Superstrong Nanotubes Show They Are Smart, Too

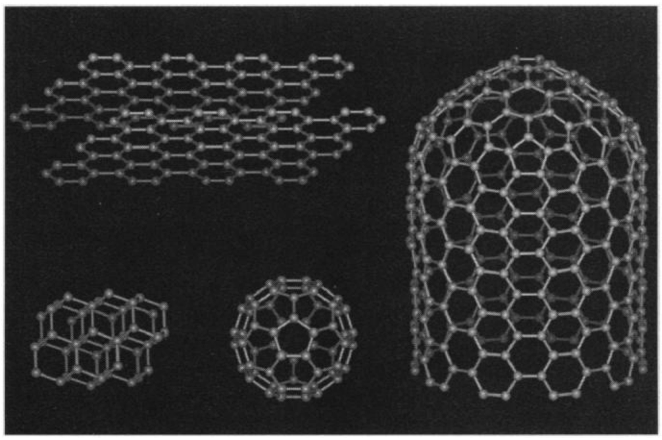
NEWS

Fullerenes may get all the headlines, but their tubular cousins have a range of electronic and mechanical abilities that will soon thrust them into the spotlight

Just 2 years ago, chemist Richard Smalley of Rice University in Houston, Texas, shared the Nobel Prize in chemistry for his part in discovering an entirely new form of carbon: spherical molecules dubbed fullerenes that are radically different from the stacked sheets of graphite and the glittering pyramidal matrix of diamond. But ask Smalley what interests him today, and he doesn't mention the prizewinning spheres. What's captured his interest and that of hundreds of other scientists are nanotubes, the fullerenes' elongated cousins.

First discovered 7 years ago by Japanese electron microscopist Sumio Iijima, nanotubes are essentially tiny strips of graphite sheet, rolled into tubes and capped with half a fullerene at each end. They are just a few billionths of a meter, or nanometer, across and up to 100 micrometers long. And although they may resemble nothing more glamorous than microscopic rolls of chicken wire, nanotubes have emerged as stars of the chemistry world. They're stronger than steel, lightweight, and able to withstand repeated bending, buckling, and twisting; they can conduct electricity as well as copper or semiconduct like silicon; and they transport heat better than any other known material.

With this roster of qualities, nanotubes "have to be good for something," Smalley is fond of saying. Indeed, there's no shortage of ideas. The current list of possible uses includes: superstrong cables, wires for nanosized electronic devices in futuristic computers, charge-storage devices in batteries, and tiny electron guns for flat-screen televisions. "I think it's inevitable that there will be a whole field of organic chemistry devoted to analyzing, [functionalizing], and separating these things," says Smalley.



RICE UNIVERSITY

Carbon's contortions. Clockwise from top left: graphite, a nanotube, a fullerene sphere, and diamond.

Cast your mind back 13 years ago to the discovery of fullerenes, and the hype may sound familiar. But this time around, researchers are confident that the promise will become reality—if they can solve some nagging fabrication problems. At least one Massachusetts materials company is convinced: Hyperion Catalysis International is already manufacturing nanotubes in bulk for use in plastics for the automotive and computer industries. The tubes help the normally insulating material conduct electrical charges away and prevent the buildup of static electricity. And researchers are already beavering away at more challenging tasks, such as turning nanotubes into electronic devices, battery components, and display elements. In comparing the likely utility of nanotubes and fullerenes, nanotube researcher Alex Zettl of the University of California, Berkeley, says: "If I were to write down all the different applications, I'd have a sheet with fullerene applications and a book for nanotubes. There's orders-of-magnitude difference in the potential."

In the pipeline

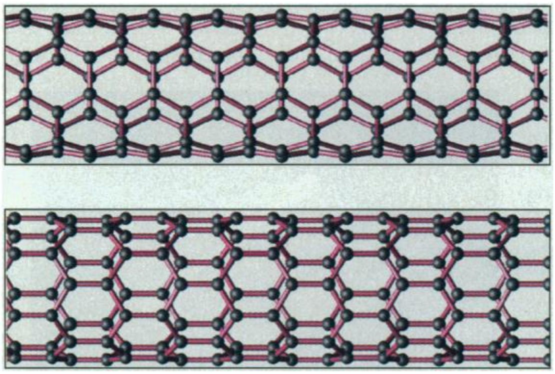
The key to this potential lies in the unique structure of nanotubes and the defects that can form in their network of carbon bonds. Nanotubes come in two classes: One, called single-wall nanotubes (SWNTs), is made up of just a single layer of carbon atoms; the other, multiwalled nanotubes (MWNTs), consists of up to dozens of concentric tubes wrapped one inside another like a coaxial cable. MWNTs—the type Hyperion is making—are typically riddled with defects, because as the tubes take shape, defects that form get trapped by overlying tubes. Single-wall tubes, by contrast, are often defect free. The defects, or lack of them, "are terribly important," says Smalley. "Virtually all of the special properties of nanotubes derive from their perfect graphitic structure."

That structure depends on the unique properties of its building material—carbon. Carbon is the elemental equivalent of the perfect neighbor, friendly and easygoing. Under intense pressure, carbon atoms form bonds with four neighboring carbons, creating the pyramidal arrangement of diamond. But carbon regularly forgoes that fourth bond and links up with just three neighbors, creating graphite's network of hexagonal rings. This arrangement leaves graphite with a host of unpaired electrons, which essentially float above or below the plane of carbon rings. In this arrangement, the electrons are more or less free to buzz around graphite's surface, which makes the material a good electrical conductor.

But graphite has one weak point—its edges. Carbon atoms at the border of a graphite sheet are out on a limb, with additional unattached bonds looking for something with which to react. That's what makes nanotubes possible. When carbon vapor is heated to some 1200 degrees Celsius, carbon rings assemble, creating a small graphite sheet. But the edges are so energetically unstable that the graphite sheet begins to curl until two edges knit themselves together. Additional carbon rings come along to form the end caps, creating the quintessential nanotube. Because it lacks any edges at all, the tube is very stable.

Like graphite, nanotubes have roving electrons that can move freely among the carbon rings. "The tubes inherit this same property," says Smalley. Theorists suggested early on that nanotubes should be good conductors, but it was not until the past year that teams have confirmed this with the help of scanning tunneling microscopes (STMs) that can pin down individual tubes and measure their conducting abilities. It is this area—using nanotubes as electronic materials—that is currently exciting the most interest among nanotube researchers. Several reports have recently demonstrated that SWNTs can function not only as conductors but also as semiconductors that can carry an electrical current under some conditions but not others. The demonstration created a buzz because semiconductor switches form the heart of computers.

Defects appear to be the key to this dual behavior. In January, teams led by Cees Dekker at Delft University of Technology in the Netherlands, as well as Charles Lieber at Harvard, confirmed theoretical predictions that the conducting properties of nanotubes are linked to the arrangement of hexagonal carbon rings around the tube. When those hexagons line up along the long axis of a nanotube, the tube conducts as easily as a metal. But twist the hexagons so that they spiral around the tube, and it will conduct like a semiconductor, carrying current only after a certain threshold voltage is applied to push it through.



VINCENT H. CRESPI/PENNSYLVANIA STATE UNIVERSITY

Twister. In-line carbon hexagons *(top)* conduct easily, while spiraling hexagons make a semiconductor.

If you can make nanotubes with two different characters, why not a single tube with a split personality? Last fall, Zettl's group isolated a single nanotube that had one metallic region and another semiconducting region (*Science*, 3 October 1997, p. 100). The hybrid tube is the result of a specific defect: Adjacent six-carbon hexagons are replaced by a five-carbon pentagon linked to a seven-carbon heptagon. This defect changes the way the rest of the hexagons wrap around the tube. One end of the tube, made up of spiraling hexagons, behaves like a semiconductor, while the other end—composed of hexagons in straight lines—is a metallic conductor. Such tubes, Zettl's group showed, can act as a molecular diode, a device that allows electrical current to flow in one direction, from a semiconductor to a metal, but not in reverse.

And researchers keep coaxing their tiny tubes to display new electronic talents. In the 12 June issue of *Science* (p. 1744), Walt A. de Heer, a physicist at the Georgia Institute of Technology in Atlanta, and his colleagues confirmed another theoretical prediction: that nanotubes can carry current at room temperature with essentially no resistance, thanks to a phenomenon known as ballistic transport. De Heer likens the normal flow of electrons to water coursing down a river, slowed by the constant friction with the riverbed and collisions with rocks. Ballistic transport is more akin to water after it has spilled over the lip of a waterfall: It simply flies through space, unimpeded by friction or collisions.

De Heer's group showed, by measuring the electrical transport down individual MWNTs, that if a tube has even one defect-free layer, electrons can stream through the tube without scattering off defects or atoms. "The upshot is that they move freely without losing energy," says de Heer. Researchers have achieved ballistic transport in other types of electronic devices, but usually over very short distances and at temperatures just a whisker above absolute zero. Ballistic transport in nanotubes is akin to the way photons fly down optical fibers without losing energy. "We're coming into an area where electronics starts to resemble optics," says de Heer. "It gives you all sorts of options for making low-loss circuitry," says Smalley. "And mind you, that's at room temperature. Room temperature!"

Although these demonstrations have come just in the past year, several groups have already begun to move on to making ultrasmall electronic devices. In the 7 May issue of *Nature*, Dekker's team reported the creation of the first room-temperature, nanotube-based

Nanotubes: The Next Asbestos?

The unrivaled mechanical properties of nanotubes, and their potential for molecular-scale electronic devices, are firing the imaginations of chemists across the world. But there is potentially one very big fly in the ointment: toxicity. Nanotubes are rigid graphite cylinders, each just one or more nanometers wide and up to 100 micrometers long. It just so happens that this resembles the shape of asbestos fibers that have been linked to cancer. Could nanotubes be toxic? "Certainly it's a concern," says Chunming Niu, a chemist with Hyperion Catalysis International, a company based in Cambridge, Massachusetts, that produces carbon nanotubes.

The dangers of asbestos first came to light in the early 1960s, when studies linked exposure to these silicate fibers with mesothelioma—a rare cancer of the lining of the chest or abdomen that's commonly fatal. Asbestos fibers were found to be so small that they could be inhaled into the deep lung, where they could stick around for decades. Once there, metals in the silicate fibers could act as catalysts to create reactive oxygen compounds that go on to damage DNA and other vital cellular components.

Whether nanotubes could reproduce this behavior is unknown: Their toxicity has yet to be tested. But already views on their safety differ sharply. "[Nanotubes] may be wonderful materials," says Art Langer, an asbestos expert at the City University of New York's Brooklyn College. "But they reproduce properties [in asbestos] that we consider to be biologically relevant. There is a caution light that goes on." Most notably, says Langer, nanotubes are the right size to be inhaled, their chemical stability means that they are unlikely to be broken down quickly by cells and so could persist in the body, and their needlelike shape could damage tissue.

DEHEER *ET AL.*

Toxic tubes? Nanotubes physically resemble asbestos fibers but without their catalytic effect.

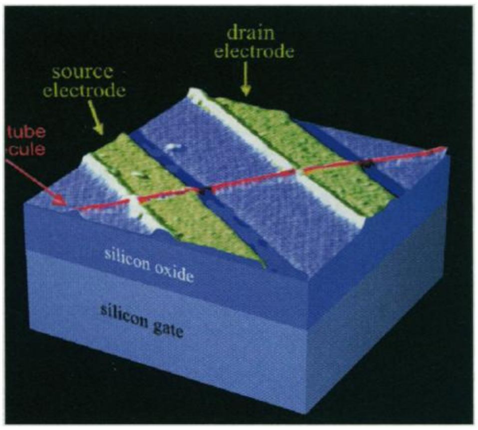
For those reasons, Niu says that Hyperion is careful about how it handles the material: "We treat our nanotubes as highly toxic material." The company produces about 300 kilograms of multiple-walled nanotubes every day and ships them to clients for use in electrically conducting plastics. But rather than shipping the nanotubes as a powder, Niu says Hyperion first incorporates the tubes into a plastic composite so that they cannot be inhaled.

Researchers such as Brooke Mossman, however, doubt that nanotubes will turn out to be dangerous even if they find their way into the body. Mossman, a pathologist and asbestos expert at the University of Vermont College of Medicine, notes that it is the ability of asbestos to generate reactive oxygen compounds that makes it carcinogenic. But the graphitic carbon structure of nanotubes is not likely to react with cellular components to produce damaging byproducts. "We've worked with a lot of carbon-based fibers and powders and not seen any problems," says Mossman.

Richard Smalley, a nanotube chemist at Rice University in Houston, agrees. In addition to being unreactive, most nanotubes when synthesized come out as a tangled mass of fibers rather than individual spears, he says. Ironically, his team recently developed the first technique to cut individual nanotubes into short, spearlike segments (*Science*, 22 May, p. 1253). But for now only a few grams of those tubes exist. Until more research determines whether nanotubes are dangerous, researchers are treating them with caution. –R.F.S.

transistor. To construct the device, Dekker and his colleagues simply laid a semiconducting nanotube across a pair of tiny gold pads grown atop an insulating layer of silicon dioxide. The silicon dioxide itself sits on a layer of silicon that served as the "gate" to switch conduction in the nanotube on and off. When the researchers applied no voltage to the gate, current was unable to pass through the nanotube from one gold pad to the other. But when they applied a voltage to the silicon layer, this created charge carriers in the nanotube, allowing current to flow between the two gold pads.

The nanotube device didn't make a particularly great transistor, for it made poor electrical contact with the gold pads. But de Heer calls it a landmark achievement nonetheless, because "it shows that these are leading to real applications." Smalley echoes the sentiment, again underscoring the point that these nanodevices work at room temperature. "It means the old dreams of molecular electronics can be redreamed," he says. And none too soon. Smalley points out that the semiconductor industry's own timeline shows that by 2006 it will have reached a physical limit of current technology to shrink silicon-based transistors. Carbon nanotubes, say Smalley and others, may be a strong contender for silicon's replacement.



Tube transistor. The switch made by lying a nanotube across contacts atop a silicon chip.

A. W. DUNN AND C. DEKKER/DIMES/DELFT UNIV. OF TECHNOLOGY

Working stiff

Even without those dazzling electronic possibilities, nanotubes' unmatched mechanical properties would still make them candidates for stardom. Nanometer for nanometer, nanotubes are up to 100 times stronger than steel. When a group led by Harvard's Lieber tested the bending strength of tubes on the end of an atomic force microscope (AFM), they found that they easily beat the stiffest silicon-carbide nanorods that are used to make high-strength composites. "This is the stiffest stuff you can make out of anything," says Smalley. Try to have a nanosized tug-of-war by pulling on opposite ends of a nanotube, and you won't find much give. "It doesn't pull apart," says Zettl.

Down the road, the stiffness of nanotubes could make them great for building strong, lightweight composites. However, they're already coming in handy for improving the capabilities of the sharp, needlelike tips of atomic imaging machines. Such imagers scan their pointed silicon tips over a surface and map its contours by either letting the tip touch the surface—in an AFM—or holding it close and passing a current from tip to surface—in an STM. When it comes to seeing fine contours, however, the normally squat tips have trouble reaching down inside atomic-scale crevices.

But in 1996 Smalley and his group showed that they could image the bottom of these trenches by attaching a carbon nanotube to the end of a silicon STM tip. Lieber and his colleagues quickly picked up on the idea as a way to obtain better images of biological molecules which, because of their pliability, posed even more of a problem for standard STM tips. Earlier this year, they reported in the *Journal of the American Chemical Society* that a nanotube-based tip did indeed allow them to create images of biological molecules with better resolution than that of conventional tips. Lieber and his team extended this feat with a report in the 2 July issue of *Nature* that they had attached different chemical groups to the end of a multiwalled nanotube, creating a nanotube-based atomic imager capable of recognizing specific chemical groups on a surface, and therefore recording not just the surface contours but identifying the actual molecules as well.

"It's great work," says Chunming Niu, a nanotube researcher at Hyperion Catalysis. An array of nanotube probe tips, each outfitted with different functional groups, could offer researchers an entirely new way to map surfaces. That could be particularly useful to biotech researchers interested in mapping the structure of cell membranes and other cellular structures, says Niu. Indeed, Lieber says that he and his Harvard colleagues are already hard at work on such applications.

Gears to guns

Compared to some potential applications of nanotubes, improving the performance of STMs may even seem unimaginative. Take the case of the nanotube gear. Researchers at NASA's Ames Research Center in Mountain View, California, have recently developed computer models of nanotube gears that have benzene groups arrayed around the tube to act as cogs. As one of these nanocylinders rolls, its tiny teeth turn the nanotube like a microscopic drive shaft.

Nanogears are likely to remain simulations for some time, however, as there's no obvious way to build them. But other seemingly exotic applications are nearing reality. In 1995, de Heer—then at Ecole Polytechnic Fédérale de Lausanne in Switzerland—and colleagues wired up an array of nanotubes to act as tiny electron guns, similar to the large-scale devices that scan the back of TV screens and generate color images. At the time, de Heer suggested that the tiny electron guns could someday be used to create flat-screen televisions. That day is fast approaching. At the Second International Vacuum Electron Sources Conference last month in Tsukuba, Japan, Yahachi Saito and his colleagues from Mie University and Ise Electronics Corp. unveiled the first nanotube-based display lighting elements (*Science*, 31 July, p. 632). Saito says he hopes to commercialize flat-panel displays using the new nanotube electron guns by the year 2000.

Other researchers are also looking into using nanotubes as a storage medium for both hydrogen gas to power fuel cells and liquid electrolytes for batteries. Hydrogen-burning fuel cells, for example, are widely considered to offer a promising clean technology for powering cars. The technology's Achilles' heel, however, is the gas tank, because high pressures are needed to store enough hydrogen to drive very far. But open-ended nanotubes can, at just below room temperature, suck up and hold onto large amounts of hydrogen with little added pressure. Raising the temperature slightly shakes the adsorbed hydrogen loose and releases the gas, making nanotubes a near-ideal hydrogen storage medium, easily beating out the current competition. "The attractive interaction between hydrogen and carbon allows you to reduce the amount of pressure you need" to store hydrogen, says Donald Bethune, a physicist at IBM's Almaden Research Center in San Jose, California, who has pioneered research in the area.

Mass production

Before these potential applications can move out of the lab, however, researchers must overcome a very large hurdle: producing enough of the stuff. Hyperion uses a catalytic process to produce hundreds of kilograms of MWNTs every day. But any industrial process is going to require tons. The situation is even worse for the more highly sought-after SWNTs, which today can be made only by the handful. A start-up company in Lexington, Kentucky, called CarboLex has recently begun selling SWNTs for about $200 a gram. At those prices, nanotubes won't be replacing graphite in tennis rackets anytime soon.

"We're still sort of stuck" in efforts to produce the tubes in bulk, says Smalley. But he is optimistic that new synthetic schemes will solve this problem. "I believe that within 10 years, some smart aleck will find a way to grow single-wall nanotubes from the gas phase off of little catalyst particles in ton amounts, just like polypropylene," says Smalley. If so, the tiny tubes face a big future.

–ROBERT F. SERVICE