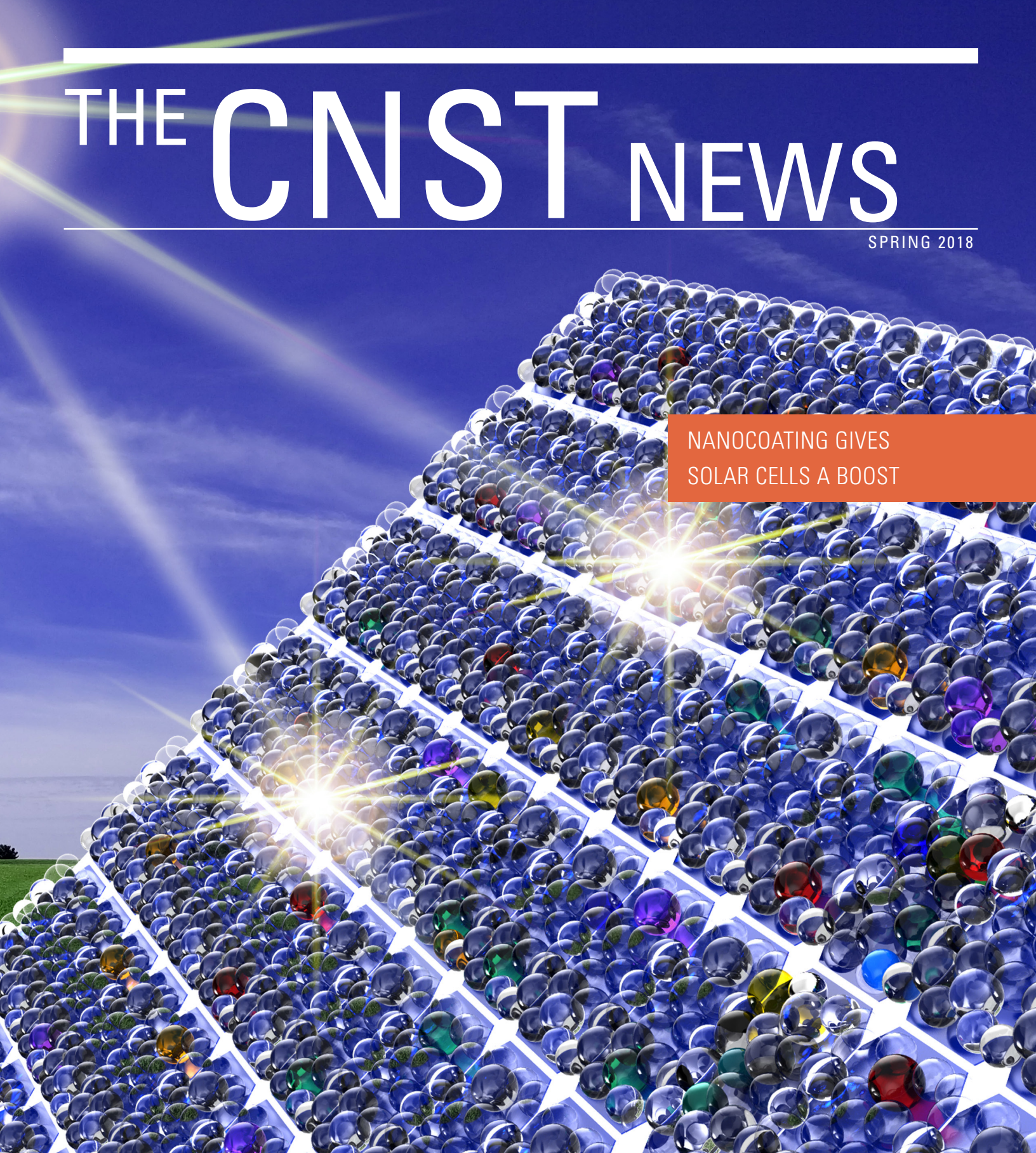

THE CNST NEWS

SPRING 2018



NANOCOATING GIVES
SOLAR CELLS A BOOST

INSIDE

DOING THE NANOSHIMMY

NANOCATALYSTS UNDER THE ELECTRON MICROSCOPE

A DETAILED LOOK AT LITHIUM IN SOLID-STATE BATTERIES

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The effect of optical couplings to nanosphere arrays above a solar cell are illustrated. The coupled light can then contribute to increase photocurrent in the solar cell. The different colors on nanospheres describe excitation of optical resonances at different visible wavelengths depending on the size of nanospheres. In the manuscript written by D. Ha and N. B. Zhitenev, nanoscale optical couplings and photocurrent enhancements with such nanosphere arrays were demonstrated using nanoscale photocurrent microscopy technique. Credit: D. Ha, K. Dill, G. Holland, N. B. Zhitenev/NIST

EDITOR |
RON COWEN

CONTRIBUTORS |
RON COWEN
CURT SUPLEE
BEN STEIN

GRAPHIC DESIGN |
KRISTEN DILL

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SRINIVASAN HONORED BY OPTICAL SOCIETY



CNST physicist Kartik Srinivasan, a project leader of the Nanofabrication Research Group, was recently elected Fellow of the Optical Society. He received the honor for his outstanding contributions to nanophotonics and quantum optics, including cavity-QED, frequency conversion and integrated optics such as photonic crystals. Pictured with him is Ursula Gibson, 2018 president-elect. Credit: Optical Society

PSST! A WHISPERING GALLERY FOR LIGHT BOOSTS SOLAR CELLS

Trapping light with an optical version of a whispering gallery, NIST researchers have developed a nanoscale coating for solar cells that enables them to absorb about 20 percent more sunlight than uncoated devices. The coating, applied with a technique that could be incorporated into manufacturing, opens a new path for developing low-cost, high-efficiency solar cells with abundant, renewable and environmentally friendly materials.

The coating consists of thousands of tiny glass beads, only about one-hundredth the width of a human hair. When sunlight hits the coating, the light waves are steered around the nanoscale bead, similar to the way sound waves travel around a curved wall such as the dome in St. Paul's Cathedral in London. At such curved structures, known as acoustic whispering galleries, a person standing near one part of the wall easily hears a faint sound originating at any other part of the wall.

Whispering galleries for light were developed about a decade ago, but researchers have only recently explored their use in solar-cell coatings. In the experimental set-up devised by a team including Dongheon Ha of NIST and the University of Maryland's NanoCenter, the light captured by the nanoresonator coating eventually leaks out and is absorbed by an underlying solar cell made of gallium arsenide.

Using a laser as a light source to excite individual nanoresonators in the coating, the team found that the coated solar cells absorbed, on average, 20 percent more visible light than bare cells. The measurements also revealed that the coated cells produced about 20 percent more current.

The study is the first to demonstrate the efficiency of the coatings using precision

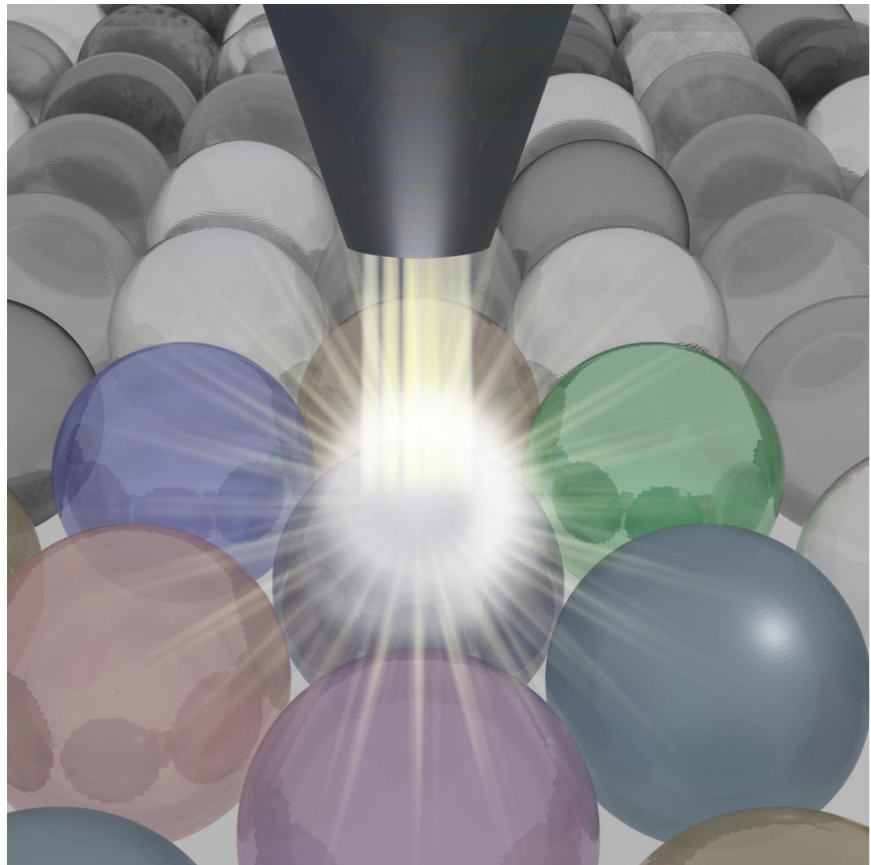


Illustration shows the nanoresonator coating, consisting of thousands of tiny glass beads, deposited on solar cells. The coating enhances both the absorption of sunlight and the amount of current produced by the solar cells. Credit: D. Ha, K. Dill, N. B. Zhitenev/NIST

nanoscale measurements, said Ha. "Although calculations had suggested the coatings would enhance the solar cells, we could not prove this was the case until we had developed the nanoscale measurement technologies that were needed," he noted.

Ha and his collaborators, Yohan Yoon of NIST and the University of Maryland's NanoCenter, along with NIST physicist Nikolai Zhitenev, [described their work](#) in a recent issue of *Nanotechnology*.

The team also devised a rapid, less costly method of applying the nanoresonator coating. Researchers had previously coated semiconductor material by dipping it in a tub of the nanoresonator solution. The dipping

method takes time and coats both sides of the semiconductor even though only one side requires the treatment.

In the team's method, droplets of the nanoresonator solution are placed on just one side of the solar cell. A wire-wound metal rod is then pulled across the cell, spreading out the solution and forming a coating made of closely packed nanoresonators. This is the first time that researchers have applied the rod method, used for more than a century to coat material in a factory setting, to a gallium arsenide solar cell.

"This is an inexpensive process and is compatible with mass production," said Ha.

DOING THE NANO-SHIMMY

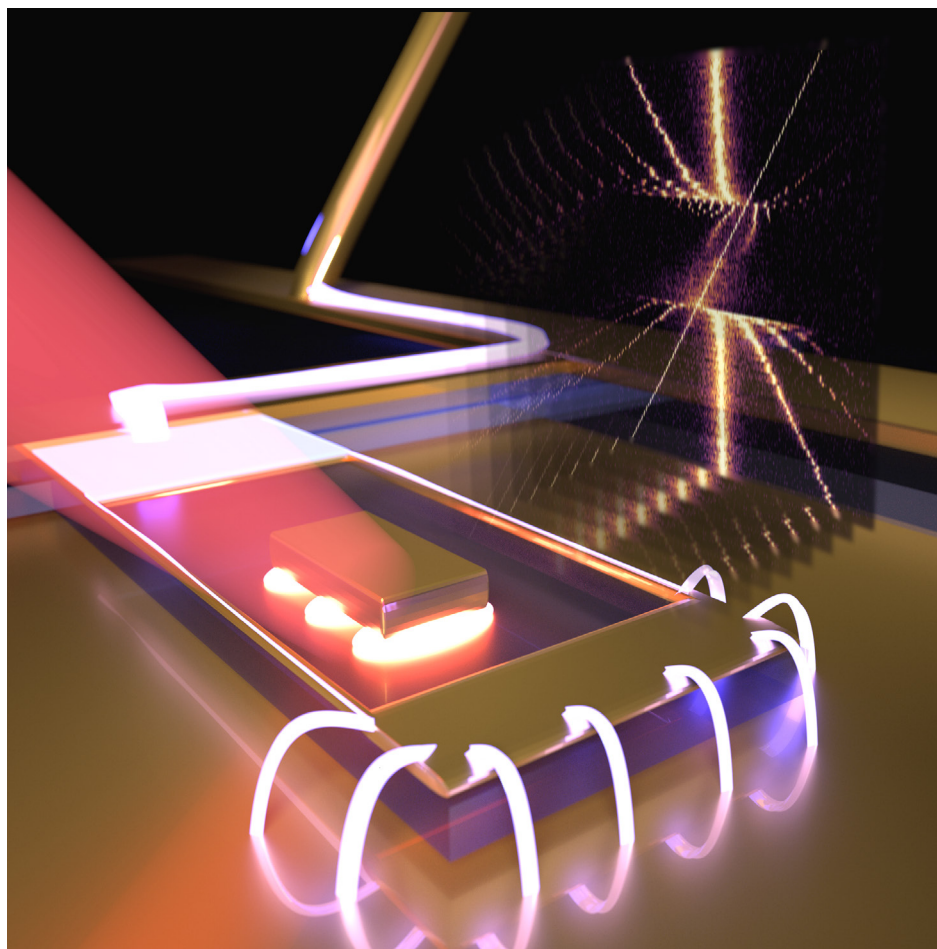
New device modulates light and amplifies tiny signals.

Imagine a single particle, only one-tenth the diameter of a bacterium, whose miniscule jiggles induce sustained vibrations in an entire mechanical device some 50 times larger. By taking clever advantage of the interplay between light, electrons on the surface of metals, and heat, researchers at the National Institute of Standards and Technology (NIST) have for the first time created a plasmomechanical oscillator (PMO), so named because it tightly couples plasmons—the collective oscillations of electrons at the surface of a metal nanoparticle—to the mechanical vibrations of the much larger device it's embedded in.

The entire system, no bigger than a red blood cell, has myriad technological applications. It offers new ways to miniaturize mechanical oscillators, improve communication systems that depend on the modulation of light, dramatically amplify extremely weak mechanical and electrical signals and create exquisitely sensitive sensors for the tiny motions of nanoparticles.

NIST researchers Brian Roxworthy and Vladimir Aksyuk [described their work](#) in a recent issue of *Optica*.

The device consists of a gold nanoparticle, about 100 nanometers in diameter, embedded in a tiny cantilever—a miniature diving board—made of silicon nitride. An air gap lies sandwiched between these components and an underlying gold plate; the width of the gap is controlled by an electrostatic actuator—a thin gold film that sits atop the cantilever and bends toward the plate when a voltage is applied. The nanoparticle acts as a single plasmonic structure that has a natural, or resonant frequency that varies with the size of the gap, just as tuning a guitar string changes the frequency at which the string reverberates.



Schematic of the first-ever plasmomechanical oscillator (PMO), developed by NIST researchers. The orange-white ovals represent the localized plasmon oscillations. The cantilever, containing the gold cuboid nanoparticle, lies dead center. The series of white curves represents the electrical field applied to the cantilever. Data at right indicates that the device can lock onto and greatly amplify weak signals that oscillate at frequencies close to the PMO. Credit: B. Roxworthy/NIST

When a light source, in this case laser light, shines on the system, it causes electrons in the resonator to oscillate, raising the temperature of the resonator. This sets the stage for a complex interchange between light, heat and mechanical vibrations in the PMO, endowing the system with several key properties.

By applying a small, direct-current voltage to the electrostatic actuator that squeezes the gap shut, Roxworthy and Aksyuk altered the optical frequency at which the resonator vibrates and the intensity of the laser light the system reflects. Such optomechanical

coupling is highly desirable because it can modulate and control the flow of light on silicon chips and shape the propagation of light beams traveling in free space.

A second property relates to the heat generated by the resonator when it absorbs laser light. The heat causes the thin gold film actuator to expand. The expansion narrows the gap, decreasing the frequency at which the embedded resonator vibrates. Conversely, when the temperature decreases, the actuator contracts, widening the gap and increasing the frequency of the resonator.

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PUTTING LITHIUM ALL-SOLID-STATE BATTERIES UNDER THE MICROSCOPE

Technology still in its infancy, lithium all-solid-state batteries may ultimately supersede the industry standard for the past 25 years, the lithium-ion battery. The solid-state battery is more compact, lighter in weight and can store more energy. And because the solid-state device doesn't contain liquid, it can't catch on fire the way lithium-ion batteries in cell phones sometimes have.

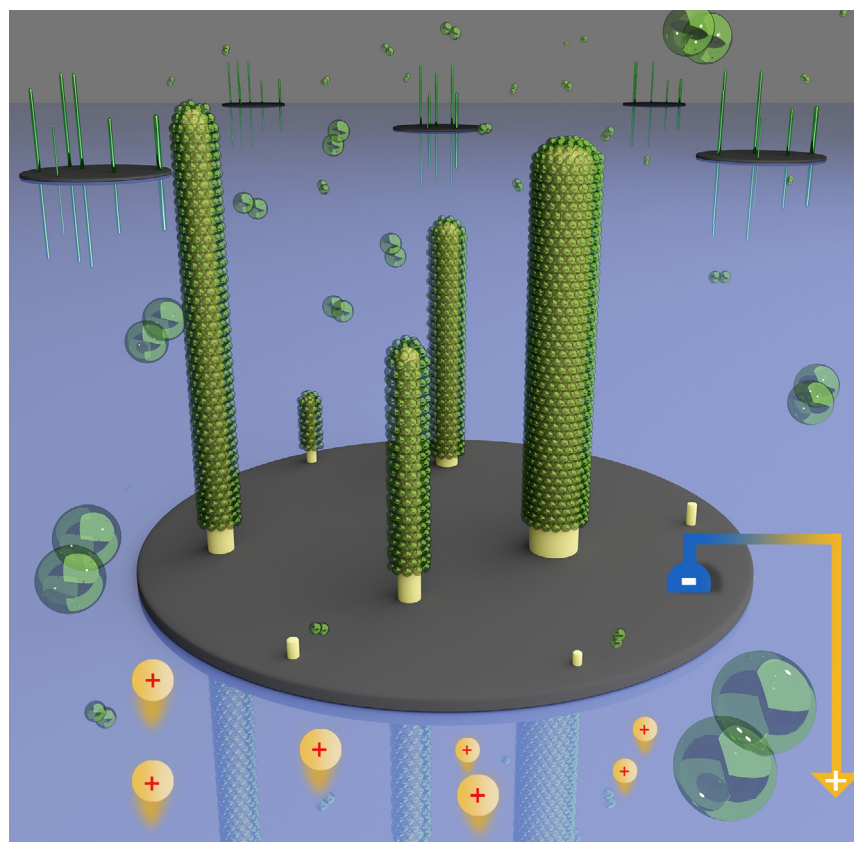
But ensuring that lithium atoms form a thick, uniform coating on a solid-state battery's negative terminal (anode)—a critical step for operating the battery at peak capacity—can prove challenging. As lithium atoms congregate on an anode, they can form such a coating, but they can also grow in clumps that grow as isolated nanostructures, such as whisker-like filaments.

The whiskers protrude from the anode and may make contact with the positive terminal (cathode), shorting out the circuit and destroying the battery. Controlling both the plating and stripping of lithium atoms as they move through the battery is therefore essential for keeping lithium solid-state batteries in good working condition.

Using nanoscale imaging techniques, researchers at the CNST and their colleagues have now documented the clustering, plating and stripping of lithium as it cycles through a thin-film model of a solid-state battery. By studying lithium cycling in different environments—under an ultrahigh vacuum and when exposed to varying concentrations of molecular oxygen—the team determined the optimal conditions to avoid or stem the growth of lithium whiskers.

Alexander Yulaev of NIST and the University of Maryland, along with NIST physicist Andrei Kolmakov and collaborators from Sandia National Laboratories and Michigan State University, described their findings in a recent *Nano Letters*.

The team used a scanning electron microscope to record images and videos of lithium activity while the model battery was in operation. The researchers also relied on



Artist's view of a model lithium solid-state battery shows lithium nanowires (yellow) protruding from carbon anode pads (gray). The presence of molecular oxygen (green) forms a lithium-oxide shell that encapsulates the lithium and restricts its uniform, three-dimensional growth. The fine balance between the battery charging rate and the concentration of oxidizing species determines the ultimate shape of the lithium deposits, which is critical to the optimal operation of a lithium solid-state battery. Credit: A. Yulaev/UMD/NIST

an Auger electron spectroscopy technique to measure the changes in chemical composition of the anode. Yulaev and his collaborators found that a balance between competing factors influence how lithium atoms are distributed on the anode: the rate at which lithium atoms are flowing onto the terminal and the concentration of molecular oxygen or other oxidizing agent that interacts with the lithium.

When exposed to relatively low concentrations of molecular oxygen (a partial pressure of about one millionth of a Pascal), the top layer of lithium atoms on the anode forms a thin shell of lithium oxide that encapsulates the rest of the lithium. During the charging process, as additional lithium atoms accumulate on the anode, cracks open

the shell, pushing lithium atoms out of the anode and forming whiskers that can cause a short circuit.

Somewhat to their surprise, the researchers found that higher concentrations of molecular oxygen (a partial pressure greater than one-hundred thousandth of a Pascal), prevented lithium from forming whiskers. The team suggests that the large oxygen concentration leads to a thicker shell of lithium oxide, which newly arriving lithium atoms cannot penetrate. The underlying lithium atoms retain their uniform distribution.

The results demonstrate the important role that trace amounts of molecular oxygen or other oxidizing agent play in the operation of solid-state batteries, Yulaev says.

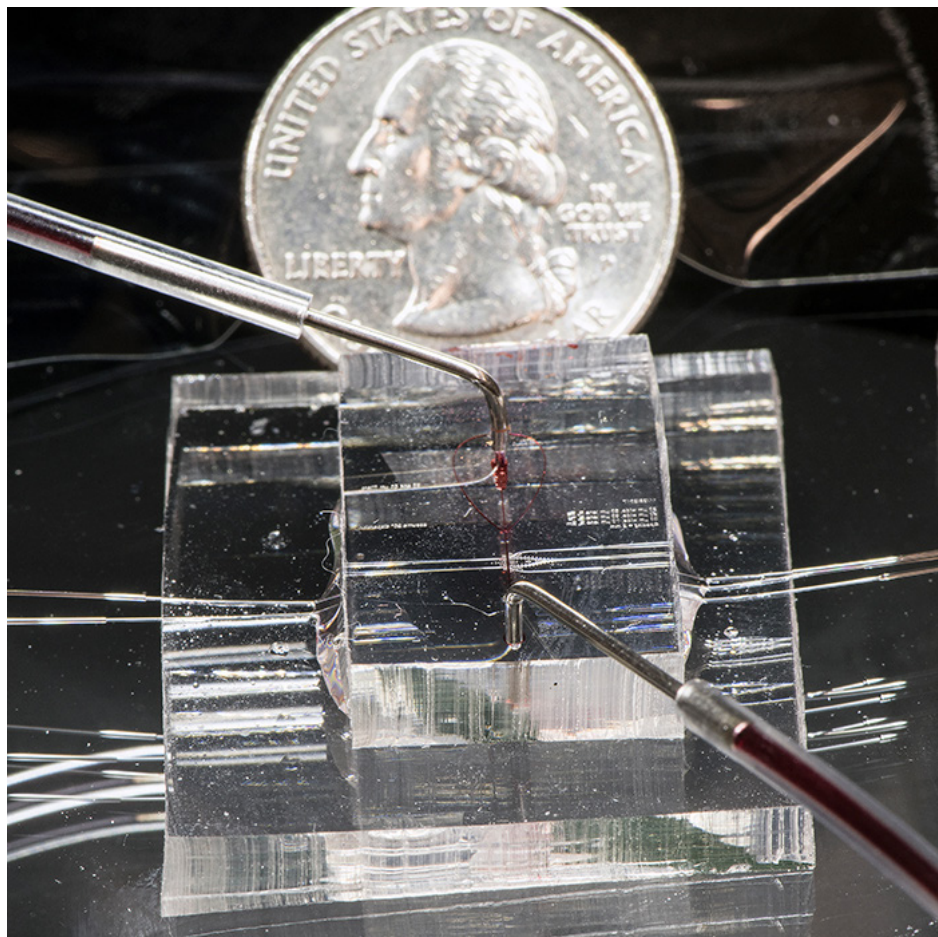
A STOPWATCH FOR NANOFUIDS: NIST FILES PROVISIONAL PATENT FOR MEASURING NANOLITER FLOW RATES

The National Institute of Standards and Technology (NIST) has filed a provisional patent application for a microflow measurement system, about the size of a nickel, that can track the movement of extremely tiny amounts of liquids—as small as nanoliters (nL, billionth of a liter) per minute. If water were flowing at that rate from a 1-liter bottle of water, it would take about 200 years to drain.

The invention is designed to fill an urgent need in the rapidly expanding field of microfluidics, in which precisely measuring tiny flow rates is critical. For example, some medical drug-delivery pumps dispense as little as tens of nL per minute into the bloodstream. For comparison, a single drop of water contains 50,000 nL. Clinical diagnostics, chemical research, cell sorting and counting, and continuous-flow micromanufacturing—essentially tiny factories that work nonstop to make small quantities of liquids—also increasingly require accurate measurements of similarly minuscule volumes.

But current state-of-the-art devices used to measure flow on that scale have one or more operational limitations. “Some require calibration, others use complex imaging systems and microscopes; some take data over many minutes, and therefore, can’t track dynamic changes, and some are not traceable to the [International System of Units](#),” said inventor Greg Cooksey, a biomedical engineer in NIST’s Physical Measurement Laboratory.

His optical microflow measurement system, fabricated at NIST’s Center for Nanoscale Science and Technology, avoids those complications. It monitors the speed of



Close-up of a microflow system with red dye in fluid channel. Credit: B. Roxworthy/NIST

fluorescent molecules in liquid as they travel down a channel about the width of a human hair, measuring the time interval between the molecules’ responses to two separate laser pulses.

Flowing down a microchannel is a fluid filled with fluorescent molecules that emit green light when exposed to a specific wavelength of blue light. However, these molecules have been chemically modified to prevent fluorescence. At one point in the channel, an ultraviolet laser destroys the chemical modification of some of the

molecules. At another point in the channel, a blue laser causes these bare molecules to fluoresce. Researchers determine flow rate by measuring the elapsed time between removing the chemical modification and fluorescence.

To exactly mark a start-time reference point, an ultraviolet laser pulse (with a wavelength of 375 nm) is fired along an optical waveguide and into the channel. There, the pulse strikes a chemically protected (“caged”) fluorescent molecule moving in the stream. “The molecule can’t fluoresce until we activate

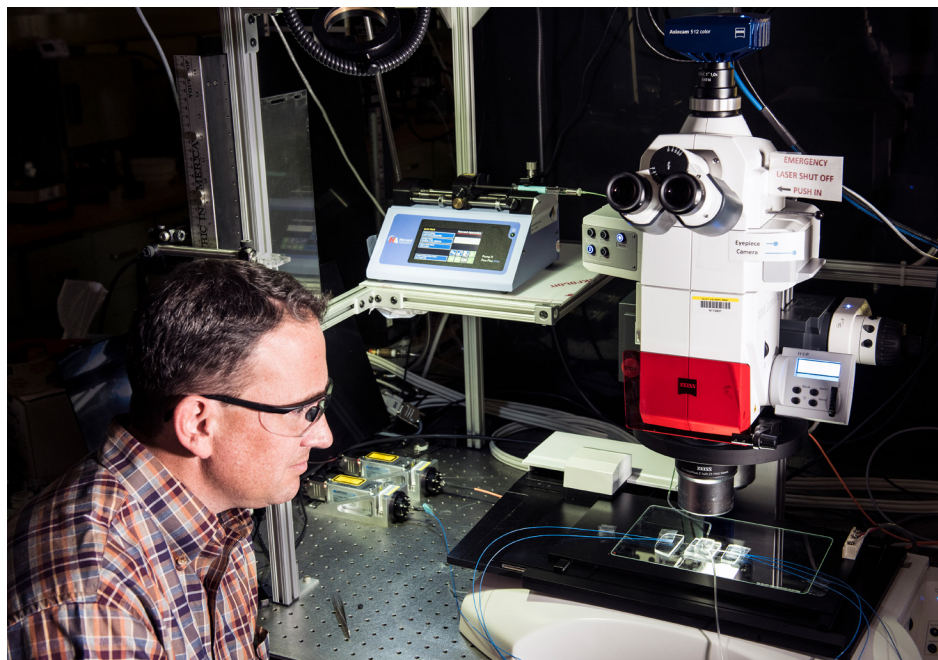
it with the UV pulse,” Cooksey said. “That, in effect, turns the molecule ‘on’ as its cage is destroyed by the laser. At that point, the molecule becomes responsive to excitation by light.”

After the activated molecule has traveled 250 micrometers—about the thickness of a playing card—downstream in the channel, it crosses the path of a blue laser (488 nm). The molecule absorbs the blue light and immediately emits green light (520 nm). That emission travels down a wave guide to an optical power meter that continuously measures changes in the emitted light’s intensity at a rate of 250,000 times per second.

The emission signals are compared to the timing of the initial activating pulses to determine the elapsed interval. The faster the flow, the less time between activation and emission.

The flow rate is deduced from careful measurements of the time between laser pulses and the channel dimensions, and those measurements are refined with calculations of flow pattern between activation and emission measurements. Therefore, the flow meter does not require calibration using an independent flow standard. In addition, it is more sensitive than most conventional technologies, and provides continuous real-time data with resolution on the order of 1 millisecond.

The invention is also capable of serving as a flow cytometer—a device that counts, or otherwise measures, properties of biological



Greg Cooksey with apparatus used to observe microflow meter. Credit: NIST

cells in a fluid stream. There are many ways of engineering cells so that they contain fluorescent “biomarkers” of various kinds, which can be measured as they flow past the detectors in the NIST device.

“That’s what we’re trying to build in addition to precision flow measurement—a platform for next-generation biological measurements,” Cooksey said. “For example, because of the precise timing built into the system, we can conduct ‘time-lapse’ studies of cell metabolism, where cells are loaded with fluorescent materials whose emission changes in proportion to their metabolism.”

Such information will be useful for studies of cancer, as cancer cells are known to have elevated rates of metabolism. “We could make as many measurements as we want

downstream,” Cooksey said. “We could use 10 of these optical interrogation points, each separated by, say, 100 milliseconds, and track the decline in light output in each cell through time.”

Alternatively, Cooksey said, they could also investigate calcium influx. “Many kinds of cells use calcium for signaling, so if we load the cell with a calcium-sensitive dye, the dye will respond as the calcium concentration changes. That would allow us to watch changes in real time in functions such as neural communication or triggering of programmed cell death.”

A provisional patent application, marking the start of the patent process, has been filed.

PRECISION TOOL COMBINES THREE MEASUREMENTS IN ONE DEVICE

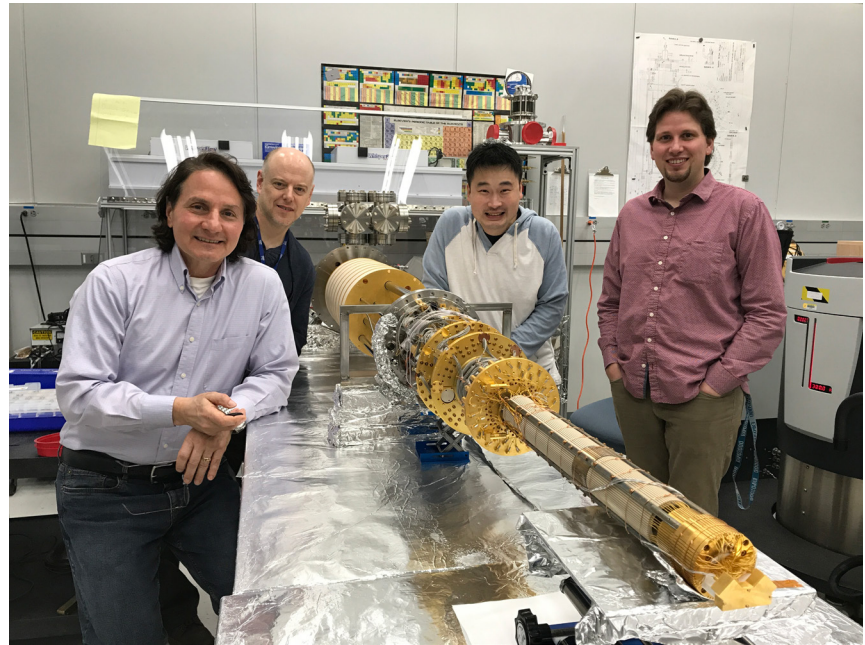
A CNST team led by physicist Joseph Stroscio has achieved a trifecta among precision measuring tools. In a single instrument, the researchers have combined a scanning tunneling microscope (STM), an atomic force microscope (AFM) and a system that measures electrical resistance. The hybrid tool is one of the first of its type that operates at temperatures one-hundredth of a degree above absolute zero and immersed in magnetic fields as high as 15 Tesla, about 150 times the strength of a small bar magnet.

NIST researchers Johannes Schwenk and Sungmin Kim described the instrument at the March meeting of the American Physical Society in Los Angeles.

With the new instrument, researchers can simultaneously conduct measurements with the STM, AFM and electrical resistance system—while current is flowing through a sample. This capability provides scientists with a new understanding of how microscopic properties of a material affect the macroscopic flow of current. Applications of the instrument include the development new types of electrical devices made from advanced electronic materials such as graphene, a single sheet of carbon atoms.

The STM part of the device produces atomic-scale images by placing a stylus just above the surface of a conducting material. The tip of the stylus is extremely sharp, formed by a single atom. A tiny, quantum-mechanical current “tunnels” from atoms on the surface to the stylus, and the tip is raised or lowered to keep the current constant. By recording the tiny vertical motion of the tip, researchers create a two-dimensional atom-by-atom contour map of the surface. An STM can also reveal the density of electrons that fall within a specific energy range at the surface of the sample, which reveals the electronic structure of the material.

In contrast, an AFM’s probe measures the atomic and molecular forces exerted by the sample, providing information on the mechanical properties, including the strength



From left to right, Joe Stroscio, Bill Cullen, Sungmin Kim and Johannes Schwenk with their hybrid AFM/STM/electric resistance measurement system. Credit: NIST

of the surface. An AFM can also produce a three-dimensional map of surface features.

Because an STM measures current flow, the material under study must either be a conductor or have a thin strip of conducting material laid on top of it. An AFM does not require current, so it can examine insulators as well as conductors.

Simultaneous operation of the STM and AFM offers several advantages in studying graphene devices—for instance, when a graphene sample abuts an insulating material such as silicon oxide. At the boundary between the two materials, an STM fails to provide accurate images, but the AFM can still provide structural information, notes Schwenk. Concurrent studies with the STM and AFM also provides information about the arrangement of atoms as well as electrons on the surface of a sample.

Combining the STM and AFM studies with measurements of electrical resistance allows researchers to see exactly where current is flowing in a device, says Stroscio. In some

cases, in the presence of a large magnetic field, the current will only flow along the edges of a sample. Studying these edge currents provides insight into the fundamental physics of how electrons flow in materials.

Although hybrid STM-AFM instruments are relatively common, “this is one of the few working machines that combines the two at temperatures of 10 millikelvin (one hundredth of a degree above absolute zero, and also includes electrical resistance measurements,” says Schwenk.

Operating the device at such low temperatures enables the instrument to examine the atomic behavior of superconducting materials, which allow electric current to flow with zero resistance when cooled below a certain critical temperature. The cold temperature also reduces the noise in the sample due to the thermal vibration of atoms. Because the hybrid tool can withstand high magnetic fields, researchers can use the instrument to probe how the electron energy levels of materials, including graphene, depend on magnetic field strength.

CNST REMEMBERS ALAN BAND

Alan Band, an electrical engineer at NIST for more than 25 years who won the Institute's Colleagues' Choice Award and was celebrated for his ability to mentor both scientists and technicians, died on April 10 after a long illness. He was 59. Alan worked at NIST's Center for Nanoscale Science and Technology since its inception in 2007, where colleagues recalled his dedication and willingness to solve electronics problems, no matter how challenging.

"Alan was absolutely one of the most friendly, helpful and knowledgeable people I have met at NIST," said Kartik Srinivasan, a project leader in CNST's Nanofabrication Group.

Elise Pilat, an electrical engineer at CNST's NanoFabrication Operations Group, met Alan soon after she started her career at NIST in 2013. "We became quick friends as we 'geeked out' about electronics and all things engineering," she recalled. Despite Alan working for a different group and having a heavy work load, "he selflessly tried to teach me everything he knew about engineering and it has been the joy of my career to learn it," she added.

For Glenn Holland, a broken turbo pump led him to Alan. The people in Holland's NIST laboratory advised him to contact Alan "because he could fix anything." While working to fix the pump, Alan suggested ways Holland could improve his project. A few years later, when Holland was looking for a new job, Alan helped him find his way to CNST's electron physics group. "It was my pleasure to share an office with him for the last nine years," said Holland.

For three years, Veronika Szalai, a project leader in CNST's Nanoscale Imaging and Spectroscopy Group, worked closely with Alan to build a magnetic resonance spectrometer for biomacromolecules, an endeavor she had never before attempted. The supporting information describing the instrument, published in a peer-reviewed journal with Alan as first author, "is a lasting record of his amazing contributions to deliver on this complex and challenging project," said Szalai. Alan had often told Szalai that her project ideally needed an entire team of engineers, but somehow Alan managed to be that entire team.

"His energy, his persistence, and his belief that any instrumentation problem—no



CNST electrical engineer Alan Band. Credit: S. Blakneship/NIST

matter how complex—can be solved with a systematic approach and confidence exemplify Alan's way," said Szalai. "He changed my research trajectory. And he changed me: He showed me not only how to do it, but helped me believe I could."

Alan supervised and mentored electronics technician David Rutter for more than 12 years. "He afforded me the opportunity to learn through the projects that we worked on together no matter how complicated," said Rutter. "Alan was always willing to consider an alternative view or differing opinion on what was being worked on to make sure of the best design possible for the CNST research staff," he added. "He will be sorely missed."

For Joseph Stroschio, a project leader and NIST fellow in the CNST's Electronics Physics Group, Alan's stand-out contribution was the electronics instrumentation that he designed and built for the CNST's scanning tunneling microscope program. "The instrumentation was largely responsible for the high-quality data that has helped the program achieve world renown," he said.

Given the accolades, it was perhaps no surprise that Band won the 2011 NIST Colleagues' Choice Award "for enthusiastic dedication to his work, original ideas for solving difficult measurement problems and unending desire to help colleagues in need." He also received the Sigma Xi Certificate

of Recognition for "Outstanding service in support of NIST research scientists" in 2009 and the NIST Bronze Medal Award in 2003 in recognition of his contribution to the Electron Physics Group's scientific programs as well as collaborative projects with other NIST laboratories.

Before joining NIST in 1991, Alan worked at the Los Alamos National Laboratory where he developed and maintained electronics for monitoring the beam position in the meson physics facility. At the Evans and Sutherland Computer Corp. in Salt Lake City, Alan designed and developed bit-slice processor boards for high-performance graphics workstations. He also held several engineering positions at Becton Dickinson Automated Immunochemistry in Salt Lake City.

In all, Alan had over 30 years of experience in biomedical and scientific instrumentation, holding positions in government and private industry as a design engineer, engineering technician and field service technician.

Alan earned his bachelor's degree from the University of Utah and an associates' degree in biomedical instrumentation technology from the Springfield Technical Community College in Massachusetts.

He leaves behind his wife of 31 years, Jeanne Dietz-Band, and three sons. Donations may be made in Alan's name to the American Cancer Society.

STROSCIO WINS KEITHLEY AWARD

CNST physicist Joseph Stroschio was honored with the 2018 Joseph F. Keithley Award for Advances in Measurement Science. He received the \$5,000 award, along with two other researchers, at the March meeting of the American Physical Society in Los Angeles. The award recognized Stroschio “for the design and construction of a series of highly sophisticated scanning probe instruments, including the development of inelastic electron tunneling spectroscopy at the single atom and single spin limit, that provided many breakthroughs in the science of measurement.”

At the awards ceremony, Stroschio spoke about his pioneering work in the development of scanning tunneling spectroscopy and the invention and evolution of scanning tunneling microscopes. The scanning tunneling microscope ushered in the nanoscience revolution, enabling scientists for the first time to image individual atoms on the surface of materials. Spectroscopic measurements taken with the microscope revealed the ability to measure electronic structure of materials with atomic spatial resolution.



Joe Stroschio (left) received the 2018 Joseph F. Keithley Award for Advances in Measurement Science at the March meeting of the American Physical Society. He was one of three winners of the award. Credit: APS

Stroschio also highlighted one of his team’s newest research efforts, developing a combined STM and atomic force microscope that routinely operates at temperatures just one hundredth of a degree above absolute zero (see related article on p. 8).

Stroschio shared the award with Wilson Ho of the University of California-Irvine and Andreas Heinrich of Ewha Womans University, in Seoul, South Korea. Stroschio was Ho’s first Ph.D. student. Last year, the Surface Society of Japan awarded Stroschio the Heinrich Rohrer Grand Medal for his research contributions to nanoscience and nanotechnology.

DOING THE NANO-SHIMMY (CONT’D.)

Crucially, the force exerted by the actuator always kicks the cantilever in the same direction in which the cantilever is already traveling. If the incident laser light is powerful enough, these kicks cause the cantilever to undergo self-sustaining oscillations with amplitudes thousands of times larger than the oscillations of the device due to the vibration of its own atoms at room temperature.

“This is the first time that a single plasmonic resonator, with dimensions smaller than visible light, has been shown to produce such self-sustaining oscillations of a mechanical device,” said Roxworthy.

The team also demonstrated for the first time that if the electrostatic actuator delivers a small mechanical force to the PMO that varies in time while the system undergoes these self-sustaining

oscillations, the PMO can lock onto that tiny variable signal and greatly amplify it. The researchers showed that their device can amplify a faint signal from a neighboring system even when that signal’s amplitude is as small as ten trillionths of a meter. That ability could translate into vast improvements in detecting small oscillating signals, Roxworthy says.

CHANGING SHAPE: THE MORPHOLOGICAL DANCE OF CATALYST NANOPARTICLES

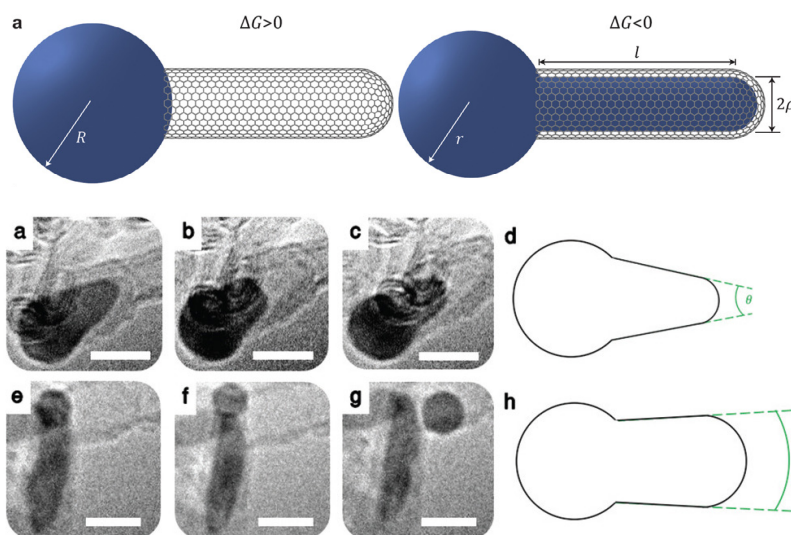
Stronger than steel and conducting heat and electricity better than copper, carbon nanotubes (CNTs) are a powerhouse material that promises to revolutionize nanotechnology. Although catalytic nanoparticles have made it easier and cheaper to manufacture these rolled-up sheets of graphene, the end product is often a mixture of many different CNTs, rather than the single type needed for a particular application.

By combining modeling with high-resolution imaging of nanoparticle catalysts as they do their work, CNST scientists and their collaborators have now documented the changes in shape and structure catalytic nanoparticles undergo to promote CNT growth—and why CNT catalysis sometimes fails to produce the desired result. The findings provide a framework for understanding similar phenomenon in a host of other catalytic reactions and suggest ways to optimize their performance, says NIST researcher Michael Zwolak.

He and CNST scientist Renu Sharma and their colleagues, including researchers from NIST's Materials Measurement Laboratory, the University of Maryland's NanoCenter and Georgetown University, recently described their results in a *Nanoscale*.

The researchers relied on an environmental transmission electron microscope to record changes in nickel catalytic nanoparticles as they interacted with a carbon source, acetylene (C_2H_2), to make CNTs. The microscope enables observations under realistic conditions because it can examine a sample that is not held at high vacuum.

The team's high-resolution movies revealed a pattern seen in earlier studies by other groups: The nickel nanoparticles, originally spherical, elongated to promote the growth of CNTs on their surface, then retracted back into a sphere, ready to repeat the process to make additional nanotubes. The nanotubes often formed multi-walled structures, with one single-walled nanotube nested inside another.



Top: When the change in the free energy of the catalyst nanoparticle is positive, the particle is favored to lie outside the growing carbon nanotube (left). When the free energy change is negative, the particle is likely to elongate and lie inside the growing carbon nanotube. **Bottom:** Snapshots of the growth of a catalyst nanoparticle for carbon nanotubes show the development of an inward (a-d) and outward (e-h) taper. Scale bar is 5 nanometers. Credit: NIST

However, the detailed observations showed something new: While catalytic growth is always a nonequilibrium process, the particle structure itself is also driven out of equilibrium. The disequilibrium triggered the catalyst nanoparticles to change their shape and structure in ways that they would not otherwise undergo. Sometimes the nanoparticles would even break apart. Using analytic theory to compute these energies, the team found that their calculations matched the experimental data.

Because earlier studies relied on limited data recorded at lower resolution, researchers could not make such determinations about the nanoparticle catalysts, nor could they accurately compare theory with experiment, Zwolak notes.

Observations with the electron microscope revealed different types of structures between the catalyst nanoparticles and CNTs. In one, CNTs began forming atop a spherical nanoparticle, a configuration that roughly resembled a head capped by a birthday hat. In these interactions, the CNTs tended to form nanofibers rather than bamboo-like multi-walled tubes. It was relatively easy, in this case, for the elongated nanoparticles

to retract to their original spherical shape because they did not have to expend much energy to do so. As the "birthday hat" became more like a top hat, the nanoparticles would become more highly elongated and the CNTs formed with longer and more uniform structures, the team found.

In yet another structure, the birthday hat configuration inverted, with the CNT fanning out from the nanoparticle. In these cases, part of the nanoparticle can become trapped in the growing CNTs and sometimes break off. The rest of the nanoparticle remained an active catalyst, but because it had lost material, it could only make smaller CNTs that were less uniform in size.

The team is still assessing what the observations mean for producing better quality CNTs. Zwolak and his collaborators suggest that researchers may want to focus on how the carbon source binds to the catalyst nanoparticles. The binding could be controlled by altering the support of the nanoparticles and changing their metallic composition. This in turn may enable engineers to better control the uniformity and design of the specific CNTs a manufacturer is aiming to produce.



CENTER FOR NANOSCALE SCIENCE AND TECHNOLOGY

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SUPPORTING THE DEVELOPMENT OF NANOTECHNOLOGY FROM DISCOVERY TO PRODUCTION

Center for Nanoscale Science and
Technology
National Institute of Standards and
Technology
100 Bureau Drive, MS 6200
Gaithersburg, MD 20899-6200
Phone: 301-975-8001
Email: cnst@nist.gov