Building the Nanofuture with Carbon Tubes

FEATURE

by Jennifer Ouellette

Since their discovery in 1991, researchers have envisioned carbon nanotubes as the most viable candidates to dominate the coming 21st century revolution in nanotechnology. Barely a decade old, these unique materials are already in use in lithium-ion batteries and as structural reinforcements, and the first flat-panel displays using nanotube components as field emitters are expected to reach the market late in 2003.

Broad commercialization awaits fabrication advances

Other potential applications in development include chemical sensors, probe tips, fuel cells, portable X-ray machines, extremely lightweight and strong fabrics, artificial muscles, and components that will dramatically reduce the weight of cars and spacecraft. "Nanotechnology, such as carbon nanotechnology, will impact almost every aspect of our lives. The only question is, when?" says Cynthia Kuper, president of Versilant Technologies (Philadelphia, PA). "The answer depends on our ability to fabricate nanotechnology materials more easily than is possible now, and turning them into useful products."

Antenna Group, Nanomix, Inc.

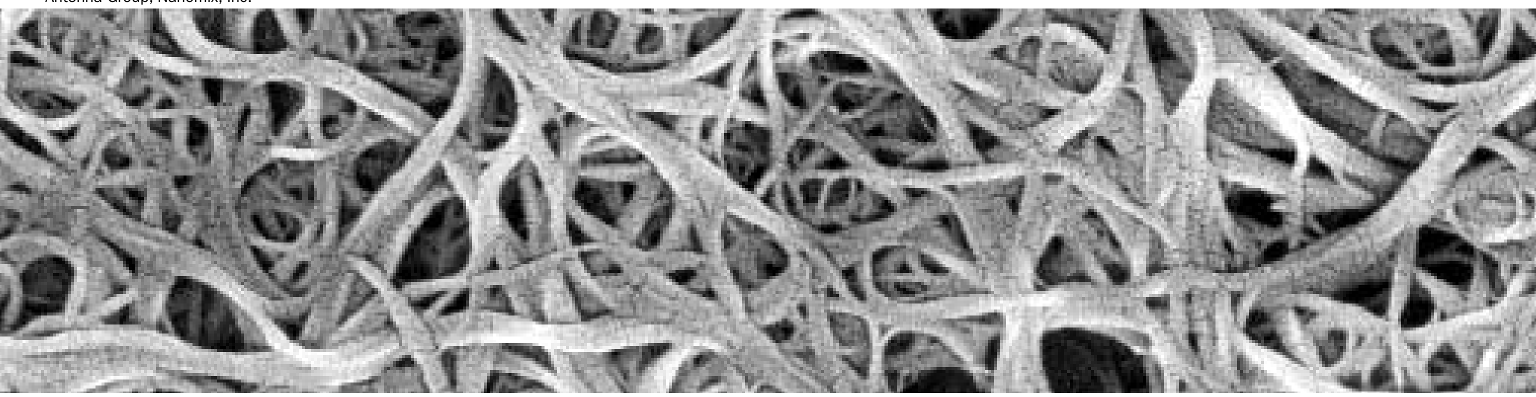


Figure 1. Scanning electron micrograph of single-wall carbon nanotubes grown with the high-pressure carbon monoxide process.

Single and multiwall

Discovered by Sumio Iijima of NEC Laboratories in Japan, carbon nanotubes are an outgrowth of the formation of carbon fullerenes, such as the C_{60} buckyball molecule. There are two basic types of nanotubes. Single-walled nanotubes (SWNTs) have one shell of carbon atoms in a hexagonal arrangement (Figure 1). Multiwalled nanotubes (MWNTs) consist of multiple concentrically nested carbon tubes, similar to the rings of a tree trunk (Figure 2). Each type has its advantages and disadvantages. MWNTs are easier and less expensive to produce because current synthesis methods for SWNTs result in major concentrations of impurities that require removal by acid treatment. But MWNTs have a higher occurrence of structural defects, which diminishes their useful properties. Some companies prefer SWNTs because they do not have such defects and their properties are consequently stronger. David Tomanek, a professor of physics at Michigan State University, helped found the start-up venture Rosseter Holdings on the island of Cyprus, which produces both types of carbon nanotubes. He believes that each of the nanotube forms will find applications for which they are best suited. For example, MWNTs will likely become the material of choice for structural reinforcement, where low price matters more than high purity (Figure 3). SWNTs will likely dominate computer circuitry if researchers can better control their diameter, which determines their properties.

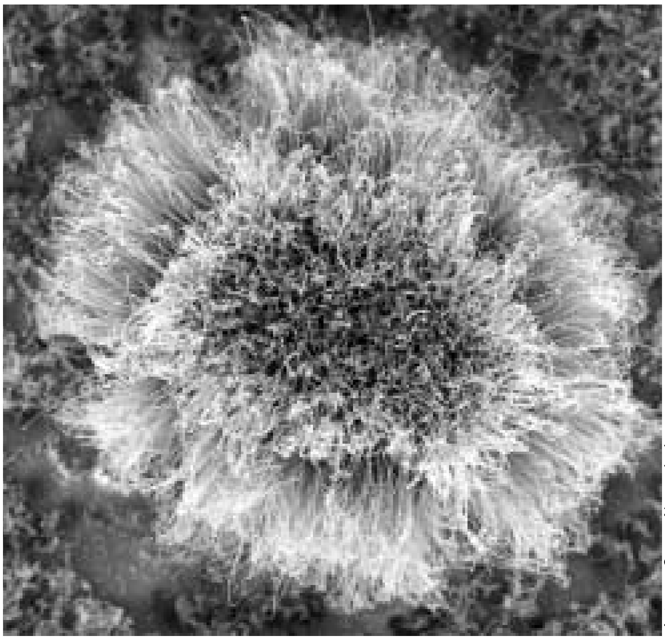
The excitement about carbon nanotubes stems from their unique properties. "There are hundreds of properties, and behind each property is a business," says Charles Janac, chief executive officer of Nanomix, Inc. (Emeryville, CA). Carbon nanotubes, for example, self-assemble from carbon vapor and can show structural perfection on the atomic scale, maintain large currents, and withstand high temperatures, and they are mechanically rigid.

Nanotubes can be combined to form the strongest material known, which Richard Smalley of Rice University, who pioneered the field with his co-discovery of buckyballs in 1985, estimates to be between 30 and 100 times stronger than steel. Yet because nanotubes are hollow, they are lightweight. They are also transparent to visible light and absorb ultraviolet light, and are excellent conductors of electricity. "If it is a perfect SWNT, electrons will flow down the structure in a coherent quantum waveguide that is unparalleled in any other structure we know," says Smalley.

Key developments

Translating any new material into a commercial industry is a daunting challenge. James Ellenbogen, senior principal scientist of Mitre Corp.'s nanosystems group (McLean, VA), cites four key recent developments that have helped bring carbon nanotubes to the brink of broad commercialization. The first is a greater understanding and better physical characterization of the materials and a corresponding awareness of their unique properties and potential applications in the commercial sector. Second, the U.S. government instituted the National Nanotechnology Initiative three years ago, whose funding is expected to reach $700 million in fiscal year 2004. The project has encouraged researchers, small start-ups, and large corporations to invest time and money in nanotube development.

A third factor is the emergence of applications. Although nanotubes first gained the interest of the electronics industry with the demonstration of nanotube transistors in the late 1990s, the first commercial uses were as structural reinforcements in composites and as an additive to graphite in lithium-ion batteries. Today, batteries used in about 60% of cell phones and notebook computers contain carbon nanotubes. "These batteries use MWNTs. They are not perfect, but they fulfill their function by making the battery last longer, making it more recyclable, and improving the energy delivery," says Tomanek.



Antenna Group, Nanomix, Inc.

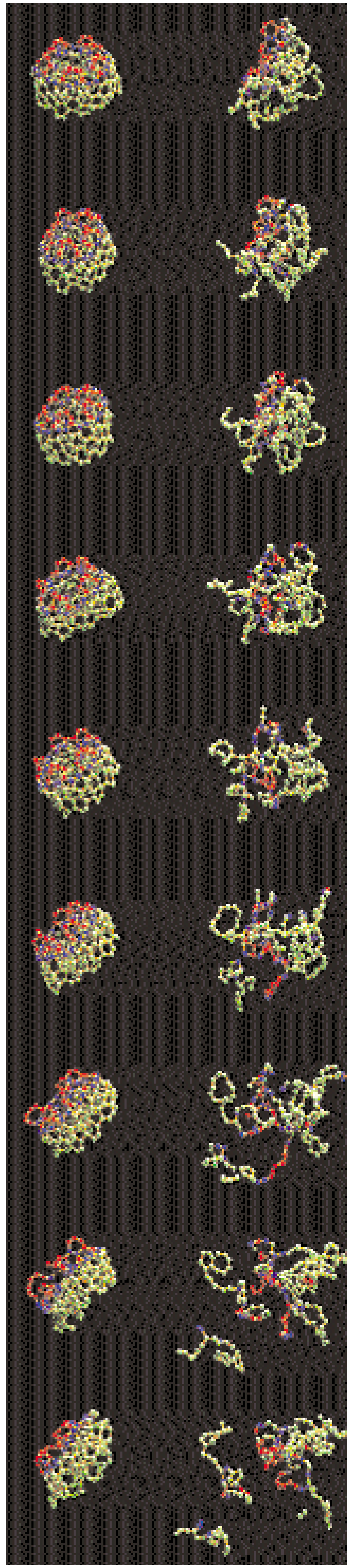
Figure 2. Scanning electron micrograph of mutliwall carbon nanotubes grown with chemical vapor deposition.

Finally, and most critical, is the recent development of mass production techniques. Ray Baughman of the University of Texas, Dallas, reports that high-purity samples of SWNTs cost about $750 per gram, and even SWNTs with substantial amounts of impurities cost about $60 per gram. "Carbon nanotubes are probably the most expensive material, pound for pound, in the world," agrees Ellenbogen. "If you could lower the cost through mass production, you could essentially remake the world out of carbon."

In the early 1990s, Hyperion Catalysis International, Inc. (Cambridge, MA), pioneered the production of MWNTs in multiton quantities, but access to the material remained limited because its purchaser agreements restricted the independent pursuit of patents by its customers. Baughman and others expect other large-scale producers of MWNTs to emerge after 2004, when Hyperion's 1987 patent, under which it makes nanotubes, expires. Mitsui Corp. plans to build a $15.2 million production facility in Japan capable of producing 120 tons of MWNTs annually. Smalley and his Rice University colleagues developed a high-pressure carbon monoxide (HiPco) flow method in 1999 capable of producing larger amounts of high-purity SWNTs. That method has become the basis for a spin-off company, Carbon Nanotechnologies, Inc. (CNI), based in Houston, and Smalley is now exploring ways to spin carbon nanotubes like spider webs (Figure 6).

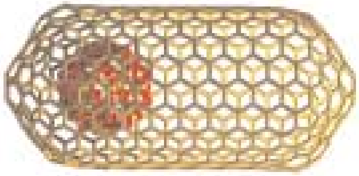
More recently, scientists have created nanoscopic "peapods," in which fullerenes are nested within nanotubes, similar to peas in a pod. The new materials have tunable electronic properties that are strongly dependent on their location along the tube, which means the discovery could have far-reaching implications for the fabrication of single-molecule-based devices (Figures 4 and 5).

There are currently between 50 and 100 producers of nanostructured carbon materials worldwide, but most are academic institutions that make small amounts



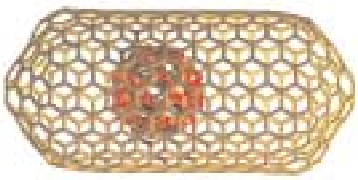
David Tomanek, Michigan State University

Figure 3. Eighteen snapshots from a computer simulation depicting the disintegration of a double-wall nanotube as the temperature rises from absolute zero to 7,800 K. The full animation is shown at http://www.pa.msu.edu/cmp/csc/simtubemlt.html.

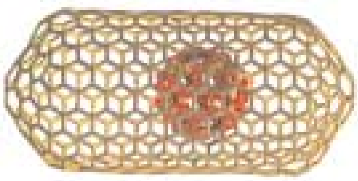


for research. Daniel Colbert, CNI's vice president for major development strategy, reports that demand for its SWNTs is growing exponentially, and he believes that SWNTs will be cost-effective in many markets. "Our pilot unit is producing much more material, and there are more and more interested parties," he says. "Rather than working on the scale of grams or tens of grams, our customers want us to work on the kilogram scale. Meeting the demand is a challenge, and we are on track to meet that demand by 2005."

CNI is targeting four key application areas—field-emission flat-panel displays, conductive plastics, high-performance fibers, and advanced composite bulk-structural materials—which Colbert estimates represent about a $5 billion market value just for the SWNT sector.



NanoDevices (Santa Barbara, CA) designed its EasyTube NanoFurnace to enable researchers to quickly and easily produce both SWNTs and MWNTs. The company shipped its first production units in early 2002. The NanoDevices design uses the carbon decomposition and catalyzed chemical vapor deposition technique to produce SWNTs and MWNTs directly on the surface of device substrates. It controls the species of nanotube through the selection of process gases. The direction and location of the nanotube growth can be controlled by rationally designing substrates and appropriately patterning the catalyst.



Applications

The next major commercial use of nanotubes probably will be that of SWNTs in field-emission flat-panel displays. Their advantages over standard liquid-crystal displays include lower power consumption, higher brightness, a wider viewing angle, faster response rate, and a wide operating-temperature range. But nanotube displays are technically complex and require concurrent advances in electronic-addressing circuitry, low-voltage phosphors, methods to maintain the required vacuum, and the elimination of faulty pixels.

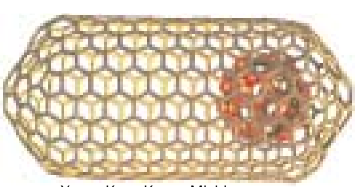


Figure 4. Four snapshots from a computer simulation depicting a nanotube-based memory element in which the two stable positions of the red metallofullerene at the ends of the capsule can be associated with "bit 0" and "bit 1." The full animation is shown at http://www. pa.msu.edu/cmp/csc/memory.html.

Young-Kyun Kwon, Michigan State University

Despite these inherent difficulties, Samsung (Tokyo, Japan) has developed a prototype full-color display, which it expects to introduce commercially by December 2003. Although display panels are a small market economically, the application is a high-profile one that should help pave the way for other uses. "There is nothing wrong with making what we call a dirty device. It is not perfect, but it works well, is reproducible and cost effective, and is better than what is on the market," says Kuper.

Conductive plastics are used for electrostatic dissipation in electronic devices, electromagnetic-interference shielding, and composite bulk-structural materials, primarily for aircraft, spacecraft, and sporting equipment such as golf clubs, but also as coatings for electronics, gaskets, and other components. Nanotubes can also be used to make high-performance fibers with double the energy absorption and increased tensile strength, and for efficient, flexible, low-cost sensors for gas-leak detection, medical monitoring, and industrial process control.

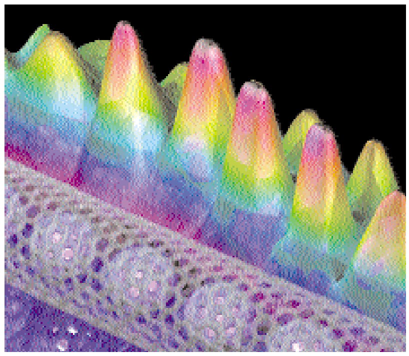


Figure 5. Depiction of a single-wall carbon nanotube peapod with C_{60} molecules encapsulated inside and the electron waves, mapped with a scanning tunneling microscope.

D. Hornbaker and A. Yazdani, University of Illinois

Nanomix plans to introduce its first leak-detection sensors made from carbon nanotubes in the second half of 2003. Such sensors are extremely small, sensitive, and low in power consumption, and can be customized to react to different chemicals. More importantly, they are inexpensive. A modern oil refinery will likely have several dozen chemical sensors to detect hydrocarbon leaks, each costing approximately $3,000. Nanosensors could cost as little as $50 each. Seiko Instruments (Chiba City, Japan) uses carbon nanotubes in the scanning-probe tips it now markets, Baughman says. The mechanical robustness and low buckling force of nanotubes dramatically increase probe life and minimize sample damage, and the cylindrical shape and small tip diameter improve resolution.

Baughman's recent work builds on his discovery that carbon nanotubes exhibit an unusual actuator effect: the tubes increase their length if the number of electrons on a tube is changed, a useful property for building artificial muscles. He and a multinational group of collaborators have demonstrated the effect using "bucky paper," a film made of bundles of SWNTs. He believes that the electromechanical actuators could open a vast field of new applications if bucky paper is used as a macroscopic material and if ropes or even individual carbon nanotubes were to be used for micro- and nanoactuator devices.

Otto Zhou of the University of North Carolina at Chapel Hill has developed a novel new X-ray machine that does not require high temperature to generate the high-energy electrons needed to produce X-rays. It uses a thin layer of carbon nanotubes operating at room temperature instead of the usual metal filaments heated inside a vacuum chamber. Because high operating temperatures easily burn out the metal filaments, the new devices will last longer. And because the devices are smaller and can operate at room temperature, it should be possible to develop portable X-ray machines for use in ambulances, airport security, and customs operations. Zhou and his colleagues are working with physicians and Applied Nanotechnologies, Inc. (Chapel Hill, NC), to market the X-ray machines within two years.

The unique properties of carbon nanotubes also make them one of the most promising candidates for a new nanoelectronic technology. They are thin (as narrow as 1 nm), but producers can control their growth up to many micrometers. They are also mechanically strong, thermally and chemically stable, and excellent heat conductors, and can be either metals or semiconductors, depending on the arrangement of their atoms. An IBM team led by Phaedon Avouris made the first arrays of nanotube transistors in early 2001, and later that year, Cees Dekker's group at the University of Delft in The Netherlands used nanotube transistors to build logic circuitry.

IBM's latest innovation reconfigures the transistor so that nanotubes are not exposed to air, and it shrinks the channel length and thickness of the dielectric layer between the gate electrode and the channel, which improves current flow. The new transistor has twice the transconductance of state-of-the-art conventional metal-oxide semiconductor field-effect transistors used in many fast electronic devices. Ellenbogen cautions that scientists still need to fabricate circuits that are at the molecular scale in their entirety, not just in their components. There is also a need for better heat dissipation and interconnects to achieve ultradense architectures, perhaps as many as 1 trillion devices/cm^2, compared with only 10 to 50 million devices/cm^2 in today's silicon devices.

Challenges

Tomanek points out that carbon nanotubes have excellent heat conductance, which is superior to that of any other material. He believes this property of carbon nanotubes will play the key role in their application in electronics. However, notes Baughman, "Silicon technology is so entrenched that it will take an overwhelmingly compelling new technology to replace it. Carbon nanotubes do not yet qualify, but the potential payoff is so great that the research is amply justified, even from a commercial viewpoint."

Despite the emergence of large-scale flow methods such as HiPco, nanotube production still faces many

Carbon Nanotechnologies, Inc., Houston

Figure 6. This pilot plant produces single-wall carbon nanotubes by a high-pressure carbon monoxide flow method and is expected to produce thousands of kilograms a week by 2005.

processing challenges. They include a strong tendency for nanotubes to agglomerate and their inability to maintain long-term order, which directly relates to exploiting the material's unique properties. Another problem is sorting nanotubes by electrical type, an important capability for fuel-cell applications and such longer-term uses as biological materials and embedded membranes.

Smalley identifies the availability of high-quality material as "the single biggest limiting factor" to quickly moving nanotubes into the commercial marketplace. "All these potential applications require SWNTs in commercial production at acceptable prices, almost certainly less than $1,000 per pound and perhaps as low as $100 per pound," he says. CNI hopes to produce thousands of kilograms of SWNTs a week by 2005. Still, Colbert admits, "Our processes are not yet as good as they will be. But it is part of the normal learning curve, and we anticipate selling into many markets." Mark Harmon, R&D manager for Carbon Solutions, Inc. (Riverside, CA), identifies impurities and high cost as the two largest obstacles to mass commercialization, although improved purifying methods have lowered prices substantially.

And although there are plenty of potentially lucrative markets, nanotubes have thus far only found their way into a few niche markets. Tomanek believes that the true commercial breakthrough for carbon nanotubes will ultimately be something scientists haven't envisioned yet. "When Charlie Townes invented the laser, he had no idea the largest application would be in the checkout counter at the supermarket," he says. "I expect the same will be true for carbon nanotubes." Ω