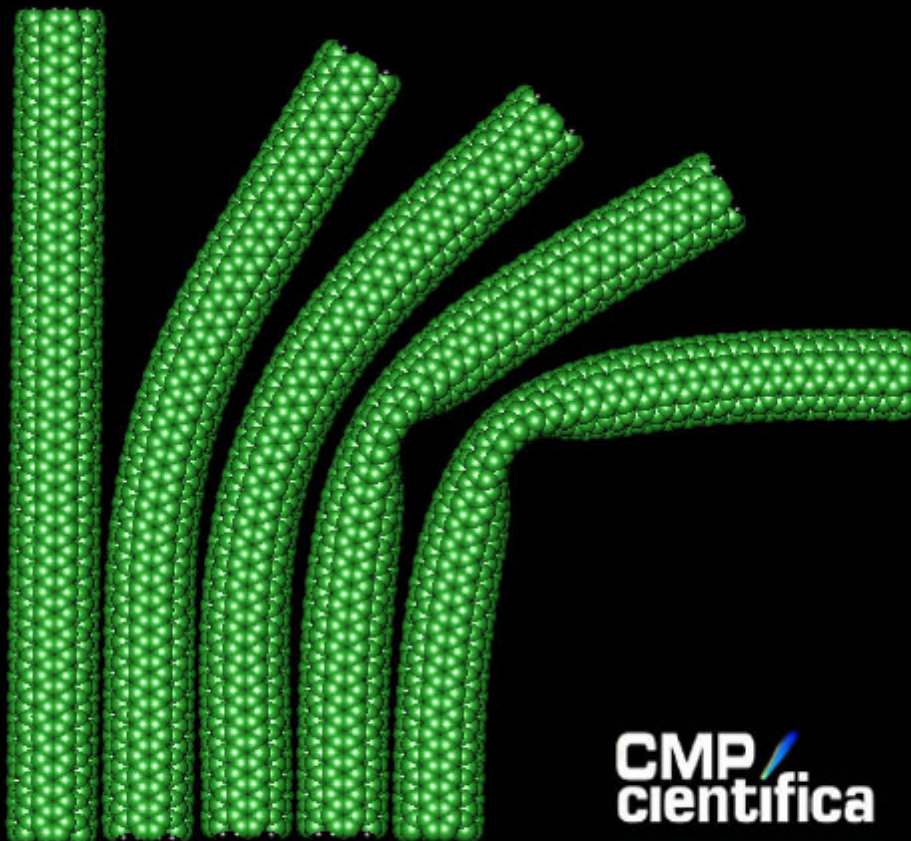


NANOTUBES

White Paper

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Cover Image: Bent Nanotubes. Courtesy of A. Rochefort, Nano-CERCA, University of Montreal, Canada.

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What is so Special about Carbon Nanotubes?

Carbon nanotubes are one of the most commonly mentioned building blocks of nanotechnology. With one hundred times the tensile strength of steel, thermal conductivity better than all but the purest diamond, and electrical conductivity similar to copper, but with the ability to carry much higher currents, they seem to be a wonder material. However, when we hear of some companies planning to produce hundreds of tons per year, while others seem to have extreme difficulty in producing grams, there is clearly more to this material than meets the eye.

In fact nanotubes come in a variety of flavors: long, short, single-walled, multi-walled, open, closed, with different types of spiral structure, etc. Each type has specific production costs and applications. Some have been produced in large quantities for years while others are only now being produced commercially with decent purity and in quantities greater than a few grams. In this brief white paper we hope to resolve some of the confusion surrounding what may be one of the most significant new materials since plastics.

Carbon Nanotubes and Related Structures

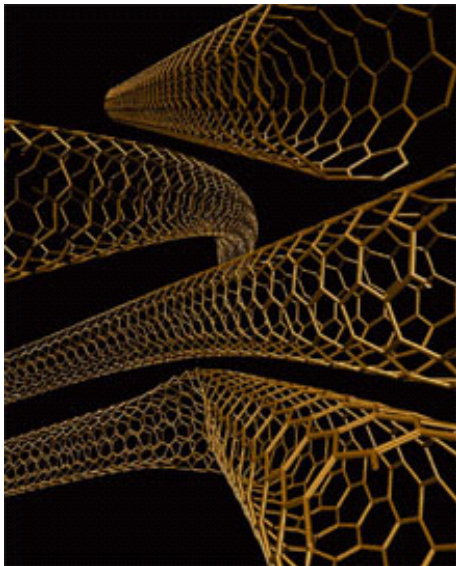


Figure 1. Bent nanotubes. Courtesy of A. Rochefort, Nano-CERCA, University of Montreal, Canada

The term nanotube is normally used to refer to the carbon nanotube, which has received enormous attention from researchers over the last few years and promises, along with close relatives such as the nanohorn, a host of interesting applications. There are many other types of nanotube, from various inorganic kinds, such as those made from boron nitride, to organic ones, such as those made from self-assembling cyclic peptides (protein components) or from naturally-occurring heat shock proteins (extracted from bacteria that thrive in extreme environments). However, carbon nanotubes excite the most interest, promise the greatest variety of applications, and currently appear to have by far the highest commercial potential. Only carbon nanotubes will be covered in this white paper.

Carbon nanotubes are often referred to in the press, including the scientific press, as if they were one consistent item. They are in fact a hugely varied range of structures, with similarly huge variations in properties and ease of production. Adding to the confusion is the existence of long, thin, and often hollow, carbon fibers that have been called carbon nanotubes but have a quite different make-up from that of the nanotubes that scientists generally refer to. To distinguish these we will refer to them as carbon nanofibers.

Introduction to Carbon Nanotubes

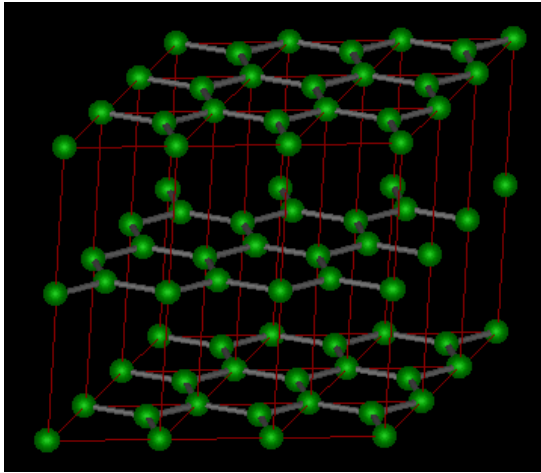


Figure 2. Layer structure of graphite.
Source: gallery of crystal structures,
Han Yang University,
Korea. [http://www.chem.hanyang.ac.kr/](http://www.chem.hanyang.ac.kr/Service/crystal)
Service/crystal.

Carbon nanotubes were 'discovered' in 1991 by Sumio Iijima of NEC and are effectively long, thin cylinders of graphite, which you will be familiar with as the material in a pencil or as the basis of some lubricants. Graphite is made up of layers of carbon atoms arranged in a hexagonal lattice, like chicken wire (see figure 2). Though the chicken wire structure itself is very strong, the layers themselves are not chemically bonded to each other but held together by weak forces called Van der Waals. It is the sliding across each other of these layers that gives graphite its lubricating qualities and makes the mark on a piece of paper as you draw your pencil over it.

Now imagine taking one of these sheets of chicken wire and rolling it up into a cylinder and joining the loose wire ends. The result is a tube that was once described by Richard Smalley (who shared the Nobel Prize for the discovery of a related form of carbon called buckminsterfullerene) as "in one direction . . . the strongest damn thing you'll ever make in the universe". In addition to their remarkable strength, which is usually quoted as 100 times that of steel at one-sixth of the weight (this is tensile strength—the ability to withstand a stretching force without breaking), carbon nanotubes have shown a surprising array of other properties. They can conduct heat as efficiently as most diamond (only diamond grown by deposition from a vapour is better), conduct electricity as efficiently as copper, yet also be semiconducting (like the materials that make up the chips in our computers). They can produce streams of electrons very efficiently (field emission), which can be used to create light in displays for televisions or computers, or even in domestic lighting, and they can enhance the fluorescence of materials they are close to. Their electrical properties can be made to change in the presence of certain substances or as a result of mechanical stress. Nanotubes within nanotubes can act like miniature springs and they can even be stuffed with other materials. Nanotubes and their variants hold promise for storing fuels such as hydrogen or methanol for use in fuel cells and they make good supports for catalysts.

But let's look at some of the different types of nanotubes, and nanotube pretenders.

One of the major classifications of carbon nanotubes is into single-walled varieties (SWNTs), which have a single cylindrical wall, and multi-walled varieties (MWNTs), which have cylinders within cylinders (see figure 3).

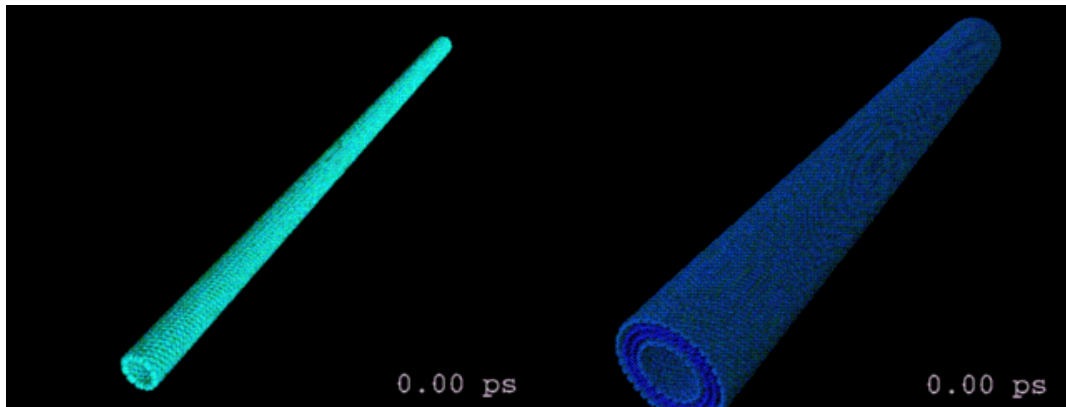


Figure 3. Computational image of single- and multi-walled nanotubes. Source: image gallery, Nanotechnology Team, NASA.

The lengths of both types vary greatly, depending on the way they are made, and are generally microscopic rather than nanoscopic, i.e. greater than 100 nanometers (a nanometer is a millionth of a millimeter). The aspect ratio (length divided by diameter) is typically greater than 100 and can be up to 10,000, but recently even this was made to look small. In May last year SWNT strands were made in which the SWNTs were claimed to be as long as 20 cm. Even more recently, the same group has made strands of SWNTs as long as 160 cm, but the precise make-up of these strands has not yet been made clear. A group in China has also found, purely by accident, that packs of relatively short carbon nanotubes can be drawn out into a bundle of fibers, making a thread only 0.2 millimeters in diameter but up to 30 centimeters long. The joins between the nanotubes in this thread represent a weakness but heating the thread has been found to increase the strength significantly, presumably through some sort of fusing of the individual tubes.

Single-Walled Carbon Nanotubes (SWNTs)

These are the stars of the nanotube world, and somewhat reclusive ones at that, being much harder to make than the multi-walled variety. The oft-quoted amazing properties generally refer to SWNTs. As previously described, they are basically tubes of graphite and are normally capped at the ends (see figure 4), although the caps can be removed. The caps are made by mixing in some pentagons with the hexagons and are the reason that nanotubes are considered close cousins of buckminsterfullerene (see figure 5), a roughly spherical molecule made of sixty carbon atoms, that looks like a soccer ball and is named after the architect Buckminster Fuller (the word fullerene is used to refer to the variety of such molecular cages, some with more carbon atoms than buckminsterfullerene, and some with fewer).

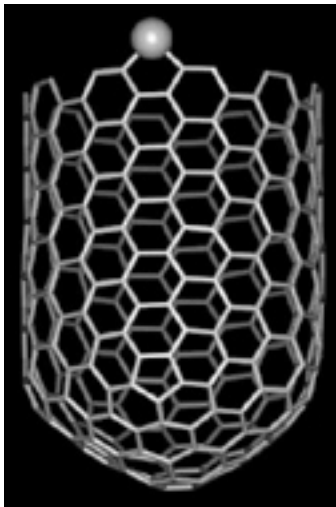


Figure 4. Simulated structure of a carbon nanotube. Courtesy of Richard Smalley's picture gallery.

metallic nanotubes), or semiconducting, which means that the flow of current through them can be stepped up or down by varying an electrical field. The latter property has given rise to dreams of using nanotubes to make extremely dense electronic circuitry and the last year has seen major advances in creating basic electronic structures from nanotubes in the lab, from transistors up to simple logic elements. The gulf between these experiments and commercial nanotube electronics is, however, vast.

There are various ways of producing SWNTs, which are briefly discussed later. The detailed mechanisms responsible for nanotube growth are still not fully understood and computer modeling is playing an increasing role in fathoming the complexities. The ambition of SWNT producers is to gain greater control over their diameters, lengths, and other properties, such as chirality (explained below).

The volumes of SWNTs produced are currently small and the quality and purity are variable. Carbon Nanotechnologies Inc. of Houston, Texas, are currently ramping up production to a half a kilogram a day, which is actually huge in comparison to amounts of SWNTs that have been made historically. Various companies pursuing specific nanotube applications produce their own material in house.

The theoretical minimum diameter of a carbon nanotube is around 0.4 nanometers, which is about as long as two silicon atoms side by side, and nanotubes this size have been made. Average diameters tend to be around the 1.2 nanometer mark, depending on the process used to create them.

SWNTs are more pliable than their multi-walled counterparts and can be twisted, flattened and bent into small circles or around sharp bends without breaking.

Discussions of the electrical behavior of carbon nanotubes usually relate to experiments on the single-walled variety. As we have said, they can be conducting, like metal (such nanotubes are often referred to as

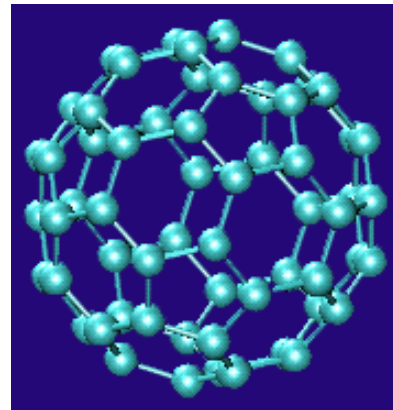


Figure 5. Buckminsterfullerene. Source: Chem Library, Imperial College of Science, Technology and Medicine, UK.

Chirality

Imagine again the chicken wire that we roll up to make the nanotube. In fact, imagine a chicken wire fence out of which will be cut a rectangle to roll into a tube. You could cut the rectangle with the sides vertical or at various angles. Additionally, when joining the sides together, you can raise or lower one side. In some cases it will not be possible to make a tube such that the loose ends match and hexagons are formed, but in other cases it will, and these represent the possible permutations of SWNTs (see figure 6). The possibilities are two forms in which a pattern circles around the diameter of the tube, often called zigzag and armchair (not the most intuitive of names, unfortunately, but they are now widely used), and a variety of forms in which the hexagons spiral up or down the tube with varying steepness, these being the chiral forms. There is theoretically an infinite variety of the latter, if you allow for infinite diameters of nanotubes.

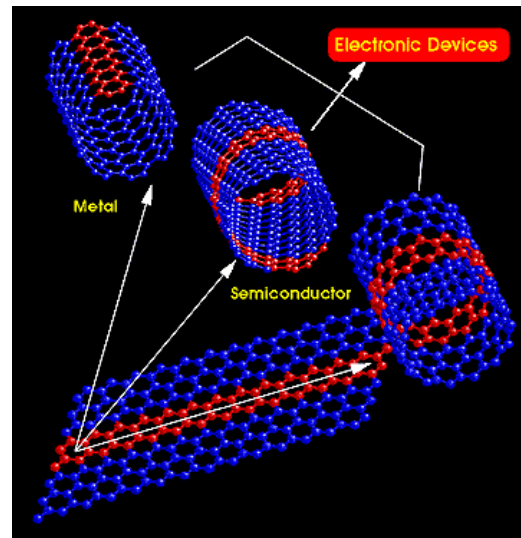


Figure 6. Schematic representation of rolling graphite to create a carbon nanotube. Source: image gallery Nanotechnology Team, NASA.

Which of these forms a nanotube takes is the major determinant of its electrical properties, i.e. whether the tube is semiconducting or conducting. For a long time, the fact that all known production methods created a mix of types has been considered one of the hurdles to be overcome if the electronic properties are to be exploited. Claims have now been made that it is possible to produce only the semiconducting kind (specifically, the zigzag form). Additionally, there are approaches that can yield only semiconducting nanotubes from a mix of semiconducting and conducting ones. One such approach relies on vaporizing the conducting nanotubes with a strong electric current, leaving only the semiconducting kind behind. A more recent approach is simply to leave the mix of nanotubes lying around for a while—the metallic ones are oxidized and become semiconducting (the process can, of course, be speeded up). In the early part of 2001 there were also reports that nanotubes had been induced to form crystals, each of which contained just one type of nanotube. This would have been a nice separation method but the silence on this approach since then suggests that these results have not been duplicated.

Multi-Walled Carbon Nanotubes (MWNTs)

Multi-walled carbon nanotubes are basically like Russian dolls made out of SWNTs—concentric cylindrical graphitic tubes. In these more complex structures, the different SWNTs that form the MWNT may have quite different structures (length and

chirality). MWNTs are typically 100 times longer than they are wide and have outer diameters mostly in the tens of nanometers.

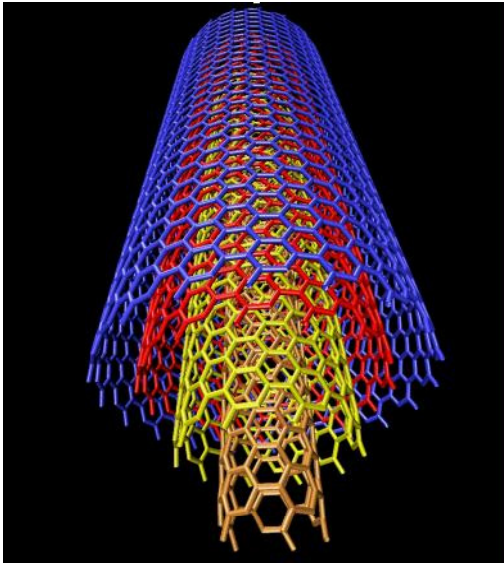


Figure 7. Representaion of a multi-walled carbon nanotube. Courtesy of A. Rochefort, Nano-CERCA, University of Montreal, Canada

Although it is easier to produce significant quantities of MWNTs than SWNTs, their structures are less well understood than single-wall nanotubes because of their greater complexity and variety. Multitudes of exotic shapes and arrangements, often with imaginative names such as bamboo-trunks, sea urchins, necklaces or coils, have also been observed under different processing conditions. The variety of forms may be interesting but also has a negative side—MWNTs always (so far) have more defects than SWNTs and these diminish their desirable properties.

Many of the nanotube applications now being considered or put into practice involve multi-walled nanotubes, because they are easier to produce in large quantities at a reasonable price and have been available in decent amounts for much longer than

SWNTs. In fact one of the major manufacturers of MWNTs at the moment, Hyperion Catalysis, does not even sell the nanotubes directly but only pre-mixed with polymers for composites applications. The tubes involved typically have 8 to 15 walls and are around 10 nanometres wide and 10 micrometers long. Other companies are moving into this space, notably formidable players like Mitsui, with plans to produce similar types of MWNT in hundreds of tons a year, a quantity that is greater, but not hugely so, than the current production of Hyperion Catalysis. This is an indication that even these less impressive and exotic nanotubes hold promise of representing a sizable market in the near future.

Nanohorns

These are single-walled carbon cones with structures similar to those of nanotube caps that have been produced by high temperature treatment of fullerene soot. Sumio Iijima's group at NEC has demonstrated that nanohorns have good adsorptive and catalytic properties (i.e. desired substances stick to them and they enhance chemical reactions), and the company is working on using them in a new generation of fuel cells for personal electronics.

Nanofibers

We use this term to refer to hollow and solid carbon fibers with lengths on the order of a few microns and widths varying from some tens of nanometers to around 200

nanometers. These materials have occasionally been referred to as nanotubes. However, they do not have the cylindrical chicken wire structure of SWNTs and MWNTs but instead consist of a mixture of forms of carbon, from layers of graphite stacked at various angles to amorphous carbon (lacking any large-scale regular structure). Because of this variable structure they do not exhibit the strength of pure nanotubes but can still be quite strong and possess other useful properties. The US company Applied Sciences Inc. is already producing tons of such material a year and there are several major producers in the Far East.

Carbon Nanotube Production Processes

Production processes for carbon nanotubes, crudely described, vary from blasting carbon with an electrical arc or a laser to growing them from a vapor, either *en masse* (usually in tangled bundles) or on nanoparticles, sometimes in predetermined positions. These processes vary considerably with respect to the type of nanotube produced, quality, purity and scalability. Carbon nanotubes are usually created with the aid of a metal catalyst and this ends up as a contaminant with respect to many potential applications, especially in electronics. IBM have very recently, however, grown nanotubes on silicon structures without a metal catalyst.

Scalability of production processes is an essential commercial consideration—some of the approaches use equipment that simply cannot be made bigger and the only way to increase production is to make more pieces of equipment, which will not produce the economies of scale required to bring down costs significantly.

Nanotube Applications

By now we hope you have an idea of the different types of nanotubes and how their qualities and ease of production vary. Reports of one company producing tons of the material, alongside reports of researchers not being able to get enough to get meaningful results from their research, should no longer be confusing. It would, of course, be useful if commentators got into the habit of making clear the type of material they are talking about.

Understanding these differences is essential for understanding the commercial potential of the various applications of nanotubes and related structures that already exist or have been proposed. The variety of these is vast, and the commercialization timelines involved vary from now to ten years from now or more. Some of the potential markets are enormous. We will leave you with a taste of the possibilities.

The materials markets are already seeing applications for composites based on multi-walled carbon nanotubes and nanofibers. In many ways this is an old market—that of carbon fibers, which have been around commercially for a couple of decades. The benefits of the new materials in these markets are the same as those of carbon fibers, just better; the main properties to be considered being strength and conductivity. Carbon fibers are quite large, typically about a tenth of a millimeter in diameter, and blacken the material to which they are added. MWNTs can offer the same

improvements in strength to a polymer composite without the blackening and often with a smaller amount of added material (called the filler). The greater aspect ratio (i.e. length compared to diameter) of the newer materials can make plastics conducting with a smaller filler load, one significant application being electrostatic painting of composites in products such as car parts. Additionally, the surface of the composite is smoother, which benefits more refined structures such as platens for computer disk drives.

When thinking about structural applications such as these, it should be remembered that, in general, as the fibers get smaller so the number of defects decreases, in a progression towards the perfection of the single-walled nanotube. The inverse progression is seen in terms of ease of manufacturing—the more perfect, and thus more structurally valuable, the material, the harder it is to produce in quantity at a good price. This relationship is not written in stone—there is no reason that near-perfect SWNTs should not be producible cheaply and in large quantities. When this happens, and it might not be too far off, the improvements seen in the strength-to-weight ratios of composite materials could soar, impacting a wide variety of industries from sports equipment to furniture, from the construction industry to kitchenware, and from automobiles to airplanes and spacecraft (the aerospace industry is probably the one that stands to reap the greatest rewards). In fact a carbon nanotube composite has recently been reported that is six times stronger than conventional carbon fiber composites.

This is an appropriate point at which to introduce a note of caution, and an area of research worth keeping an eye on. Just because the perfect nanotube is 100 times stronger than steel at a sixth of the weight doesn't mean you are going to be able to achieve those properties in a bulk material containing them. You may remember that the chicken wire arrangement that makes up the layers in graphite does not stick at all well to other materials, which is why graphite is used in lubricants and pencils. The same holds true of nanotubes—they are quite insular in nature, preferring not to interact with other materials. To capitalize on their strength in a composite they need to latch on to the surrounding polymer, which they are not inclined to do (blending a filler in a polymer is difficult even without these issues—it took a decade to perfect this for the new nanoclay polymers now hitting the markets).

One way of making a nanotube interact with something else, such as a surrounding polymer, is to modify it chemically. This is called functionalization and is being explored not just for composite applications but also for a variety of others, such as biosensors. For structural applications, the problem is that functionalization can reduce the valuable qualities of the nanotubes that you are trying to capitalize on. This is an issue that should not be underestimated.

Of course, in theory you don't need to mix the nanotubes with another material. If you want to make super-strong cables, for example, the best solution would be to use bundles of sufficiently long nanotubes with no other material added. For this reason, one of the dreams of nanotube production is to be able to spin them, like thread, to

indefinite lengths. Such a technology would have applications from textiles (the US military is in fact investigating the use of nanotubes for bullet-proof vests) to the 'space elevator'. The space elevator concept, which sounds like something straight out of science fiction (it was, in fact, popularized by Arthur C. Clarke) involves anchoring one end of a huge cable to the earth and another to an object in space. The taut cable so produced could then support an elevator that would take passengers and cargo into orbit for a fraction of the cost of the rockets used today. Sounds too far out? It has, in fact, been established by NASA as feasible in principle, given a material as strong as SWNTs. The engineering challenges, though, are awesome, so don't expect that 'top floor' button to be taking you into orbit any time soon.

The materials market is a big one, and there are others, which we'll come to, but smaller ones exist too. Nanotubes are already being shipped on the tip of atomic force microscope probes to enhance atomic-resolution imaging. Nanotube-based chemical and biosensors should be on the market soon (they face stiff competition from other areas of nanotechnology). The thermal conductivity of nanotubes shows promise in applications from cooling integrated circuits to aerospace materials. Electron beam lithography, which is a method of producing nanoscale patterns in materials, may become considerably cheaper thanks to the field emission properties of carbon nanotubes. Recent developments show promise of the first significant change in X-ray technology in a century. Entering more speculative territory, nanotubes may one day be used as nanoscale needles that can inject substances into, or sample substances from, individual cells, or they could be used as appendages for miniature machines (the tubes in multi-walled nanotubes slide over each other like graphite, but have preferred locations that they tend to spring back to).

Big markets, apart from materials, in which nanotubes may make an impact, include flat panel displays (near-term commercialization is promised here), lighting, fuel cells and electronics. This last is one of the most talked-about areas but one of the farthest from commercialization, with one exception, this being the promise of huge computer memories (more than a thousand times greater in capacity than what you probably have in your machine now) that could, in theory, put a lot of the \$40 billion magnetic disk industry out of business. Companies like to make grand claims, however, and in this area there is not just the technological hurdle to face but the even more daunting economic one, a challenge made harder by a host of competing technologies.

Despite an inevitable element of hype, the versatility of nanotubes does suggest that they might one day rank as one of the most important materials ever discovered. In years to come they could find their way into myriad materials and devices around us and quite probably make some of the leaders in this game quite rich.