



## The Carbon Nanotube - Miracle Material

by John G. Cramer

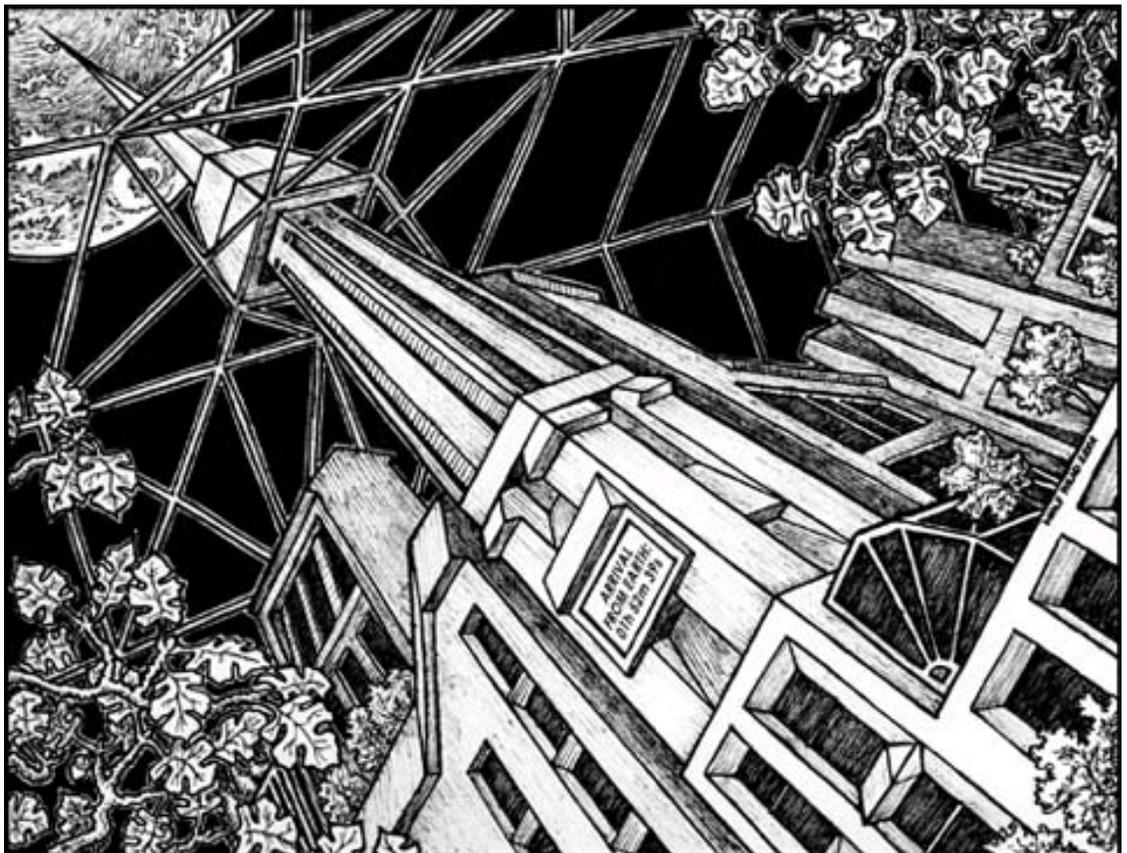
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Suppose you read a science fiction story in which a new material had been discovered. It was supposed to conduct electricity better than copper or silver, but it could also be made into a semiconductor for transistor fabrication. It was far stronger than steel, strong enough to support much more than its own weight as a fiber hanging down to the surface of the Earth from geosynchronous orbit, yet so compact that such a fiber long enough to reach from Earth to Moon could be rolled up and stored inside a poppy seed. The material could absorb and store vast



quantities of hydrogen, thereby storing fuel for powering fuel cells and pollution-free automobile engines. It could also change its length by 10% in an electric field, forming an artificial muscle, and could be used in reverse to produce electrical energy when flexed, for example by wind or ocean waves. It could be used to emit electrons to make wall-size ultra-thin video displays. It could be used to cut or strengthen other materials. And it was made from one of

the commonest of materials of all, ordinary soot.

I think you will agree that a story line involving such a material would strain your suspension of disbelief to the breaking point. How could the author ask us to swallow such a ridiculous fabrication? And yet, there is an actual material that, even as you read this, is emerging from the physics laboratories of the world, and it has all of these properties. It is the carbon nanotube, a new form of carbon discovered in 1991.

The nanotube is a molecular cousin of a form of carbon that is perhaps more familiar, the  $C_{60}$  molecule or buckyball, an array of 60 carbon atoms forming a soccer-ball-like icosahedron. If the buckyball could be sliced in half, with a "belt" made of a connected loop of 10 carbon atoms inserted in the cut, it would form another stable configuration, a  $C_{70}$  molecule that is a larger and somewhat elongated buckyball. If instead one inserted two or three 10-carbon loops, this would make even more elongated  $C_{80}$  or  $C_{90}$ . The process could be repeated to produce an arbitrarily long tube, with endcaps made of half-buckyball hemispheres. The object thereby produced is a species of carbon nanotube.

Alternatively, a nanotube might be produced by starting with a planar one atom thick sheet of graphite. Graphite is an array of linked carbon atoms lying in a plane, with the carbons forming the vertices of linked hexagons, like the cross section of a honeycomb. In principle, a skilled nano-tailor could cut a strip out of such a graphite sheet, join the cut edges to form a tube, and then cap the open tube ends with half buckyballs. Again, the result is a carbon nanotube.

However, there are several ways that the nano-tailor could have cut the strip from the graphite sheet. A graphite sheet of hexagons can be oriented so that one set of hexagon sides is vertical. In this case, a horizontal cut along a row of hexagons goes alternately up and down in a zig-zag, following the hexagon edges. This is called a "zig-zag" cut.

If the strip used to form the nanotube is made such that the open end of the rolled tube forms such a zig-zag, it is called a *zig-zag nanotube*.

If the length of the strip along this edge spans, say 6 hexagons, then the resulting nanotube is identified as having the index (6,0).

The first number is related to the circumference of the nanotube and the following 0 tell us it as the zig-zag configuration.

On the other hand, the graphite sheet could also have been oriented so that one set of hexagon sides was horizontal.

In this case, a horizontal cut along a row of hexagons goes up, across, down, and across, following the edges. This is called an "armchair" cut because the cut line resembles a row of armchairs arranged side-by-side. If the strip used to form the nanotube is made such that the open end of the rolled tube forms such an armchair pattern, it is called an armchair nanotube.

If the length of the strip along this open edge spans, say 6 ups and downs, then the resulting nanotube is identified as having the index (6,6).

For all armchair nanotubes, the second index number must match the first, and is related to the circumference of the nanotube.

There are also "chiral" nanotubes that, if viewed end-on, show a clockwise or counter-clockwise spiral pattern. These are intermediate between the zig-zag and armchair configurations and are characterized by the index (m,n), where  $0 < n < m$  for counter-clockwise spirals and  $0 < m < n$  for clockwise spirals.

Some, but not all, nanotubes are good electrical conductors. This is because nanotubes are small enough that quantum mechanical effects dominate their electrical conductivity. In particular, the quantum wave functions of the conduction electrons are either reinforced or destroyed by the symmetries of the nanotube. For example, nanotubes with indices (6,0), (6,6), (9,0), and (9,9) are all excellent electrical conductors. On the other hand, nanotubes with indices (7,0), (8,0), (6,2), and (7,5) are all semiconductors, materials in which there are no free conduction electrons. If a nanotube is an electrical conductor at all, it is a very good conductor indeed, because the electrical conduction is the result of coherent participation by all the carbon atoms in the nanotube. Consequently, nanotubes have a theoretical maximum current density that is 1000 times higher than that of excellent metallic conductors like silver and copper.

We find that nanotubes produced in a strong electric current often form concentric multi-layer nanotubes. For example, published electron microscope images show nanotubes with two, five, and seven concentric walls. Theoretical calculations show that it should be fairly easy to produce such concentric nanotubes with layers that are alternately insulators and conductors. Therefore, a nanotube “coaxial cable” with a conducting core and conducting jacket separated by one or more insulating layers should be possible. Such a nanotube should have interesting applications, not only for signal transmission at the nanoscale, but also for creating linear capacitors with a very high capacitance for storage of electrical energy.

The semiconductor nanotubes also have their uses. Scientists at IBM have deposited nanotubes randomly on a microchip pattern of conducting copper, then applied a large current pulse to burn away the conducting nanotubes. They have then demonstrated field-effect transistor behavior in surviving semiconductor nanotubes.

Nanotubes are among the sharpest objects in nature, leading to other interesting electrical applications. If a sharp object is placed at a high electrical potential, an extremely large electric field develops near the pointed end. If the pointed tip is made electrically negative, it will emit electrons that are accelerated in the strong field. This phenomenon is called *field emission*. Samsung Electronics has produced a prototype ultra-thin very high resolution flat-panel display that uses the field emission from nanotubes to fluoresce phosphor pixels placed opposite in planar geometry. This is a big step towards the “video wallpaper” that is a common techno-prop of science fiction.

The mechanical strength and low mass density of nanotubes is also impressive. They share many of the strength properties of their molecular cousin, the diamond. For example, nanotubes are expected to have a tensile strength equal to that of diamond, about 130 GPa (18,900,000 pounds per square inch). For comparison, the best steel has a tensile strength of about 5 GPa (725,000 pounds per square inch). On the other hand, nanotubes should have about the mass density of graphite, about 1.9 times that of water or about 1/3 the density of steel.

In his novel *The Fountains of Paradise*, Arthur C. Clarke described an orbital elevator or “skyhook” that used a 22,000 mile long cable to raise and lower payloads from the Earth’s surface to geosynchronous orbit and beyond. A cable that hangs from geosynchronous orbit to Earth and has a density that is 1.9 times that of water will produce a tension on the highest part of the cable of 92 GPa (13,300,000 pounds per square inch). This is only about 2/3 of the estimated tensile strength of nanotubes, so a uniform cylindrical cable of any diameter that is fabricated with nanotubes should be able to function as a skyhook. The 22:1 tapering techniques that would be needed with weaker materials are unnecessary with nanotubes fabrication.

To put it another way, the relevant quantity for judging construction materials for skyhook construction is the ratio of tensile strength to density. Under this criterion, carbon nanotubes should be about 80 times better than steel and about 16 times better than the best plastic materials so far considered for this purpose. Moreover, nanotubes have already shown the tendency to form themselves into bundles or “nano-ropes” that should be an ideal skyhook construction material.

Unfortunately, present fabrication techniques can make carbon nanotubes only a few tenths of a millimeter long. This falls far short of the lengths (a few meters) required for skyhook cable fabrication, or even the centimeter lengths required for strengthening composite materials.

It has been discovered that shining laser light of the right wavelength on a nanotubes can make it vibrate in a “radial breathing mode”, in which the entire nanotube alternately increases and decreases its diameter. The light wavelength that excites this vibration mode depends directly on the diameter of the nanotube. Therefore, the technique can be used to measure diameters of nanotubes and perhaps, by applying a pulse of high laser-light power, to destroy unwanted nanotubes of a selected diameter.

Vibration techniques have also been used to estimate the spring-related properties of nanotubes,. Vibrations of the free end of a nanotube that is clamped at the other end are measured. This work indicates that nanotubes can make exceptionally stiff springs, with a Young's modulus that is 5 times higher than that of steel (1.0 TPa as compared to 0.2 TPa).

Under compression, nanotubes appear to be more forgiving than other materials, because they tend to fold rather than fracture. They are seen in electron microscope images to form bends and kink-like ridges under compression and torsion, and to relax elastically when the distorting forces are removed. It has been suggested that mechanical compression of nanotubes can achieve such a large mechanical energy density that stressed nanotubes should be considered as candidates for explosives as well as for mechanical energy storage devices.

Because of their tubular geometry and variable diameter, nanotubes can also be considered as pipes for transporting other atoms or as test tubes for containing them. Techniques have been developed for opening and closing nanotube ends. Nanotubes encasing silver nitrate molecules have been used to deposit nano-beads of silver. It has also been discovered that nanotubes holes provide excellent high-density storage for hydrogen gas.

This brings us to the problem of how to make nanotubes. For long nanotubes we would like to be able to pull single nanotube fibers (or even complete nano-ropes) out of some hot carbon source medium. Unfortunately, the only fabrication method presently available is to vaporize carbon in an arc discharge (20 volts at 100 amps), with a small amount of iron, cobalt, or nickel added to the arc. This creates nanotubes in at best sub-millimeter lengths.

However, the nanotube fabrication technology is rapidly evolving, and there are already at least nine commercial nanotube suppliers. I predict that this is a growth industry. Watch this column for further developments.

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