

CARBON NANOTUBES

Carbon is an extraordinary element, considering the diversity of materials it forms. Ranging from sparkling gems to sooty filth, these materials have been studied and used for centuries, and carbon science was long thought to be a mature field. So when a whole new class of carbon materials—the fullerenes, such as C_{60} —appeared in the last decade, many scientists were surprised.^{1,2} The consequences have reached well beyond the fullerenes themselves to include major changes in our concepts and understanding of long-known carbon materials. It is in this context that the story of carbon nanotubes starts.³

History

With the study of C_{60} and C_{70} , it was soon realized that an infinite variety of closed graphitic structures could be formed, each with unique properties. All that was necessary to create such a structure was to have 12 pentagons present to close the hexagonal network, as explained by Euler's theorem (see the box on page 28). Given that C_{70} was already slightly elongated as compared to C_{60} , tubular fullerenes were imagined.

In 1991, when a group at the Naval Research Laboratory first submitted a theoretical paper on the electronic structure of such small tubes,⁴ the results were deemed too speculative for publication because the synthesis of nanotubes seemed unlikely in the near future. The researchers predicted, among other things, that by simply turning a sheet of graphite into a small tube, the structure would have a carrier density similar to that of metals, unlike graphite. And they predicted that the tube would have no Peierls distortion (bond alternation resulting in the formation of a gap) at room temperature, unlike other conjugated materials such as polyacetylene.

At the same time, in Japan, Sumio Iijima of NEC had been using transmission electron microscopy to analyze a sample of carbon soot received from Yoshinori Ando of Meijo University. The sample had been retrieved from a carbon arc machine normally used to make C_{60} . Iijima observed that the sample contained tubules. Although

Seamless cylindrical shells of graphitic carbon have novel mechanical and electronic properties that suggest new high-strength fibers, submicroscopic test tubes and, perhaps, new semiconductor materials

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cylindrical carbon tubes and fibers were known,⁵ these nanotubes appeared perfectly graphitized and capped at each end with pentagons, just like the fullerene molecules. Most important of all, Iijima noticed that the carbon atoms in each nanotube's closed shells were arranged with various degrees of helicity: The path of carbon bonds formed a spiral around the tube.⁶

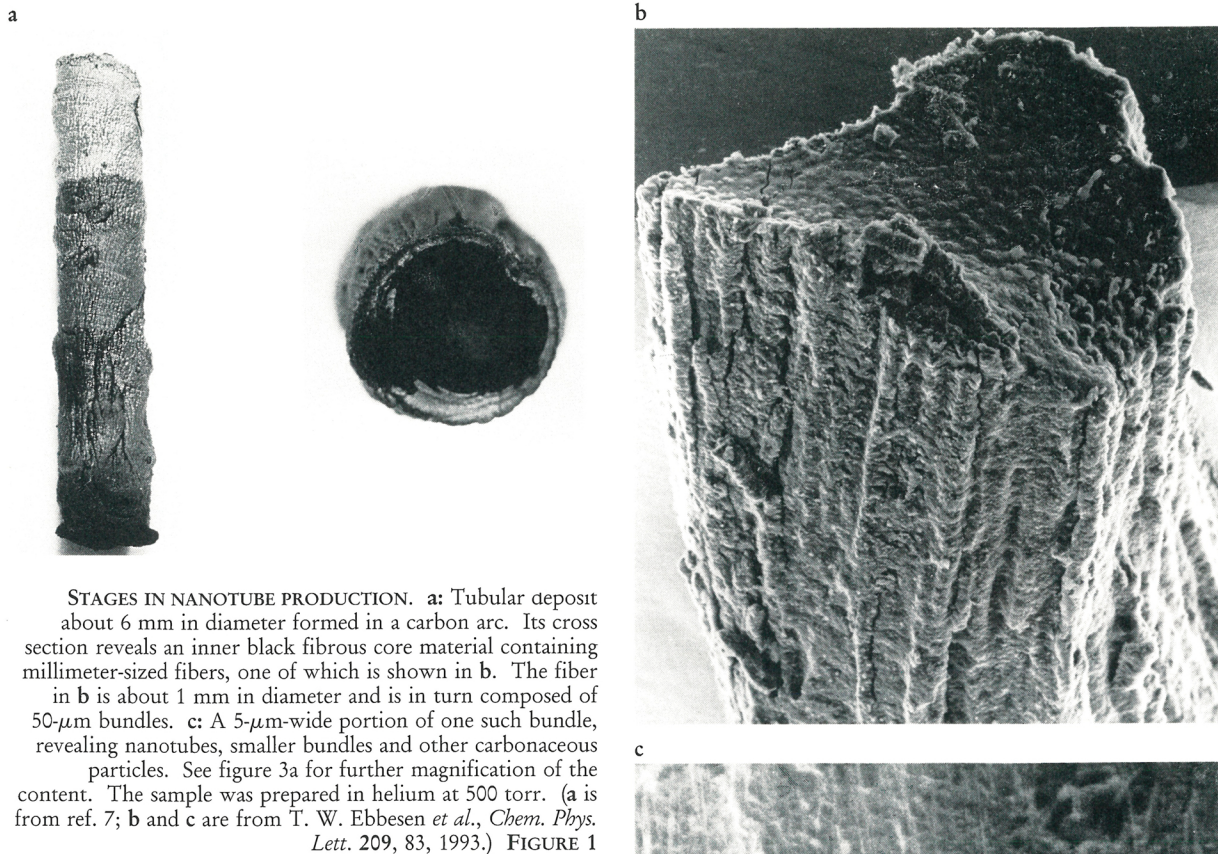
The excitement of this discovery was amplified when several theoretical studies revealed that the nanotube would be either metallic or a semiconductor, depending not only on the diameter but also on the helicity.⁷ From a materials point of view, carbon nanotubes were seen as the ultimate fiber, with an exceptional strength-to-weight ratio. So by the spring of 1992, the expectations for nanotubes were running very high. The problem was that the nanotubes were present only in minute quantities in the carbonaceous deposits, so that it would be hard to extract them or do any studies of their properties.

At that time, our molecular science group in the NEC Fundamental Research Laboratory in Tsukuba, Japan, was busy studying fullerenes, which we generated with the carbon arc method.² One day while trying to make modified C_{60} with boron, we found quite by chance that under different operating conditions the arc would produce nanotubes in high yields.⁸ The deposits came in a tubular form as shown in figure 1, with an outer hard shell and an inner soft fibrous core containing the nanotubes and nanoparticles. With gram quantities now in hand, it was possible to start evaluating nanotube properties. Last year there were more than 180 papers published on the subject, and what follows is only a small sampling of the total activity in the field.

Structure and production

How does one define a carbon nanotube? Ideally, a nanotube consists of one or more seamless cylindrical shells of graphitic sheets. In other words, each shell is made of sp^2 (trivalent) carbon atoms that form a hexagonal network without any edges. A nanotube can be thought of as a tubular microcrystal of graphite. The tube is typically closed at each end, according to Euler's theorem (see box), by the introduction of pentagons in the hexagonal network. Figure 2 shows examples of multishell nanotubes. Each layer in the tip contains at least six pentagons. The interlayer spacing is about 0.34 nanometers and typical of turbostratic graphite, in which the position of each layer

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relative to the next is not correlated. A given nanotube will be composed of shells having different helicities. In fact, the different degrees of helicity in each shell are necessary to obtain the best fit between the successive shells in a tube and minimize the interlayer distance. The nanotubes are typically longer than a micrometer, with diameters ranging from 1 to 20 nm. As a result of these dimensions and this aspect ratio, nanotubes are expected to have some features of low-dimensional materials.

Nanotubes are not always perfect seamless shells of graphite. Their quality depends on the method used to generate them and the exact conditions of the particular method. Making nanotubes is simple, but making good-quality samples with high yields and highly graphitized shells—that is, a continuous seamless hexagonal network—is not trivial.

There are now several methods³ for making nanotubes, but the carbon arc method⁸ remains the most practical for scientific purposes and yields the most highly graphitized tubes simply because the process has a very high temperature—of 4000 K. Only with the properly graphitized material can one expect to find any correlation between theoretical predictions and experiments. Furthermore these samples can be purified, as I discuss below.

The deposit generated in the arc has a hierarchical structure, with nanotubes organized in small bundles, which are themselves organized (together with nanoparticles) into 50- μm fibers packed to form larger fibers visible to the eye, as shown in figure 1. The alignment of the nanotubes in the deposit along the axis of the arc current, the yield of nanotubes and their structural quality all depend on the conditions of the arc. The most critical parameters are the inert gas pressure, the growth rate,

the cooling rate, the stability of the arc plasma and many variables that are hard to quantify.^{3,8} Nanotube yields of about 60% of the core material are obtainable under optimal conditions.⁸

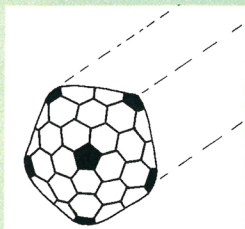
The growth mechanism of the nanotubes is a complex and fascinating subject in itself. Why do nanotubes form in the first place—and in such high yields—at such high temperatures when they are not thermodynamically the most stable structures? In other words, why tubes and not balls? This and other important questions were raised and discussed by Richard Smalley of Rice University in

Euler and the Nanotube

The flat sp^2 hexagonal sheets of graphite can be given three-dimensional shapes by sp^2 - sp^3 rehybridization and by the introduction of rings other than hexagons. The graphitic geometry induced by the presence of pentagons and heptagons clearly follows Euler's theorem, which relates the number of vertices, edges and faces of an object. From it a more practical expression can be derived for sp^2 hexagonal networks:^a

$$\dots 2n_4 + n_5 - n_7 - 2n_8 \dots = \sum (6-x)n_x = 12(1-g)$$

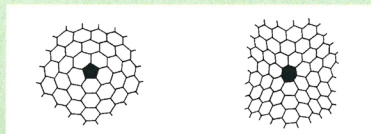
Here, n_x ($x > 2$) is the number of polygons having x sides (notice that it is not necessary to count the hexagons) and g is the genus ($g = 0$ for a closed sphere, $g = 1$ for a torus having a hole, and so on). This equation is very useful in that it tells what the presence of rings (polygons) does to the geometry of the hexagonal network and how many are necessary to obtain a closed structure—that is, a total disclination of 4π . For instance, for $g = 0$, $n_5 = 12$. In other words, 12 pentagons



are necessary to close the hexagonal network in the absence of heptagons, octagons and so on. This is the case of C_{60} . Each tip of the closed nanotubes corresponds to half a sphere, and thus the ends must contain at least 6 pentagons, as illustrated above.

If 12 pentagons induce a total of 4π disclination, then one pentagon induces a $4\pi/12$ (also referred to as a 60°) disclination. Heptagons produce a negative 60° disclination. (See the sketch at the top of the next column.)

The addition of one heptagon requires the presence of one extra pentagon to close the structure. In other words, a

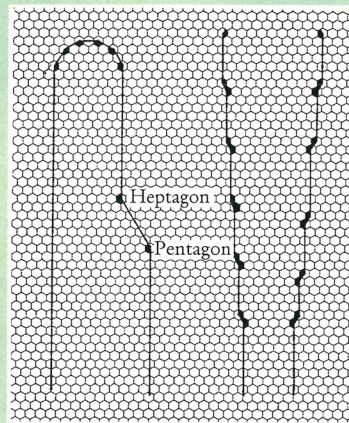


pentagon-heptagon pair produces no net disclination but may change the diameter and the helicity of a

nanotube. If the pentagon and heptagon are attached by one side as a linked pair, they may be very hard to detect in a nanotube, but if many of them happen to be oriented in a similar direction, then the nanotube will become wider and wider as illustrated at the right.

An example of such a widening nanotube is shown in figure 2b, from which it can be estimated that a pentagon-heptagon pair must be present every 3 nm. Notice that the nanotube is open at the tip, forming a structure similar to half a torus.

According to Euler's theorem, such a torus can be formed by having six pentagons on the outer periphery and six heptagons on the inner periphery.



Reference

- a. H. Terrones, A. L. Mackay, *Carbon* **30**, 1251 (1992). B. I. Dunlap, *Phys. Rev. B* **49**, 5643 (1994).

trying to understand the nanotube growth mechanism. He suggested that the high electric field, due to the voltage drop in the space-charge sheath near the cathode, might be responsible for keeping the nanotubes open and might result in elongated structures.⁹

More detailed analysis of the physics of the arc plasma by Eugene Gamaly of Australian National University indicates that the electric field is not after all the major player and that the growth of nanotubes is the result of the competition between two types of carbon species present near the cathode surface: the anisotropic unidirectional carbon ions accelerated across the gap, and the thermally evaporated carbon from the cathode with isotropic velocity distribution.¹⁰ In other words, the introduction of an axis of symmetry in the reaction zone due to the unidirectional carbon species results in elongated structures. The suggested bimodal distribution of carbon species seems to agree well with the bimodal distribution of products—namely, nanotubes and nanoparticles (which are polyhedral and have no particular axis of symmetry—as can be seen in figure 3a.³

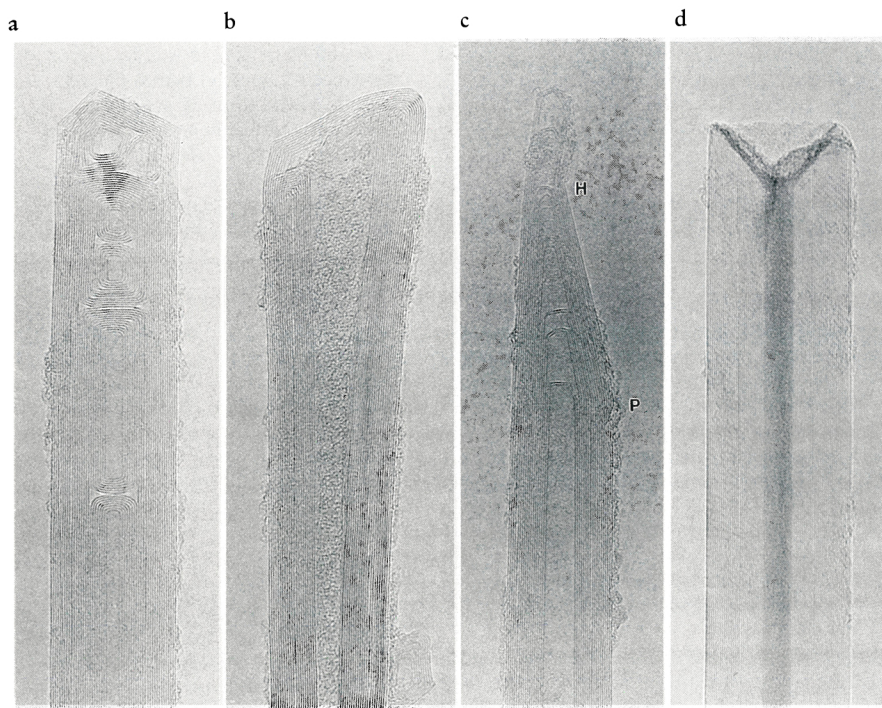
Analysis shows that such an axis of symmetry always exists in the reaction coordinates in all the methods used to generate nanotubes. For instance, in the catalytic growth of single-shell nanotubes, the catalytic particles provide this asymmetry in three dimensions. In this technique, metal catalysts such as cobalt, iron and nickel are mixed into the carbon rods consumed in the arc plasma, resulting in significant quantities of single-shell nanotubes with diameters centered around 1.2 nm. This

method was considered very promising when it was first reported by Don Bethune and his coworkers at IBM and Iijima and Tetsuya Ichihashi at NEC, because these nanotubes would allow a much better comparison with theory than would the multishell nanotubes.¹¹ However, separating these single-shell nanotubes from the residual metal and soot has been a big obstacle, and developing a purification technique remains the biggest challenge.³

It took a long time to find a way of purifying the multishell carbon arc tubes. At NEC, after trying various standard purification methods without success, we discovered that the nanotubes could be purified by oxidation in an oven at about 1000 K, with the nanoparticles being consumed faster than the nanotubes.³ Oxidation works because the nanotubes are consumed from the tip inward, and therefore their greater aspect ratio gives them a survival advantage; figure 3b shows the dramatic differences after oxidation. Hence, although the yield was quite small (about 1%), macroscopic quantities of purified multishell nanotubes were finally available and could be studied for their properties.

Defects

As with any other material, the issue of defects cannot be neglected when trying to measure and analyze nanotube properties. The required purity and perfection depend on the type of property to be measured. And the quality of the nanotube sample depends sensitively on the methodology. So it is not surprising that results have not always been consistent from one research group to another. This



NANOTUBE tip structures (a,b,c) and a filled nanotube (d). All are multishell nanotubes. The one in **b** is vase shaped with an open tip having a semitoroidal structure (see box for explanation). The nanotube in **c** has a carbon pentagon (P) and heptagon (H), resulting in a thinner tube before closing at the very tip. The nanotube in **d** is filled with bismuth oxide. The scale of each of these transmission electron micrographs is indicated by the fringe spacings, which are about 0.34 nm. (**b** is from T. W. Ebbesen, T. Takada, *Carbon*, vol. 33, p. 973, 1995; **d** is from P. M. Ajayan *et al.*, *Nature* 367, 522, 1993.) **FIGURE 2**

fact has led to suggestions that typical nanotubes are not tubes but are composed of small pieces of graphitic domains patched together like papier-mâché or rolled up like scrolls. There is no doubt that such structures exist, but they are not representative of all samples.

There is much evidence to support the view that nanotubes are seamless cylinders. For instance, when nanotubes are oxidized in an oven at high temperature, they are consumed from the tip inward, layer by layer as has been shown independently by Edman Tsang, Peter Harris and Malcolm Green at the University of Oxford and our own group.¹² If nanotubes had seams, one would expect that the seams would oxidize first, everywhere along the tube.

That does not imply that the nanotubes are defect free. They may contain a number of defects, which fall into three categories: topological defects, rehybridization defects and incomplete bonding.

Topological defects are due to the presence of rings other than hexagons in the structure (except at the ends, where six pentagons are necessary for closure). It appears that a common topological defect is the pentagon-heptagon pair in which the pentagon and heptagon are attached to each other, forming what chemists know as the azulene structure. This 5/7 pair produces no net disclination (see box) but may slightly change the diameter and the helicity, or chirality, of the tube, depending on its orientation relative to the tube axis. Such 5/7 pairs are hard to detect unless many happen to be oriented in the same overall direction, in which case the nanotube diameter will gradually widen. Such widening is observed from time to time (figure 2), and frequencies of one 5/7 pair every 3 nm can be estimated.

Mingqi Liu and John Cowley of Arizona State University have shown that nanotubes are not always cylindrical but may be polygonal.¹³ The presence of the pentagons at the tip (see box) might induce nanotubes to grow with a polygonal cross section instead of relaxing to a cylindrical shape. The edges have a stronger sp^3 character than do the flat areas, the more so the greater the degree

of curvature, forming sp^3 defect lines in the sp^2 network. These rehybridization defects will no doubt affect the properties.

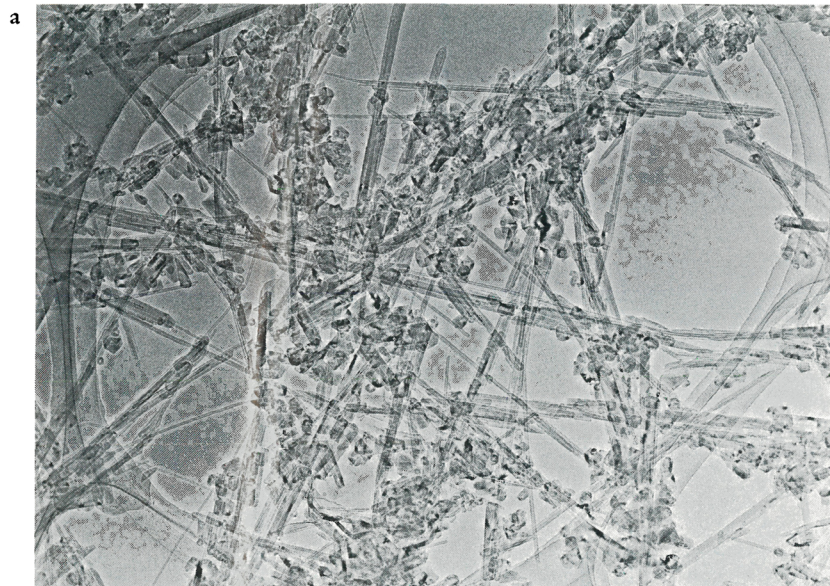
Finally, incomplete bonding due to dislocation edges are also observed, but their frequencies do not suggest that they are a major problem in normal arc-produced samples.

One might wonder why the nanotubes grown in the arc at 4000 K still contain defects. It is most likely due to the fact that kinetics, and not thermodynamics, dominate the growth process.³ As a result, there is not sufficient time for annealing the structure. As with other graphitic materials, further high temperature treatment (at about 3100 K) reduces the amount of defects, as discussed below.

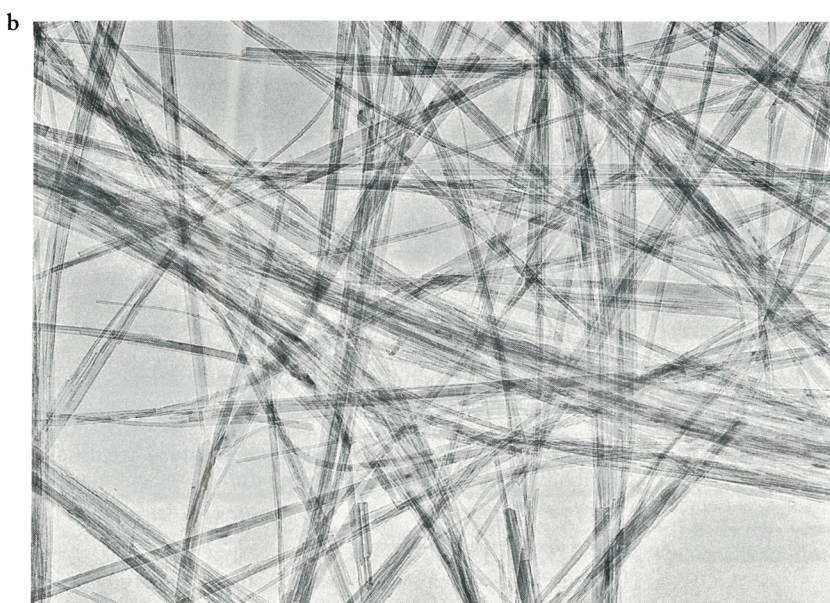
Electronic properties

The electronic properties of carbon nanotubes are of great interest in light of the theoretical predictions, but they have also been the most challenging to measure due to the small diameter of the tubes. Only very recently has one been able to attach probes directly to single nanotubes to measure transport properties. Most studies have been on bulk material, from which a great amount of information has been learned. Electron spin resonance (ESR) studies, for example, reveal that a fraction of the nanotubes are indeed metallic (or narrow bandgap semiconductors). And there has been no indication of Peierls distortion (such as instability to bond alternation in polyacetylene), in agreement with theoretical calculations.^{4,7} Furthermore, ESR studies of carbon nanotubes also illustrate well the issues of sample preparation and defects, as results have varied significantly from one group to another.

Seeing this problem, we decided that annealing the nanotubes at high temperature in argon would reduce the amount of defects. Indeed, the results are not only different, but cleaner. A single conduction-electron signal having Pauli paramagnetic temperature dependence is observed, and no localized spins appear at low temperature



CORE FIBROUS MATERIAL of a carbon arc deposit (figure 1c) before (a) and after (b) purification by gas-phase oxidation. Notice in a the presence of polyhedral particles, also known as carbon nanoparticles. The transmission electron micrographs cover a region about $2.5\text{-}\mu\text{m}$ wide. **FIGURE 3**



transport in a weakly disordered and low-dimensional electronic system. Both two-dimensional weak localization and the presence of a Landau level (quantized state of an electron in a magnetic field) at the crossing of the valence and conductance bands contribute to the positive magnetoconductance. At very low temperatures, aperiodic fluctuations, known as universal conductance fluctuations, appear superimposed on the weak localization and Landau level effects (figure 5b). The fact that such a nonannealed nanotube has features of a disordered transport system is consistent with the ESR studies before and after annealing, which indicate the presence of defects in such samples.

The greatest challenge ahead is to place four probes directly on a single nanotube. That would allow accurate measurement of the transport properties of both annealed and nonannealed nanotubes and thereby enable comparison with theoretical predictions about

the effect of the diameter and helicity on those properties.

after annealing. Perhaps the most dramatic change can be seen in the g -value (roughly the ratio of the spin-orbit coupling energy and the energy separating the coupled states), which becomes almost temperature independent after annealing, as shown in figure 4. The average Pauli paramagnetic susceptibility of the annealed purified nanotubes is greater than 4.5×10^{-8} electromagnetic units per gram, which is larger than that of graphite. This measure is a minimum because if the sample contains wide-bandgap semiconductor nanotubes that go undetected in the ESR, the susceptibility will be even larger.

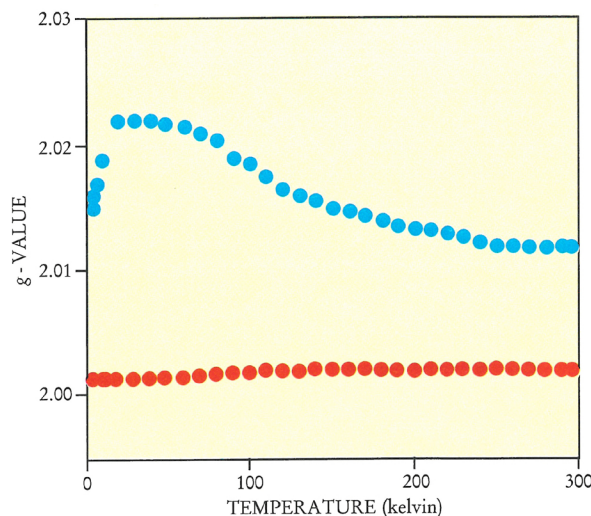
Recently, Luc Langer and his coworkers at the Catholic Universities of Louvain and Leuven in Belgium were the first to succeed in attaching probes directly to a single multishell nanotube to measure transport properties. They attached two leads to a nonannealed nanotube and measured the magnetoeconductance down to 20 mK under various field strengths. The results (figure 5a) show some remarkable features that are consistent with quantum

the effect of the diameter and helicity on those properties.

Material properties

As with carbon fibers, perhaps the most important potential application of carbon nanotubes is based on the use of their mechanical properties, in particular their high strength-to-weight ratio. In this regard, seamless nanotubes are expected to be the ultimate fiber. Again, due to their very small size, there are not yet any hard experimental values for their tensile strength, Young's modulus and so on. There are, however, many observations that nanotubes are very strong and flexible. For example, nanotubes will buckle and deform, but they recover without any damage, as shown on the cover. This property stems from the ability of the sp^2 carbon atoms to rehybridize when the bonds are deformed out of plane, the degree of sp^2 - sp^3 rehybridization being dependent on the curvature. At the same time, the in-plane rigidity and strength of graphite sheets must also be present in the nanotubes.

TEMPERATURE DEPENDENCE of the g values of the conduction electron spin resonance of purified nanotubes before (blue circles) and after (red circles) high-temperature annealing at about 3100 K. (From M. Kosaka, T. W. Ebbesen, H. Hiura, K. Tanigaki, *Chem. Phys. Lett.* 233, 47, 1995.) FIGURE 4



Other features of nanotubes that offer intriguing possibilities for material science and nanoscale experiments are the inner hollow cavity and the outer surface. For instance, the inner hollow cavity can serve as a nanoscale test tube or mold, while the outer shell could be decorated to yield catalysts with unique properties due to the high curvature.¹⁴

For such goals, it is extremely important to understand the wetting properties of nanotubes, because they govern what liquid will spontaneously cover the outer surface, be drawn inside by capillarity, mix to form a composite and so on. Capillarity is an indicator of wetting ability, as can be seen from the Young–Laplace equation

$$\Delta P = (2\gamma/r) \cos \theta$$

which relates the pressure difference ΔP across the liquid/vapor interface in a capillary to the surface tension γ of the liquid, the radius of curvature r of the meniscus and the contact angle θ between meniscus and surface. The contact angle is a direct measure of the strength of liquid/solid interactions relative to the cohesive forces in the liquid. The liquid will be drawn spontaneously into the capillary when ΔP is positive—in other words, when θ is less than 90° . In such a case the contact angle θ is said to be wetting. It is hard to predict the contact angle, and so we decided to evaluate the wetting properties of nanotubes by testing their capillarity action on various substances according to their surface tension. The results, shown in the table, indicate that nanotubes are wet only by low-surface-tension liquids, with a limit of about 200 mN/m. Hence, typical metals will not be drawn in by capillarity. Only by applying outside pressure sufficiently high to compensate for the negative ΔP will the liquid metal go in where it can be trapped by lowering the temperature below its melting point.¹⁴

Preceding and later capillarity work on metal oxides by P. M. Ajayan and his colleagues all fit within this limit.¹⁵ Figure 2d gives an example of a nanotube filled with bismuth oxide. Most recently, the researchers have shown that V_2O_5 ($\gamma = 88$ mN/m) will cover both the inside and outside of the nanotube, acting like a template for the formation of nanoceramic fibers. We predicted that the low-surface-tension limit was sufficiently high to allow wetting by organic solvents and thus was favorable for doing chemistry. This idea was confirmed independently by a simple and elegant experiment by the Oxford re-

searchers.¹⁶ They used nitric acid ($\gamma = 43$ mN/m) to open the nanotube tips by oxidation and fill the nanotube with a metallic compound dissolved in the acid. In other words, the nitric acid acts first as a tube opener and then as a low-surface-tension carrier to introduce material inside the nanotube that otherwise would not have gone in spontaneously. This technique should be very useful for filling nanotubes with a variety of materials.

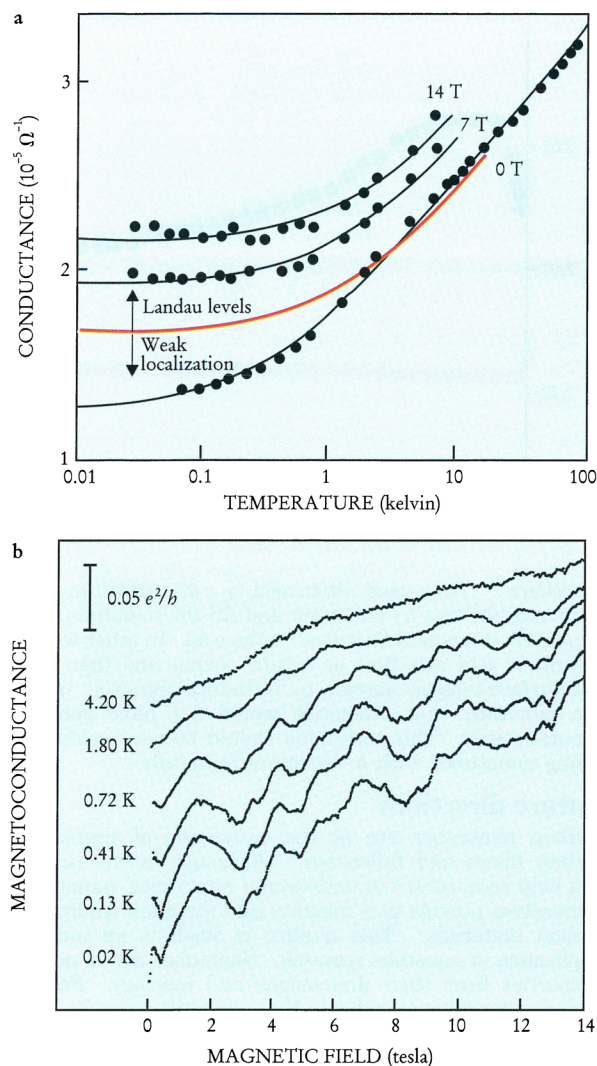
Future directions

Carbon nanotubes are at the crossroads of traditional carbon fibers and fullerenes.³ Although carbon science can help researchers to understand nanotubes, nanotubes themselves provide new insights into the more traditional carbon materials. This quality in itself is an indirect application of nanotube research. Nanotubes derive unique properties from their dimensions and topology. For instance, experiments indicate that nanotubes can be used as atomic-scale field emitters¹⁷ and as pinning material in high- T_c superconductors.¹⁸ Further studies of their

Nanotube wetting abilities*

Substance	Surface tension (millinewtons per meter)	Wetting
HNO ₃	43	Yes
S	61	Yes
Cs	67	Yes
Rb	77	Yes
V ₂ O ₅	80	Yes
Se	97	Yes
Pb oxides	(PbO ~ 132)	Yes
Bi oxides	(Bi ₂ O ₃ ~ 200)	Yes
Te	190	No
Pb	470	No
Hg	490	No
Ga	710	No

*Wetting properties of nanotubes in terms of surface tension of selected substances in their liquid state. The Pb and Bi oxides had unknown stoichiometry in the experiments.



ELECTRICAL AND MAGNETIC CONDUCTANCE. **a:** Electrical conductance of a single multiwalled 20-nm nanotube as a function of temperature at the indicated magnetic fields. The colored curve separates the contributions to the magnetoconductance from the Landau levels and the weak localization. **b:** Plot of magnetoconductance as a function of magnetic field, showing the appearance of universal conductance fluctuations at low temperatures. (From L. Langer, V. Bayot, E. Grivei, J.-P. Issi, J. P. Heremans, C. H. Olk, L. Stockman, C. Van Haesendonck, Y. Bruynseraede, *Phys. Rev. Lett.* **76**, 479, 1996.) **FIGURE 5**

mechanical properties are extremely important, because that category is where the direct application perhaps has the most potential; nanotube-reinforced materials are one possibility. Low-cost methods for generating large quantities of perfectly graphitized nanotubes will be necessary for such bulk applications. In this regard, further analysis of their growth mechanism is warranted. Nanotubes made from elements other than carbon also open exciting avenues for future research.¹⁹

Although there has been considerable activity in this field, much work remains to be done, in particular directly on individual nanotubes. This work is perhaps the most challenging, but it opens the door to broader studies relating bulk properties to graphitic materials with specific geometrical designs. Only when researchers can do this systematically will they be able to fully tap the wealth that is hidden in carbon.

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