Carbon Nanotubes and Nanofibres: Exotic Materials of Carbon

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(Received February 2, 2000, Accepted September 11, 2000)

Nanotube research has developed rapidly over the last decade, following the bulk production of C_{60} and structural identification of carbon nanotubes. This review summarises achievements in nanotube and nanofibre technology, in particular, various routes to filamentous carbon and their remarkable mechanical and electrical conducting properties. These advances are paving the way to nanoscale technology and promise to provide a wide spectrum of applications.

KEYWORDS : Carbon nanotube, Nanofibre, Fabrication

1. Introduction

Fullerenes consist of closed (sp^2 hybridized) carbon networks, organised on the basis of 12 pentagons and any number of hexagons except one. This definition encompasses elongated fullerenes, known as nanotubes⁽¹⁾⁻³⁾ (Fig.1).

Nowadays, carbon nanotubes can be produced by diverse techniques such as arc discharge⁽⁴⁾, pyrolysis of hydrocarbons over catalysts^(5), 6), laser vaporisation of graphite^(7), 8), and by electrolysis of metal salts using graphite electrodes^(9), 10).

Theoretical calculations predicted that carbon nanotubes would behave as metallic, semiconducting or insulating nanowires depending on their diameter and the hexagonal pattern along the

direction of the tube axis (termed *helicity* or *chirality*)^(11), 12). More interesting, transport measurements on bulk nanotubes^(13), 14), individual multi-layered tubes⁽¹⁵⁾ and single-walled tubules^(6), 17) revealed that their electronic properties depend markedly on their crystallinity, diameter and helicity. Mechanical strength measurements also show that multi-layered nanotubes are much stronger than conventional carbon fibres⁽¹⁸⁾ and are extraordinarily flexible when subjected to large strain.

Recent nanotubes applications include: (i) gas storage of Ar ⁽¹⁹⁾ and H_2 ^(20), 21); (ii) STM probes⁽²²⁾ and field emission sources^(13), 23); (iii) high power electrochemical capacitors⁽²⁴⁾ and (iv) the production of nanorods (*e.g.* TiC , NbC , Fe_3C , GaN , SiC & BC_x) using carbon nanotubes as reacting templates⁽²⁵⁾.

2. Carbon nanotubes and Nanofibres

2.1 Structure

The interlayer spacing within multi-walled nanotubes ($d_{(002)} = 3.4 \text{ \AA}$) is slightly greater than that of graphite ($d_{(002)} = 3.35 \text{ \AA}$). This fact is ascribed to a combination of tubule curvature and van der Waals force interactions between successive graphene layers. Nanotube diameters are usually $< 10\text{-}20 \text{ nm}$, and they could be up to several microns in length. When the diameter of the tube becomes larger than 15 nm , it should be termed as nanofibres, because the tube larger than 15 nm polygonizes when it is heat-treated, meaning that the structural property is not exactly the same as the tubes with smaller diameter. Since the diameter effect of the tubes is outside the scope of this paper, 'nanotubes' will be used hereafter as a term including both nanotubes and nanofibres.

It is important to mention that filamentous carbons can exhibit a wide range of diameters ($1 \text{ nm}\text{-}10 \text{ }\mu\text{m}$), thus possessing diverse potential technological applications. For instance, the bulk properties of graphite dominate the characteristics of large

Fig.1 Representation of a nanotube, which can be regarded as an elongated fullerene.

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Fig.2 Comparison of size diameters and $d_{(002)}$ spacings (determined by X-ray powder diffraction) of various filamentous carbon. Note that nanofibres are located within the interface of carbon nanotubes (quantum properties) and bulk thick carbon fibres.

Fig.3 Molecular models of single-walled nanotubes with different helicities: (a) zig-zag arrangement; (b) armchair configuration; (c) and (d) two different helicities.

diameter fibres (> 100 nm), whereas carbon nanotubes (< 10 – 20 nm OD) obey quantum effects. **Fig.2** shows a comparison of size diameters and $d_{(002)}$ spacings (determined by X-ray powder diffraction) of various filamentous carbons⁶³. It is noteworthy that carbon nanofibres (or vapour grown carbon fibres) are located within the interface of nanotubes and bulk (thick) carbon fibres. Therefore, it is expected that filaments within the intermediate range: $10 < \text{diameter} < 100$ nm, may exhibit

Fig.4 Graphene sheet. There are many ways to roll it over and therefore, different types of tubules. This vector convention is used to define each point on the lattice. Unitary vectors a_1 and a_2 are necessary to determine the rolling direction expressed by vector C_n .

properties between those of bulk graphite and quantum wires.

2.1.1 Straight and Crystalline nanotubes

As discussed previously, carbon nanotubes consist of nested hexagon-rich cylinders, composed of sp^2 hybridized carbon, and terminated by caps containing 12 pentagons (six per end). Starting from a flat *graphene* layer, it is possible to construct a cylinder by rolling it up in different ways. Two of these are "non-helical" so that the graphite lattices at the top and the bottom of the tube are parallel. The latter arrangements are termed 'armchair' and 'zig-zag'. Armchair nanotubes exhibit two C-C bonds on opposite sides of each hexagon, which are perpendicular to the tube axis, whereas in the zig-zag arrangement, these bonds are parallel to the tube axis (**Fig.3a-b**). In all other conformations, the C-C bonds lie at an angle to the tube axis and a helical structure results (see **Fig.3c-d**).

Early theoretical calculations indicated that the electronic properties for a single-walled nanotube will vary as a function of its diameter and helicity^{11, 12}, and more interestingly, the tubes may be semiconductors or metallic.

2.1.2 Constructing Nanotubes and their properties

The way of constructing a single-walled nanotubes, from a graphene sheet, starts by the selection of an origin $(0, 0)$, followed by choosing a second lattice point in the sheet given by (m, n) (see **Fig.4**)¹². By rolling up the sheet so that the chosen lattice point is superposed in the origin, the desired tubule can be generated (**Fig.4**).

The index (m, n) expresses the lattice point which can be used to determine tube diameter and helicity (or chirality).

The vector $\alpha = 1.42 \times \sqrt{3}$ Å determines the direction of rolling and therefore, the diameter can be expressed as

$$d = \frac{a\sqrt{m^2 + mn + n^2}}{\pi} \dots\dots\dots (1)$$

Note that the C-C distance is 1.42 Å.

The universal description of chiral tubules encompasses the range of orientations for $\frac{(2m+n)}{3} = \text{integer}$. In order to determine an armchair and zigzag structure in terms of (m, n) and the inclination angle θ , it is necessary to fulfill the following

Fig.5 (a) Hemispherical cap of a carbon nanotubes-headed arrows denote likely pentagon sites (interlayer spacing, ca. 0.34 nm), and (b) possible structures for nanotubes tips depending upon the introduction of pentagons within the mainly hexagonal framework.

conditions :

$$\theta = 0, (m, n) = (p, 0), \text{ where } p \text{ is integer (zigzag) } \cdots \cdots (2)$$

$$\theta = \pm 30^\circ, (m, n) = (2p, -p) \text{ or } (p, p) \text{ (armchair) } \cdots \cdots (3)$$

The chiral angle θ (angle between C_n and the zigzag direction) is defined as:

$$\theta = \arctan \left[\frac{\sqrt{3}n}{2m+n} \right] \cdots \cdots \cdots (4)$$

Various studies predict that all armchair fibres are metallic, as are zigzag tubules when m is a multiple of three⁽²⁾. The metallic conductivity condition for these structures can be written:

$$\frac{(2m+n)}{3} = \text{integer} \cdots \cdots \cdots (5)$$

If Eq (5) is not satisfied, it is hypothesised that the tube may exhibit semiconducting properties.

2.1.3 Nanotube Tips

Nanotube end-caps provide a rationale for the growth and helicity of a tube. As noted already, six pentagons (regularly or randomly distributed) are necessary and sufficient to close one end of a nanotube. However, five pentagons are capable of closing a nanotube in a cone-like shape⁽²⁶⁾. **Fig.5** shows a carbon nanotube cap and their associated morphologies, depending upon the pentagonal arrangement within the cap. The strain introduced by the pentagons renders the caps chemically reactive. Confirmation of this process is provided by oxidation, which takes place in air at ca. 750°C⁽²⁷⁾ (see also section 2.2.2).

2.1.4 Helicoidal and hemitoroidal nanotubes

In the beginning of the last decade, Mackay & Terrones⁽²⁸⁾ proposed, for the first time, that the introduction of heptagons into the hexagonal graphite network would produce negative curvature. Iijima *et al*⁽⁴⁾ introduced this concept when they observed 30 degree bends with carbon nanotubes, explained on the basis of the presence of one extra pentagon per heptagon (see **Fig.6**). Helicoidal and toroidal graphite containing 5, 6 and 7 membered carbon rings were also predicted theoretically⁽²⁹⁾, and evidence for its existence was reported soon after^(6), 30).

Helicoidal nanotubes have been reported in samples obtained by pyrolysis of acetylene over a cobalt catalyst⁽⁶⁾. During this process (see section 2.3), the catalytic particle plays a crucial role in the nanotube growth, since accretion of carbon atoms appears to take place on the metal surface. As a result, it is possible that different rates of carbon agglomeration may arise within the nanotube walls. These are responsible for the bent structures (e.g. spirals and helices; see section 2.3). These helices are multi-walled and complex, however, the simple archetypal single wall helix (**Fig.7**) has yet to be synthesised.

Hemitoroidal nanotube tips (axially-elongated concentric doughnuts; **Fig.8**) have been produced by passage of an arc between graphite rods^(4), 31) (**Fig.8** (b)). In addition, the formation of hemi-toroidal-linked structures between adjacent concentric walls in pyrolytic produced carbon nanotubes has been observed^(26), 30) (**Fig.8** (c)). These structures appear to form as a result of optimal graphitisation of two or more adjacent concentric graphene tubules.

The arrangement for these "sock-like" (inwardly-folded;

Fig.8 (a) structures can be envisaged as cauterised rim-seals, which link the inner or the outer tubes, thereby avoiding dangling

Fig.6 Nanotube cap exhibiting negative curvature due to the presence of a pentagon-heptagon pair; the 30° -pentagon declination (right hand bend) cancels the 30° -heptagon inclination (left top bend), ending with six pentagons at the hemispherical cap (interlayer spacing, ca. 0.34 nm).

bonds. These structures can be thought of as concentrically growing nanotubes which have been forced into U-turns in order to generate a more stable graphene configuration. Due to the presence of pentagon-heptagon pairs, the electronic properties for these structures may well diverge from those of conventional nanotubes.

2.2 Arc Discharge Nanotube Production

Optimum conditions for nanotube generation involve passage of a direct current (100 A) through two graphite (6-8 mm

Fig.7 Simulated single-wall corkscrew carbon nanotube produced by interspersing five and seven-membered rings judiciously within the mainly hexagonal network.

(a)

(b)

(c)

Fig.8 (a) Molecular model of a hemi-toroidal nanotube cap, consisting of two concentric nanotubes joined together at their top rims; (b) Hemi-toroidal nanotube caps found in the cathode deposit after arcing hexagonal BN/graphite mixtures (interlayer spacing, ca. 0.34 nm) and (c) Hemitoroidal graphites observed in pyrolytic produced carbon nanotubes.

diam) electrodes (separation *ca.* 1 mm) in a He atmosphere (500 Torr). During arcing, a deposit forms at a rate of 1 mm/min on the cathode (negative electrode), whereas the anode (positive electrode) is consumed. This deposit exhibits a cigar-like structure, in which a grey hard shell is deposited on the periphery. The inner core, which is dark and soft, contains carbon nanotubes and polyhedral particles.

Inner core deposits contain bundle-like structures, which contain randomly distributed nanotubes and polyhedral particles. It is possible that, as a result of carbon vapour condensation generated by the arc and by temperature gradients, carbon ion may result in the formation of anisotropic structures (tubules) on the cathode. It is believed that an open-end mechanism (see below) may play a role in the generation of elongated structures. Polyhedral particles may arise from frustration associated with axial open-growth, possibly caused by arc instabilities such as current and localised abrupt pressure changes.

2.2.1 Deposit formation and growth mechanisms

Two main 'atomistic' growth mechanisms have been proposed in order to explain the formation of individual carbon nanotubes. The first, by Iijima and coworkers⁴⁾, states that carbon atoms (*e.g.* C, C₂, C₃ units) attach to the edges of a growing carbon cylinder, which closes when conditions are not suitable for growth. An alternative scheme, by Endo and Kroto¹⁾, proposes that nanotubes are essentially elongated giant fullerenes which grow by direct insertion of carbon species, accreted from the vapour phase, into the closed network.

However, experiments using hydrogen as a buffer gas in the arc discharge lead to the formation of C-H bonds at the tips, thus inhibiting nanotube closure. In addition, the observation that small diameter carbon tubules are contained within larger diameter tubules provide evidence that the inner tube is denied access to a carbon source during growing. These results support the open-ended mechanism for nanotube formation proposed by Iijima and coworkers.

Bulk nanotube growth mechanisms have also been proposed, the latest and more complete being due to Gamaly and Ebbesen³²⁾. This model deals with the carbon velocity distribution in the reaction zone near the cathode surface and contains two groups of carbon species, designated fast and slow. The fast carbons are thought to be anisotropic (one symmetry axis) and are held to be responsible for the nanotube length. The second (slow) group exhibits an isotropic carbon velocity distribution (Maxwellian), which is possibly responsible for nanotube width, and hence multilayered nanostructures. This second group may be responsible for the formation of polyhedral nanoparticles, and may favour nanotube capping after arcing is discontinued.

Ajayan *et al.* analysed cathode deposits by SEM³³⁾, and stated that nucleation and growth of nanostructures occur only in a high density carbon vapour, and that porous-like microstructures form as part of the inner core cathode deposit.

2.2.2 Nanotube purification

Carbon nanotubes produced by arc discharge techniques can be freed from polyhedral particles by differential oxidation²⁷⁾ [see Fig.9]. Unfortunately, the method suffers from the drawback that more than 95% of the original material is destroyed, and the remaining nanotubes lose their end caps.

Fig.9 TEM images: (a) bulk material containing nanotubes and polyhedral particles, 1 : 2 ratio; (b) oxidised sample (10.5% of the original mass remaining), exhibiting a decrease in the number of polyhedral particles; (c) oxidised sample (1% of the mass remaining), showing essentially pure nanotubes.

However, non-destructive methods for separating carbon nanotubes from polyhedral particles have been reported. These involve the use of well-dispersed colloidal suspensions of tubes/particles, coupled with surface-active agents (surfactants, polymers or other colloidal particles), which prevent aggregation. Subsequent filtration of the suspensions, using porous filters³⁴⁾ and size exclusion chromatography³⁵⁾, yield size-graded almost pure nanotubes. Nevertheless, large scale purification using these methods may be difficult to achieve.

2.3 Hydrocarbon pyrolysis over catalysts

Pyrolysis of hydrocarbons (*e.g.* benzene, acetylene, naphthalene, ethylene, etc.) in the presence of catalysts (*e.g.* Co, Ni and Fe deposited on substrates such as silicon, graphite or silica), provides an alternative route to fullerenes and carbon nanotubes. It is noteworthy that prior to the discovery of fullerenes in 1985, pyrolytically grown nanofibres/nanotubes had actually been observed and structurally identified by several authors^{36), 37)}. Even at that early stage, a growth mechanism was postulated involving

metal (catalyst) particles, which were held to be responsible for the agglomeration of carbon and subsequent axial growth of the fibre.

2.3.1 Filament growth

It is now well recognised that pyrolysis of hydrocarbons and of carbon monoxide over catalysts (*e.g.* Co, Ni, Fe, Pt, Cu) at high temperatures ($> 600\text{ }^{\circ}\text{C}$) yields to graphite filaments and nanotubes³⁷⁾.

Several authors have proposed mechanisms to account for the formation of carbon filaments and nanotubes by pyrolysing hydrocarbons over catalysts. At present, the following mechanisms, have been widely recognised:

Carbon diffusion 'through' catalytic particles: Baker *et al*³⁷⁾ postulated that decomposition of acetylene on the exposed surfaces of the metal catalyst, resulted in gaseous hydrogen and carbon. The carbon then diffuses through the catalytic particle and precipitates at the other end of the filament. The exothermic nature of hydrocarbon decomposition results in a temperature gradient across the catalyst, which appears to be a crucial factor associated with the model in question. Thus, carbon is precipitated at the colder zone of the particle, allowing the filament to grow. This process continues until the catalytic activity of the leading particle is 'neutralised'.

Carbon diffusion 'on' catalytic particles: Baird *et al* in 1974³⁸⁾ and Oberlin *et al* in 1976³⁹⁾ postulated that carbon filaments are formed by surface diffusion on the particle (**Fig.10**). This process should be easier if the catalyst particles are liquid.

Carbon nanotubes produced in this way may account for preferential carbon growing on selected faces of the catalytic particle [*i.e.* the Fe particle is oriented with its (100) axis along the filament axis, whereas Fe/Co or Fe/Ni alloys prefer the (110) orientation].

Diffusion parameters can also depend critically on the dimensions of small particles. A recent model accounts for the formation of hollow filaments, based upon the precipitation of carbon on the catalytic particle. Here, graphite planes grow parallel to the exterior fibre planes and a hollow core is formed. However, other studies on the filament tips where the metal particle is located, suggested that the basal planes were positioned at an angle to the filament axis³⁹⁾. In this case, the Ni particles were aligned with respect to its (112) axis, parallel to the filament axis (cone-like structures).

Fig.10 Schematic illustration of the growth mechanism proposed for carbon fibres and filaments formed by pyrolysing benzene over catalytic particles (From Oberlin *et al.*).

From the above argument, it is clear that there may not be a unique growth mechanism for the production of carbon filaments and nanotubes. Changing parameters, such as type of hydrocarbon, catalysts, particle size and temperature, leads to different filaments possessing various morphologies and degrees of crystallinity. However, any pyrolysis experiment in the presence of catalysts results in the formation of elongated structures. Therefore, deposition of 'uniform catalyst particles' must play a vital role in preferential nanotube generation, thus controlling diameter and length.

2.3.2 Aligned multiwalled nanotubes

Ajayan and co-workers were the first to report aligned nanotube arrays by cutting thin slices (50-200 nm thick) of a nanotube-composite polymer⁴⁰⁾. However, the alignment strongly depended upon the thickness of the composite slice and the process becomes impractical for larger areas.

Alternative bulk growth processes using laser etching of cobalt thin films provides an efficient route to catalysts which, in conjunction with the pyrolysis of organic precursors (*e.g.* 2-amino-4,6-dichloro-s-triazine, etc.) yields aligned nanotubes⁴¹⁾. These tubes are of uniform length ($\leq 100\text{ }\mu\text{m}$) and diameter (30-50 nm od) and grow perpendicularly to the catalytic substrate 'only' in the etched regions [**Fig.11**]. The orientation of the catalyst particles, ablated during etching, appears to be crucial, nanotubes with preferred helicity being favoured (*e.g.* armchair 25-30 %). It is possible that matrices consisting of aligned nanotube bundles may be useful as novel mechanically strong composite materials and as ultra-fine field emission

Fig.11 SEM images of aligned nanotube bundles: a) Low magnification of adjacent bundles in which nanotubes appear fairly aligned; b) Higher magnification of one bundle showing aligned nanotubes [uniform length (20 μm) and diameters (30-50 nm)].

sources^{(13), (23)}.

Another recent report describes the large scale synthesis of aligned carbon nanotubes, of uniform length and diameter, by passage of acetylene over iron nanoparticles embedded in mesoporous silica⁽⁴²⁾. The latter two methods, based on the pyrolysis of organic precursors over templated/catalysts supports, are by far superior by comparison with plasma arcs, since other graphitic structures such as polyhedral particles, encapsulated particles and amorphous carbon are notably absent. Subsequently, Rao and co-workers (The Indian Institute of Science) reported a simple and low cost route to aligned MWNT's, by pyrolysis of ferrocene at 1000 °C in the absence of any additional hydrocarbon⁽⁴³⁾.

Recently, a modified pyrolytic process has been used by a research team from the Chinese Academy of Sciences, Beijing to produce MWNT's an order of magnitude longer (2 mm) than is usually achieved using this method⁽⁴⁴⁾. Furthermore, Dai and co-workers at Stanford University have developed successfully an efficient route to construct 3 dimensional regular arrays of nanotube towers (base: 50×50 μm²; height: < 250 μm), by ethylene pyrolysis over chemically patterned Fe/Si substrates⁽⁴⁵⁾. Field emission studies of the latter material exhibits low operating voltages and high current stability, comparable to the best field emission previously reported for arc discharge MWNT's or SWNT's.

2.4 Nanotubes produced by laser vaporisation

Laser vaporisation of graphite at high temperature (1200 °C) in an inert atmosphere (Ar) produces multi-walled carbon nanotubes^{(12), (46)}. The growth mechanism states that a graphitic flake, with at least one pentagon, is first created from the carbon vapour formed by graphite vaporisation. Under specified high temperature conditions, this flake may anneal, thus creating fullerenes, which may nucleate and form onions. If the carbon density is high enough, successive concentric graphite layers form around the template and multi-walled nanotubes are produced. Crystalline bundles of single-walled nanotubes

If graphite/Co-Ni mixtures are used as a target during laser vaporisation at 1200 °C, bundles or ropes of single-walled nanotubes are produced⁽⁸⁾. These usually appear to contain mainly (10,10) nanotubes (13.8 Å diameter) packed in a crystalline form. X-ray powder diffraction reveals that these ropes or bundles consist of 100-500 single-walled tubes packed in a two dimensional triangular constant lattice of 17 Å⁽⁸⁾. A 'scooter' growth mechanism was proposed to account for the generation of these ropes. Initially, Ni or Co chemisorbs to the open end of a graphene sheet, binding to its edge and catalysing rearrangements of carbon rings (generated in the gas phase), thus favoring the axial growth of the tubes⁽⁸⁾. It is not obvious why single atoms would scooter around the edge of these tubules. Therefore, it is more likely that Co and/or Ni clusters are responsible for the growth of such tubular structures. In this context, a novel growth mechanism, based on the absorption of Ni/Co atoms on the surface of C₆₀⁽⁴⁷⁾, was proposed. This model suggests that a metal-coated fullerene acts as a growing template and, once growth has been initiated, nanotube propagation may occur without the particle been involved. If the resulting nanotube is conical, rather than cylindrical, growth will cease rapidly,

especially if the propagating walls converge.

Bundles of single-walled nanotubes can also be produced using arc discharge techniques in presence of Co or Ni. Very recently, bundles of single-walled nanotubes were obtained in high yield by plasma arcs, using graphite anode mixtures containing yttrium and nickel⁽⁴⁸⁾. These bundles are deposited on a 'collaret', formed around the cathode, generated after arc vaporisation.

Recently, the pyrolysis of metallocenes (e.g. ferrocene, nickelocene, cobaltocene, etc.) in conjunction with hydrocarbons (e.g. acetylene, benzene, ethylene), sometimes in the presence of sulfur, at 700-1200 °C, has been used to generate bundles of aligned SWNT's⁽⁴⁹⁾. However, the quality and yields of these pyrolytically grown tubes need to be improved further before this becomes a valuable commercial method for their production.

A disadvantage, associated with the methods described above, arises from the presence of catalytic particles. In this context, recent reports have shown that separation of single-walled nanotube bundles from the catalytic particles can be achieved by chemical methods. Tohji *et al*⁽⁴⁹⁾ described a technique that led to a 95% purity sample of separated single-walled nanotubes, accompanied by polyhedral particles and small concentrations

Fig.12 (a) TEM image showing single-walled nanotube bundles, with encapsulated metal particles, produced by arc discharge techniques using Ni-Y/graphite mixtures; inset shows a cross section of a bundle of 6 tubes; (b) HRTEM image showing single walled nanotubes (SWNT's) and bundles (courtesy of J. P. Zhang).

of encapsulated metal particles.

2.5 Electrolytic fabrication of nanotubes

Surprisingly, fullerene-related nanomaterials are formed under electrolytic conditions^{(9), (10)}. Using graphite electrodes immersed in molten LiCl under argon, some 20-30% of the carbonaceous material formed may consist of graphitic nanotubes.

The condensed-phase apparatus⁽¹⁰⁾ was used with LiCl. After electrolysis of graphite electrodes immersed in the molten ionic salt (e.g. LiCl at 600 °C), After removal by filtration, the solids revealed the presence of carbon nanotubes and other graphite-like nanostructures.

Nanotubes produced in this way are similar to those formed in the carbon arc processes (*i.e.* multi-walled structures possessing interlayer spacings of *ca.* 0.34 nm).

It is clear that the cathode immersion depth, as well as the current, play important roles in controlling the type of nanomaterial formed. It is possible that a combination of the electrical potential and metal atom/cluster, or radical reactions (involving lithium metal atoms or ions) with the carbon electrode at the surface of the cathode may be involved in network fabrication, leading to nanomaterials. In other words, molten droplets of Li may form by localised electrolysis at prominent points on the carbon cathode surface. These droplets may dissolve carbon, which is subsequently transformed into nanotubes. As a consequence, these nanotubes, may concentrate the electric field of the cathode, serving as an enhanced site for electrolysis of molten LiCl.

3. Mechanical and conducting properties

HRTEM observations indicate that nanotubes are flexible (see Fig.13). For instance, they can be bent mechanically by sonication, grinding or by being embedded in a polymer resin⁽⁴⁰⁾. Theoretical calculations predicted these properties noting that the tubes would soften with decreasing radius⁽⁴⁰⁾. It has also been predicted that the tube stiffness is dependent on helicity (e.g. zig-zag tubes would be less stiff than the armchair tubes).

Young's modulus measurements of individual multi-walled carbon nanotubes were first carried out by Treacy, *et al.*⁽¹⁸⁾. The authors reported that the nanotubes possess an average Young's modulus of $Y = 1.8$ TPa, which is much higher than that of commercially available carbon fibres ($Y \sim 800$ GPa).

In this context, carbon nanotubes can be bent through large angles, without undergoing catastrophic failure (Fig.13). The latter measurements confirm that carbon nanotubes are extraordinarily flexible under large strain, which makes them good candidates for super-strong carbon-fibre-reinforced materials.

The first transport measurements on single bundles of carbon nanotubes, using two gold contacts attached by lithographic techniques, revealed a temperature-dependent resistance, which fitted well (2-300 K) a simple two-band semi-metal model⁽⁵¹⁾. Subsequent measurements showed the presence of thermal activated electrical behaviour with band gaps ranging from 6 to 260 meV⁽⁵²⁾. More recent conductivity measurements on 'aligned' bundles of carbon nanotubes⁽¹³⁾ showed that the material, behaved as conducting rods, and exhibited anisotropy in respect of transport properties for different alignment configurations. For instance,

Fig.13 (a) Molecular model of a collapsed nanotube showing bending within the hexagonal network; (b) aligned and deformed tubes embedded in a polymer resin [85], arrows indicate the nature of bending within the tubes; the larger tube has been twisted but the smaller one shows no such defect (courtesy of P. M. Ajayan); (c) SEM image of a carbon nanotubes (contained in the inner core of a vapour grown carbon fibre) surviving a mechanical fracture in liquid nitrogen. This suggests that nanotubes (which act as growing templates for carbon fibres) possess high flexural strength.

measurements on a single bundle-like particle taken from the inner core cathode deposits ($0.5 \times 0.6 \times 1.1$ mm³) and consisting of smaller bundles composed of randomly distributed nanotubes, revealed a nearly temperature-independent conductivity along the bundle axis. However, further microwave contactless conductivity measurements showed that inner core cathode deposits (nanotubes/nanoparticles generated by arc discharge methods) exhibited thermal activated behaviour with activation energies of *ca.* 70 meV (somewhat smaller than those reported for individual nanotubes).

Transport measurements on single multi-layered nanotubes

revealed that each nanotube exhibits unique conductivity properties¹⁵⁾, leading to both metallic and non-metallic behaviour (resistivities at 300 K of *ca.* $1.2 \times 10^{-4} - 5.1 \times 10^{-6}$ Ohm cm; activation energies < 300 meV for semiconducting tubes). In addition, bundles of single-walled nanotubes have been shown to behave as metals with resistivities in the 0.34×10^{-4} and 1.0×10^{-4} Ohm cm range⁸⁾.

The most recent achievement in this respect, involves transport measurements on a single-walled nanotube (1 nm in diameter), showing that it behaves as a quantum wire, in which electrical conduction seems to occur via well-separated, discrete electron states that are quantum-mechanically coherent over long distances¹⁶⁾.

Using a scanning tunneling microscope (STM)^{16), 17)}, various authors imaged single walled carbon nanotubes with atomic resolution, and observed chiral winding patterns of hexagons along the tube axis. Further local density of states measurements on different tubes, revealed for the first time clear experimental verification of the theoretical band structure predictions. Basically, the results demonstrate that nanotubes can be either metals or semiconductors depending on small variations in the chiral angle or diameter.

4. Future applications

Various applications of carbon nanotubes are envisaged, among which nano-scale engineering and electronics are prominent. For example, very recently Tans, Vershueren & Dekker fabricated a three-terminal switchable device based upon a single nanotube molecule⁵³⁾. This transistor, which operates at room temperature, consists of a semiconducting single-walled nanotube connected to metal nanoelectrodes. The performance, in terms of switching speed due to low capacitance, is excellent⁵³⁾.

Furthermore, a method devised to control the length and, consequently, the electronic properties of individual nanotubes by STM nanostructuring has been reported⁵⁴⁾. This technique allows one to cut nanotubes into shorter sections, which may be useful for future construction of molecular machinery and/or nano-scale circuits.

Integration of multiple devices into circuits may be feasible in future if molecular self assembly methods can be controlled, thus producing nanotubes with desired dimensions and properties. Bent tube, which is a good candidate structure for such devices, arises as a result of pentagon insertion (outer rim with positive curvature) matched by the inclusion of a heptagon (inner rim with negative curvature) on opposite sides of the tubule (Fig.14).

Therefore, chirality changes by 30° may cause significant variations in the electronic properties (e.g. from metallic conductor to semiconductor because a bend can transform a zig-zag configuration into an armchair arrangement). The properties of these bent structures have been widely investigated by Lambin *et al*⁵⁶⁾. These structures may behave as nano-switches. Collins *et al* observed abrupt transport changes (from graphite-like response to highly non-linear) along single walled nanotubes⁵⁷⁾. These changes may be due to the presence of defects such as pentagon-heptagon pairs. However, further investigation is needed in order to confirm this and other topological defect

Fig.14 Molecular simulation model showing the change in helicity by 30° (from zig-zag to armchair) two different electronic properties (e.g. semiconductor and metallic conductor) are possible.

calculations within graphite networks (e.g. pentagon-heptagon, pentagon-octagon, etc.).

Novel structures based upon sp^2 carbon, such as concentric giant fullerenes⁵⁸⁾, graphite cones⁵⁹⁾, graphitic cubes⁶⁰⁾, discs⁵⁹⁾ and helices⁶⁾, have been successfully generated, and await transport and mechanical studies. Predicted structures remained to be constructed⁶¹⁾.

Investigation on nanotubes and related fullerene-like structures for hydrogen storage is a necessary precursor to the development of fuel-cell electric vehicles. In addition, the fabrication of Li^+ batteries using these novel forms of filamentous carbon need to be tested in detail.

It may prove possible to develop polymer matrices of highly crystalline nanotubes or nanofibres for the fabrication of high performance composites with high electrical transport and thermal conductance. The mechanical properties of these novel composites may well be stronger and lighter than steel, thus paving the way to novel technologies.

Acknowledgement

Present work (M. T., T. H., and M. E.) is supported by a grant-in-aid for "Research for the Future Program", Nano-Carbon, from the Japan Society of Promotion of Science.

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