Making the Switch to Nanoparticle-Enhanced Coatings

The EPA’s Nanomaterial Extramural Research Program

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Global Nanotechnology Initiatives

To gauge nanotechnology’s effect on global businesses and their readiness for change, Lux Research recently analyzed 1,331 of the world’s largest companies and interviewed leading executives at 35 of the most pioneering ones directly. These corporations put $3.2 billion into nanotech R&D in 2005 and earned $32 billion in revenues from nanotech-related products. Among their findings:

• Nanotechnology will impact different industries in radically different ways. In high-impact industries like pharmaceuticals, semiconductors, and aerospace, companies like Merck and Boeing will develop wholly new product lines, find cost reduction/performance improvements on the order of 20% or more, and need to develop new processes for innovations like drug-device hybrids and roll-to-roll printable electronic devices. Even in medium-impact sectors like automotive and food, companies like Ford and Kraft are seeing large incremental improvements that will be felt at the bottom line as nanotechnology makes hybrid vehicles run longer and functional foods deliver more nutrition.

• Today 148 firms have structured nanotech initiatives, doubling to 290 in 2008. By then, corporate nanotech R&D spending will increase to $12 billion; 80% of high-impact companies will have nanotech in normal product development, and many of the 217 firms seeing a medium level of impact from nanotechnology will have formalized today’s loose projects.

“We have seen significant increases in corporate nanotechnology activity in the last 18 months, with companies now firmly staking out their competitive positions,” said Lux Research Senior Analyst Mark Bünger. “Many large corporations are already selling products that incorporate emerging nanotechnology, and scores of others are in late-stage product development or trials. But even the leaders say they’re not organized effectively, and many of their competitors have not even begun to set up shop.”

Visit www.luxresearchinc.com for more information.

ON THE COVER
An artist’s impression of the sorting of green and red microtubules in nanochannels. Kinesin motors on the walls push the microtubule forward while an external experimentalist can steer the direction by exerting an electrical force on the tube. Researchers from Delft University of Technology’s Kavli Institute of Nanoscience have discovered how to use the motors of biological cells in extremely small channels on a chip. For more information, see the tech brief on page 20. (TU Delft/Tremani)

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FEATURES

5 Small Talk
Tech notes and nano news on patents, grants, industry partnerships, and new products and technologies.

7 Perspective
Today’s energy crisis coupled with the impressive performance properties of materials enabled by the addition of nanoparticles may be the final incentive needed to initiate a shift for the coatings industry. Sally Ramsey, chief chemist and co-founder of Ecology Coatings, discusses how the use of 100-percent-solids UV-curable coatings with nanoparticles can take industry to more energy-efficient manufacture.

9 In Depth
Government support for basic R&D in its early stages is required in order to realize nanotechnology’s full potential. In this issue of Nanotech Briefs, Nora Savage, PhD, an environmental engineer with the U.S. Environmental Protection Agency (EPA), discusses the numerous environmental R&D activities that are either currently underway or will soon be started within the EPA.

24 Inside:
Scheduled for completion in March 2007, the Center for Functional Nanomaterials (CFN) at Brookhaven National Laboratory will provide state-of-the-art capabilities for the fabrication and study of nanoscale materials. As a premier user facility, the CFN will serve as an enabler of advanced materials research in the northeastern U.S.

TECHNOLOGIES

Electronics
12 Mechanical Energy Converted to Electrical Energy for Self-Powered Nanoscale Devices

Manufacturing/Fabrication
14 Fabrication of Transparent Alumina (Al₂O₃) Nanofibers
15 Templates For Fabricating Nanowire/Nanoconduit-Based Devices

Test & Measurement
17 Environmental Chamber Aids Nano-Studies of Metal Oxides

Materials
19 Carbon Nanotube Thermal Interface Materials Reduce Computer-Chip Heating

Bio/Medical
20 Biological Motors Sort Molecules One by One on a Chip

MEMS
23 Nanoscale Drive Mechanisms for Integrated MEMS/NEMS
Fabricating Molecular Electronics

Scientists from Philips Research and the University of Groningen (Eindhoven, the Netherlands) have for the first time fabricated arrays of molecular diodes on standard substrates with high yields. The molecular diodes measure 1.5 nm and are suitable for integration into standard plastic-electronics circuits. Based on construction principles known as molecular self-organization, molecular electronics is a new approach for manufacturing electronics circuits in addition to today's conventional semiconductor processing.

Molecular electronics holds the potential to fabricate elements for electronics circuits with a functionality that is embedded in just a single layer of molecules. Instead of using photolithography or printing techniques to etch or print nano-scale circuit features, molecular electronics can be engineered to use organic molecules that spontaneously form the correct structures via self-organization.

The technology developed by the scientists uses monolayers that are confined to predefined holes in a polymer that has been applied on top of the bottom electrode. The key to their success is the deposition of an additional plastic electrode layer on to the monolayer prior to the deposition of the metallic electrode. The plastic electrode protects the monolayer and enables a non-detrimental deposition of the gold electrode.

"Based on a molecular self-assembly process, we have developed a reliable way to fabricate well-defined molecular diodes," said Dr. Bert de Boer, an assistant professor within the Materials Science CentrePlus at the University of Groningen. "It will enable us ... to do reliable and reproducible measurements on molecular junctions, which is essential for the exploration of the potential applications of molecular electronics."


RNT Awarded $1 Million In SBIR Funds

RNT (Hunt Valley, MD), the developer and manufacturer of NanoFoil®, has been awarded $1 million by the National Science Foundation (NSF). The award, presented in two $500,000 grants, will be used to continue development and commercial expansion of its material and process technology.

The NSF awards are Phase II-B awards from the agency’s Small Business Innovation Research (SBIR) program. One award is for the development of NanoFoil for “Reactive Multilayer Joining of Metals and Ceramics;” the other designates funds towards the development of NanoFoil for “Reactive Mounting of Heatsinks” for Thermal Interface Management (TIM).

"With increasing demand for our NanoFoil technology, the NSF grants will be instrumental in allowing us to complete some outstanding development and expand commercial delivery of our product," said Timothy P. Weihs, Ph.D., RNT Co-Founder and Chief Technology Officer. "We are very pleased that the NSF, whose goal is to promote scientific progress, has recognized the significant benefits NanoFoil technology has for reaction initiation and joining applications, and is actively supporting further development."

Activities possible as a result of the NSF funding are the automation of bonding of electronic components using NanoFoil, as well as the fabrication of a fully integrated TIM product for mass-scale manufacture for CPU and other chip-cooling applications.

E-Textiles “Grown” in Washing Machine

NanoSonic, Inc. (Blacksburg, VA) has unveiled a new twist in the manufacturing process of electronic textiles. Materials engineers with the company are “growing” novel, electrically conductive textiles in a makeshift washing machine, incorporating NanoSonic’s Metal Rubber™ as an integral component. “We can spin gold and silver into flexible fabrics, and they are electrically conductive and nearly transparent,” said Rick Claus, NanoSonic President and professor of engineering at Virginia Tech.

The new nanotextiles could be used for a number of applications including as a shield for potentially harmful and disruptive radio frequency (RF) radiation. Although there is no federally mandated RF exposure standard, research is continually questioning potential hazards of RF electromagnetic fields associated with consumer goods such as cell phones and the effects of living near an electric power line.

According to the inventors, some of the other advantages of NanoSonic’s novel e-textiles are its reduced weight, low manufacturing costs (with only aqueous byproducts), its ability to stretch without the incorporated metal and polymer nanoparticles separating, and durability to withstand repeated washings.

To date, several types of flexible fabrics, foams, and fibers that incorporate the properties of Metal Rubber™ have been produced. The inventors have met another challenge of working with nanomaterials; they have up-scaled production to macro-sized materials, as large as a 4’ x 8’ sheet of plywood one might buy at a local hardware store.


Commercializing Quantum Dot Lasers

Fujitsu Limited and Mitsui & Co., Ltd. (Tokyo, Japan) have established a new optical device venture, QD Laser, Inc. (QDL), leveraging venture capital funding from both companies and Fujitsu’s quantum dot laser technology.

Quantum dot lasers are significantly superior to conventional semiconductor lasers in that they feature higher performance in such aspects as temperature-independent operation, low-power consumption, long-distance transmission, and high speed. It is anticipated that quantum dot lasers will become a core technology to realize high-performance light sources for optical telecommunication, for which data traffic is continuing to increase rapidly.

Utilizing quantum dot semiconductor crystallization technology developed thus far by Fujitsu, and laser design and process technologies, QDL will offer quantum dot lasers to the optical telecommunication light source market for use in optical access and optical LAN within buildings.

By achieving commercialization of its quantum dot laser technology through the growth of QDL, Fujitsu expects to enhance its competitiveness in the optical access market, for which full-fledged global expansion is anticipated. In addition to providing technical support through joint research, Fujitsu will also offer business management support. Fujitsu’s capital investment to QDL will be made through a corporate venture capital fund managed by Fujitsu.

Mitsui’s equity investment in QDL will be made from Mitsui’s principal funds that are managed by Mitsui Ventures. In addition to supporting QDL through strategy planning, operational management, and capitalization and fund-raising strategy, Mitsui Ventures will also support global marketing of QDL’s technologies, enhancing growth and expansion of the new venture.

From your car to your television to your golf clubs, nearly every product manufactured requires the application of a coating for protection and aesthetics. Although pressured by environmental regulatory constraints and efficiency demands in the face of global competition, the multi-billion-dollar OEM coatings industry has been slow to embrace the next generation of coating technologies. Widely recognized for their inherent advantages, 100-percent-solids ultraviolet (UV) curable coatings provide reduced production of polluting emissions and hazardous waste, increased production rates, a smaller footprint in the manufacturing plant, and improved durability in the final product. To date, the sum of those parts has not been enough to overcome the inertia that dominates much of U.S. manufacturing. Today’s energy crisis coupled with the impressive performance properties enabled by the addition of nanoparticles may be the final incentive needed to initiate that shift for the coatings industry and its manufacturing customers.

Most conventional coatings require substantial energy inputs to cure. Even the newest of the surface finishing techniques commonly used today — powder coating — requires raising the temperature of large masses of metal for more than 20 minutes at a time, an energy-intensive undertaking that is accomplished through IR radiation or natural gas-fired ovens. When conventional liquid coatings are used, those same processes must be employed to drive off carriers, either organic solvents or water. Waterborne coatings can be air-dried, with significant costs in terms of production time, space, and ventilation requirements. If the bottleneck created by more than one hour of drying time isn’t enough of a disincentive, performance is also an issue. Waterborne coatings can cause flash rusting. Hardness, abrasion resistance, corrosion resistance, and adhesion are often below the levels seen for either conventional liquid coatings or for powders, clearly a less-than-perfect solution.

In contrast, 100-percent-solids UV-curable coatings cure very quickly, usually in seconds. The rapidity drives up to 80 percent reductions in energy required, a serious carrot in today’s energy market. When combined with enhanced production speed, space savings, and environmental advantages, the energy savings make next-generation coatings an attractive solution to the fossil fuel blues.

With the economic argument leading the way, nanotechnology comes to the forefront as an enabler.
of an entirely new set of desirable performance properties to match. The incorporation of nanoparticles into Ecology Coatings’ 100-percent-solids UV-curable technology enhances coating application qualities including improved flow characteristics, reduced thinning on sharp edges, and minimized defects. Nanoparticles also can increase the hiding power of pigmented coatings by a factor of 20 percent.

One of the more interesting applications of nanoparticles is in matting or producing flat coatings, a particular challenge in 100-percent-solids coatings. Most matting agents substantially increase viscosity, a problem that is usually addressed by the addition of thinners. By definition, thinners cannot be used in a 100-percent-solids formulation. Through a proprietary method, Ecology Coatings disperses amorphous nanoparticles in a variety of monomer components to produce a matte coating with almost no increase in viscosity.

Another important application for nanoparticles is moisture resistance, or simply the creation of a barrier to water, air, or both. Such barriers are essentially a function of filling space, an objective for which a combination of nanoparticles and larger-sized particles is particularly effective. By adjusting the dosage of particles or the dosage of coating itself, the resistance can be fine tuned to specifically block water, air, or solvents. Because resistance is not achieved through hydrophobicity, this technique maintains printable and overcoatable surfaces.

Nano-enabled moisture resistance is particularly useful as a tool against microorganisms that thrive in a moist environment. When water is absorbed by drywall and other porous substrates, spores landing on the surface access the moisture to propagate quickly. Sealing a porous surface blocks access to water and thus inhibits growth. A coating that acts against such microbes in multiple pathways is particularly effective for minimizing the rapid development of resistance. For example, the addition of antimicrobials that function in a catalytic manner and/or larger microbe-resistant particles such as silver compounds can create an effective coating for combating organism growth.

While many organisms need moisture to grow, many electronics find it fatal, a problem conventionally solved by using glass to protect electronics. However, glass has drawbacks; namely it is breakable, heavy, and inflexible. Serving as air and vapor barriers, coatings with nanoparticles can be used as a direct replacement to glass for more porous materials. In testing done in accord with ASTM D 3985-02, an Ecology Coatings product lowered air permeance 6 to 200 times depending on the thickness of the coating used.

In addition to serving as a direct barrier, coatings can enable other protective barriers. Although plastics like polycarbonate are lighter and more flexible than glass, its use as a replacement has been limited by a propensity for scratching and vulnerability to common solvents. Enabled by nanoparticles that maintain clarity and unprecedented hardness, Ecology Coatings’ polycarbonate product addresses both of these issues.

While industry may find many advantages in the use of a new generation of coatings, our interests will be best served by close attention to potential health and environmental concerns associated with new technologies. Since much is yet to be learned, it would be wise to err on the side of caution by using the strictest of industrial hygiene practices. Since the advent of clean air and water regulations in the U.S., the finishing industry has managed and mitigated these types of health issues. Tools to minimize both particulate exposure and release are already in place to manage potential risks. Now is the time to continue and expand the use of that toolset as we move forward.

As we look towards the future, we look forward to a better understanding of coating materials and continued improvements to the technology. Use of 100-percent-solids UV-curable coatings with nanoparticles can take industry to more energy efficient manufacture. Use of lighter materials made durable by coatings will result in fuel savings for consumers and end users. Improvements in the control and confinement of air, water, and solvents may help in the construction of devices and infrastructure for alternative energy sources. Driven by energy volatility and enabled by nanomaterials, we are riding the tipping point for a move toward better products to meet our voracious energy demands.

For more information, contact Sally Ramsey at uv@ecologycoatings.com. Visit Ecology Coatings at www.ecologycoatings.com.
The challenge for environmental protection is to ensure that, as nanomaterials are developed and used, unintended consequences of exposures to humans and ecosystems are prevented or minimized. In addition, knowledge as to how best to apply nanotechnology for pollution prevention, detection, monitoring, and clean-up is also needed. The key to such understanding is a strong body of scientific information, and the sources of such information are the numerous environmental research and development activities that are either currently underway or will soon be started within government agencies, academia, and the private sector. Collaboration and communication in this field is important and will undoubtedly play a pivotal role in both how and when critical research questions are addressed.

Since 2001, various federal agencies have sponsored extramural and intramural research in nanotechnology — both applications and implications. Agencies include the EPA; the National Institutes of Health (NIH); the National Science Foundation (NSF); the National Institute for Occupational Safety and Health (NIOSH); the Departments of Agriculture, Defense, and Energy; the National Toxicology Program (NTP); the National Institute for Standards and Technology (NIST); and the National Institute of Environmental Health Sciences (NIEHS).

More recently the National Toxicology Program (NTP) has engaged in eco and human health research on specific engineered nanomaterials including quantum dots, fullerenes and carbon nanotubes, and titanium dioxide.

The NEHI (Nanotech Environmental and Health Implications Workgroup of the NSE) is identifying critical research needs for the development of comprehensive risk assessments for nanomaterials as well as research needs for a number of potential applications for nanotechnology. A brief summary of EPA’s identified research needs is listed below. A more comprehensive description of EPA’s draft nanotechnology research needs can be found in EPA’s draft Nanotechnology White Paper, which is currently undergoing external peer review.

Treatment and remediation techniques can be greatly improved through the use of nanotechnology. The potential exists to develop inexpensive remediation and treatment technologies that enable the rapid and effective clean up of recalcitrant compounds, especially those located in difficult to access areas.

Nanotechnology can enable the development of rapid, accurate, miniature environmental sensing and monitoring devices. Such devices would allow for early alerts to first responders and the general public of toxic releases in the atmosphere, water supplies, and in subsurface areas. Anticipated capabilities of nano-enabled sensors would include the

**IN DEPTH**

**The U.S. Environmental Protection Agency’s Nanomaterial Extramural Research Program**

Developing Improved Data for Nanomaterial Risk Assessments

*Nora Savage, PhD*

*Environmental Engineer*

*U.S. EPA*

*Washington, DC*
ability to detect minute concentrations of a variety of compounds simultaneously, to instantly record and store the collected data, to issue warnings for dangerous concentrations of toxic compounds, to isolate these compounds in order to minimize environmental and human exposures, and to remediate potentially harmful compounds that enter the environment.

Direct applications to the environment may include nanoscale monitoring systems, control or clean-up systems for conventional pollutants, and desalination or other chemical modifications of soil or water. Nanoscale particles may affect aquatic or terrestrial organisms differently than larger particles due to their potential to cross and/or damage cell membranes, and differences in other chemical and physical properties (U.S. EPA, 2003). Furthermore, use of nanomaterials in the environment may result in novel byproducts or metabolites that also may pose significant risks.

The unique properties that make nanomaterials useful and novel are also likely to be the properties that could impact humans and the environment under specific conditions. Critical research is needed to explore the methodology and likelihood of nanomaterial release into environmental media and potential for significant human or ecosystem damage resulting from anticipated exposures.

Life-cycle analysis (LCA) is an approach to evaluating the environmental consequences of a product through all stages along the life cycle of a compound, including production, use, recycling, and disposal. Adequate information on the use of nanomaterials is a critical data need in applying LCA analysis. The processes that are involved in the production of nanomaterials and their incorporation into consumer products are not centrally reported. Exposure to nanomaterials from a specific product may vary considerably based on the stage of life of the material.

The potential for adverse health effects from exposure to engineered nanomaterials may result from either inadvertent release of materials during manufacture, use, or disposal or recycling; through the generation of unintentional byproducts during environmental application; or through the intentional introduction of these materials for cosmetic, health, or other purposes. Little data exist on the deposition and fate or specific susceptibility from exposure to engineered nanomaterials or their associated byproducts. It also is unclear how standard test methods will be used to identifying novel toxicities associated with the unique physicochemical properties of intentionally produced nanomaterials (ILSI, 2005).

In the implications area, the research community relies on reproducible and standardized testing protocols and well-characterized testing materials to effectively utilize and extrapolate study data. Understanding the physical and chemical properties of engineered nanomaterials and developing standard testing protocols is necessary in the evaluation of hazard (both toxicological and ecological) and exposure of these materials.

Data concerning the transformation of specific compounds — individually and in complexes with other compounds — and the interactions that may occur between the compound and its surroundings are critical to developing environmental protection policies. While there are historical data and models...
for conventional pollutants, such data and models may not be sufficient for characterizing engineered nanomaterials. Consequently, research is needed to understand fully how these compounds may differ in reaction with each other, with other compounds, and with environmental media, and the mechanisms by which these interactions occur.

The fundamental properties concerning the environmental fate of nanomaterials are not well understood (European Commission, 2004). Consequently, it is essential to determine the fate of nanomaterials in the environment, and the availability of these materials to living organisms, waters, and the atmosphere. Evaluation and modification of existing methods, or the development of new test methods, to support these investigations must be carried out, as well as the development of property estimation methods.

Potential exposures to nanomaterials include workers exposed during the production and use of nanomaterials; general population exposure from releases to the environment during the manufacture, use, or disposal/recycling of nanomaterials or products composed of nanomaterials; and ecosystem exposure during the manufacture, use, or disposal/recycling of nanomaterials or products containing nanomaterials (Aiken 2004). Information concerning duration, type, and route of exposure, as well as information on quantities and types of engineered nanomaterials, is currently lacking.

Ecosystems may be affected through inadvertent or intentional releases of engineered nanomaterials. Drug and gene delivery systems, for example, are not likely to be used directly in the environment but may contaminate soils, surface waters, or wastewater treatment systems (from human use and excretion) through run-off from concentrated animal feeding operations or from aquaculture applications.

Assessing potential health effects of engineered nanomaterials requires determining to what extent existing databases can be used to predict or assess the toxicity of engineered nanomaterials. The limited instillation studies conducted to date suggest that the toxicological assessment of specific engineered nanomaterials may be difficult to extrapolate from existing databases (Lam, et al. 2004; Warheit D.B. et al. 2004). Although the toxic effects of engineered nanomaterials have not been fully characterized or understood, it is known that these materials differ from their bulk counterparts in certain physical or chemical properties. There is a critical need to develop methodologies for characterizing and testing nanomaterials in a systematic and comparable way such that research results can be appropriately evaluated and compared.

As a result of their smaller size, nanoparticles may pass into cells directly through cell membranes or via cellular transport mechanisms, and may penetrate the skin and distribute throughout the body. There is also a concern for systemic effects (e.g., migration to target organs and the cardiovascular and neurological systems) in addition to portal-of-entry (e.g., inhalation, dermal, oral) toxicity.

For more information, contact Nora Savage, PhD, at Savage.Nora@epamail.epa.gov. Visit the EPA at www.epa.gov.
Mechanical Energy Converted to Electrical Energy for Self-Powered Nanoscale Devices

Current-producing arrays could be built from millions of nanowires.

Georgia Institute of Technology, Atlanta, GA

A new technique for powering nanometer-scale devices without the need for bulky energy sources such as batteries has been developed. By converting mechanical energy from body movement, muscle stretching, or water flow into electricity, these “nanogenerators” could make possible a new class of self-powered implantable medical devices, sensors, and portable electronics.

While a broad range of nanoscale devices have been proposed and developed, their use has been limited by the sources of energy available to power them. Conventional batteries make the nanoscale systems too large, and the toxic contents of battery-
ELECTRONICS

ies limit their use in the body. Other potential power sources also suffer from significant drawbacks.

The nanogenerators developed by Georgia Tech researchers use the very small piezoelectric discharges created when zinc oxide nanowires are bent and then released. By building interconnected arrays containing millions of such wires, it is believed that enough current could be produced to power nanoscale devices.

To study the effect, the researchers grew arrays of zinc oxide nanowires, and then used an atomic-force microscope tip to deflect individual wires. As a wire was contacted and deflected by the tip, stretching on one side of the structure and compression on the other side created a charge separation — positive on the stretched side and negative on the compressed side — due to the piezoelectric effect.

The charges were preserved in the nanowire because a Schottky barrier was formed between the AFM tip and the nanowire. The coupling between semiconducting and piezoelectric properties resulted in the charging and discharging process when the tip scanned across the nanowire. The strain was released when the tip lost contact with the wire, and the researchers then measured an electrical current. To rule out other potential sources of the current, the researchers conducted similar tests using structures that were not piezoelectric or semiconducting.

The researchers grew the nanowire arrays using a standard vapor-liquid-solid process in a small tube furnace. The arrays contained vertically aligned nanowires that ranged from 200 to 500 nm in length and 20 to 40 nm in diameter. The wires grew approximately 100-nm apart.

A film of zinc oxide also grew between the wires on the substrate surface, creating an electrical connection between the wires. An electrode for measuring current flow was attached to the conductive substrate.

Though attractive for use inside the body because zinc oxide is non-toxic, the nanogenerators could also be used wherever mechanical energy — hydraulic motion of seawater, wind, or the motion of a foot inside a shoe — is available. The nanowires can be grown not only on crystal substrates, but also on polymer-based films. Use of flexible polymer substrates could one day allow portable devices to be powered by the movement of their users.

Current also could be produced by placing the nanowire arrays into fields of acoustic or ultrasonic energy. Though they are ceramic materials, the nanowires can bend as much as 50 degrees without breaking.

This work was performed by Zhong Lin Wang and Jinhui Song of Georgia Institute of Technology. Visit www.nanoscience.gatech.edu/zlwang .

A scanning electron microscope image (A) shows an array of Zinc Oxide Nanowires. A schematic (B) of how an AFM tip was used to bend nanowires to produce current. Output voltages (C) produced by the array as it is scanned by the AFM tip. (Credit: Z. L. Wang)
Fabrication of Transparent Alumina (Al₂O₃) Nanofibers

The technique of electrospinning allows the development of high-quality transparent alumina fibers.

Department of Chemical Engineering, The University of Toledo, Toledo, OH

Alumina (Al₂O₃) is a well-known structural material and enjoys the status of Holy Grail among functional ceramics. Porous alumina, also known as activated alumina, is extensively used as an industrial adsorbent and catalytic support. Its applications range from transparent thin films as optical windows to particulates, platelets, and fibers as reinforcements in lightweight, ultra-strong metal matrix composites. Its fabrication in nanofibrillar form with high aspect ratio is expected to enhance its role in the above and a number of other processes.

While it is rather difficult to fabricate and maintain alumina in nanofibrillar architecture by conventional and some of the sophisticated methods, electrospinning has made it possible.

The fabrication, processing, and characterization of transparent one-dimensional Al₂O₃ nanofibers has recently been achieved by electrospinning polymer-ceramic (polycer) composite fibers from a 1:1 mixture of aluminum precursor in acetone and polyvinylpyrrolidone (PVP) in ethanol. Using a high-voltage DC source, 7 to 9 kV is applied between the needle of a syringe containing the mixture and a collector to initiate the electrospinning.

The transformation of polycer to ceramic is followed by a series of heat-treatment, and phase and morphological examination using Raman spectroscopy, X-ray diffraction, scanning, and transmission electron microscopy coupled with energy dispersive spectroscopy and selected area electron diffraction techniques.

This work was performed by Abdul-Majeed Azad and his research group at the Chemical Engineering Department of the University of Toledo. Visit www.eng.utoleo.edu/~aazad.
A
n effort is underway to develop processes for making templates that could be used as deposition molds and etching masks in the fabrication of devices containing arrays of nanowires and/or nanoconduits. Examples of such devices include thermoelectric devices, nerve guidance scaffolds for nerve repair, photonic-band-gap devices, filters for trapping microscopic particles suspended in liquids, microfluidic devices, and size-selective chemical sensors. The technology is an extension of previous work conducted by JPL, UCSD (University of California, San Diego), and Paradigm Optics Inc., which developed a process to fabricate macroporous scaffolds for spinal-cord repair.

Highly-ordered, optical-fiber arrays consisting of dissimilar polymers comprise the template technolo-

Figure 1. An Image from a scanning electron microscope shows the array of 100-nm diameter holes etched in a PMMA matrix.
The selective removal of the fiber cores in specific solvents creates the porous templates to be filled with a “top-down” deposition process such as electrochemical deposition, sputter deposition, molecular beam epitaxy, and the like.

Typically, the fiber bundles consist of polystyrene (PS) fiber cores, which are clad with varying thickness poly(methyl methacrylate) (PMMA). When arranged in hexagonal, close-packed configuration and pulled, the fibers form highly-ordered arrays comprised of PS fiber cores surrounded by a continuous matrix of PMMA. The ratio of PMMA cladding thickness to PS core diameter determines the spacing between PS fiber cores and typically ranges from 3:1 to 1:1.

Essentially, the simultaneous heating and drawing or pulling in the longitudinal direction of polymer-fiber arrays fuses the fibers together. Since the fusing process is a constant volume process, a lateral or cross-section reduction is accompanied by a commensurate increase in length. Thus, the degree of pulling determines the final core dimensions.

Compared to previous work, where the fiber cores were in the range of 100 to 200 microns, the
extent of pulling was significantly increased, thus resulting in a significant reduction in feature dimensions. The scanning electron microscope (Figure 1) image reveals the close packed array 100-nm diameter holes etched in a PMMA matrix (center image). The background image indicates that the hole monodispersity and order is maintained over relatively large areas. The original template length or fiber length was greater than 1 cm and the cross sectional dimension was 1 cm by 0.4 cm (Figure 2). In principle, the depth of the holes could be far greater than 1 mm, which could result in features with aspect ratios (length/diameter) in the 1,000 to 10,000 range.

This work was done by Jeffrey Sakamoto of Caltech for NASA’s Jet Propulsion Laboratory and Todd Holt and David Welker of Paradigm Optics, Inc. For further information, access the Technical Support Package (TSP) free on-line at www.techbriefs.com/tsp under the Manufacturing & Prototyping category.

In accordance with Public Law 96-517, the contractor has elected to retain title to this invention. Inquiries concerning rights for its commercial use should be addressed to:

Innovative Technology Assets Management
JPL
Mail Stop 202-233
4800 Oak Grove Drive
Pasadena, CA 91109-8099
(818) 354-2240

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Figure 2. The Nanotemplate, approximately 1/2×1/2×1/8 inch (12.7×12.7×3.2 mm), contains about 60 fibers.

TEST & MEASUREMENT

Environmental Chamber Aids Nano-Studies of Metal Oxides

Experiments establish nano-level copper-oxidation model.

Argonne National Laboratory, U.S. Department of Energy, Argonne, IL

An environmental chamber constructed by Argonne’s Materials Science Division allows researchers to watch materials as they grow step-by-step while interacting in elevated-temperature, reactive-gas environments. The first experiment in the new chamber revealed intriguing information about how copper oxidizes at the nano level and established a new basic model for understanding oxidation.

The initial study found that clean copper surfaces are more resistant to oxidation than previously expected when exposed to oxygen. These findings could lead to improved electronic com-
ponents. Industry is interested in using copper in some devices that are processed at high temperatures with oxygen present, but has been concerned that the copper might oxidize, leading to degraded electrical properties. The chamber also may help researchers find better ways to produce hydrogen from hydrocarbons.

Oxides can be protective, as when alumina forms on aluminum surfaces, or damaging, as when iron rusts and fails. Understanding these processes at the atomic level will allow researchers to manipulate oxidation to create better materials.

Oxide studies have traditionally been conducted on thick, mature oxide layers on bulk materials. More recently, transmission electron microscopy (TEM) has revealed local oxidation processes at the mesoscopic level — the scale at which one can reasonably discuss the properties of a material or phenomenon without having to discuss the behavior of individual atoms. But the new environmental chamber permits X-ray diffraction measurements at Argonne's Advanced Photon Source (APS) to reveal oxidation at the atomic level — including chemical and microstructural evolution — in a controlled environment over a sample's entire surface.

ANL scientist Pete Baldo built the Environmental Chamber that allows materials scientists to watch materials oxidize.

With heat and time, small islands oxidize on the Copper Substrate. As seen in this transmission electron microscope image taken after 20 minutes at 350°C, the islands are about 200 nm.
For this study, a thin film of copper was placed in the chamber, and both the temperature and gas environments were controlled. As oxygen was added to the chamber, it initially formed an ordered monolayer over the copper. According to the researchers, as the oxygen level increased it reacted with the copper and small “nano-islands” of copper oxide appeared on the surface, which measured approximately 100-nm wide and a few nanometers thick. Once the islands formed, the temperature and oxygen levels were varied to study the islands’ growth. Research revealed which conditions caused the islands to grow or shrink. Scientists determined the phase boundary — the dividing line that distinguishes between growing or shrinking — for several temperatures.

This work was performed by Jeff Eastman, Dillon Fong, Paul Fuoss, Lynn Rehn, Guangwen Zhou, Pete Baldo, and Loren Thompson of Argonne’s Materials Science Division. Visit www.msd.anl.gov.
Biological Motors Sort Molecules One by One on a Chip

Transport system uses electrical charges to direct individual molecules.

Delft University of Technology’s Kavli Institute of Nanoscience, Delft, The Netherlands

Researchers from the Kavli Institute of Nanoscience have discovered how to use the motors of biological cells in extremely small channels on a chip. Based on this, they built a transport system that uses electrical charges to direct the molecules individually. To demonstrate this, the researchers sorted the individual molecules according to their color.

The biological cell is a complex of many different small protein factories. The necessary transportation of materials within the cell occurs across a network of microtubules — long, tubular-shaped proteins that extend in a star-shaped formation from the nucleus of the cell to the walls of the cell. Molecular bio-motors, such as the enzyme kinesin, can walk in small steps (of 8 nm) with a load of material along these microtubule-networks and thus provide transport within the cell.

Researchers are currently exploring the possibility of inserting these kinesin motors and microtubules in an electrically directed transport system made by using nano-fabrication techniques.

It will be necessary to find more efficient thermal-interface materials in the future because as computer chips become increasingly more compact, more circuitry will be patterned onto a smaller area, producing additional heat. Excess heat reduces the performance of computer chips and can ultimately destroy the delicate circuits.

This work was performed by Timothy Fisher and Jun Xu of Purdue University. Visit http://nanotron.ecn.purdue.edu. © (Velcro® is a registered trademark of Velcro Industries B.V.)

COMMERCIAL APPLICATIONS

- Biological motors
- Steering individual molecules
- Electrical transport
The researchers turned the system around: the kinesin motors are fastened in large quantities on a surface with their “feet” up; the microtubules (measuring approximately 1 to 15 micrometers in length) were then transported over the “carpet” of motors. A particular challenge of the research was to ensure beforehand that the microtubule tubes could be transported in a determined direction and were not dislodged by collisions of the motor carpet.

An important step in achieving this control was to allow microtubule-transport to occur in small, closed, liquid channels. This made it possible to apply a strong electrical field locally at the Y-junction in the channels; therefore, the electrical force could be exerted on the individual microtubules. It was discovered that by using this electrical force, the

Sorting green and red microtubules in Nanochannels. Kinesin motors on the walls push the microtubule forward while an external experimentalist can steer the direction by exerting an electrical force on the tube.
front of the microtubule could be pushed into the determined direction.

To demonstrate this, the researchers allowed a mixture of green and red fluorescent microtubules to arrive at a Y-junction. By changing the direction of the electrical force, depending on the color of the microtubule, the researchers were able to collect the green and red microtubules in different reservoirs.

This work was performed by Cees Dekker, Martin van den Heuvel, and Martijn de Graaff for Delft University of Technology’s Kavli Institute of Nanoscience. Visit www.mb.tn.tudelft.nl.
Researchers at Berkeley Lab have invented a device that harnesses the incredible force of surface tension at the nanoscale, which can become the dominant force for systems this small. The Berkeley Lab nanoelectromechanical (NEMS) actuator offers several features that will enhance switching and motor functions for microelectromechanical (MEMS) devices: it’s nanoscale, yet simple to construct and manufacture in bulk; it’s extremely powerful with a mechanical frequency range from DC to gigahertz; and the action is frictionless and driven by extremely low voltage. The new actuator can also be integrated into existing semiconductor architectures and manufacturing processes and functions at semiconductor operating temperatures.

In the Berkeley Lab invention, a molten metal droplet governed by DC current grows and shrinks on a nanotube substrate like a miniature hydraulic press, applying force to a lever, mirror, or other object. The mechanism is reversible and increasing or reducing the voltage can control its speed.

The technology is scalable, simple to construct, and uses DC voltage as low as 1 V. The system also is compatible with existing semiconductor architectures, manufacturing processes, and operating conditions.

The technology is available for licensing or collaborative research.

This work was performed by Alex Zettl and his team from Berkeley Lab’s Materials Sciences Division. Visit www.lbl.gov/Tech-Transfer/techs/lbnl2008.html#2008a.

**COMMERCIAL APPLICATIONS**

- Motors
- Electromechanical switches
- Drives
- Microfluidic control valves

Metal Atoms Are Transported via electric current from the large metal droplet on the right to the small one on the left.
The Center for Functional Nanomaterials

With construction planned for completion by March 2007 and experiments due to begin shortly thereafter, the U.S. Department of Energy’s (DOE) Brookhaven National Laboratory’s Center for Functional Nanomaterials (CFN, Upton, NY) is on schedule to provide researchers with new fabrication techniques to study materials at nanoscale dimensions. The CFN — one of five Nanoscale Science Research Centers — is a 94,500-square-foot state-of-the-art laboratory/office facility expected to attract an estimated 300 researchers from the Northeast annually.

The DOE’s Office of Basic Energy Sciences is funding the $81-million CFN project. The building will house specialized equipment such as electron microscopy facilities and lithography-based fabrication facilities. The CFN will occupy nine square acres, accommodate 150 people, and will be considered “green” — energy efficient and environmentally friendly — based on the U.S. Green Building Council’s rating system.

The goal of the CFN is to help solve energy problems in the U.S. by exploring materials that use energy more efficiently and by researching practical alternatives to fossil fuels, such as hydrogen-based energy sources and improved solar energy systems. Science at the CFN is organized around three scientific themes, which are identified below. The nanoscience themes are expected to evolve and change with time.

Scientific Themes

“The Center for Functional Nanomaterials will be at the forefront of research that is expected to lead to new technologies, such as faster computers, new communications devices, improved solar energy, and new energy alternatives,” said Congressman Tim Bishop during the official groundbreaking ceremony.

Under the energy banner, research will focus on three key areas: nanocatalysis, the acceleration of chemical reactions using nanostructures; biological and soft nanomaterials, such as polymers and liquid crystals, in which specialized design is expected to lead to new functions; and electronic nanomaterials that exhibit unprecedented control of electrons, which are expected to lead to new communication and energy-control devices.

Nanocatalysis uses tiny structures, a few billionths of a meter in dimension, to speed up chemical reactions essential to modern life. Metal-containing nanoparticles are essential ingredients in industrial chemical production and energy-related processes. For example, fuel cells for powering electric vehicles use bimetallic particles of platinum and ruthenium to catalyze the conversion of chemical energy into stored electrical energy. These particles are less than 100 nm in size and make up only a few percent of the catalyst’s weight, yet provide the active sites where chemical reactions take place.

Biological and soft nanomaterials include polymers, liquid crystals, and other relatively “soft” materials that fall into a state between solid and liquid.

One particular focus of this research is on the structure and behavior of soft matter deposited on-
to nanopatterned interfaces. This work is designed to help scientists learn and control how materials transfer forces and electric charge, and how these properties are influenced by the surface on which the film is grown. Applications for this research include flexible computer or television displays.

Within the electronic nanomaterials theme, research will focus on how electric charge and magnetism move and interact within nanomaterials. Nanoscale electronic materials research is expected to revamp the U.S. energy storage and distribution network, and transform the electronics industry by producing very small, fast circuits.

Scientists at the CFN will focus on studying how electrons transfer between diverse materials; in particular, the properties of carbon nanotubes will be studied. Carbon nanotubes possess exceptional electric and structural properties, making them attractive for many applications. For example, CFN scientists demonstrated that a single nanotube can emit ultraviolet light when a voltage is applied across it, creating the world’s first electrically controllable BNL light emitter.

Facilities & Equipment

Housed in a new building consisting of offices and laboratories, and located next to the National Synchrotron Light Source (NSLS), the centerpiece of the CFN will be composed of five state-of-the-art groups of laboratories called Laboratory Facilities, as well as a Theory and Computational Center, and a set of advanced endstations on beamlines at the NSLS. The Laboratory Facilities will include advanced capabilities in nanopatterning, transmission electron microscopy, nanomaterials synthesis, ultra-fast laser sources, and powerful probes to image atomic and molecular structures.

In addition, the CFN will offer clean rooms; general laboratory space; wet and dry laboratory space; materials-synthesis equipment; scanning-probe and surface-characterization facilities; and electron microscopy, spectroscopy, and lithography-based fabrication facilities.

User Program

The CFN will be operated as a national user facility, accessible to researchers at universities, industrial laboratories, and national laboratories through peer-reviewed proposals. The equipment will be offered to users under a proposal system, and the user program will provide access to the Laboratory Facilities and related facilities staffed by laboratory scientists, postdoctoral appointees, and technical support personnel who are active in nanoscience research. Prior to the completion of the facility, the CFN is offering a set of capabilities attractive to scientists working on the nanoscale.

For more information about Brookhaven’s CFN, visit the Web site at www.cfn.bnl.gov.