NANOTUBES

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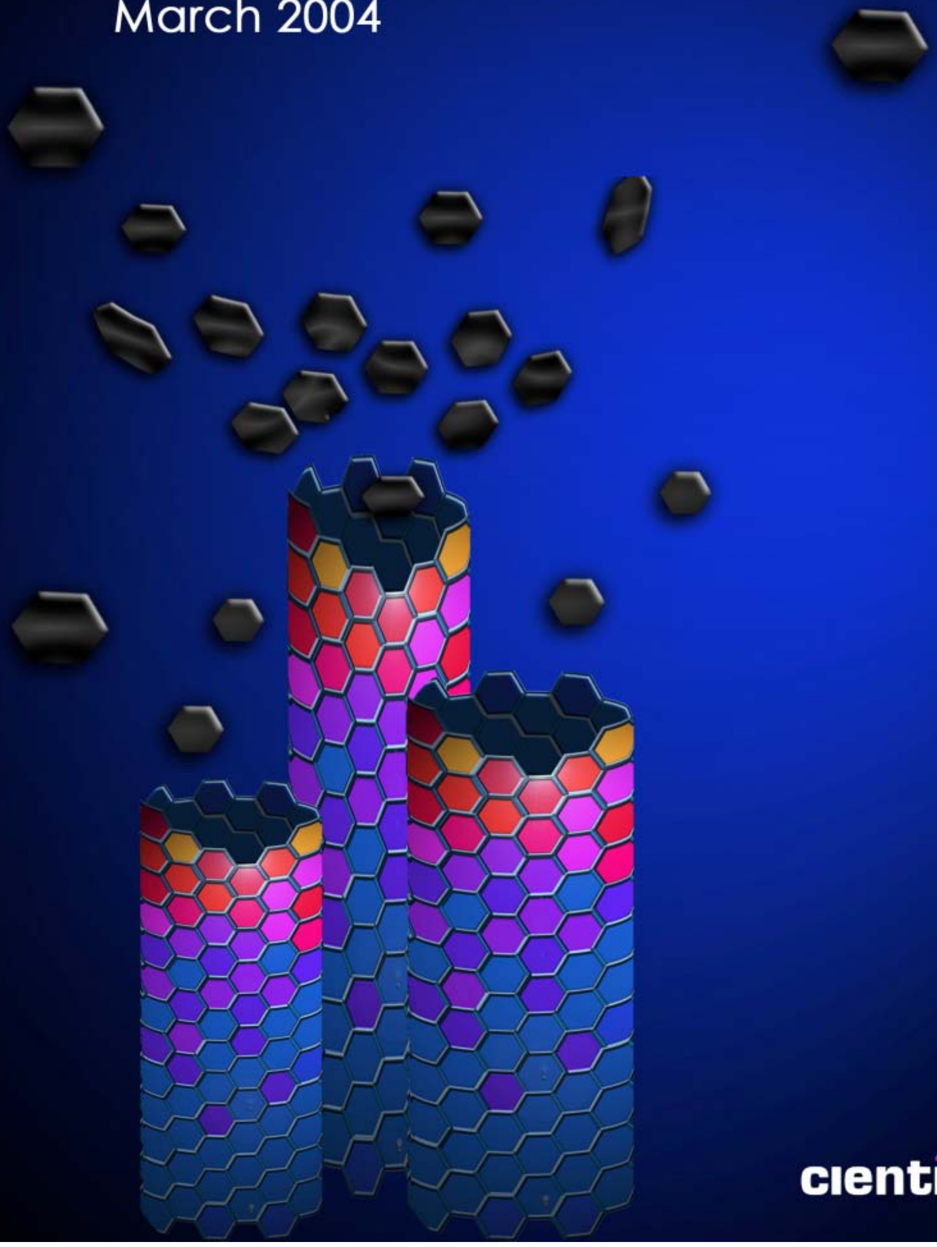
March 2004



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The authors

- Cristina Román is Managing Director and Senior Scientific Consultant at Científica, with a scientific background in macromolecular organic and physical chemistry. She received her PhD for a thesis on the development of highly functional dendritic structures for applications in materials science. She worked at Johnson & Johnson Pharmaceutical R&D on the development of new pharmaceutical processes based on supercritical fluid technology and as an advisor in the study of nanodevices as drug carriers.

- Paul Holister is Chief Information Architect at Cientifica. He is co-author of the Nanotechnology Opportunity Report™, described by NASA as "the defining report in the field of nanotechnology," and editor-in-chief of the X Report and TNT Weekly, which has been running since 2000 and is widely read across the entire nanotechnology community, from academics to investors. After early training in biochemistry, Paul worked for some years in scientific publishing and for many more in the IT industry, as a consultant, business analyst, and system designer.

- Tim Harper is the founder and CEO of Científica, and co-author of the Nanotechnology Opportunity Report™. Tim has been described by TIME Magazine as "the face of European nanotechnology" and he has been profiled in TIME Magazine's Digital Europe Top 25, as one of Europe's top 25 entrepreneurs. Small Times Magazine described Tim as "Europe's pre-eminent nanotech spokesman outside of government." Tim was an engineer at the European Space Agency's R&D center in the Netherlands. He managed the micro and nanoscale characterization facility, and has published extensively on analytical techniques and characterization of advanced materials.

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Executive summary

First Ever Comprehensive Global Overview

The 2004 Nanotubes report is the world's first global survey of the producers, the technologies, the application and markets for carbon nanotubes. Long touted as the ultimate engineering material, getting to market has been hampered by high prices and production bottlenecks.

The 2004 Nanotubes report surveyed all 44 global producers, ranging from single walled nanotubes to nanofibres. CNT production has now reached a tipping point where the combination of decreasing prices and increased availability will enable more widespread applications. The Nanotubes report covers production, prices, and applications.

Production Capacity Ramps Up

- Current estimated global production of carbon nanofibers is more than 40 tons a year, and is expected to reach more than 58 tons by 2006.
- Total global production capacity of multi-walled nanotubes is higher than 99 tons a year and expected to increase to at least 268 tons annually by 2007.
- Current global production of single walked nanotubes can be estimated to be at least 9000 kg/year. The production is expected to increase up to more than 27 tons by 2005 and to reach 100 tons by 2008.

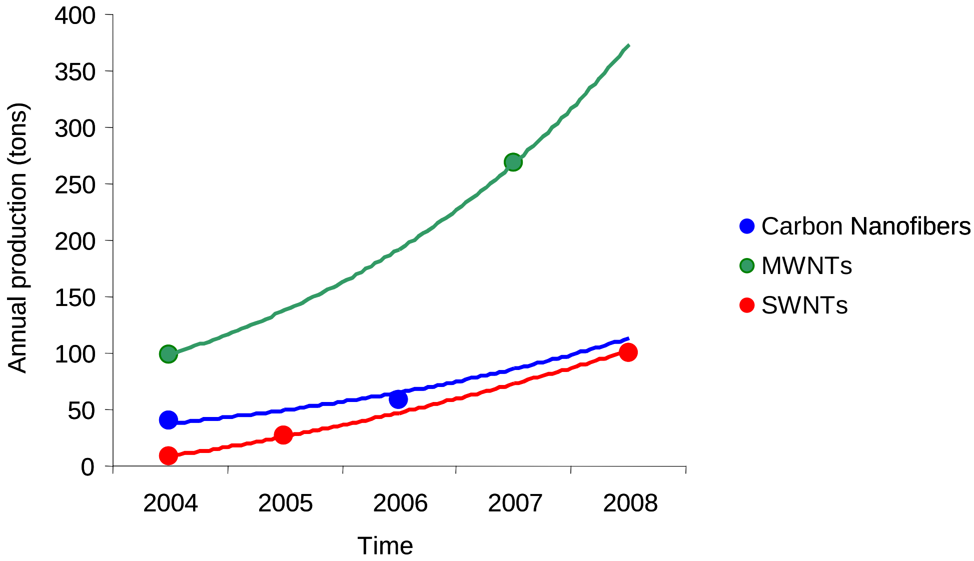

Figure 1. Estimated future global production.

The Global landscape

China has already overtaken Japan in both the number of companies and total production capacity of all varieties of carbon nanotubes.

- Almost one third of the companies producing nanofibers are located in the US, followed by European, Japanese and Chinese producers in the same proportions.

- Major nanofiber production takes place in the US, which represents nearly 40% of the total production capacity, followed by China and Japan with approximately 30% of total production. Although the number of producers is similar, production of carbon nanofibers in Europe is small compared with other regions.

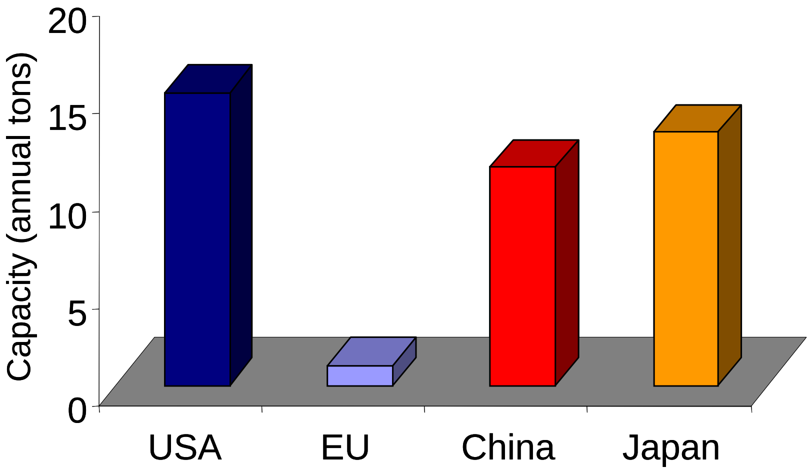

Figure 2. Nanofibers production capacity.

- Almost one half of the MWNT production takes place in the US, followed by Japan with approximately 40% of total production.

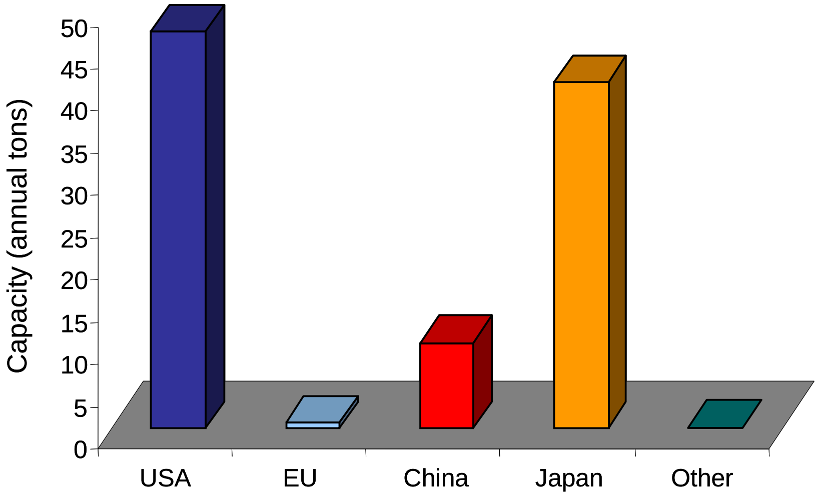

Figure 3. MWNT production capacity.

- The US leads production of SWNTs with holding more than 70% of total capacity. Next is China, with 22%, and the EU, with approximately 4% of total production.

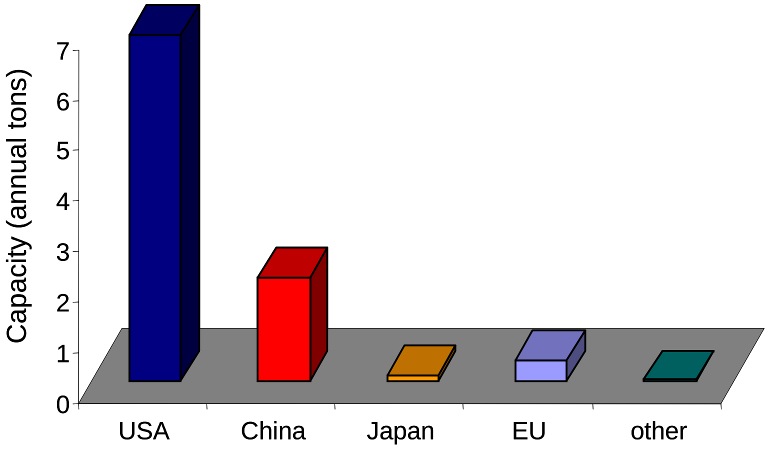

Figure 4. SWNT production capacity.

Introduction to nanotubes

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). Carbon nanotubes, though, excite the most interest, promise the greatest variety of applications, and currently appear to have by far the highest commercial potential. As a result they constitute the bulk of the Nanotubes report, but the potential of other forms of nanotube, especially those that fall within the burgeoning field of molecular engineering, should not be passed over.

Carbon nanotubes

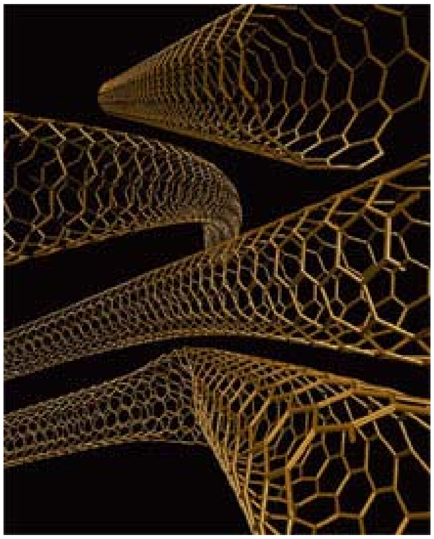

Figure 5. Bent nanotubes. Courtesy of A. Rochefort, Nano-CERCA, University of Montreal, Canada

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 carbon nanotubes come in a variety of flavors: long, short, single-walled (SWNTs), multi-walled (MWNTs), 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. The variations in production volumes, prices and properties make for a very diverse set of applications, which need to be looked at for each flavor of nanotube. Taken altogether, the possible impact of carbon nanotubes on the world is immense, with market sizes for new products based on them running into the hundreds of billions if they fulfill all their potential. A lot of this could be seen within 5 years, with more following within a decade.

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.

Carbon nanotubes were discovered in 1991 by Sumio Iijima of NEC (*Nature*, **354**, 56) and are effectively long, thin cylinders of graphite. 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 allows a pencil to leave a mark on paper.

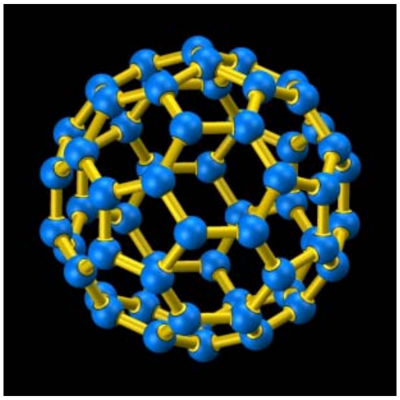

Figure 6. Buckminsterfullerene. Courtesy of Prof. Lauher. State Univ. of N.Y., Stony Brook ,USA. http://www.chem.sunysb.edu/msl/.

Graphite sheets are relatively flexible and the energy required to roll them up into a nanotube is more than returned by the bonding of the carbons at the edge of the sheet. The carbons at the end of the tube can be, and usually are, bonded by closing the tube. This is achieved by the insertion of pentagons to create curvature and is responsible for nanotubes normally being classified as part of the fullerene family, a collection of caged carbon molecules of which the buckyball is the most famous. This consists of 60 carbon atoms in an arrangement that looks like a soccer ball. If you add ten carbon atoms to the middle of a buckyball then you get another fullerene, C70, which is somewhat elongated. Another 10 give you C80 and this process can be continued to create a carbon nanotube. It is worth noting, though, that a lot of the interesting properties of carbon nanotubes are most related to the long graphene (the generic term for the structure of graphite) tube. This makes nanotubes quite different from the other fullerenes, and they are normally considered separately.

As mentioned earlier, there is a wide variety of carbon nanotubes, but they can be largely separated into two classes, single-walled and multi-walled, generally abbreviated to SWNTs and MWNTs.

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 2), although the caps can be removed.

The theoretical minimum diameter of a carbon nanotube is around 0.4 nanometers, which is about the width of two silicon atoms side by side, and nanotubes this size have been made—a team at the Hong Kong University of Science and Technology molded nanotubes with a diameter of 0.4 nanometer using the channels of zeolite crystals. Average diameters tend to be around the 1.2 nanometer mark, depending on the process used to create them.

Lengths, on the other hand, can be significant, typically 100 times the diameter (this ratio is called the aspect ratio), but sometimes up to 10,000 times. In theory an indefinite length is possible and something many would like to achieve. Indeed, some promise has been seen in this respect lately, as will be seen later.

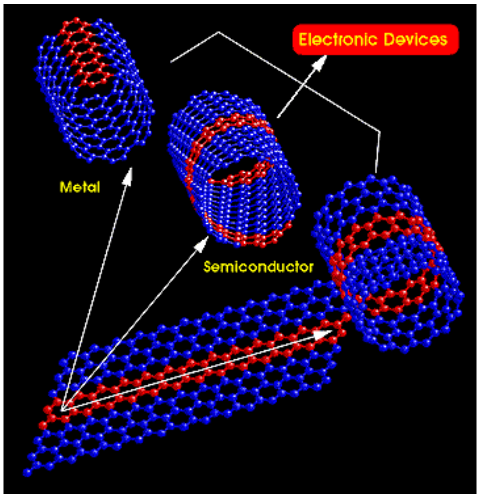

Figure 7. Schematic representation of rolling graphite to create a carbon nanotube. Courtesy of Nanotechnology Team, NASA.

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 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 few years have 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 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).

Chirality

The best way to picture the property of chirality is to imagine rolling up a rectangle of chicken wire into a tube (see Figure 4). The rectangle can be cut with the sides vertical or at various angles. Additionally, when joining the sides together, one side can be raised or lowered. 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. 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.

Which of these forms a nanotube takes is the major determinant of its electrical properties; armchair nanotubes are excellent conductors of electricity, while helical and zigzag nanotubes both act as semiconductors.

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.

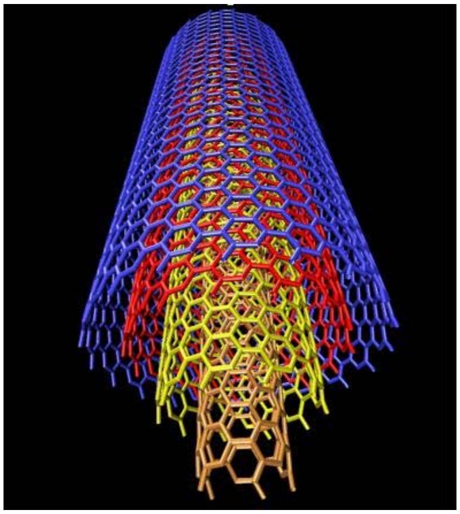

Figure 8. Representation of a multi-walled carbon nanotube. Courtesy of A. Rochefort, Nano-CERCA, University of Montreal, Canada.

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. MWNTs are often described as having diameters from 10 to 200 nanometers, with numbers of walls varying from two up to a few tens. However, the larger MWNTs are often so far removed from the pure nanotube structure that they don't really warrant the name and well-formed MWNTs will normally not be wider than around 20 nanometers, with around 15 walls. This is, of course, an arbitrary line since the structures actually represent a continuum.

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. Production is scheduled to be ramped up significantly, as is mentioned later.

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 are often referred to as nanotubes but they do not have the cylindrical chicken wire structure of SWNTs and MWNTs, where the walls of the tube are parallel to the central axis.

In nanofibers the angle between the graphite planes and the tube axis is non-zero, and the resulting structures are sometimes referred to as stacked-cone structures. When they exhibit only small angular deviations from the axis and are not solid cylinders but hollow, they are often called multi-walled carbon nanofibers (MWNFs). The terminologies 'graphitic carbon fibers' (GCFs) and 'vapor-grown carbon fibers' (VGCFs) have long been used to denote solid cylinders.

Nanofibers mostly 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 (e.g. around 7 gigapascals tensile strength for the heat-treated Pyrograf I product from Applied Sciences, which compares with under 5 gigapacals for the best traditional carbon fibers) and possess other useful properties, such as good electrical and thermal conductivity.

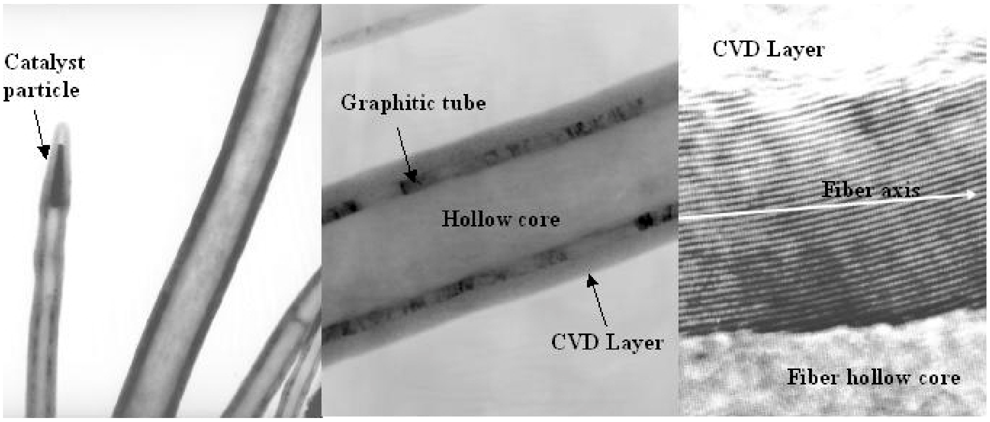

Figure 9. Hollow carbon nanofiber, consisting of an outer layer of amorphous carbon and an inner layer of graphitic carbon . Image courtesy of Applied Sciences, USA.

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.