CARBON NANOTUBES:

OPPORTUNITIES AND CHALLENGES

This is Part II of a two-part discussion of carbon fibers and carbon nanotubes. This article discusses carbon nanotubes, and Part I covered carbon fibers in the September issue.

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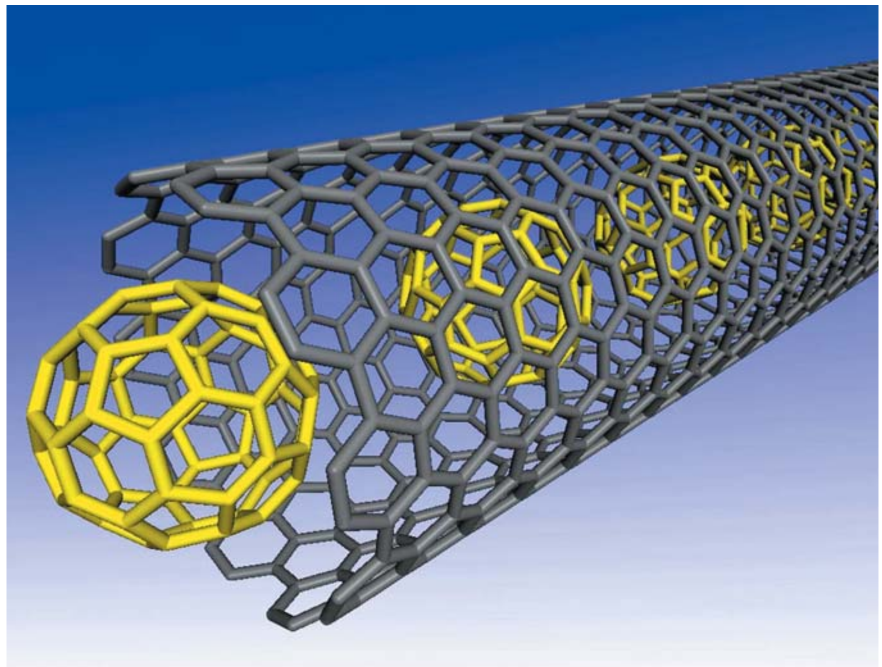
Fullerenes are commonly defined as "any of a class of closed hollow aromatic carbon compounds that are made up of twelve pentagonal and differing numbers of hexagonal faces." Higher-order fullerenes include carbon nanotubes (CNTs), which can be described as fullerenes that have been stretched along a rotational axis to form a tube.

There are two general types of nanotubes. Multi-walled tubes (MWNTs) resemble many pipes nested within each other. Shortly after MWNTs were discovered, single-walled nanotubes (SWNTs) were observed.

Single-walled tubes resemble a single pipe that is potentially capped at each end. Multi-walled carbon nanotubes (MWNTs) range from double-walled NTs to carbon nanofibers. Vapor grown carbon fibers (VGFs) are the extreme of multi-walled tubes. They are thicker and longer than either SWNTs or MWNTs, having a cross-sectional area of about 500 Angstroms, and are between 10 and 100 microns long.

Carbon nanotubes represent the link between well-established carbon materials and the new field of nanotechnology. The applications of these carbon materials in areas as diverse as construction, transportation, medicine, electronics, and energy suggests that the first technology age of the 21st century will be known as the carbon age.

This article describes how carbon nanotubes are made, discusses some of the barriers to wider applications, and lists some current and potential applications.



This diagram shows a single-wall carbon nanotube with buckminsterfullerenes inside. Image courtesy Case Western Reserve University, www.nanopedia.case.edu.

Producing nanotubes

Many methodologies have been developed to produce carbon nanotubes in sizable quantities, including arc discharge, laser ablation, high pressure carbon monoxide (HiPco), and vapor liquid solid (VLS) growth. It is worth noting that the latter is often referred to as chemical vapor deposition (CVD); however, this is actually an incorrect use of the term.

Nanotubes were first observed in 1991 in the carbon soot of graphite electrodes during an arc discharge that was intended to produce fullerenes. Because of the high temperatures caused by the discharge in this process, the carbon contained in the negative electrode sublimed. The fullerenes ap-

The previously unknown allotrope of carbon, C_{60}, was discovered in 1985, and in 1996 the Nobel Prize in Chemistry was awarded to Curl, Kroto, and Smalley for this discovery. Named "Buckminsterfullerene," it has a spherical shape often compared to the typical black and white soccer football, hence the nickname buckyball.

Mechanical properties of CNTs vs. carbon fibers

Characteristic	Pitch-based carbon fibers	PAN-based carbon fibers	Vapor-grown carbon fibers	Multi-wall carbon nanotubes	Single-wall carbon nanotubes
Density, g/cm^3	1.57-1.81	2.0	2.0	2.6	1.4
Tensile strength, MPa	600-2500	2100	4000	150000	150000
Young's modulus, GPa	30-300	520	300	1200	1054

peared in the soot that formed, while the CNTs were deposited on the opposing electrode.

Tubes produced by this method were initially multi-walled carbon nanotubes. However, in 1993 it was discovered that with the addition of cobalt to the vaporized carbon, it was possible to grow single-walled nanotubes.

This plasma-based process is analogous to the more familiar electroplating process in a liquid medium. It produces a mixture of carbon forms, and requires further purification to separate the CNTs from the soot and the residual catalytic metals. Producing CNTs in high yield depends on the uniformity of the plasma arc, and the temperature of the deposit forming on the carbon electrode.

Higher yield and purity of SWNTs may be prepared by a dual-pulsed-laser vaporization of a Co/Ni-doped graphite rod with a high-powered laser in a tube furnace operating at 1200°C. By this method, it is possible to grow SWNTs in a 50% yield without the formation of an amorphous carbon overcoating. Although arc-discharge and laser vaporization are currently the principal methods for producing small quantities of high quality SWNTs, both methods have drawbacks.

- The first is that they involve evaporating the carbon source, making scale-up on an industrial level difficult and energetically expensive.
- The second issue relates to the fact that vaporization methods grow SWNTs in highly tangled forms, mixed with unwanted forms of carbon and/or metal species. The SWNTs thus produced are difficult to purify, manipulate, and assemble for building nanotube-device architectures for practical applications.

To overcome some of the difficulties of these high-energy processes, Richard Smalley and coworkers developed a chemical catalysis method based on either hydrocarbon or carbon monoxide feedstock. A major advance in recent years is the growth of carpets of aligned carbon nanotubes.

Performance and applications

The physical properties of CNTs in general and SWNTs in particular make them extremely attractive for the manufacture of nano devices. SWNTs have been shown to be stronger than steel, while their electrical conductivity is comparable to that of copper, with anticipated current densities up to 10^{13} A/cm^2 and a resistivity as low as 0.34×10^{-2} Ω-cm at room temperature. Finally, they have a high thermal conductivity (3000 to 6000 W-m/K). The table shows the mechanical properties of various CNTs compared with carbon fibers.

Given the present high cost of CNTs it is not surprising that initial commercial applications involve small to modest loadings or specialty applications. The high aspect ratio of CNTs, in combination with their superior conductivity, means that they require much lower loadings than traditional fillers. Carbon black typically requires 30 or 40% by volume loading to confer conductivity, at which point the mechanical properties of the composite are often severely degraded.

On the other hand, only 0.005 wt% loading of aligned MWNTs enable epoxy to become conductive. It is also likely that modest loadings of SWNTs will actually enhance the structural properties of the composite.

Pure CNTs are the best thermally conductive material ever discovered, and applications exploiting their heat management potential are being investigated. As the electronics world strives to fit more and more functionality into less and less space, overheating is becoming a major problem. CNTs may have a potential role in electronics packaging as well as that of active components.

Electromagnetic interference shielding in electronic devices from laptops to mobile phones is becoming increasingly important to preventing interference with and from other portable electronic devices. The electrostatic dissipation properties of CNT coatings and composites offer significant performance/loading as compared to other conductive fibers. Unlike their micron brethren, CNTs also have potential applications in a wide range of medical treatments. Their size in combination with their ability to generate heat upon exposure to radio waves, as well as their potential as drug vectoring agents, offers a new frontier for carbon materials in the treatment of disease.

Commercial status

Because of their thermal and electrical conductivity and other properties, the demand for CNTs is increasing rapidly in electrical, mechanical, and medical applications. The global carbon nanotubes market is projected to exceed $1.9 billion by 2010, at an annual growth rate of more than 80% during the analysis period.

The United States currently dominates the world market in terms of revenues, while the European carbon nanotubes market is projected to be the fastest growing at a rate of over 100%. At present, the United States and Asia-Pacific combine to account for over 75% of the global CNT market. However, the Asia-Pacific region will increase its share to become a leading market, with revenues expected to reach $2.5 billion by the year 2012.

The MWNT market was estimated at $290 million for 2006. Revenues generated from MWNTs are high due to their simple production process and low cost compared to SWNTs. However, in the coming years, the SWNT market is projected to overtake the MWNT market, and is projected to cross $5 billion by the year 2012, at a very high annual growth rate of 200%. Development and use of cost-effective production methods are expected to increase the worldwide CNT market.

Various application sectors such as electronics, batteries, composites, and research institutions were the reasons for rapid growth over the last couple of years. However, high cost is one of the major issues in the carbon nanotubes industry. Expansion of manufacturing facilities is expected to fuel the production of CNTs, while reducing prices.

Barriers to mass markets

• Cost: SWNTs now cost $600/g. That will need to decline significantly to become a commercially viable material.

• Quality control: Consistently high quality is needed.

• Basic science: Thorough understanding of the effects on performance and properties of adding CNTs to any material is important to ensure the correct use of CNTs.

It should be noted that these problems are the same that plagued the commercialization of carbon fibers. Key players dominating the global carbon nanotubes market include Catalytic Materials, Hyperion Catalysis International, ILJIN Nanotech, Nanocyl, Nanoledge, Raymor Industries, Rosseter Holdings, Shenzhen Nanotech Port, SouthWest NanoTechnologies, Sun Nanotech, and Unidym.

Unlike carbon fibers, it is not sufficient to just manufacture the raw materials. It is also necessary to make chemical derivatives for many applications. CNTs may be functionalized by a wide range of chemical methods. A growing number of commercial entities now provide (or use) functionalized CNTs, including Zyvex, Nantero, NanoRidge, and NanoComposites.

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