electrons orbiting close to the nucleus are energized and move outward, which for a split second reveals the element's fingerprint.

The STM needle doesn't actually touch the surface of the atoms it's mapping. It rides on an extremely thin electron buffer. For the topographical image to be accurate, this buffer must remain consistent as the needle moves. And herein lies the nub of the problem when combining X-rays with an STM: When the energized electrons blast out of their inner orbits, they can distort that buffer.

Hla and his research team invented a switching mechanism that allows the STM needle to read the atomic fingerprint a split second after the X-ray blast. They have essentially fooled the system so that the needle doesn't recognize the burst of energy caused by the X-rays, he said. He likened it to the World War I fighter planes that had machine guns mounted directly in front of the pilot. Engineers had to figure out a precise timing mechanism so that with the trigger depressed the bullets fired only after the propeller blade swept by, otherwise it would be blown to bits.

Hla was recently granted a patent on this technique. He also holds a patent on a technique that uses an STM needle to probe one of the world's smallest molecular superconductors. Moreover, he is an expert in moving atoms from one spot to another. As a demonstration, taped to his office wall is a picture of atoms he maneuvered to form the letters OU.

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