OAK RIDGE NATIONAL LABORATORY

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

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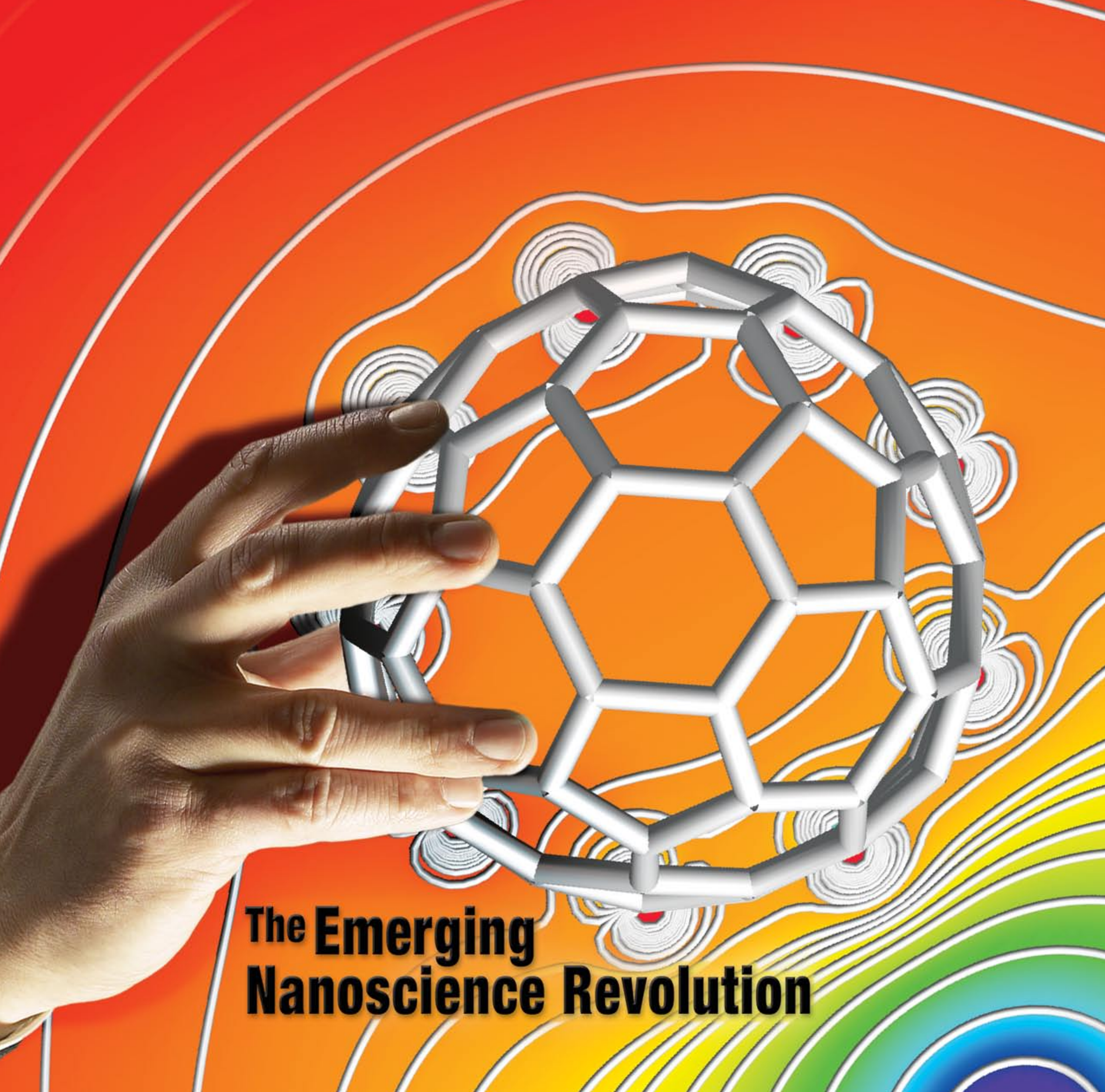

The Emerging Nanoscience Revolution

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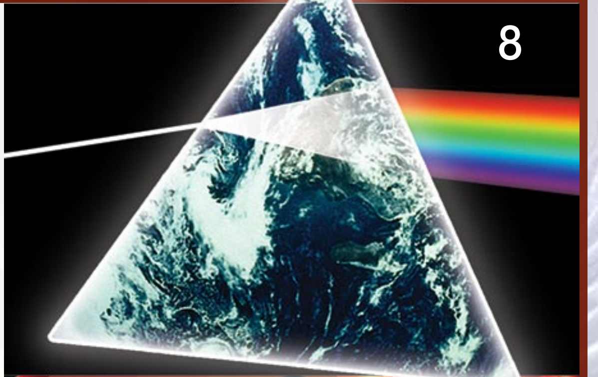
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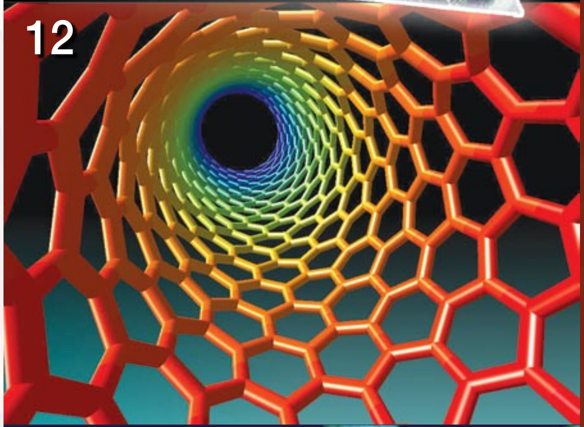
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COVER: Electric field induced by an electric charge affects a carbon nanostructure in ways related to differences in the field’s direction and strength. Visualization based on calculations made by ORNL’s Vincent Meunier et al.

JOINING THE EMERGING Nanoscience Revolution

For researchers who dream of controlling materials properties down to the atomic level, 2005 marks a milestone for a revolutionary new science. Oak Ridge National Laboratory is opening the Center for Nanophase Materials Sciences (CNMS), the first of five new Department of Energy Nanoscale Science Research Centers. Located adjacent to the Spallation Neutron Source, the $65 million facility houses state-of-the art instruments and is open to users from universities, national laboratories, and commercial firms, as well as the University of Tennessee and ORNL.

The six-year journey from conception to completion of the CNMS began in 1999 when ORNL researchers joined DOE in planning for the National Nanotechnology Initiative. Meanwhile, ORNL invested internal funds to strengthen the Laboratory's nanoscience research capabilities and prepared a successful proposal to build DOE's first nanoscience center in Oak Ridge. With construction of its building completed at the beginning of May 2005, the CNMS announced a Call for Proposals and hosted an Inaugural User Meeting with more than 270 participants. During FY2004-2005 ORNL also operated a limited "jump start" nanoscience research program that resulted in support for 75 user projects. The revolution was truly taking flight.

This issue of the *ORNL Review* highlights the role of the CNMS in creating a highly collaborative environment that will accelerate nanoscience discovery and drive technological advances. Because nanoscale science is highly integrative, we are striving to bring together the best ideas, instruments, and individuals to form a highly interactive and multidisciplinary CNMS user research community. We are guided by the Department of Energy's challenge to design a nanoscience center that would "enable research of a scope and depth beyond current national capabilities."

The CNMS will meet this challenge by providing new capabilities for nanomaterials synthesis and characterization, nanofabrication, theory and modeling of nanoscale phenomena, and, ultimately, the design of functional nanomaterials. Equally important, the CNMS also will create scientific synergies by exploiting ORNL strengths in neutron science, leadership computing, materials synthesis, and instrument development, each of which provides opportunities for international leadership in nanoscience. The facility will be aided by a new generation of unique, state-of-the-art instruments that combine nanoscale imaging with simultaneous nanomaterials' manipulation and properties' measurements, and, on occasion, special sample environments.

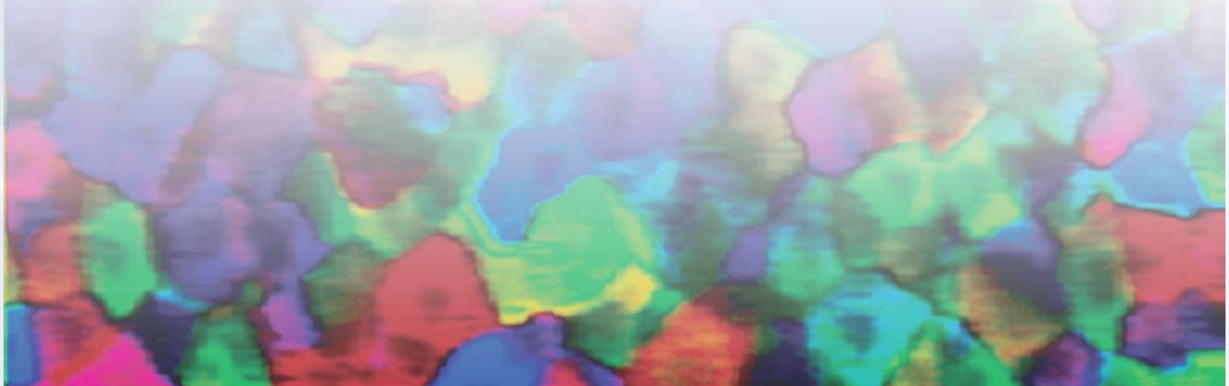
Using the Spallation Neutron Source, which opens in 2006, and the recently upgraded High Flux Isotope Reactor, the CNMS will exploit neutron scattering's unique capabilities — complementary to other techniques — to probe polymeric and bio-inspired materials, as well as magnetic materials and phenomena.

The CNMS' Nanomaterials Theory Institute will make use of the expertise and supercomputers at DOE's new National Leadership Computing Facility at ORNL to address several grand challenges of computational nanoscience. The Institute already is pursuing these challenges by establishing "NanoFocULs" laboratories that bring together users with world leaders in computational nanoscience, to develop community-based codes.

Pursuing yet another scientific synergy, CNMS researchers will focus on "science-driven synthesis" as a tool for discovery to reveal new phenomena and obtain new functionalities. The new Nanofabrication Research Laboratory will be used to develop ways of achieving the controlled synthesis and directed assembly of functional nanomaterials needed for nanotechnology. The materials processing and nanoscale patterning capabilities in the laboratory's "clean room" already are attracting local science-based firms, reinforcing predictions that the CNMS could be an incubator for commercial nanotechnology.

Our dreams have been realized. Our real work is just beginning.

Douglas H. Lowndes, Scientific Director,
Center for Nanophase Materials Sciences



THE NEXT Small Thing

With new facilities and capabilities, ORNL will help researchers make advances in nanoscience and nanotechnology that could boost Tennessee's economy.

Tiny particles 100,000th the width of a human hair may someday make a huge difference in the world's economy. Sunscreens, cosmetic powders, therapeutic drugs, magnetic recording tapes, polishing agents, and automotive catalyst supports are among the commercial products that contain nanoparticles. Successes in manipulating matter at the nanoscale have spawned laptop computers more powerful than mainframe systems that supported Apollo lunar missions, composites 10 times as strong as steel, and tiny lasers on chips that make possible portable CD players. Carbon nanotubes invisible to the human eye are being developed to replace hair-sized carbon fibers in composite materials used for sports equipment, jet aircraft, and space vehicles.

Nanoscale materials can be as small as a benzene molecule, equal to one billionth of a meter, or one nanometer. As the underlying materials for new commercial products get progressively smaller, the economic prospects for nanoscale materials grow larger. Economists estimate that the world market for nanotechnology will exceed $1 trillion by 2015.

The atom-by-atom understanding of functional matter is known as nanoscience. Researchers are discovering that the properties of a material finely divided into an invisible powder or other nanoscale structures are often different from the properties of the same material in bulk form. The gold in earrings, for example, does not rust because it is inert and will not react with oxygen in air. However, gold nanoparticles with diameters of 4 nanometers are highly reactive and may be used to catalyze chemical reactions. Clearly, nanoscience is a revolutionary new scientific field that will change in fundamental ways our understanding of nature.

Equally revolutionary is nanotechnology, which focuses on the development of devices and other systems at length scales between 1 and 100 nanometers. At Oak Ridge National Laboratory, researchers seek to combine carbon nanotubes with polymers to form new composites and coatings that promise to be stronger and better able to store hydrogen or to conduct heat, light, and electrical current. Using molecular manufacturing and self-assembly techniques, other researchers are building new devices, such as nanomotors, nanorods, and nanosensors.

In ORNL laboratories, nanofibers tipped with DNA are penetrating and reprogramming living cells. Nanoprobes are following the actions of proteins in cells. According to ORNL Corporate Fellow Tuan Vo-Dinh in his editorial in the new scientific journal *NanoBiotechnology*, “the futuristic vision of nanorobots patrolling inside our bodies and armed with lightning nanorods that can be activated remotely to recognize and kill diseased cells might someday no longer be the ‘stuff of dreams.’ ”

Understanding biological and physical systems at the molecular level is a major goal of nanoscience research at ORNL. Thanks to new scientific facilities and the right combination of equipment and expertise, ORNL is well positioned to help researchers make new discoveries and develop new devices involving nanoscale materials.

In 2006 the Department of Energy’s Spallation Neutron Source at ORNL will be providing researchers with the world’s most powerful pulsed beams of neutrons, enabling a more precise understanding of where atoms are and how they move in novel materials.

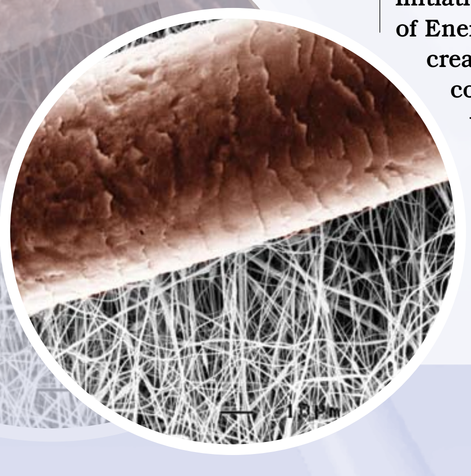
ORNL also is partnering with industry to build the world’s most powerful open scientific computer. By delivering trillions of calculations per second, this marvelous machine will allow researchers to attack previously insoluble problems in nanoscience and nanotechnology. The National Leadership Computing Facility at ORNL will enable scientists to simulate nanoscale materials as large systems of atoms and nanoscale phenomena over long time scales. The facility’s incredibly powerful supercomputers will help engineers design functional nanomaterials and engage in the virtual synthesis of new materials.

Nearby on Chestnut Ridge adjacent to the Spallation Neutron Source, the Center for Nanophase Materials Sciences is prepared to take advantage of its co-location with SNS and remote access to ORNL’s new supercomputer. For example, researchers at the nanocenter will synthesize novel, nanoscale materials that can be analyzed at SNS and modeled at ORNL’s computational facilities.

CNMS is providing distinctive research capabilities in four areas: materials synthesis and characterization; nanofabrication; theory, modeling, and simulation; and nanomaterials design. CNMS supports partnerships, collaboration, and education. The nanocenter’s overarching goals are to accelerate discovery and drive technological advances for American industry.

Research at CNMS and nanocenters elsewhere should lead to tougher and stronger nanocomposites; nanomembranes and nanofibers for water purification and desalination; more effective catalysts using smaller amounts of precious metals; highly sensitive and selective, solid-state, biological and chemical sensors; long-lasting, rechargeable batteries; improved solar cells and fuel cells; targeted drug delivery through cell walls; neural prosthetics for treating paralysis and blindness; and point-of-care medical diagnostics. In an early project at CNMS, a small, microfluidic machine was devised that shows promise in quickly and reliably synthesizing therapeutic drugs tailored to individual patients’ needs.

Commercializing nanotechnology advances based on new knowledge to help Tennessee’s economy is a key part of ORNL’s agenda. The Laboratory will anchor the East Tennessee Nano Initiative. UT-Battelle, which manages ORNL for the Department of Energy, is helping expand access to venture capital. Having created some 60 new companies since 2000, UT-Battelle is committed to taking ORNL’s nanoscience discoveries and using them to help grow Tennessee’s economy through the creation of new nanotechnology companies. These firms could provide products and services in the areas of materials, manufacturing techniques, information technology, health care, and energy production. For Tennessee and for the nation, the economic implications of the next small thing could be huge indeed.



The width of a carbon nanotube (bottom) is 100,000th that of a human hair (top).

Stairway at ORNL's nanocenter.

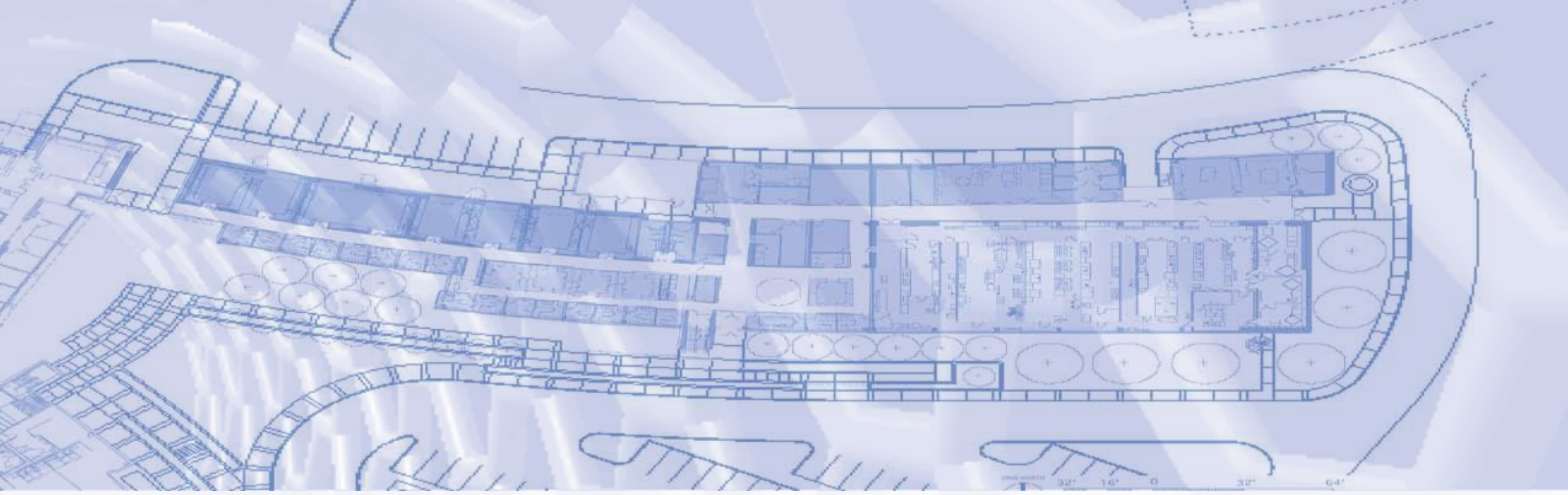
The Center for Nanophase Materials Sciences

DOE's first nanoscale research center opened to its first users in late 2005 at ORNL.

The Center for Nanophase Materials Sciences is the Department of Energy's newest user facility at Oak Ridge National Laboratory and one of a dozen new buildings constructed during the past three years on the ORNL campus. Planning for CNMS began in 2001 with the preparation of a peer-reviewable proposal for a unique kind of user facility—one housing a user program that would provide the scientific community with not only state-of-the-art equipment but also the research expertise to support the multidisciplinary areas of nanoscience and nanotechnology. The proposal built on traditional ORNL strengths in nanomaterials synthesis, characterization, and theory, modeling, and simulation. The plan included both "hard" and "soft" materials, as well as hybrid and biological materials.

After the panel review, DOE selected ORNL to house the first of what would eventually be five Nanoscale Science Research Centers of the agency's Office of Science. Supported by DOE's Office of Basic Energy Sciences, CNMS is the first of the five new facilities to be completed. A foundation for the CNMS user program is its convenient location next door to the Spallation Neutron Source. Equally important are the nanocenter's ties to other DOE user programs at ORNL, including the National Leadership Computing Facility resources in the Center for Computational Sciences, the High Flux Isotope Reactor, and the microscope facilities in the Shared Research Equipment User Program, the High Temperature Materials Laboratory, and the Advanced Microscopy Laboratory.

Following the initial peer review, CNMS construction has been on a fast track. Several building features as well as the selection of scientific themes and the initial equipment set were based on input from the academic and industrial community. These useful suggestions were collected in a series of planning workshops beginning in 2002.



The nanocenter has 85,000 sq. ft, including a 10,000 sq. ft nanofabrication clean room facility. Designers included spaces to provide opportunities for interactions among staff researchers and users. CNMS offers amenities such as plenty of sunlight and coffee areas on every floor that, according to their professors, are important for today's graduate students. The construction line item contains the initial suite of technical equipment needed for research on macromolecular materials, catalysts, functional nanomaterials, and magnetism and transport in nanoscale materials. In addition to providing remote access to the National Leadership Computing Facility (one of the world's most powerful unclassified supercomputers) for high-end computing challenges, CNMS operates its own computer cluster for theory, modeling, and simulation research.

Construction of the CNMS began in August 2003. Beneficial occupancy of the facility occurred less than 2 years later, in April 2005. The first users in the new facility were welcomed in October 2005, with final completion of the facility, including installation of all of the technical equipment, expected in October 2006. The first neutron beams are also expected at the SNS in 2006, marking the dawn of an exciting era for nanoscience and neutron science at ORNL.

The User Program

As a DOE national user facility, the CNMS makes its unique capabilities available to scientists from around the world. Use of the nanocenter's facilities and collaborative support from CNMS staff are free of charge for users conducting non-proprietary research that is intended for publication in the open literature. User research proposals are brief and focused. The proposal's core is a narrative research description of no more than two pages. Selection of researchers who will be granted access to the CNMS is based on the scientific and technical quality of their proposals. The CNMS relies on a Proposal Review Committee, which consists of external members to evaluate the user proposals and provide ratings that guide prioritization of user access.

Due to its multidisciplinary nature, a nanoscience user program differs in two fundamental ways from the user programs at traditional user facilities such as those for neutron sources, light sources, and microscopy. First, nanoscience user facilities have a much broader spectrum of research instruments and other equipment that require different levels of expertise for operation, that have vastly different throughputs, and that may be used both independently and interdependently. Equally significant, extensive collaboration between users and CNMS staff will be an important component of virtually all of the user research programs.

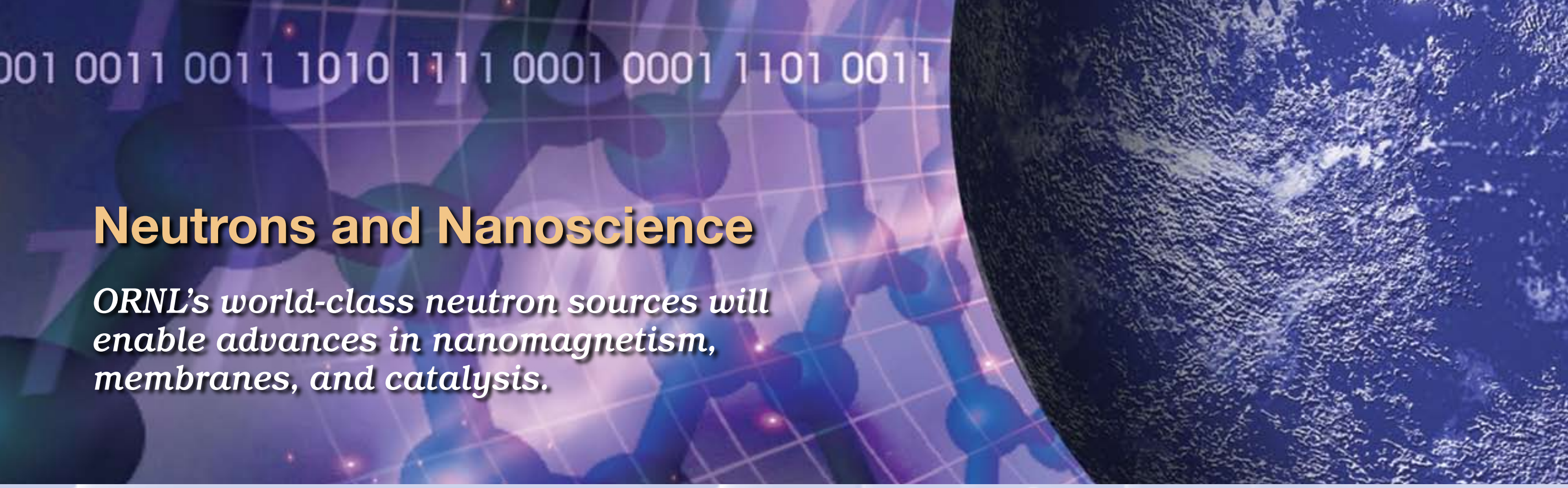
With encouragement and funding from the Department of Energy, the CNMS in the fall of 2003 began operating a limited "jump-start" user program, relying on existing ORNL facilities and staff distributed among the Laboratory's various research divisions. The program's objectives were to nurture a vibrant and active user community during the nanocenter's planning and construction period, as well as to gain experience in the operation of a user program that, in several respects, was breaking new ground.

The user community responded very favorably during the jump-start period. In response to two calls for user proposals, in August 2003 and in September 2004, the CNMS received 72 and 63 user proposals respectively. Forty-three projects were approved following the first call and 32 following the second. CNMS staff and the jump-start users became well seasoned by the experience. Both groups looked forward to utilizing the lessons learned in jump-start practice when the nanocenter became fully operational.

In the fall of 2005 CNMS began regular operations. The center now offers a wider variety of capabilities, supports a larger number of projects, provides more extensive access to individual projects, and makes longer-term commitments to, for example, multi-year projects that involve larger research teams. The CNMS is initially planning to announce calls for user proposals semiannually following the first full call that closed in July 2005. Eventually, the calls for proposals will parallel those of the CNMS sister user facilities, allowing external users to prepare a single proposal for accessing multiple ORNL facilities for their research. The CNMS expects to have 100 users in fiscal-year 2006 and as many as 250 users by the end of FY2008.

CNMS has a Scientific Advisory Committee to advise ORNL management on the nanocenter's scientific directions and overall quality of its user program. Jerzy Bernholc of the Department of Physics at North Carolina State University chairs this committee. Members of this committee include Bill R. Appleton, former ORNL deputy director for science and technology and now director of the Nanoscience Institute for Medical and Engineering Technologies at the University of Florida, and Richard E. Smalley, professor at Rice University who won the Nobel Prize for his discovery of buckyballs.

For more information on the CNMS, visit our web site at http://www.cnms.ornl.gov/—*Linda L. Horton, director of the CNMS User Program* Ⓡ



Neutrons and Nanoscience

ORNL's world-class neutron sources will enable advances in nanomagnetism, membranes, and catalysis.

Like a child playing with toy building blocks, researchers are creating new materials, objects, and devices from nanoscale blocks as small as individual atoms. These creations have unique properties that, when understood, will enable the design of new "functional" materials to carry out specific tasks—a type of "nanotechnology." The properties of materials and devices are dictated by the arrangement, or structure, of their building blocks, and by the way these nanoscale blocks move over time. The ability of neutrons to measure the positions and motions of atoms and molecules makes these nuclear particles essential research tools in nanoscience and nanotechnology.

Not surprisingly, the Department of Energy elected to build the agency's first nanoscience center at Oak Ridge National Laboratory to give researchers direct access to the world's most powerful probes of nanostructured materials located in the neutron scattering facilities at the High Flux Isotope Reactor and the Spallation Neutron Source. Coupled with the Laboratory's unique high-performance computing capability, these "neutron microscopes" can provide unique "images" at the nanoscale of the properties of materials synthesized at DOE's Center for Nanophase Materials Sciences.

Neutrons cover all the length scales of interest in nanoscience, from the atomic structure of individual building blocks to the configuration of assembled, functional structures, making them essential tools for the elucidation of the structure and function of nanostructured materials. At the same time neutron probes enable researchers to determine the motions, or dynamics, of nanoscale building blocks over a wide range of time scales ranging from ultrafast structural relaxation to slow diffusion processes—a remarkable time scale that spans 10 orders of magnitude.

Moreover, because they have a magnetic moment, neutrons behave like small magnets, making them extremely sensitive to magnetic structure on the nanoscale. Advanced techniques allow researchers to align these small neutron magnets and use them to probe both the structure and temporal variations of magnetic particles in nanomaterials such as nanomagnets, molecular magnets, and electronic devices. Significantly, neutrons travel easily through most materials without causing damage. Researchers can take measurements deep inside the surface, and in situ under a wide range of environments, including vacuum, high or low temperature, high pressure, or intense magnetic fields. Critical measurements can be made even during the synthesis and subsequent processing of the material.

A variety of examples demonstrate the value of neutrons to nanoscience.

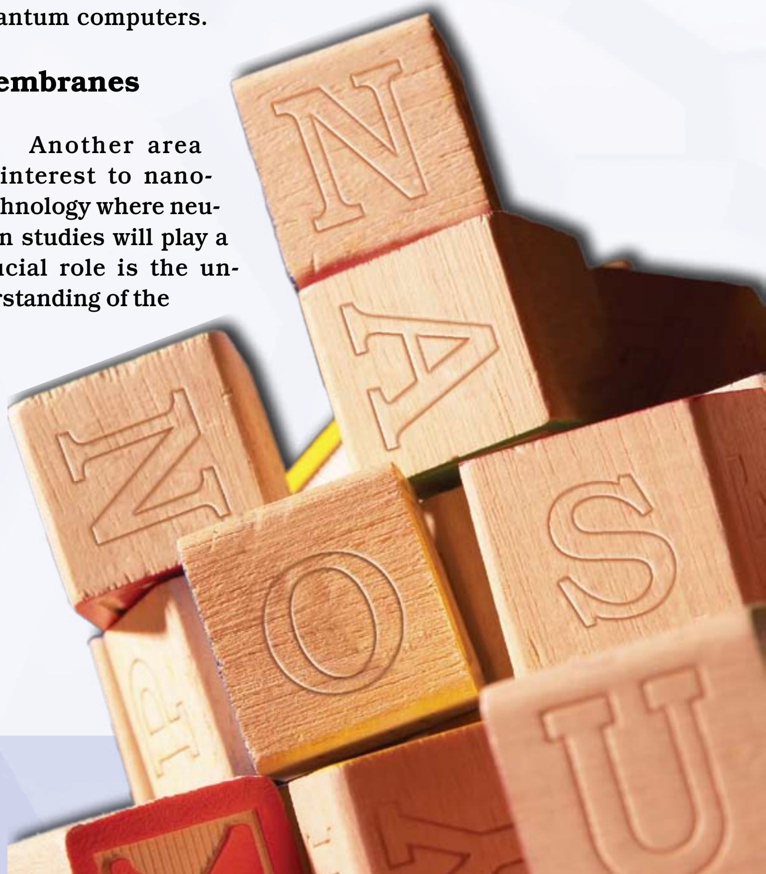
Nanomagnetism

For years, information has been transmitted by means of electric currents or charge flowing through electronic circuits. Today, however, the electronics industry has adopted technologies that use electron "spin"—electrons acting like small spinning tops—rather than charge to store and transmit information, enabling faster devices and higher-density storage media. Examples include magnetic random access memories and the read heads on modern computer hard disks. These so-called "spintronic" devices rely on the relative alignment of the electron spins to the magnetic direction in nanostructured thin-film devices, which determines the way they can flow through the device.

Polarized neutron reflection studies provide unique information on magnetic direction in deeply buried layers, and laterally, across the surface. Such information is required to understand and further develop these devices. Future advances in instrumentation using the intense neutron beams at SNS will allow these studies to be extended to understanding the dynamical processes that give rise to switching phenomena and the interactions of magnetic nanoparticles—important steps on the path to developing quantum computers.

Membranes

Another area of interest to nanotechnology where neutron studies will play a crucial role is the understanding of the



structure and dynamical properties of complex fluids confined in nanometer-scale architectures. Such fluids include polymers, surfactants, and small-molecule liquids that exhibit novel properties when confined in one, two, or three dimensions. In particular, controlled synthesis of membrane structures will provide an interface to biological systems and allow researchers to probe, modify, or mimic live cells, cell components, and molecular structures relevant to biology.

The control of the passage of materials and information across cell membranes is one of the most critical and little understood phenomena for biological function, and hence life itself. Because of their sensitivity to light atoms, neutrons are ideal probes for determining membrane structure. In the past, neutron scattering studies have been used to determine, for example, the structure of pneumolysin, the toxin from *Pneumococcus* bacteria which causes pneumonia, middle ear infections, and meningitis and promotes cell death by creating pores in the cell membrane.

Ongoing neutron studies are aimed at determining protein crystal structures and understanding how membranes fuse and transmit information. In the future, using a unique combination of synthesis of materials at CNMS and neutron characterization techniques at HFIR and SNS, researchers coming to ORNL will be able to study protein and lipid interactions in membranes suspended over specifically synthesized nanostructured scaffolds, which may be adapted to promote controlled insertion of proteins, molecules, or functional structures into the membrane.

Of course, a full understanding of biological systems requires additional information on their dynamics. By definition living organisms move, and do so on time scales spanning from vibrations to slow folding processes, all of which are vital to function. Neutrons come to the rescue once again, easily covering the relevant time domain. Novel instrumentation under development for SNS will allow simultaneous measurements of membrane structures 10 to 1000 nanometers wide and their movements ranging from picoseconds to microseconds.

Biosensors, microfluidic devices, and structural templates for tissue engineering and drug delivery are evidence that the development of improved structures that mimic biological functions in a controlled manner have increasingly important applications in everyday life.

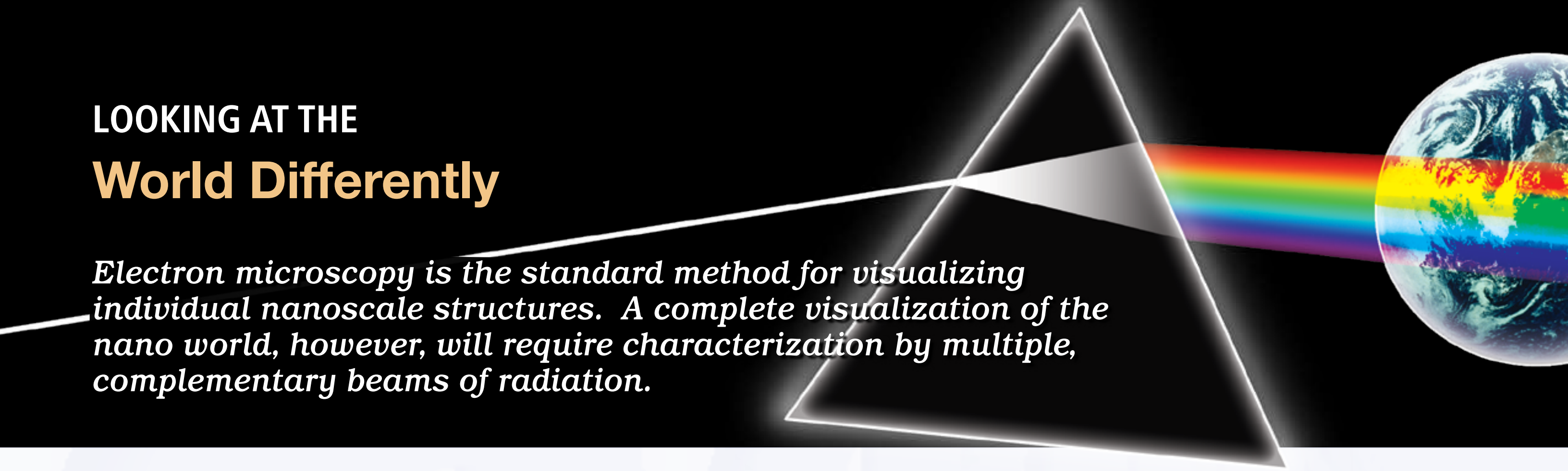
Catalysis

Many commercial products are made possible by chemical reactions driven by catalysts. Because most catalytic reactions take place on surfaces, the increased surface area afforded by nano-sized particles is of great interest. Neutrons provide invaluable information on the sizes and surface structures of nanoparticle catalysts and adsorbed molecules. Researchers seek to determine how these adsorbed molecules change during contact with a catalyst surface and relate these changes to the catalyzed chemical processes. Relating the structures of both the adsorbed species and catalytic particle is crucial to understanding the catalytic process. These techniques have led to the understanding of the role of nanostructured cerium oxide particles in platinum-based catalytic converters for automobiles.

However, understanding the structure alone may not be sufficient to fully interpret a functioning catalyst. The catalytic process is dynamic; adsorbed molecules undergo rapid transformations including diffusion, rotation, and vibration, all of which have a role in the catalytic process. Fortunately, neutrons also can be used to characterize dynamic processes and relate them to structural properties. Once again, all this data can be obtained under real operating conditions. Neutrons have been used to study processes that deactivate or poison catalysts. As our understanding of the chemical processes involved improves, so does the demand for more detailed information. In the future polarized neutron techniques will allow researchers to follow spin-dependent processes involving paramagnetic molecules and obtain an even more detailed understanding of the chemistry of catalytic reactions.

While efficient catalysts are important in our search for clean, environmentally friendly energy sources, the role of neutrons to support this goal does not stop at catalysts. Neutrons are also used to study how well carbon nanotubes can store hydrogen, a primary need for an efficient hydrogen-based economy, and how well various membranes work in advanced fuel cells.

Neutrons offer an important key to unlocking the secrets of nature at the nanoscale. Discovering these secrets will accelerate the development of nanotechnology, which promises new energy, health, and environmental solutions in the years ahead.—*Ian S. Anderson, SNS Experimental Facilities Division Director* ®



LOOKING AT THE World Differently

Electron microscopy is the standard method for visualizing individual nanoscale structures. A complete visualization of the nano world, however, will require characterization by multiple, complementary beams of radiation.

When we wish to tell someone that we understand, we often say, "I see," a phrase confirming that the ability to visualize something is an essential part of understanding. In the emerging field of nanoscale science and technology, the visualization of nanoscale structures will be essential to understanding them. Among imaging methods where the specimen is irradiated by an incident radiation, the instruments that best provide this ability are electron microscopes. Whereas an optical microscope is limited to the micrometer scale, an electron microscope can resolve features as small as a fraction of a nanometer. In addition, unlike photons, electrons interact strongly with matter, producing signals that provide data about a sample's physical and chemical properties.

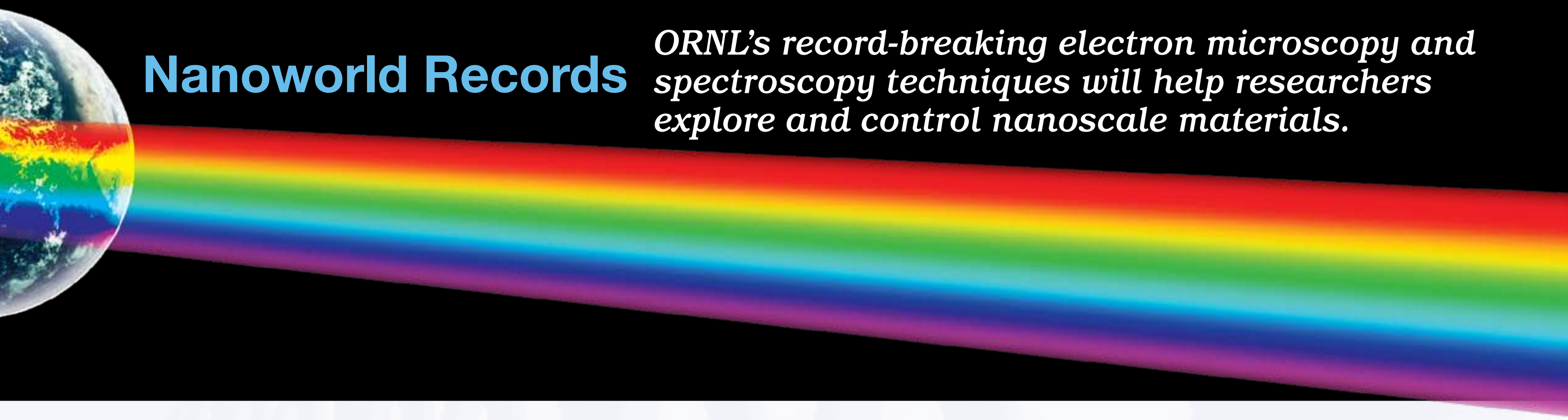
Although powerful, electron microscopy gives an incomplete view of the nano world, just as looking at a flower with light of only one wavelength—for example, with red laser light —would give an imperfect idea of the flower's true colors. We can now look beyond electron microscopy imaging by simultaneously illuminating our specimen with multiple radiations. Chosen from the "rainbow" of electromagnetic and particle beams available, giving us in effect two or more "eyes," each of these radiations is capable of discerning different kinds of information from the same region of our sample.

So-called "dual-beam" microscopes, which have both electron and ion sources, are commercially available and are becoming common tools for advanced materials analysis. When ions strike the sample surface, they sputter, or erode, the surface at roughly a nanometer per second. Thus, an ion beam can be used as a scalpel to cut into the specimen, revealing previously unknown internal details. The ions also generate secondary particle emissions, both electrons and ions, from a very shallow region of the surface. The secondary electrons carry information about the surface topography and crystal structure, while the secondary ions can be collected and identified to analyze the chemical composition of the top few atomic layers of the surface. By using the incoming ion beam also to erode the surface, scientists can study the variation in a sample's composition not only in the place of the surface but also as a function of depth. Such a dual-beam microscope will be available at ORNL's new Center for Nanophase Materials Sciences.

Photon beams with wavelengths that span the electromagnetic spectrum provide a wide range of specimen excitations. Consider the additional information obtained when a fine beam of X rays is projected onto a specimen. Like electron beams, X-ray beams can stimulate emissions of X rays from the specimen, potentially enabling the determination of the specimen's elemental composition and chemical formula. However, in contrast with electron beams, X-ray beams generate negligible background signal. Consequently, "X-ray fluorescence" can detect the presence of a few parts per million of an element, albeit at more limited spatial resolution, while conventional electron beam fluorescence is typically limited to several percent concentration.

Lower-energy photons—those from light in the visible or infrared spectrum— can also be employed as an additional beam for "Raman spectroscopy" studies of a variety of nanostructures, including nanotubes, polymers, and semiconducting thin films. In this technique the wavelength of the incoming light is changed by interaction with a sample. A measurement of the differences provides a unique fingerprint that can identify different polymer types, show whether carbon nanotubes are acting more like semiconductors than metallic conductors, or measure the local mechanical strain in thin-film layers.

In summary, the secrets of the nano world will be fully illuminated by imaging and analysis with a variety of complementary beams of particles or radiation. We anticipate in the near future the development of poly-beam instruments that will take advantage of the additional information provided by X-ray photons, light beams, and possibly other, more exotic radiation sources.—*David C. Joy, ORNL-University of Tennessee Distinguished Scientist, and Ian M. Anderson, Metals and Ceramics Division, ORNL* ®



Nanoworld Records

ORNL's record-breaking electron microscopy and spectroscopy techniques will help researchers explore and control nanoscale materials.

ORNL has achieved two world records in electron microscopy and spectroscopy, heralding a giant leap forward in nanoscience. The records resulted from research by Steve Pennycook's Electron Microscopy Group in ORNL's Condensed Matter Sciences Division (CMSD). The research reinforces the notion that ORNL is gathering a variety of tools to help researchers navigate the nanoworld.

In 1959 Richard Feynman, renowned American physicist at the California Institute of Technology, first mentioned nanoscience in one of his famous lectures. He predicted that nanoscience would be greatly accelerated if the resolution of electron microscopes could be enhanced by a factor of one hundred.

That leap in resolution occurred 45 years later with the achievement of one ORNL world record by an aberration-corrected, Z-contrast scanning transmission electron microscope (STEM) housed in ORNL's new vibration-free Advanced Microscopy Laboratory. The instrument obtained incredibly sharp images of single lanthanum atoms at a world-record resolution of 0.6 angstrom (Å).

"Our microscope allows us to see heavy atoms, such as bismuth, on a substrate of light atoms, such as silicon, giving a direct, real space image of single atoms," Pennycook says. "The bright atoms in the image have a much higher atomic, or Z, number than the lighter atoms in the substrate, which show up dark and provide contrast."

In 1988 Pennycook worked with VG Microscopes to develop the first Z-contrast STEM for ORNL research. In 2001, after sharpening the instrument's electron beam probe, Pennycook "saw" silicon atoms with a world-record resolution of 0.8 Å. In 2002 the Nion Company of Kirkland, Washington, built and delivered a spherical aberration corrector for ORNL's 300-kilovolt Z-contrast STEM, again breaking the world record.

Yet another world record was achieved when CMSD's Maria Varela used the electron energy loss spectroscopy capability of a Z-contrast STEM to carry out a spectroscopic analysis of a single lanthanum atom embedded in calcium titanate. She identified and located the atom based on the amount of energy lost as the microscope's electron beam as passed through the lanthanum atom.

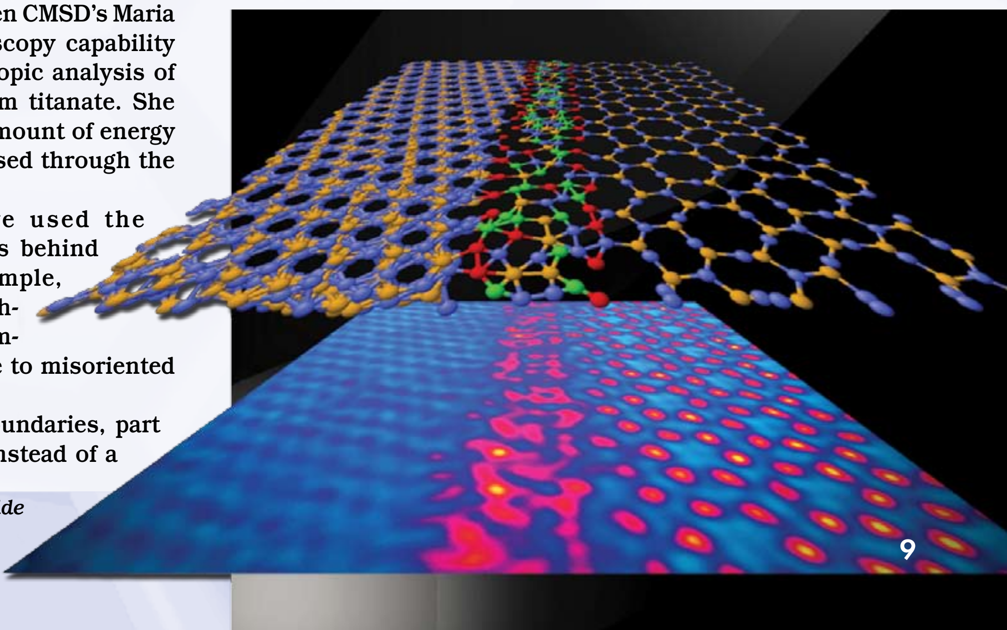
Pennycook and his colleagues have used the Z-contrast STEM to help explain mechanisms behind materials phenomena. Researchers, for example, have observed blockages of current flow in a high-temperature superconductor containing yttrium-barium-copper oxide (YBCO) that they attribute to misoriented grain boundaries low in oxygen.

"When oxygen is missing from grain boundaries, part of the superconductor becomes an insulator instead of a conductor," Pennycook says. "Several scientists observed that, if YBCO is doped with calcium, more current passes across the boundary, They thought calcium replaces yttrium and supplies additional current carriers."

Pennycook and colleagues from Brookhaven National Laboratory studied YBCO samples with and without calcium doping using the Z-contrast STEM. Their objective was to figure out why a perfect-crystal YBCO superconductor carries very little current. Pennycook's studies convinced him that the sources of the problem were the very high strains in the YBCO grain boundaries, which caused oxygen to be expelled. Pennycook found that the introduction of calcium atoms can heal the strains placed on the superconductor's grain boundaries by the perfect YBCO crystalline film. Surprisingly, the calcium atoms healed the strains by replacing copper and barium atoms normally in the boundary.

"The scientists who advocated calcium doping of superconductors were right for the wrong reasons," Pennycook says, adding that he believes nanoscale grain boundary engineering can prevent areas of YBCO superconductors from becoming insulators. "To keep the oxygen from escaping, the superconductor could be doped with big atoms to plug grain boundaries that are stretched or with little atoms when the boundaries are compressed. The aberration-corrected Z-contrast STEM helps scientists see which dopant atoms are the right size for healing misoriented grain boundaries."

Pennycook's group has also determined why nickel aluminide for turbine blades is less brittle when doped with boron and why silicon nitride for more efficient car engines becomes even stronger when doped with lanthanum atoms. His insights stem from microscope images that are crucial to the exploration and control of the nanoworld. Ⓡ



Sharp microscope image of film between silicon nitride grains shows attached lanthanum atoms.

Imaging the Invisible

Advanced scanning probe microscopy tools are opening new worlds of nanofabrication.

Some mark the dawn of the nanoscience era in 1982, when two IBM researchers invented the scanning tunneling microscope. The STM for the first time provided real-space imaging of single atoms, suddenly making possible the study and manipulation of the electronic and atomic structure of materials at the atomic level. Two decades later, imaging detailed features of surfaces using the STM helps physicists improve semiconductor and microelectronic devices, enables chemists to see how well a catalyst stimulates chemical reactions on surfaces, and allows biologists to examine DNA molecules.

Using the STM, ORNL researchers study the structure of a conductive surface by employing an extremely sharp probe that scans the surface at a distance on the order of an atomic radius. Electrons tunnel between the surface atoms and the single atom forming the probe tip, producing an electrical current. Slowly scanning across the surface, the probe rises and falls to keep the current constant, thus maintaining the distance. The probe's vertical movements are recorded, creating a profile of the surface that the computer translates into a two-dimensional map.

John Wendelken of ORNL's Condensed Matter Sciences Division has led the development of novel techniques for growing and manipulating nanostructures using the STM as an imaging and fabrication tool. Wendelken and his team have used the STM to crack iron-containing molecules to make magnetic iron wires only 5 nanometers wide, establishing a pathway for STM-assisted chemical vapor deposition. Thus, fabricated nanostructures, as well as buffer-layer-grown iron nanoparticles, are shown by the STM to be in alignment with the surface crystal structure of a copper substrate.

Wendelken's team also demonstrated in separate experiments that cyclopentadiene (C_5H_5) molecules deposited on a silver substrate form "rings" that represent the substrate's electronic response to the C_5H_5 molecules. At a certain STM tip voltage-current setting, the C_5H_5 molecule jumps to the next lattice site before the ring image is completed. The resulting zigzag tracks show the paths of the molecules being "swept" across the surface in the so-called "molecular broom" effect. "Understanding this tip-controlled molecular dynamics holds the key to future molecular fabrication technologies," Wendelken says.

Wendelken, Ward Plummer, and colleagues at ORNL are working with STM designers to build advanced ultrahigh-vacuum scanning microscopy probes for the Department of Energy's Center for Nanophase Materials Sciences at ORNL.

"We are buying and helping develop a cryogenic four-probe STM," says Wendelken. "This instrument will enable researchers to grow, prepare, and manipulate samples. The instrument is so unique that we expect to attract researchers from the world's outstanding universities."

This STM will enable studies of quantum transport in nanoscale systems and fabrication and characterization of nanoscale devices. Combining cutting-edge imaging capabilities, the STM will guide deposition of metallic and semiconducting films using molecular beam epitaxy.

Another instrument to be housed at the CNMS will be the low-temperature, high-field "ultimate" STM. ORNL, the University of Tennessee, and the University of Houston are fabricating this CNMS partner instrument. The ultimate STM will be used for single-atom and single-molecule spectroscopy, the generation of atomic-resolved spectroscopy maps, and studies of quantum responses of nano-objects.

ORNL's Sergei Kalinin helped pioneer several advanced scanning probe microscopies that will be available to users at CNMS. These techniques include electromechanical imaging of biological systems and scanning impedance microscopy, designed to address frequency-dependent electromechanical properties and electron transport in systems as diverse as carbon nanotubes and oxide nanowires, electronic devices, and biological systems. The nanocenter will also have ambient and ultrahigh-vacuum microscopes capable of piezoresponse force microscopy and atomic force acoustic microscopy.

Kalinin and colleagues used atomic force acoustic microscopy to study a butterfly wing. When the wing "sample" was vibrated mechanically, acoustical waves—tiny blasts of sound—were transmitted to the probe tip and detected. The contrast between the hard and soft regions of the wing provided insights on the butterfly wing's elasticity and durability.

As if on the wings of a butterfly, ORNL's researchers will probe into worlds their predecessors could only imagine. Ⓡ

A NEW ATTRACTION

ORNL researchers synthesize and characterize magnetic nanostructures that are capturing the interest of the electronics industry.

Magnetic iron nanostructures grown on copper using different methods.

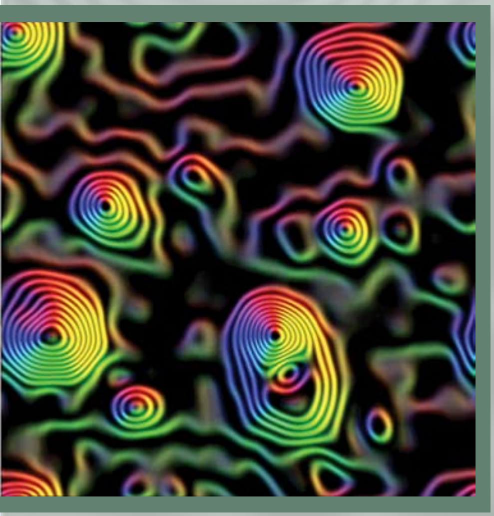
Jian Shen, a recipient of the Presidential Early Career Award in Science and Technology in 2004, is a research theme leader at the Department of Energy's Center for Nanophase Materials Sciences. Many predict that Shen's novel techniques for growing and studying magnetic nanostructures will attract a growing number of guest scientists to ORNL's new nanocenter.

Shen and his colleagues in the Low Dimensional Materials by Design Group in ORNL's Condensed Matter Sciences Division have developed novel methods for growing artificially structured materials layer by layer, wire by wire, and dot by dot. These two-dimensional, 1-D, and 0-D structures can be made of either traditional or nontraditional magnetic materials or hybrids of both types.

The physical properties of these nanostructures can be "tuned beyond nature" by controlling the size, shape, and density of each individual layer, wire, or dot in a nanostructure. Thus, iron nanodots and iron horseshoe magnets have dramatically different magnetic properties.

Nanomagnetism research is particularly important to the electronics industry. High-density magnetic data storage devices must have nanometer-sized arrays of magnetic nanodots. Because they are so small, these nanodots usually become magnetic only at very low temperatures. Such data storage devices would be practical only if they could operate at room temperature or higher. "We were able to tune the interaction between nanodots to obtain ferromagnetism well above room temperature," Shen says.

Shen and his colleagues are synthesizing nanostructures from three types of materials and studying the effects of spatial confinement on these materials' magnetic and electron transport properties. They are working with strongly correlated materials, such as compounds containing manganese oxide. These manganites exhibit colossal magnetoresistance—a huge change in electrical resistivity when subjected to a magnetic field. The ORNL team will seek to determine how much the magnetoresistance is affected by the reduced dimensions of manganite nanowires and nanodots.



Magnetic flux lines for nickel nanoparticles.

Courtesy Brookhaven National Laboratory

Shen's group is also studying dilute doped magnetic semiconductors, such as silicon or germanium nanostructures doped with magnetic elements such as manganese atoms. If created properly, these materials could be both ferromagnetic and semiconducting, making them potentially useful for spintronic devices, a new technology that exploits quantum properties of electron spins for a new generation of electronic devices.

Shen and his associates at the University of Tennessee are examining a third class of materials—semiconducting polymers in nanostructures embedded with nanodots or nanowires made of traditional magnetic materials such as iron, cobalt, or nickel. The resulting hybrid material could be used to improve the efficiency of organic light-emitting diodes.

Researchers studying nanomagnetism at ORNL's nanocenter will have a unique collection of tools for synthesizing and characterizing magnetic nanostructures. Electron beam (e-beam) lithography and other e-beam writing tools will be available to synthesize magnetic nanowires and etch nanopatterns to form electrodes.

"These wires are so small that a traditional contact to measure resistance and conductivity would not work," Shen says. "So we must make a nanoscale electrical contact for the outside world to measure the wires' properties."

To image changes in a nanomaterial's magnetic structure as the temperature changes, researchers will use a scanning electron microscope with polarization analysis.

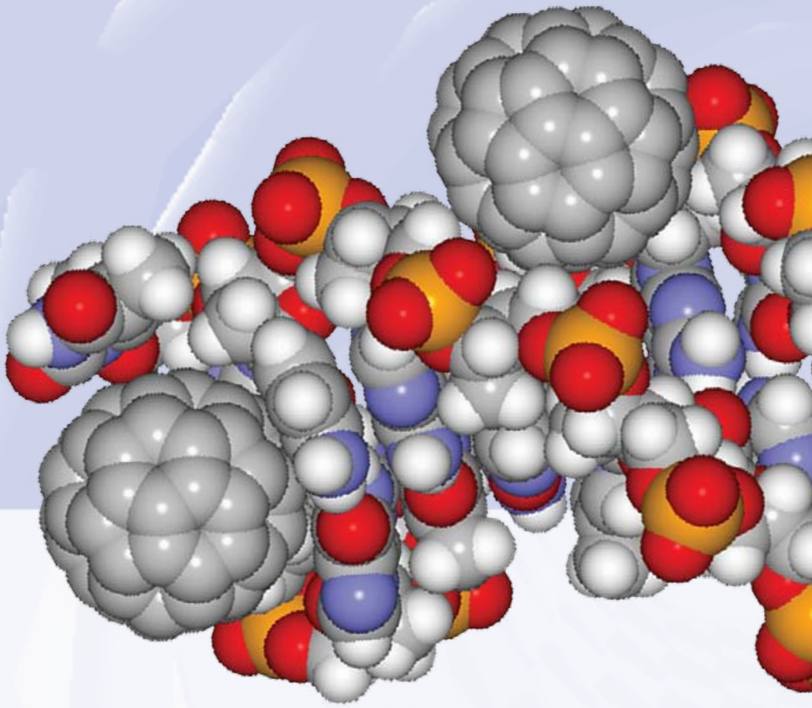
Electron beams are bent by magnetic fields, so ordinary electron microscopes cannot image these fields well. "Our unique microscope will allow researchers to measure magnetic moments in nanosized samples with high resolution," Shen says. "We will also have a scanning tunneling microscope with spin polarization to provide similar information."

The proximity of ORNL's Spallation Neutron Source is ideal for nanomagnetism studies, says Shen, because the intensity of the source's pulsed neutron beams will allow studies of the dynamics and magnetic structure of very small samples of magnetic material.

"Neutrons can penetrate stacked magnetic films used in data storage and provide a depth profile of magnetization in the vertical direction," Shen says. "Neutrons also give chemical information about the structure, allowing magnetic properties to be correlated with chemical composition. We anticipate that this information may guide the design of modular structures with improved magnetic properties needed for high-density data storage and other applications."

NEW TOOLS FOR
Nanoscience

Theory and modeling help explain nanoscale interactions.



Researchers at Oak Ridge National Laboratory, along with colleagues at other institutions, are synthesizing, characterizing, and manipulating nanoscale structures. While opening a broad range of opportunities in both fundamental and applied science, their work also poses formidable experimental challenges. Because the experimental observations are being made at the nanoscale, many such measurements cannot be interpreted without a theoretical model of the interaction between the measuring "device" and the measured structure.

For example, in a neutron scattering experiment on complex nanostructures, a model is required to describe interactions between neutrons and the atoms in the nanostructure in order to extract information about the location of the atoms. In another example, to understand the information obtained from an atomic force microscope moving across a surface, a model is needed to describe how the AFM tip interacts with the molecules on the surface.

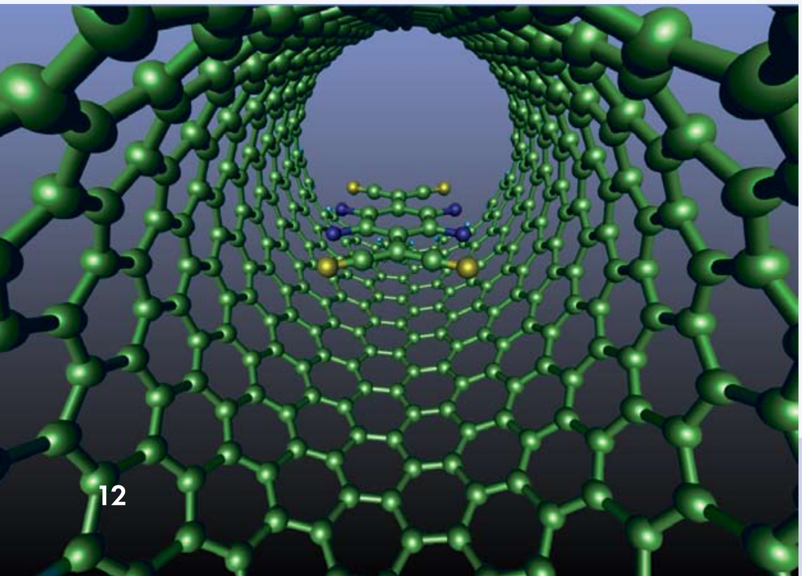
Additionally, achieving high reproducibility and product quality in the large-scale manufacture of nanostructured materials, most likely by self-assembly, requires deep understanding of the connection between nanofabrication and the manipulation of macroscale processing variables, such as temperature, pressure, exposure time, and concentration. As a result of these and other considerations, from the beginning of the National Nanotechnology Initiative, theory, modeling, and simulation have been expected to play a very significant role in nanoscience and nanotechnology. The result has been strong interplay between theory and simulation on the one hand, and experiment on the other, leading to rapid advances in various areas of nanoscience, as well as improvements in both theory and experiment.

ORNL's Vision

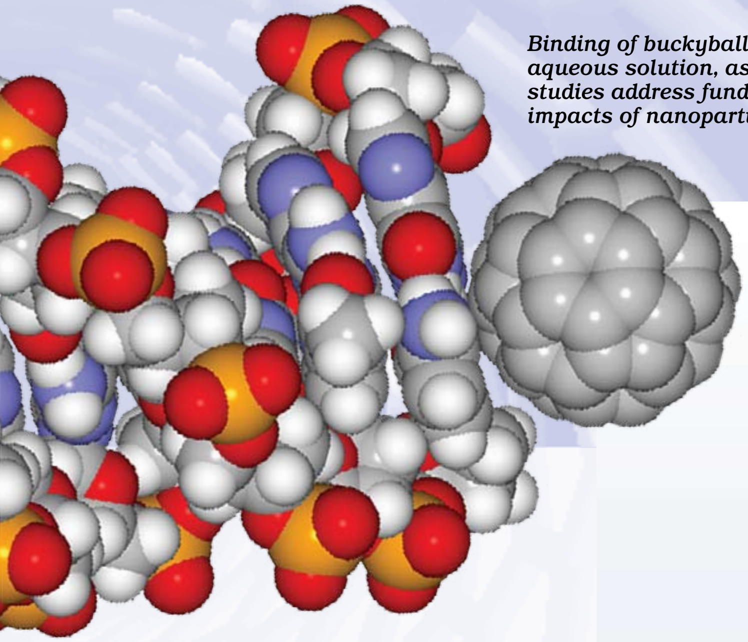
ORNL's successful proposal to build the Center for Nanophase Materials Sciences articulated a vision in which a theory, modeling, and simulation group plays a major role in support of the experimental programs. The proposal also anticipated the development of new theoretical insights into complex nanoscale phenomena and new theoretical and simulation capabilities. The Nanomaterials Theory Institute is the realization of this vision.

The institute, which occupies the top two floors of the office block of the nanocenter, currently has space for 20 researchers and visitors, with the flexibility to expand to 36. The institute already has 10 user projects supported by NTI staff. The projects include the electronic structure of inorganic nanostructured materials, electron transport between inorganic surfaces and organic molecules (related to molecular electronics devices), self-assembly of polymer nanostructures, and the nanostructural properties and mechanism of an enzymatic catalyst that might be used to optimize the energy obtained from biomass. Additionally, several projects are methodological, aimed at developing new theories or algorithms.

The institute draws on ORNL's traditional strengths in materials modeling and theoretical and computational chemistry and physics. Expertise exists at the Laboratory in a number of areas relevant to theoretical and computational nanoscience. Supported by these capabilities, NTI researchers can model the most fundamental electronic structure level in which the quantum mechanical Schrödinger's equation is solved for electronic or spin degrees of freedom. Theorists can do atomistic simulation by describing systems at the level of atoms and molecules and the forces between them using force fields derived from more fundamental methods. Likewise, scientists can provide more coarse-grained descriptions, known as mesoscale simulation methods, which are used to describe systems with larger spatial structures and longer relaxation times, such as polymer nanostructures and biomolecular nanosystems.



Stable position of a tetrafluorotetracyano-p-quinodimethane encapsulated in a single-wall carbon nanotube, as predicted by first-principles calculations.

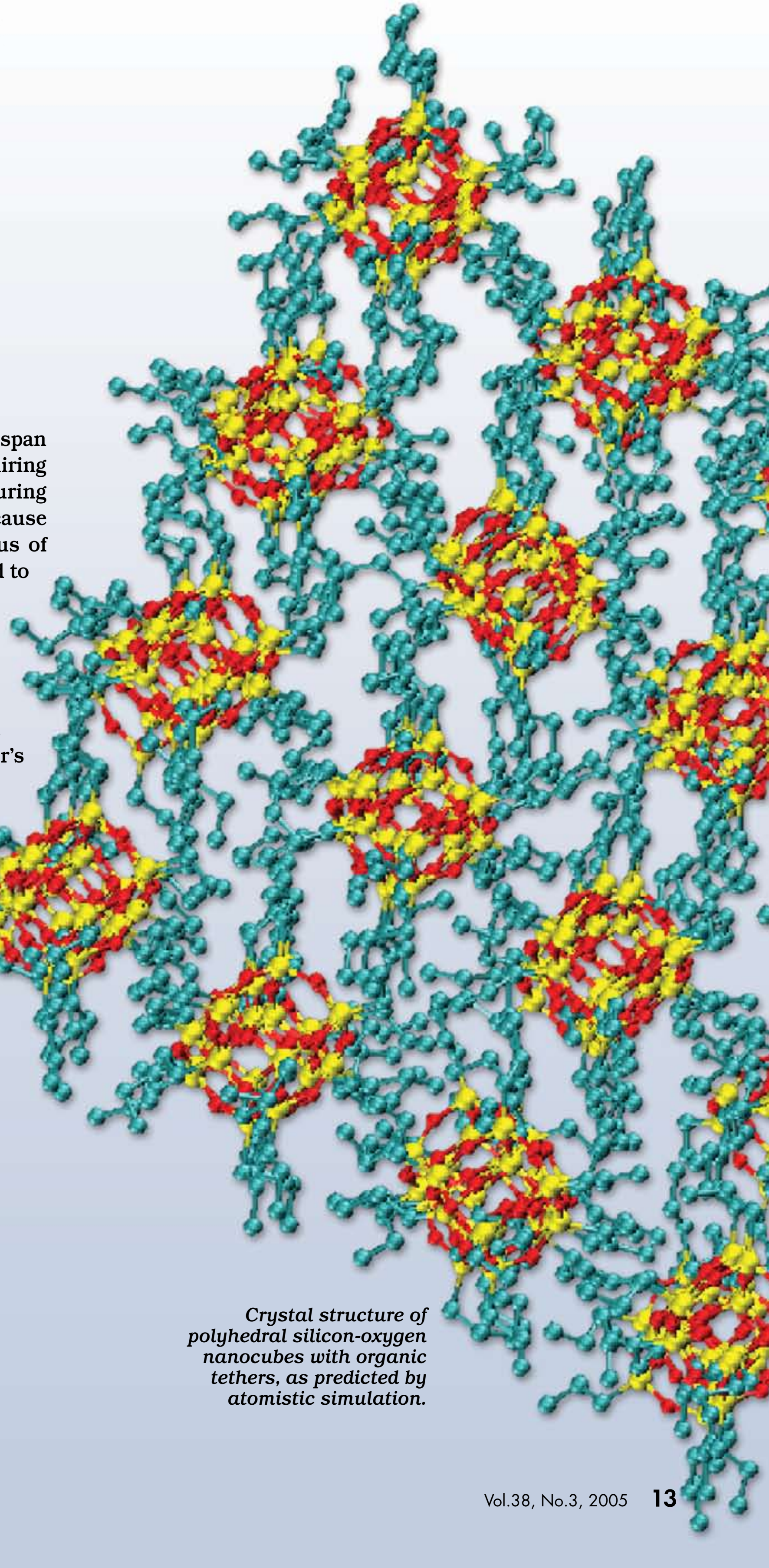


Binding of buckyballs, made of 60 carbon atoms, with DNA in aqueous solution, as predicted by an atomistic simulation. Such studies address fundamental aspects of the potential health impacts of nanoparticles released to the environment.

NTI's User Projects

The 10 user projects that the NTI currently supports span the range of these methods. The institute is currently hiring staff to support existing and future user needs by ensuring representation of expertise in all of these theory areas. Because state-of-the-art instrument development is a primary focus of the CNMS, the center also is securing the expertise needed to support new instrument design. Through collaboration with ORNL's Condensed Matter Sciences Division, the institute's researchers are focusing on developing the theoretical description of, and simulation methods for, neutron scattering from nanostructures, whether they are magnetic, metallic, organic, biological, or some combination of these. The theory support now being offered to the nanocenter's experimental users suggests that over the next few years, NTI researchers will have increasing opportunities to become intimately involved in user-driven experimental programs.

Nanoscience offers the possibility of bringing together into complex nanoscale structures materials that were once regarded as incompatible. For example, by working at the nanoscale level, inorganic surfaces might be chemically bonded to biological molecules to make new biomimetic devices in a controlled and reproducible fashion. The reason: at the nanoscale level the exploitation of the principles of physics, chemistry, and biology becomes feasible, as the similarities of physical, chemical, and biological systems come into play at the atomic and molecular level. Hence, in creating functional nanostructures, the nanoscientist has a palette to work with that is far broader than that of a traditional materials scientist, physicist, or chemist. The wide variety of nanoscale systems that researchers are developing provides both daunting challenges and exciting opportunities for the NTI theory

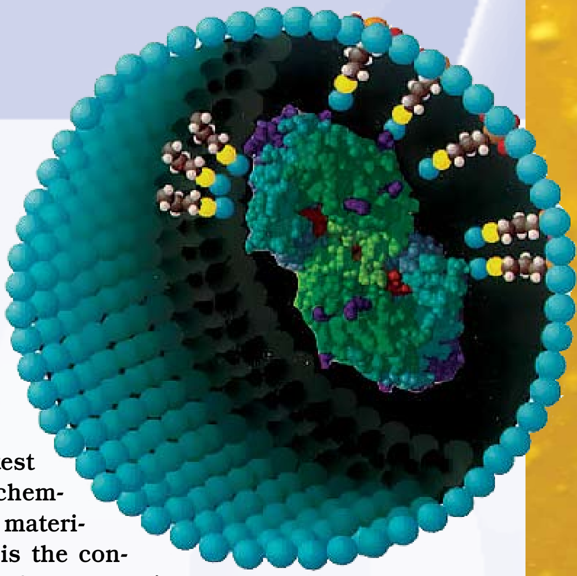


Crystal structure of polyhedral silicon-oxygen nanocubes with organic tethers, as predicted by atomistic simulation.

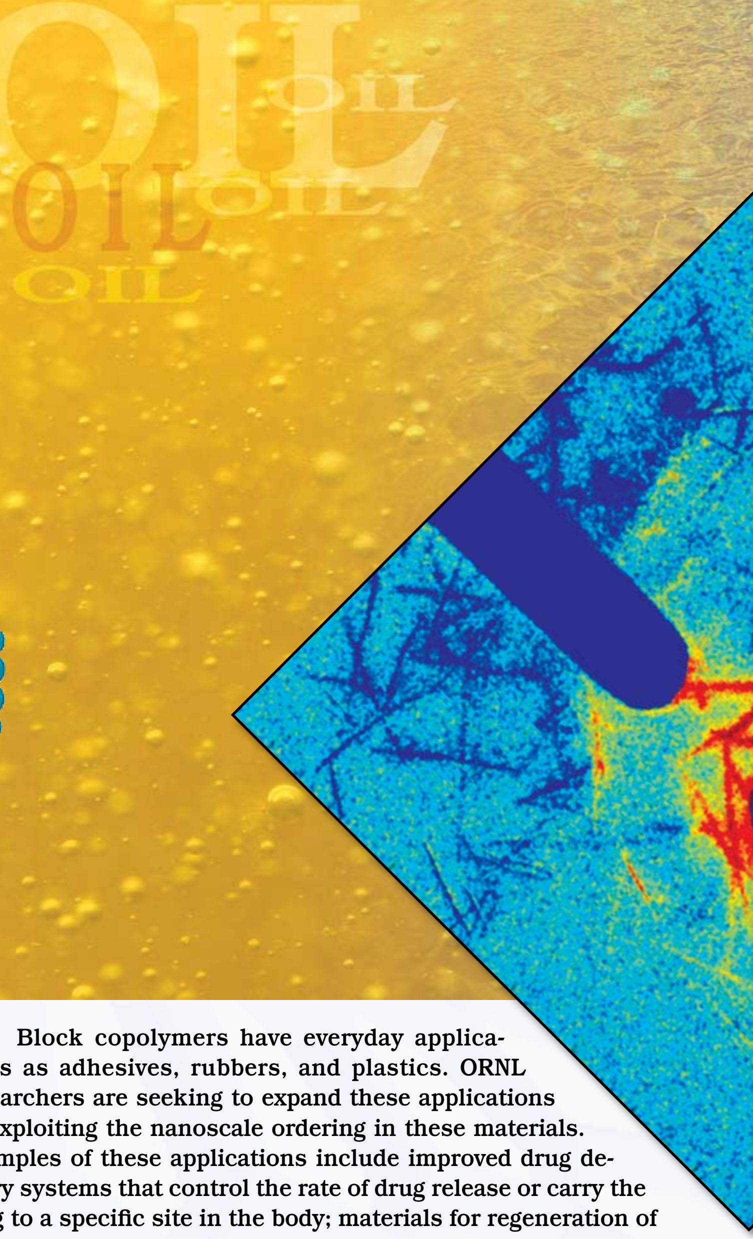
Visualizations by Vincent Meunier and B. G. Sumpter.

Producing Polymers

ORNL and UT researchers design, synthesize, and characterize new kinds of polymers.



Enzyme bound inside 30-nm silica pore to increase enzyme stability.
Courtesy Pacific Northwest National Laboratory.



Among the greatest challenges facing chemistry, physics, and materials science today is the controlled synthesis of mesoscopic materials—particles with characteristic dimensions of 1 to 100 nanometers—with well-defined structures and properties, and the assembly of these materials into macroscopic functional devices. One way to address these challenges is the "bottom-up" approach used by nature: Start with single molecules (monomers) of controlled size, shape, and functionality, such as amino acids, and assemble them to produce a new material with unique properties, such as an enzyme. These macromolecules are called polymers—many (poly) monomers.

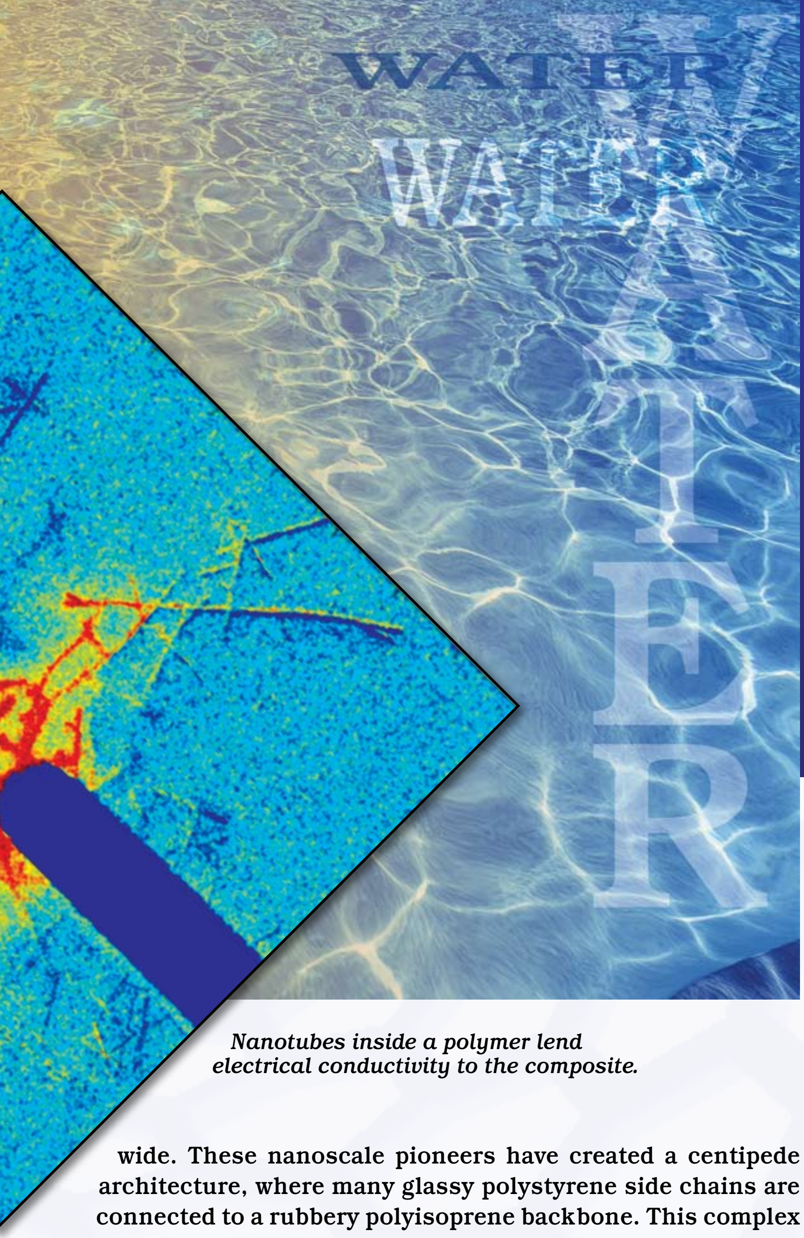
Polymers derive many of their properties from the number and kind of monomers connected together, a phenomenon related to the polymer's length and molecular weight. Natural polymers, such as cellulose, starch, proteins, and DNA, and synthetic polymers, such as polyethylene in milk jugs, polyvinylchloride in drain pipes, and polystyrene in plastic peanuts and cups, are used every day. Researchers still hope, however, to create new, complex, multi-functional materials that possess greatly enhanced mechanical, optical, catalytic, chemical, or electrical properties.

Scientists working in the Macromolecular Complex Systems research theme at the Center for Nanophase Materials Sciences focus on the design, synthesis, and characterization of polymers with well-controlled, and often complex, architectures. A research area of particular interest is block copolymers, in which two different types of polymers are chemically bound together. Two different polymers will usually not mix, but because they are bound together they cannot separate, as would a mixture of oil and water. The two polymers instead separate on the nanoscale, forming tiny domains that may be spherical, cylindrical, layered, or bi-continuous, depending primarily on their composition.

Block copolymers have everyday applications as adhesives, rubbers, and plastics. ORNL researchers are seeking to expand these applications by exploiting the nanoscale ordering in these materials. Examples of these applications include improved drug delivery systems that control the rate of drug release or carry the drug to a specific site in the body; materials for regeneration of living tissue, such as cartilage cells for arthritic knees; sensors for detecting specific chemical or biological agents; lightweight, flexible materials that can harvest energy from sunlight; and "super-elastomers," materials that can be reversibly stretched to 20 times their initial length.

Some of these applications take advantage of the ability of certain polymer molecules of designed architecture to change their shape, or to associate or dissociate with other polymer molecules, based on a change in their environment. Nature utilizes such effects extensively in living organisms, so scientists seek to mimic nature in materials research. ORNL researchers have developed a block copolymer, derived in part from a natural amino acid, which can associate with, or dissociate from, another polymer in response to a change in temperature or pH. At temperatures above 32°C and pH greater than 4, the individual polymer chains aggregate to form micelles, electrically charged particles combining water-hating and water-loving polymers that might be used to deliver hydrophobic drugs.

Working with visiting professors from Germany and Massachusetts, they have developed super-elastomers. Together, they are taking advantage of the unique molecular topologies available at Oak Ridge to create using specialized polymerization techniques available only in a few laboratories world-



Nanotubes inside a polymer lend electrical conductivity to the composite.

wide. These nanoscale pioneers have created a centipede architecture, where many glassy polystyrene side chains are connected to a rubbery polyisoprene backbone. This complex shape gives rise to super-elasticity as a result of enhanced coupling of the rubbery backbone with dispersed, nanosized glassy domains of polystyrene.

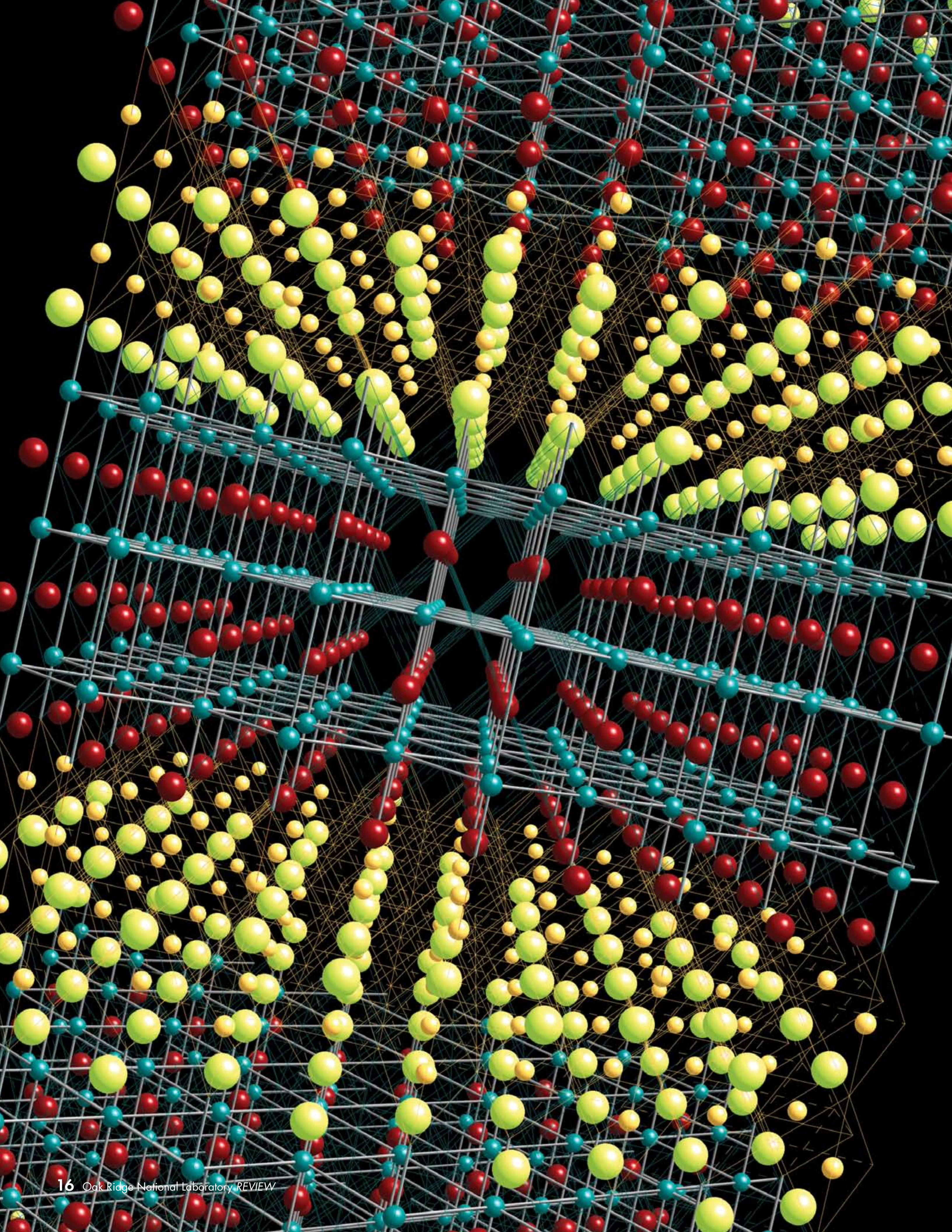
A new ORNL capability is the synthesis of deuterated polymers. By substituting deuterium for ordinary hydrogen, a particular polymer or portion of the polymer can be made to scatter neutrons strongly, while not affecting the polymer's other properties. This capability makes neutron scattering a particularly useful technique for studying the structure and properties of polymers and multicomponent polymer mixtures. However, custom synthesis of well-defined, well-characterized monomers and polymers labeled appropriately with deuterium is required. Recent workshops sponsored by the National Science Foundation highlighted the critical need for custom-deuterated synthesis facilities convenient to neutron scattering facilities.

Upon completion of the Spallation Neutron Source (SNS) and the upgrades to the High Flux Isotope Reactor (HFIR) by 2006, Oak Ridge National Laboratory will assume world leadership in neutron scattering. Located adjacent to the SNS and close to HFIR, ORNL's nanocenter envisions a synergistic relationship with these facilities. Nanocenter researchers seek to fulfill a critical national need by working closely with neutron scientists to create custom-synthesized materials (polymers, lipids, surfactants) that are optimized for a particular neutron scattering experiment.

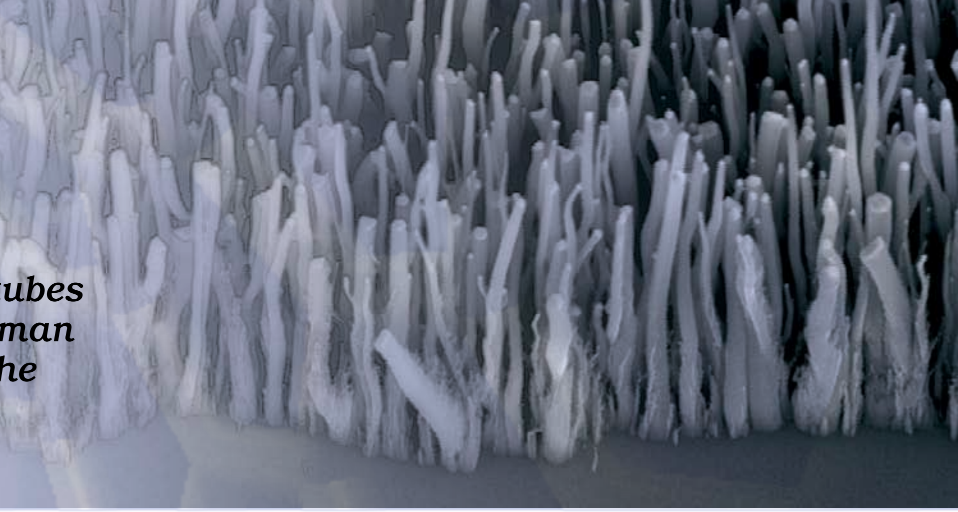
In addition to synthetic capabilities, ORNL's nanocenter will have a broad range of state-of-the-art equipment for characterizing the structure, composition, molecular weight, and thermal and physical properties of polymers. These instruments include gel permeation chromatography with light scattering and viscosity detectors; high-resolution nuclear magnetic resonance spectroscopy; near-infrared spectroscopy; matrix-assisted laser desorption/ionization time-of-flight mass spectrometry; simultaneous static and dynamic light scattering; spectroscopic ellipsometer, differential scanning calorimetry and thermogravimetric analysis; transmission electron microscopy and scanning electron microscopy; atomic force microscopy, and rheometers.

The characterization made possible by these instruments will be especially important when trying to control the structure at the nanoscale and to understand the nanoscale physics and chemistry. In a "jump-start" project, students from Professor Timothy Long's group at Virginia Tech sought help in characterizing the novel polymers they synthesized. These polymers can associate in aqueous media and, therefore, have potential for use in controlled gene or drug delivery.

In the Nanomaterials Theory Institute headed by Peter Cummings, the Center for Nanophase Materials Sciences has world-class expertise and facilities for theory, simulation, and modeling of soft materials such as synthetic polymers and biomaterials. Researchers from both the center and the institute are working together to identify opportunities where theory and modeling can favorably impact user programs, complement experimentation, and aid in the design of experiments.—*Phillip Britt, ORNL's Chemical Sciences Division, and Professor Jimmy Mays, UT-ORNL Distinguished Scientist* Ⓡ



A Limitless Potential



ORNL is producing carbon nanotubes 100,000 times smaller than a human hair that could impact much of the world's economy.

Researchers believe carbon nanotubes may prove to be the most promising nanoscale materials for multifunctional applications. These hollow tubes of carbon often have multiple, concentric layers of carbon sheets, like rings of a tree. A single-wall carbon nanotube (SWNT)— one sheet of carbon atoms rolled into a tube— has special properties resulting from a structure much more like that of a one-dimensional molecule than bulk graphite. A typical SWNT is a few microns long and approximately 100,000 times smaller than a human hair, with a diameter around one nanometer.

Despite being long and thin, nanotubes are extremely strong and difficult to break. An optimized composite made from SWNTs is predicted to be 100 times stronger than stainless steel, with only one-sixth the weight. SWNTs are lightweight and incredibly resilient, snapping back to their original shape after terrible deformation. For these reasons, scientists are developing carbon nanotubes to replace hair-sized carbon fibers in composite materials for uses as varied as sports equipment, jet aircraft, and space vehicles.

The electronic properties of nanotubes are equally impressive. Depending on how carbon atoms are arranged, a particular nanotube may be either metallic or semiconducting. Because metallic nanotubes have been shown to conduct electrical currents without loss, they are envisioned as candidates for next-generation wires and power transmission cables. However, roughly two-thirds of SWNTs synthesized today are semiconducting. Requiring little power to switch them "on and off," these nanotubes are already being developed as transistors for next-generation "molecular" electronics. Semiconducting SWNTs are electroluminescent, emitting light when injected with electrons and holes.

Nanotubes readily emit electrons under a remarkably low applied electric field. New field-emission displays and ultrathin X-ray sources based upon this effect are now available.

Experiments demonstrate that individual SWNTs conduct heat more efficiently than almost any other material, making nanotubes potential tools to cool everything from laptop computer chips to the leading edges of wings on hypersonic aircraft.

The sharpness and length of carbon nanotubes make them ideal for probing surfaces, cells, and even molecules. One finding suggests that nanotubes combined with catalytic metal nanoparticles can store enough hydrogen to make lightweight, hydrogen-powered vehicles practical.

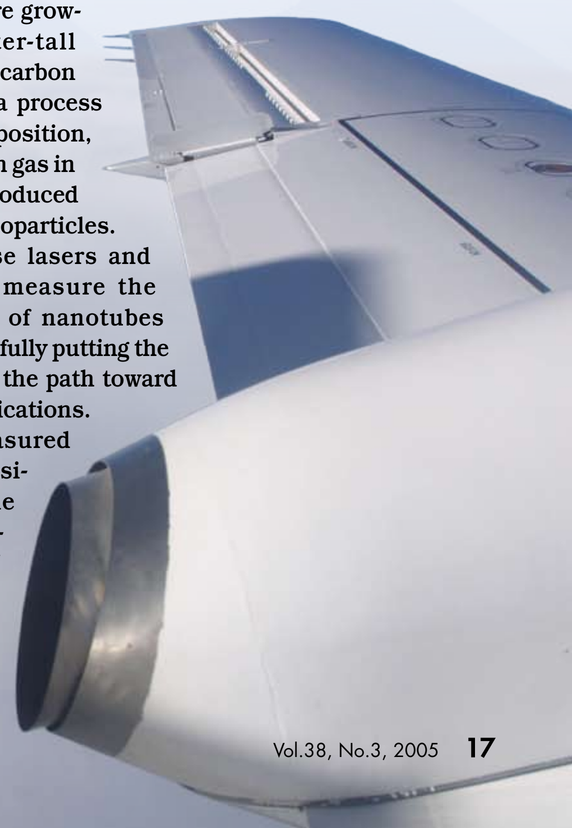
Because of the seemingly unlimited applications of carbon nanotubes, the race is on worldwide to find out how to manufacture them economically in large quantities. ORNL researchers are exploring applications of carbon nanotubes (see next article), but their chief focus has been the basic science of how nanotubes grow, how to sustain their growth, and how to grow them with high levels of purification.

For more than seven years, David Geohegan and Alex Puretzky, both of ORNL's Condensed Matter Sciences Division, have made nanotubes by creation of a high-temperature plasma with a laser. Using time-resolved optical probes of this laser ablation process to learn how SWNTs grow, they detected a miniature "big bang" when laser light vaporizes a carbon target impregnated with catalytic nickel and cobalt powders. About a millisecond after a hot plasma is formed at 3500°C, both the carbon and metal condense into tiny clusters and particles from which only SWNTs grow at rates of 1-5 microns/second while floating in hot argon within a 1200°C furnace. This relatively high growth rate lasts for only about a second. Growth then mysteriously stops.

At ORNL laser ablation produces 1 gram a day of carbon nanotubes. ORNL's new Advanced Laser Processing and Synthesis Facility promises to make SWNTs up to 30 times faster. Phil Britt's team in ORNL's Chemical Sciences Division has developed methods to purify laser-grown nanotubes by removing the unconverted amorphous carbon and almost all the metal catalyst.

Researchers are growing three-millimeter-tall "forests" of aligned carbon nanotubes through a process of chemical vapor deposition, in which hydrocarbon gas in a hot furnace is introduced to metal catalyst nanoparticles. The researchers use lasers and movie cameras to measure the lengths of trillions of nanotubes while they grow, hopefully putting the nanotube forests on the path toward multifunctional applications.

Although measured in an almost infinitesimal small scale, the scientific and economic potential of these nanotubes appears to be literally without limits. ®



Model of an artificial oxide solid built from lanthanum manganite ($LaMnO_3$) and strontium titanate ($SrTiO_3$) building blocks. Synthesis as well as computer simulations and measurements of the electronic structure are being performed at ORNL. Visualization by Leon Petit

Breaking the Mold

The potential of nanotube-polymer composites made at ORNL is attracting growing interest.

Natural bio-composites fascinate Ilia Ivanov, a University of Tennessee research assistant professor who makes light, strong, multifunctional composites of polymers and carbon nanotubes. “As we develop composites, a good model is the beetle, which surprisingly has a high level of complexity and multifunctionality,” he says. “The beetle’s exoskeleton is strong and lightweight yet has built-in thermal management, self-repair, and sensory capabilities.

“Today’s advanced man-made composites, on the other hand, are generally heavy materials with a single function. Because of their properties, carbon nanotubes and other nanomaterials could break this paradigm, bringing unique multifunctionality to everyday composite materials, while making them stronger and lighter.”

Over the past few years, with funding from the Department of Energy, National Aeronautics and Space Administration, Defense Applied Research Projects Agency, and ORNL’s internal Laboratory Directed Research and Development Program, Ivanov— working with Dave Geohegan, Phil Britt, and many other collaborators across ORNL and UT—has explored methods of fabricating and testing the multifunctionality of nanotube composites. “Testing the properties of the small amounts of material we make has been difficult,” Ivanov says. “ORNL’s George Pharr and Andrei Rar helped us examine the mechanical properties of aligned nanotube composites. We found that even though nanotubes occupy a tiny fraction of the polymer’s volume, the resulting nanocomposite becomes stiffer in the direction in which the tubes align. We hope to apply this finding to the design of novel, directionally enhanced structural materials.”

Compared with the pure polymer, the nanotube-polymer composite demonstrates much better thermal stability, suggesting that the nanocomposite could survive harsh environments. Furthermore, this material conducts heat almost anisotropically in the direction of nanotube alignment. According to measurements performed by Hsin Wang and his ORNL colleagues, the thermal diffusivity of nanotubes in this composite is near that of copper and aluminum, indicating that this material could serve as a thermal interface for such disparate applications as cooling computer chips and emergency personnel and astronauts in protective suits.

To understand how heat is transported in nanomaterials, Ivanov will be using a novel fixture designed by Mike Watson at NASA’s Ames Laboratory. The device will enable thermal transport measurements on a single nanotube, nanowire, nanotube bundle, or tiny bit of a nanocomposite material.

Ivanov and colleagues have shown that the exposed ends of nanotubes protruding from a nanocomposite surface can serve as electrodes for the detection of small concentrations of redox-active species, chemicals that can donate or borrow electrons.

The ORNL team and UT’s Bin Hu found that nanotubes can be perfect electron-and-hole conductors when illuminated, suggesting that nanotube composites could make brighter organic light-emitting devices using lower voltages, as well as photovoltaic cells that produce higher electrical currents from sunlight.

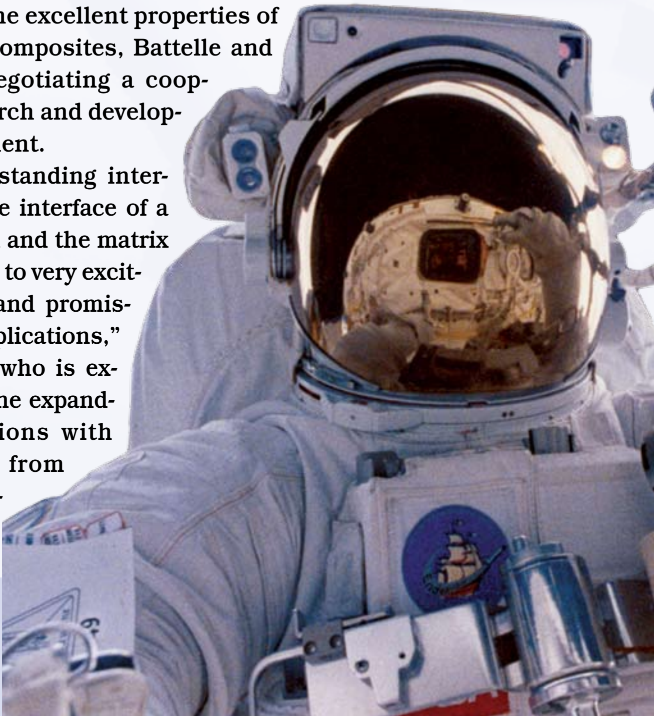
Because of their excellent electrical conductivity and high aspect ratio, nanotubes are perfect candidates for making a coating designed to conduct electricity. Such a transparent, antistatic coating could be useful in the canopies over airline pilots’ cockpits, where electrical charges build up.

Ivanov showed that conductive nanotube membranes made in Geohegan’s lab can be deposited on a metal, glass, or plastic surface. A nonconductive polymer can be made conductive if coated with a nanotube membrane.

“Our conductive nanotube membrane coating is much more flexible than the indium titanium oxide coating on today’s computer monitors and television screens,” Ivanov says. “These new membranes might someday replace the oxide coatings, the cost of which has doubled in the past few years.”

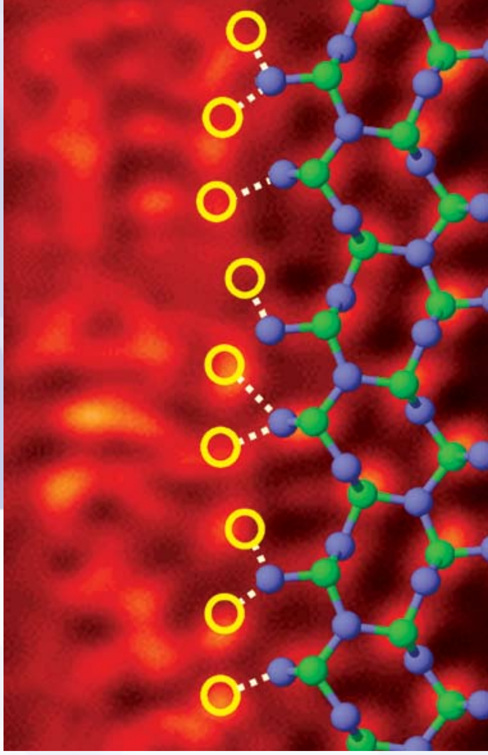
Battelle, a member of the UT-Battelle partnership that has managed ORNL for DOE since 2000, is interested in making transparent, electrically conductive nanotube composites. Because of the excellent properties of ORNL nanocomposites, Battelle and ORNL are negotiating a cooperative research and development agreement.

“Understanding interactions at the interface of a nanomaterial and the matrix holds the key to very exciting science and promising, novel applications,” says Ivanov, who is excited about the expanding interactions with researchers from outside organizations. ®



Researching in Bulk

Bulk materials can be synthesized to create nanoparticles that improve the materials' properties.

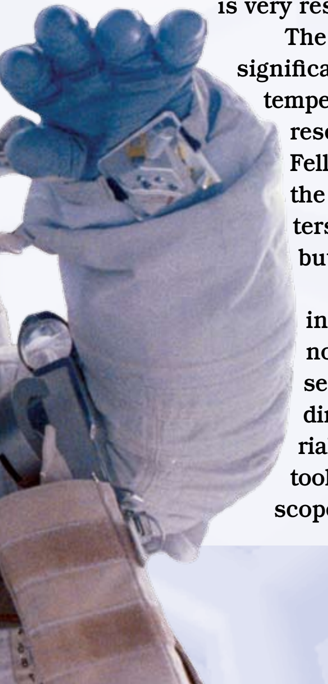


Silicon nitride grain boundary doped with lanthanum atoms.

Swiss chocolates, cosmetics, and sunscreens—all these products contain nanocrystals that give them their appealing properties. Scientists classify such products as bulk nanostructured materials, a growing area of research at ORNL. The chief building block of these materials is often the nanocluster—a cluster of atoms or molecules measuring only a few nanometers in any direction.

A new phenomenon in which stable oxygen-enriched nanoclusters significantly strengthen ferritic steels is being investigated by David Hoelzer and collaborators in ORNL's Metals and Ceramics Division. The nanoclusters were discovered in a ferritic steel that was mechanically alloyed (MA) with yttrium oxide. Research shows that the MA ferritic steel containing the nanoclusters exhibits a dramatic improvement in high-temperature strength over that of any other iron-based alloy. A primary goal achieved by ORNL staff researching this phenomenon was determining the critical elements and processing conditions that favor the formation of nanoclusters in ferritic steels. The project's success was aided by advanced characterization tools, such as the atom probe microscopes available at ORNL.

ORNL research indicates that the MA ferritic steel may be suitable for high-temperature applications, such as advanced nuclear reactors, because of the high number density and uniform dispersion of the nanoclusters. These 2- to 5-nm nanoclusters containing yttrium, titanium, and oxygen have been found to have remarkable stability at temperatures as high as 1300°C. At 600 to 800°C, the temperatures expected in an advanced reactor, tests reveal that the nanocluster-strengthened ferritic steel is very resistant to deformation and rupture.



The reasons why nanoclusters are stable and significantly strengthen the ferritic steel at high temperatures are currently being investigated in a research project led by ORNL Senior Corporate Fellow C.T. Liu. The project's findings may allow the phenomenon of strengthening by nanoclusters to be applied not only to iron-based alloys, but also to other important alloy systems.

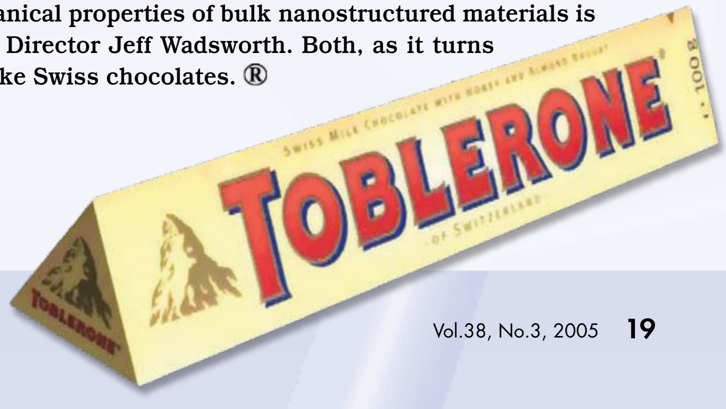
"Several ORNL research groups are forming crystalline nanostructures within bulk noncrystalline materials by aging, heating, or seeding the bulk material," says Linda Horton, director of ORNL's Center for Nanophase Materials Sciences. "At the center we have special tools, such as state-of-the-art atom probe microscopes, to help researchers determine whether crystalline nanoclusters are forming in a noncrystalline matrix."

Paul Becher is leading a project with ceramics researchers at Pennsylvania State University in which they use heat but no pressure to densify nanocrystalline zirconium oxide powders to at least 95% of theoretical density with grain sizes down to 30 nanometers. The researchers hope to determine whether these strong ceramic materials can be plastically deformed without breaking, as some scientists believe. Results thus far show such nanocrystalline oxide electrolytes have exceptionally high ionic conductivity, making them potentially usable in fuel cells.

An ORNL project led by Craig Blue involves heat-treating noncrystalline (amorphous) silicon on polymer substrates in a large-area format to incorporate evenly dispersed silicon nanocrystals, using the Laboratory's powerful Vortek infrared plasma lamp. This type of flexible electronics, in which the electronic properties of both nanocrystalline and amorphous silicon are exploited, could prove useful for photovoltaics. The lamp might be an economic technique for fabricating nanocrystalline and amorphous silicon thin-film composites for rooftop solar cells, which convert sunlight into electricity for buildings. Use of this type of silicon thin-film composite as solar cells could greatly boost the photon collection efficiency and reduce the cost of rooftop solar panels.

Yet another ORNL project focuses on fabricating membranes based on the materials used at the Oak Ridge Gaseous Diffusion Plant to enrich a gas in fissionable uranium. Researchers are striving to tailor membranes for such uses as fuel cells, water purification, catalyst supports, protein separation, and filters for homeland security.

One pioneer of research on the bulk behavior of nanostructured materials is Carl Koch, a former ORNL scientist now at North Carolina State University. Another expert on the mechanical properties of bulk nanostructured materials is ORNL Director Jeff Wadsworth. Both, as it turns out, like Swiss chocolates. ®



Layered Film That Stacks Up

Using pulsed laser deposition, ORNL researchers have grown perfect ferroelectric superlattices with surprising properties.

ORNL researchers can deposit thin films of a complex oxide simultaneously onto 11 substrates, each heated to a different temperature.

As recently as two years ago, most researchers seeking to build metal-oxide thin films with atomically abrupt interfaces were convinced that molecular beam epitaxy was the only technique that could provide the required control. Pulsed laser deposition—using laser light to vaporize target material, which is deposited on a substrate—was not considered suitable for this task. But MBE, which typically operates at much lower oxygen pressures than pulsed laser deposition, presents challenges when applied to insulating oxides because of defects formed that muddle attempts to characterize accurately the film's electronic properties.

In 2004, Ho Nyung Lee surprised his fellow researchers in the Thin Film and Nanostructured Materials Physics Group in ORNL's Condensed Matter Sciences Division. "Ho Nyung Lee used pulsed laser deposition to fabricate perovskite nanostructures with a degree of perfection we had not seen before," says Hans Christen. Unlike MBE, pulsed laser deposition forms these oxides without the need for separate heat treatment in oxygen after the film is grown.

So he wouldn't be shooting in the dark, Lee used reflection high-energy electron diffraction during film growth. "With the diffraction as his flashlight, he realized the importance of slowing down the process to precisely control the amount of material deposited for each crystalline unit of the film," Christen says. "Now, he can stack atomically smooth layers of different composition to create a perfect ferroelectric superlattice, with hundreds of individually controlled layers that together are about 200 nanometers thick."

Ferroelectric materials store electronic charge at their surfaces because of the asymmetric displacements of ions within their crystalline structure. The displaced ions give each layer positive and negative sides. This polarization can be "switched" by applying a voltage across a ferroelectric crystal. If electrodes are applied to two sides of a crystal, a current pulse flows during such polarization reversal, making these materials potentially useful in data storage devices.

Lee, working with Christen, Matt Chisholm, Chris Rouleau, and Doug Lowndes, synthesized and characterized "asymmetric three-component ferroelectric superlattices" with a "strong polarization enhancement" that was the subject of a letter published in the January 27, 2005, issue of *Nature* magazine.

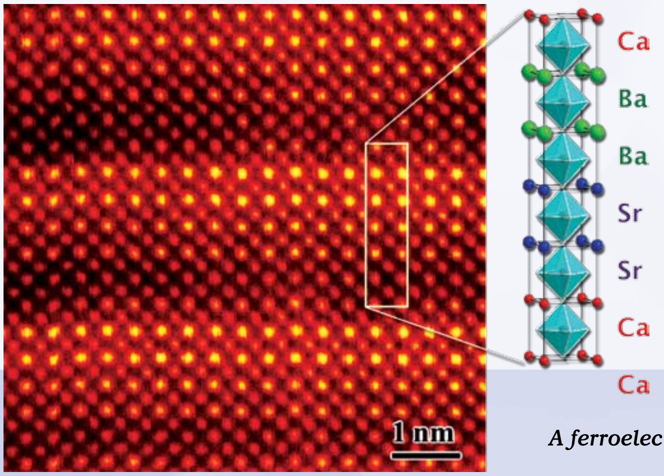
The superlattices described by the ORNL researchers in the *Nature* letter consist of dozens of repetitions of barium titanate ($BaTiO_3$), strontium titanate ($SrTiO_3$), and calcium titanate (CaTiO3), stacked with atomic precision on top of conducting, perfectly flat strontium ruthenate ($SrRuO_3$) layers. Each repetition is 3 to 10 nm thick.

Barium titanate, accounting for only a fraction of the total material in the superlattice, is the only ferroelectric compound among the constituents. Yet, partly because "strain" is maintained—that is, the crystalline film is forced to grow in alignment with the $SrTiO_3$ substrate—the ORNL superlattice has 50% greater polarization than similarly grown pure $BaTiO_3$. This feature —for the first time—confirms theoretical predictions made by two theorists at Rutgers University. Although containing excellent ferroelectric properties, the ORNL superlattice is not the best available ferroelectric material for applications such as memory devices.

"The purposes of this study were to prove we could make a perfect ferroelectric film using pulsed laser deposition, to determine the mechanisms on an atomic scale that influence the material's properties, and to learn how to control and modify the material's properties," Christen says. "Such information could allow us to engineer future ferroelectric films for specific applications and would ultimately help us understand atomic-scale mechanisms in other oxide nanostructures."

The critical issue is the material's behavior directly at each interface between layers. "Our data revealed that the specific interface structure and local asymmetries played an unexpected role in the polarization enhancement," Christen says.

Researchers are now ready to go beyond tailoring ionic displacements at interfaces to changing the electronic configuration in materials such as lanthanum manganite. Aided by excellent tools and strong collaborations, the big picture is coming into focus, helping ORNL researchers improve the behavior of their thin films. ®

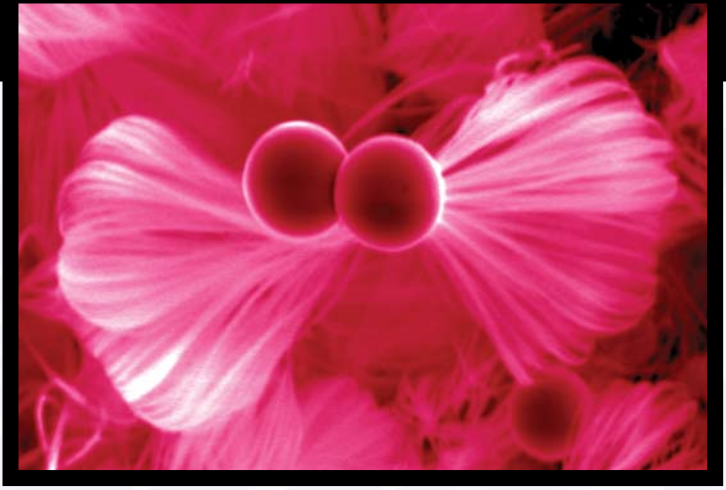


A ferroelectric lattice.

Catalysis at the Nanoscale

Scientists are learning how to make effective catalysts from nanoparticles.

Germanium beads on a zinc oxide nanowire (right).



Gallium-catalyzed silicon dioxide nanowire assembly (left).
Images from Zhengwei Pan

In 1897 French chemist Paul Sabatier discovered that passing a mixture of ethylene and hydrogen over a column of heated nickel transformed the ethylene into ethane. Sabatier, who won the Nobel Prize for chemistry in 1912, later used "finely divided" nickel to catalyze other hydrogenations, the process employed today on oils for food production. Some suggest that Sabatier's heterogeneous catalysis was among the earliest predecessors of today's nanotechnology.

In heterogeneous catalysis, chemical reactions in gases or liquids are accelerated by introducing a solid phase that ideally contains large enough amounts of the right kind of site for chemical reactants to adsorb, react, and desorb. Because optimization of the catalyst requires increasing the numbers of sites to expand surface area, the catalytic particle size must be decreased. In contemporary laboratories, active catalysts tend to consist of carefully prepared nanometer-sized particles on supports with nanometer-sized pores or structural features. Modern catalysts typically consist of multiple-component active phases that may include a support tailored to disperse, isolate, or otherwise enhance the structure or properties of individual catalytic particles.

One goal of catalysis research is to understand how decreasing the size of catalytic particles alters the intrinsic catalytic performance beyond simply expanding surface area. A corollary goal is learning how to design and prepare catalysts with the most effective size and structure. Achieving these goals is the aim of research conducted by the Heterogeneous Catalysis and Surface Chemistry Group in ORNL's Chemical Sciences Division and at the Center for Nanophase Materials Sciences.

One surprising catalytic material studied at ORNL is gold. Because gold is chemically inert, the metal does not react with oxygen (i.e., rust) in air. This property makes gold valuable as jewelry. Intriguingly, gold, once thought to have no catalytic activity because of its inertness, is now known to be extremely active in catalyzing certain oxidation reactions, but only if the gold is in the form of particles 2 to 5 nanometers in diameter. Researchers are seeking to determine the reasons for this size constraint on the catalytic activity of gold. Because gold particles tend to grow readily by migrating and merging under high-temperature conditions, a major goal of research is to stabilize the sizes of gold particles by, for example, trapping them in nanosized pores or tailoring the surface properties of the material supporting the gold particles.

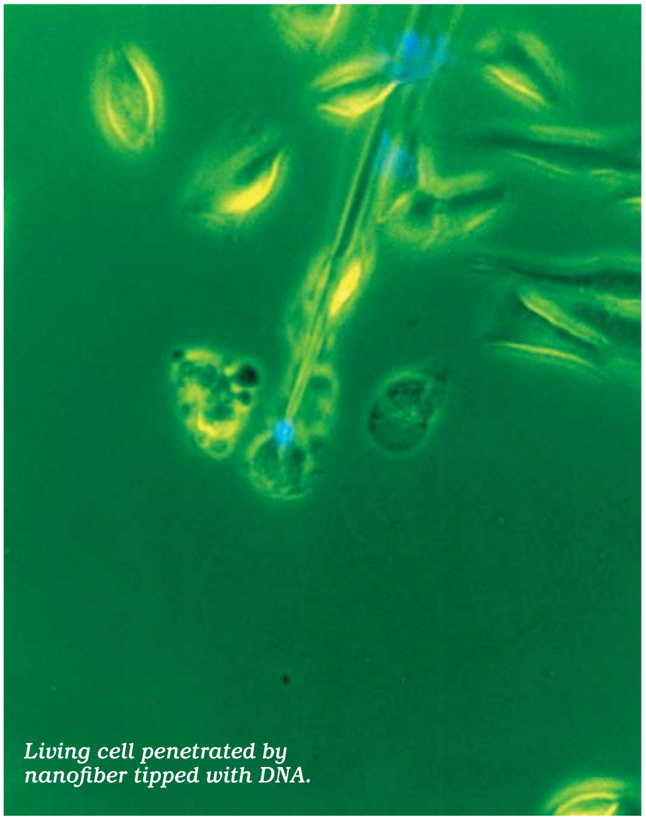
Sheng Dai and Wenfu Yan have found ways to adjust surface properties of oxides by introducing single-layer coatings of various compositions, thereby tailoring the interaction between gold particles and the oxide support. Gold particles supported in this way can be highly stable and can exhibit high catalytic activity for oxidation of carbon monoxide, an automotive exhaust pollutant. Properties of the gold particles have been determined through the analysis of X-ray absorption by David Mullins and Viviane Schwartz, who can directly assess both the gold oxidation state and the average gold particle sizes. From analysis by high-resolution Z-contrast electron microscopy, Steve Pennycook and Andy Lupini, both of ORNL's Condensed Matter Sciences Division, have demonstrated that gold particles apparently must not only be very small but should also have a raft-like shape, to exhibit optimum catalytic activity. Computational approaches by Sergey Rashkeev are now revealing how the stability and adsorption energetics of gold particles are related to their morphologies.

At ORNL's nanocenter, four laboratories will be used to study the relationship between nanoscale structure and catalysis. Researchers in two of the labs will use state-of-the-art methods to synthesize candidate catalytic materials, allowing users to try their ideas for preparing and modifying support materials. Multiple techniques will be used to analyze the composition, structure, and particle and pore sizes of nanostructured catalysts. Several catalytic reactors will be available for testing the catalytic performance of candidate catalysts for various chemical reactions.

One can imagine that Sabatier would have felt right at home in Oak Ridge.—*Steve Overbury, Chemical Sciences Division* Ⓡ

Nature's Way

"Nanobiotechnologists" are imitating, harnessing, and probing nature at the level of the living cell.



Living cell penetrated by nanofiber tipped with DNA.

The world's a stage, and nature is a splendid stage manager. Understanding how nature works and imitating nature at work are among the goals of nanobiotechnology.

Some 20% of the 75 "jump-start" user projects approved for ORNL's Center for Nanophase Materials Sciences are classified as nanobiotechnology. Dozens of Oak Ridge scientists are engaged in nanobiotechnology studies, cutting-edge research where materials, imaging, computational, and biological sciences merge.

Mitchell Dokycz, leader of biochemical and biophysics programs in ORNL's Life Sciences Division, defines nanobiotechnology in terms of the four types of projects in which his group is engaged. "We have used biological materials in innovative ways, such as training bacteria to light up when they sense a specific chemical," he says. "We have used synthetic materials in natural ways, copying nature's way of doing things. We have created devices that are hybrids of nanoscale and biological materials. Finally, we have used nanoscale probes to interrogate biological systems."

Michael L. Simpson, an ORNL-University of Tennessee joint faculty appointee and leader of the Nanobiological Materials Sciences Group in the Laboratory's Condensed Matter Sciences Division, says the types of users at the nanocenter will include researchers from the biomedical, fundamental biology, and biomimetics communities. They will pursue applications such as drug delivery, therapeutics, nanoscale electrochemical sensors, and advanced computation.

ORNL researchers and users at the nanocenter will have access to state-of-the-art instruments for nanobiotechnology research. "We will fabricate new nanostructures using an electron beam writer and characterize them using microscopes, spectroscopy tools, and e-beam holography," Simpson says. "We are nano-enabling systems biology research by getting down to the contents of living cells."

One grand challenge of nanobiotechnology, Doktycz says, is to understand what happens at the interfaces between living and nonliving entities. Here are several examples.

Mengdawn Cheng of the Environmental Sciences Division has shown that 10-nanometer manufactured particles can do more damage to both human and mouse lung cells than micron-sized particles. Nanometer-sized particles emitted by aircraft and automotive vehicles contribute largely to smog found in the world's metropolitan areas.

ORNL Corporate Fellow Eli Greenbaum leads studies of the toxicities that arise at the interface between a microelectrode array and surviving retinal tissue in the typical eye of a legally blind person suffering from retinal degenerative disease.

ORNL Corporate Fellow Thomas Thundat and colleague Ming Su have used gold nanoparticle–labeled probe DNAs to amplify the mass change on Thundat's revolutionary microcantilevers so they bend more. In this way, a target DNA strand that binds with the probe DNA is more easily detected.

The research group of ORNL Corporate Fellow Tuan Vo-Dinh examines proteins in a living cell penetrated by a nanoscale optical fiber tipped with an antibody probe. The group has developed DNA probes based on silver nanoshells and nanoparticles that have detected the AIDS virus and a breast cancer gene by changing their surface-enhanced Raman scattering signals.

Timothy McKnight, Simpson, and their ORNL colleagues penetrate living cells in a checkerboard arrangement in a massively parallel fashion with thousands of vertically aligned carbon nanofibers tipped with plasmid-DNA. The genes in the injected DNA stimulate the cells to produce proteins encoded by the foreign genes. One of the expressed proteins is green fluorescent protein (GFP), which turns the cell green, visibly indicating gene expression in the cell-nanofiber hybrids.

UT and ORNL researchers, including Doktycz, Simpson, and McKnight, created a microarray biosensor using ink-jet technology to spit single droplets of cells into alternating tiny wells in a synthesized carbon nanofiber membrane. Each of the

NANOFABRICATION IN THE CLEAN ROOM

The Nanofabrication Research Laboratory, housed in a wing of the ORNL nanocenter, occupies a room that is clean to the extreme. The "clean room," which occupies almost 10,000 sq. ft of the 80,000-sq.-ft nanocenter, is designed to have extremely low levels of airborne particles, acoustic noise, vibrations, and electromagnetic interference. The clean room's air is highly filtered to remove a large fraction of the particles present in ambient air. The clean room air is 10 times cleaner than the cleanest hospital air and 1,000 times cleaner than the air people normally breathe.

A clean room is needed at the ORNL nanocenter so that "the sensitive tools used to fabricate nanostructures can achieve the best performance," says Richard Kasica, a research engineer in ORNL's Engineering Science and Technology Division. Too many airborne particles and vibrations, for example, could undermine the nanocenter's extensive, novel synthesis capabilities.

The most impressive tools in the clean room for science-based synthesis of nanoscale materials and structures are a unique, state-of-the-art electron beam (e-beam) lithography system and a dual-beam scanning electron microscope/focused ion beam (SEM/FIB) system. Kasica, who has considerable experience in e-beam lithography, is training researchers from ORNL and elsewhere in the use of the clean room's various tools. The tools also include optical lithography, plasma etching, and techniques for depositing and etching away electrically conductive metals and insulators. Scanning probe microscopies are also used in nanofabrication, but they are located elsewhere in the nanocenter.

According to Kasica, this particular e-beam lithography tool will have a few more features than those found on the other 17 systems currently installed across the world. The system at ORNL is the world's fastest writing tool for creating nanosized features over an area as large as 200 millimeters in diameter. For basic research purposes at CNMS, this tool will probably be used on substrates as small as 50 mm2.

"This e-beam lithography tool can quickly scan a substrate, put down square pixels, and connect them, with less error in alignment," Kasica says. "It's like stitching together patches to make a quilt."

The dual-beam SEM/FIB system, which produces electrons and ions from a tank of liquid gallium, will be used to deposit material, etch it away, and make patterns on a substrate. Rarely are patterning, depositing, and etching—the elements of nanofabrication—made available in one tool. The microscope in this system, which is rapidly gaining popularity for sample preparation and analytical work, produces images to ensure precision in researchers' nanofabrication projects, which will include nanoelectronic devices, nanoscale sensors, and drug delivery devices.

bacterial cells grown in the wells has a GFP gene coupled to a chemically sensitive promoter. When the sensor is exposed to that chemical, the promoter induces expression of the GFP gene, causing the cells to glow green.

One exciting "jump-start" nanobiotechnology project that involves Simpson, McKnight, and Gomez Wright of ORNL's Nuclear Science and Technology Division would fabricate a device that could create custom-tailored medical compounds faster than ever before. The project, which is being carried out in the nanocenter's clean room (see sidebar), is led by Joseph Matteo, founder and chief executive officer of the local research firm NanoTek. The company is building a small, microfluidic machine to synthesize quickly and reliably drugs and medicines tailored to individual patients' needs, as well as diagnostic imaging agents.

Matteo's device, which uses ORNL-developed technology to manipulate ions in a stream of solution, operates at high speed using low volumes of fluids. Potential commercial applications include short-order manufacture of drugs and other chemicals with a short shelf life; a better way to make short-lived radioactive compounds for medical diagnostic imaging technology, such as positron emission tomography; and bio-threat detection.

A primary function for this closed-loop, information-driven, serial discovery machine is to synthesize a drug, test the drug against a patient's fluids, feed the test results back to the synthesis process, and optimize the drug to get the desired improvement in patient health.

If the concept works, the findings could demonstrate the feasibility of "point of use" drug synthesis, ushering in a new era of personalized medicine, where patients visit doctors, undergo tests, and receive medicines formulated especially for them in minutes. The discovery, in turn, may speed up nature's way of healing the body. Ⓡ

PROFILE

JIM ROBERTO:

Weighing in on Nanoscale Research

As ORNL's Deputy Director for Science and Technology, Jim Roberto says that his professional goal has always been to find a place where he can contribute most effectively. A physicist who has made his way upward through administrative ranks, his favorite moments in the lab were when he could sit down and analyze all the data that had been collected, putting together the pieces of the puzzle. Now, he has the opportunity to analyze a Laboratory's worth of research and see how those pieces fit into a much bigger picture, although he still "misses all the details."

Roberto joined ORNL in 1974 after earning a B.S. in aeronautics and astronautics from the Massachusetts Institute of Technology and a Ph.D. in applied physics from Cornell University. His research interests have included X-ray and neutron scattering, ion-surface interactions, materials for fusion reactors, and nanoscale science and technology. Formerly the Associate Laboratory Director for the Physical Sciences, Roberto was appointed to his current position in 2004. He is a fellow of the American Association for the Advancement of Science and a recipient of the 2004 National Materials Advancement Award from the Federation of Materials Research Societies.

Q: During the transition in early 2000 from Lockheed-Martin to UT-Battelle, what was happening with the Center for Nanophase Materials Science?

At about the time of the contract change, the Department of Energy's Office of Basic Energy Sciences commissioned a national study, led by ORNL Corporate Fellow Doug Lowndes and involving a number of laboratories and universities, to look into nanoscale science research. One recommendation of the study was that DOE establish nanomaterials research centers and co-locate them with DOE's major synchrotron and neutron facilities. This recommendation helped precipitate a call for proposals for what are now the DOE nanoscale science research centers. ORNL was one of five laboratories that responded to the call, one of three chosen for the second round of the competition, and the first approved for construction. DOE was subsequently able to get funding for all five facilities, and they are currently in various stages of development. Our facility has been completed, and equipment is being installed. Operations will begin in October 2005.

Q: What have been your biggest contributions and your biggest challenges in shaping the Lab's research agenda?

ORNL is the nation's leading materials laboratory. One of my goals has been to further strengthen materials research and leverage this strength to advance the broader missions of the Laboratory. Nanoscience offers the organizing principle. Nanoscale science and technology will revolutionize almost everything we do from basic research to energy and national security. We focused on developing the best tools for nanoscale research—the nanoscience center and the world's best neutron sources, computers, and electron microscopes—and strengthening the related research programs. We formed partnerships with the University of Tennessee and other universities to further strengthen our science and recruiting. And we encouraged integration across the disciplines based on a shared understanding that progress will occur at the nanoscale. For example, chemistry at the molecular scale is directly connected to biology, materials, computing, national security, and many energy and environmental technologies. We have a wonderful opportunity to strengthen chemistry as a result of this integration. The most powerful tool for determining nanoscale structure and dynamics is neutron scattering, and the Spallation Neutron Source and upgraded High Flux Isotope Reactor will uniquely strengthen materials, biology, chemistry and many other programs. Biology is perhaps the most complex nanoscale science, and our multidisciplinary capabilities in nanoscale research offer truly revolutionary possibilities. Building on the efforts of many people and our traditional strengths in materials and other disciplines, we have positioned the Laboratory for leadership in the 21st century. While my role in this has been modest, the outcome has been quite astounding.

Q: Where does the SNS-HFIR package position ORNL in the neutron-scattering world?

ORNL will undoubtedly have the world's best capabilities for neutron scattering. We've been visited by international review committees that have acknowledged this. SNS will provide the world's best pulsed neutron scattering facilities by a factor of ten, and the upgraded HFIR will provide unsurpassed capabilities for experiments that are best performed using a steady-state source. The Europeans have an interest in building a pulsed source, and the Japanese are building one. But SNS has its own upgrade path, and we believe we will stay ahead of the curve.

Q: Where do you think nanotechnology and our energy problem will meet?

The major areas are materials design and catalysis, where you try to control nanoscale structure and chemistry to get the properties you want for energy applications, and genomics, where you try to control biological systems and processes to the same end. The big impacts will be in materials for extreme environments, functional materials for photovoltaics and fuel cells, lightweight materials for transportation, catalysts for energy conversion and process efficiency, and new approaches to biomass and microbial and photochemical energy processes. These are fundamental challenges to advances in energy, and progress in all of these areas depends on the ability to understand and control complex assemblies of atoms and molecules at the nanoscale.

Q: What is ORNL's role in addressing the social and ethical concerns that accompany the production of nanoparticles?

We have a significant role. First, we must ensure that our research is done safely. A lot of effort has been devoted to designing the nanoscience center so that our staff and users will not be exposed to potentially dangerous substances. We have created a state-of-the-art work environment that is safe and environmentally benign. Second, the National Nanotechnology Initiative requires that a portion of the federal investment in nanoscale science and technology be devoted to examining societal, environmental, and health effects. We are studying some of these effects at ORNL. The problem is complex, because nanoscale particles can take many forms in various applications.

Q: You've watched the Lab's research focus shift over the past three decades. What do you think the Lab's signature research capabilities will be over the next 5, 10, 20 years?

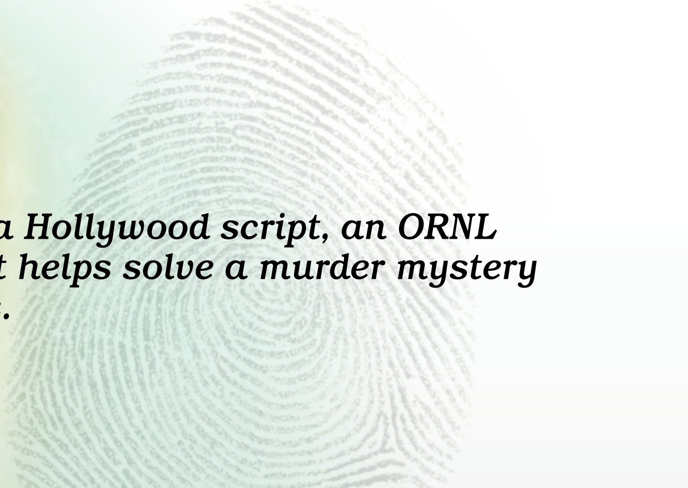
ORNL has a strong tradition in science and technology, but this is by far the most exciting time in my tenure at the Laboratory. We are DOE's largest science, energy and materials laboratory. We have developed new opportunities in neutron science, nanoscience and computational science. We have the base and facilities for international leadership across a broad spectrum of science and technology. Delivering on this unprecedented potential for the Laboratory is our biggest challenge and opportunity. We begin from a very strong position, but the proof will be when the truly pioneering experiments come out of SNS, when our computing revolutionizes the study of complex systems, and when our nanoscience produces breakthroughs across science and technology. This will keep us busy for a while.

Q: What is next?

Many believe that computing will eventually become a third branch of science. Experimental research will always be important, but as we go to more complex systems, the range of experiments required to explore them is just not practical. We will have to use computers to guide our experimental work in the most productive directions. To do that, we must be leaders in simulation science, and that will require significantly greater computing capability than we have now. We will maintain our leadership in neutron science by doubling the performance of the SNS twice, first by upgrading the facility's power and then by adding a second target station. At the nanoscale, a lot of biology is physics and chemistry. By combining our physical sciences strengths with our biology expertise, we can make a unique contribution to biology and develop a next-generation genomics facility. And by integrating across our disciplines, we can develop technologies and facilities that address the global energy problem, perhaps the most significant challenge of our time. We stand on the verge of a scientific and technological revolution based on our ability to characterize, manipulate, and understand materials and biological systems at the nanoscale. We are very fortunate to be at this Laboratory at this time with the capabilities we have created.—*Eva Millwood* Ⓡ

The "Real" CSI:

As if in a Hollywood script, an ORNL scientist helps solve a murder mystery in Texas.



In March 2004, a woman who had been missing for a week was found strangled and stabbed to death in a field in Collin County, Texas. Around her body lay pieces of partially burned logs. Her murderer apparently had tried to ignite the wood pieces in an attempt to burn her body. The attempt failed because the wood was too green.

The sheriff's office obtained warrants to search the homes of people who had known the murdered woman. A criminal investigator found similar, partially burnt wood pieces at the site of a gathering attended by a male suspect. The investigator theorized that the woman's murderer had cut more wood from the same tree, and perhaps took the wood elsewhere.

The sheriff's office collected and numbered 14 logs—some from the murder site and the others from the place of gathering the suspect attended. The wood pieces were sent to Henri Grissino-Mayer, an expert in tree-ring analysis who had relocated from the University of Arizona to the Geography Department at the University of Tennessee at Knoxville.

Grissino-Mayer determined that the logs came from the mesquite tree, which grows too erratically to be useful for studies of annual tree rings. Thinking that a chemical technique might show the wood pieces came from a particular location, Grissino-Mayer contacted a Tennessee Valley Authority chemist. She suggested that he contact Madhavi Martin, a physicist in ORNL's Environmental Sciences Division. Martin had begun studies of the chemical composition of wood, using laser-induced breakdown spectroscopy.

Grissino-Mayer called Martin and asked if she would apply her LIBS technique to the analysis of wood pieces to help solve a murder mystery. Martin agreed. She received three boxes of wood pieces, each piece about 2 feet long and 6 inches in diameter.

Martin was not told that, of the 14 logs she was asked to analyze, 10 were retrieved from the crime scene and 4 from another place the suspect had been. "I analyzed all 14 pieces and found they had an identical spectrum," she says. "They all came from the same tree or from trees found in the same geographical area. I examined the burned parts of the logs and the unburned parts. The data revealed that the wood pieces had the same elemental content."

Equipped with this key piece of evidence, authorities connected the suspect to the crime scene. In June 2005 a jury found the suspect guilty of murder.

LIBS is a technique that produces a chemical "fingerprint" of wood or any other material, based on heavy metals and other trace elements. A tree draws metals from the soil into its wood structure. Trees in one location may have high concentrations of titanium, represented in the spectrum as a tall peak. Trees in another location may have little, if any, titanium.

In LIBS a high-intensity, pulsed laser is focused through a lens onto a solid, liquid, or gaseous sample. The hot laser pulse breaks down the sample, creating a plasma. As the plasma cools, excited atoms of different elements emit light of distinct wavelengths. The light is collected by optical fibers, delivered to a spectrometer, and detected by an intensified charge-coupled detector. The computer-controlled spectrometer is triggered to acquire and read out the data simultaneously on the display screen, to provide rapid elemental analysis of materials.

Through various collaborations, Martin has used LIBS to detect and measure concentrations of heavy metals in emissions from coal-fired power plants, sulfur and carbon in coal gasification plant emissions, and silver and palladium dispersed in cellulose membranes developed for fuel cells. She also has examined silicon and carbon in layers enveloping nuclear fuel cores to determine if layer thicknesses are uniform.

Martin laughs at the notion her research may be equally valuable to the writers of CSI, noting that LIBS also enables her to distinguish between real money and counterfeit bills. Ⓡ

Collaboration at a Superfund Site

ORNL scientists play key roles in the first comprehensive study of microbial gene expression at an acidic mine.

Using mass spectrometers and bioinformatics tools, Oak Ridge researchers made key contributions to the first comprehensive study of gene expression in a community of microbes thriving in an unusually harsh acidic environment. Their work helped their collaborators understand how these microbes survive as a community in a Superfund site at Iron Mountain, California.

In a paper published May 5, 2005, in the online *Science Express*, scientists from Lawrence Livermore and Oak Ridge national laboratories, the University of California, Berkeley, and Xavier University in New Orleans identified more than 2,000 proteins produced by five key microbial species in the community. More than 500 of the proteins appear to be unique to the community, and many do not resemble known proteins.

The proteins were identified largely by ORNL chemist Bob Hettich and Nathan VerBerkmoes, a postdoctoral researcher, both in the Chemical Sciences Division. Using "shotgun" mass spectrometry, they determined the molecular masses and fragmentation patterns of proteolytic peptides from these proteins To identify the peptides from the experimental data, they turned back to the genomes. These DNA sequences of microbial genes in this natural community were identified in 2004 by the Department of Energy's Joint Genome Institute in California and ORNL researchers. The sequences specify the order in which chains of amino acids are linked together to make proteins.

The genomes allowed Manesh Shah of ORNL's Life Sciences Division and other researchers to predict the proteins in each member of the biofilm community. Shah, for example, used computational tools to search the microbial genome database. He then disseminated appropriate data to help the researchers predict the protein fragments that would result if the proteins were chopped into pieces. Correlating the experimental results with the predicted data allowed the researchers to reconstruct the complete proteins and then associate each protein with a particular organism.

"This first large-scale, proteomics-level examination of a natural microbial community from the environment demonstrates the best approach for conducting research in systems biology," Hettich says of the DOE-funded work. "We assembled a strong multidisciplinary research team with critical expertise in each area of systems biology." (See systems biology issue of *ORNL Review*, Vol. 38, No. 1, 2005.)

Jill Banfield, professor of earth and planetary science and of environmental science, policy, and management at UC Berkeley, leads a research team that has conducted a nine-year study of the Iron Mountain microbial community, which consists of bacteria and archaea. The study was the first microbial community characterized at the genetic level. Banfield's team extracted samples of the pink biofilm floating on the water at the abandoned iron mine and prepared them for mass spectrometry analyses.

Michael Thelen, a protein biochemist at Lawrence Livermore, helped unravel the functions of some extracellular proteins in the microbial community. He determined that many unfamiliar proteins are enzymes whose function is to maintain the correct structure of other proteins exposed to sulfuric acid and toxic heavy metals.

Thelen also found that some microbes specialize in fixing nitrogen for the community. One bacterial member of the community, *Leptospirillum group II*, makes a cytochrome protein in abundance, which may capture an electron as the first step in oxidizing iron, a source of energy that allows the intake of airborne nutrients—carbon and nitrogen. The iron was leached out of iron sulfide rock.

"We also found that a different bacterium, *Leptospirillum group III*, apparently makes more of the polysaccharide that is needed as a matrix or housing material for the biofilm community," Thelen says. "These organisms evolved to adapt to their specific environment. They come up with genes distinct enough from those of other organisms to enable them to survive in that particular niche."

Raymond Orbach, director of DOE's Office of Science, says, "Now scientists can investigate not only the 'community genome' but also the resulting 'community proteome' for enzymes and pathways that can help clean up some of the worst environmental sites in the nation." ®

...and the WINNERS are...

Accomplishments of Distinction at Oak Ridge National Laboratory

ORNL researchers won three ***R&D 100 Awards*** in 2005 from *R&D* Magazine in recognition of the year's most significant technological innovations. With 122 of these prestigious awards, ORNL leads DOE national labs and is second only to General Electric. The winners are: SEMCO Revolution, a compact, energy-efficient, rooftop air conditioner that can independently control humidity and temperature while delivering any specified percentage of outdoor air into commercial and institutional buildings, developed by ORNL's **Jim Sand** and John Fischer of SEMCO; SensArray Integrated Wafer, a tool for monitoring temperatures during the manufacture of semiconductors, developed by ORNL's **Robert Lauf**, **Don Bible**, and **Carl Sohns** and five SensArray researchers; and SeizAlert, a low-cost compact wearable prototype device designed to alert the wearer and medical personnel of an impending epileptic seizure, developed by ORNL's **Lee Hively**, **Kara Kruse**, **Vladimir Protopopescu**, and ***Nancy Munro***.

R&D 100 Award winners (left to right) Carl Sohns, Kara Kruse, Lee Hively, Vladimir Protopopescu, and Nancy Munro.

Jizhong Zhou has been elected a ***fellow of the American Society for Microbiology***. He was cited "for his pioneering advances and leadership in developing and applying integrated genomics technologies to address research challenges in functional genomics, including understanding the diversity, structure, mechanisms, and dynamics of microbial communities and extremophilic metal-reducing bacteria important to bioremediation, global changes, and carbon sequestration."

Gary Van Berkel has been awarded the ***Biemann Medal by the American Society for Mass Spectrometry*** for his achievements in and contributions to better understanding the electrochemical nature of the electrospray ion source. The Biemann Medal recognizes significant achievements in basic or applied mass spectrometry made by an individual early in his or her career.

The Institute of Electrical and Electronics Engineers (IEEE) recently named six ORNL researchers as IEEE senior members: **Norbert Holtkamp**, **Burak Ozpineci**, **Melissa C. Smith**, **Ida Lee**, **Lynne Parker**, and **Jie J. Wu**. Senior member is the IEEE's highest professional grade, representing 7% of the institute's membership.

Robert Harrison, **Tony Mezzacappa**, and **Thomas Thundat** have been named ***UT-Battelle Corporate Fellows***. Harrison is chief architect of the world's leading computational chemistry code; Mezzacappa was the first to model neutrino transport during supernova explosions, a theoretical and numerical feat long thought impossible; and Thundat is a leader in the field of nanomechanical sensors. ®

Next Issue . . .

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