

CARBON NANOTUBES AND RELATED STRUCTURES

New Materials for the Twenty-first Century

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1

Introduction

Take Carbon for example then
What shapely towers it constructs
A. M. Sullivan, *Atomic Architecture*

Carbon, in fact, is a singular element . . .
Primo Levi, *The Periodic Table*

The ability of carbon to bond with itself and with other atoms in endlessly varied combinations of chains and rings forms the basis for the sprawling scientific discipline that is modern organic chemistry. Yet until recently we knew for certain of just two types of *all-carbon* crystalline structure, the naturally occurring allotropes diamond and graphite. Despite the best efforts of some of the world's leading synthetic chemists, all attempts to prepare novel forms of molecular or polymeric carbon came to nothing: the elegant all-carbon structures proposed by Roald Hoffmann, Orville Chapman and others remained firmly in the realm of pure speculation. Ultimately, the breakthrough which revolutionised carbon science came not from synthetic organic chemistry but from experiments on clusters formed by the laser-vaporisation of graphite.

Harry Kroto, of the University of Sussex, and Richard Smalley, of Rice University, Houston, had different reasons for being interested in the synthesis of carbon clusters. Kroto had been fascinated since the early 1960s in the processes occurring on the surfaces of stars, and believed that experiments on the vaporisation of graphite might provide key insights into these processes. Smalley, on the other hand, had been working for several years on the synthesis of clusters using laser-vaporisation, concentrating chiefly on semiconductors such as silicon and gallium arsenide. But he was also interested in what might happen when one vaporises carbon. In August 1985, the two scientists came together at Rice and, with a group of colleagues and students,

began the now famous series of experiments on the vaporisation of graphite. They were immediately struck by a surprising result. In the distribution of gas-phase carbon clusters, detected by mass spectrometry, C_{60} was by far the dominant species. This dominance became even more marked under conditions which maximised the amount of time the clusters were ‘annealed’ in the helium. There was no immediately obvious explanation for this since there appeared to be nothing special about open structures containing 60 atoms. The eureka moment came when they realised that a *closed* cluster containing precisely 60 carbon atoms would have a structure of unique stability and symmetry, as shown in Fig. 1.1. Although they had no direct evidence to support this structure, subsequent work has proved them correct. The discovery of C_{60} , published in *Nature* in November 1985 (1.1), had an impact which extended way beyond the confines of academic chemical physics, and marked the beginning of a new era in carbon science (1.2–1.5).

At first, however, further progress was slow. The main reason was that the amount of C_{60} produced in the Kroto–Smalley experiments was minuscule: ‘a puff in a helium wind’. If C_{60} were to become more than a laboratory curiosity, some way must be found to produce it in bulk. Eventually, this was achieved using a technique far simpler than that of Kroto and Smalley. Instead of a high-powered laser, Wolfgang Krätschmer of the Max Planck Institute at Heidelberg, Donald Huffman of the University of Arizona and their co-workers used a simple carbon arc to vaporise graphite, again in an atmosphere of helium, and collected the soot which settled on the walls of the vessel (1.6). Dispersing the soot in benzene produced a red solution which could be dried down to produce beautiful plate-like crystals of ‘fullerite’: 90% C_{60} and 10% C_{70} . Krätschmer and Huffman’s work, published in *Nature* in 1990, showed that macroscopic amounts of solid C_{60} could be made using methods accessible to any laboratory, and it stimulated a deluge of research.

Carbon nanotubes, the primary subject of this book, are perhaps the most important fruits of this research. Discovered by the electron microscopist Sumio Iijima, of the NEC laboratories in Japan, in 1991, these ‘molecular carbon fibres’ consist of tiny cylinders of graphite, closed at each end with caps which contain precisely six pentagonal rings. We can illustrate their structure by considering the two ‘archetypal’ carbon nanotubes which can be formed by cutting a C_{60} molecule in half and placing a graphene cylinder between the two halves. Dividing C_{60} parallel to one of the three-fold axes results in the zig-zag nanotube shown in Fig. 1.2(a), while bisecting C_{60} along one of the five-fold axes produces the armchair nanotube shown in Fig. 1.2(b). The terms ‘zig-zag’ and ‘armchair’ refer to the arrangement of hexagons around the circumference. There is a third class of structure in which the hexagons are arranged helically

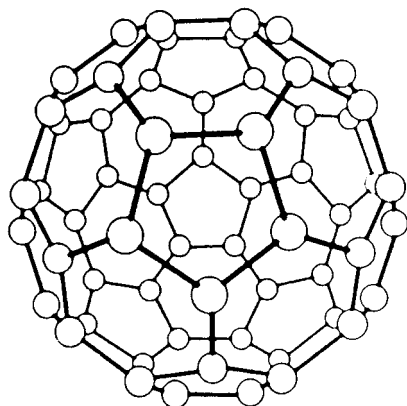


Fig. 1.1. C₆₀: buckminsterfullerene.

around the tube axis (see Chapter 3). Experimentally, the tubes are generally much less perfect than the idealised versions shown in Fig. 1.2, and may be either multilayered or single-layered.

Carbon nanotubes have captured the imagination of physicists, chemists and materials scientists alike. Physicists have been attracted to their extraordinary electronic properties, chemists to their potential as ‘nanotest-tubes’ and materials scientists to their amazing stiffness, strength and resilience. On a more speculative level, nanotechnologists have discussed possible nanotube-based gears and bearings. In this book, an attempt has been made to cover all of the most important areas of nanotube research, as well as discussing related structures such as carbon nanoparticles, carbon onions and ‘inorganic fullerenes’. This opening chapter begins with a brief account of the discovery of carbon nanotubes and then describes some of the basic characteristics of arc-evaporation-synthesised nanotubes. The pre-1991 evidence for the existence of nanotubes is discussed, and some of the directions in which nanotube research is developing are summarised. Finally, the organisation of the book is outlined.

1.1 The discovery of fullerene-related carbon nanotubes

Iijima was fascinated by the Krätschmer–Huffman *Nature* paper, and decided to embark on a detailed TEM study of the soot produced by their technique. He had good reasons for believing that it might contain some interesting structures. Ten years earlier he had studied soot formed in a very similar arc-evaporation apparatus to the one used by Krätschmer and Huffman and found a variety of novel carbon architectures including tightly curved, closed

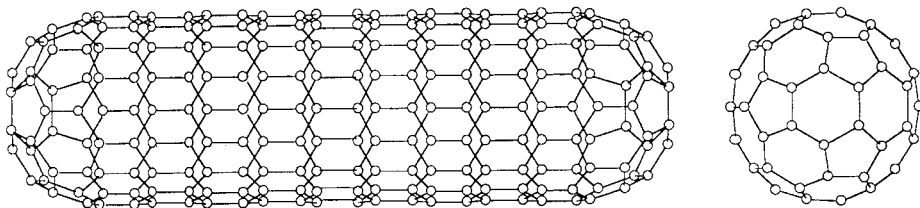
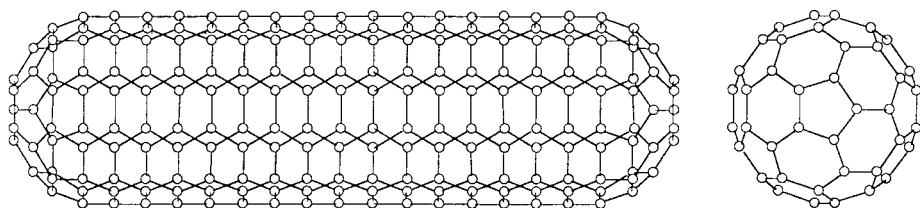
a**b**

Fig. 1.2. Drawings of the two nanotubes which can be capped by one half of a C_{60} molecule (1.7). (a) Zig-zag (9,0) structure, (b) armchair (5,5) structure (see Chapter 3 for explanation of indices).

nanoparticles and extended tube-like structures (1.8, 1.9). Might such particles also be present in the K–H soot? Initial high resolution TEM studies were disappointing: the soot collected from the walls of the arc-evaporation vessel appeared almost completely amorphous, with little obvious long-range structure. Eventually, Iijima gave up sifting through the wall soot from the arc-evaporation vessel, and turned his attention to the hard, cylindrical deposit which formed on the graphite cathode after arc-evaporation. Here his efforts were finally rewarded. Instead of an amorphous mass, the cathodic soot contained a whole range of novel graphitic structures, the most striking of which were long hollow fibres, finer and more perfect than any previously seen. Iijima's beautiful images of carbon nanotubes, shown first at a meeting at Richmond, Virginia in October 1991, and published in *Nature* a month later (1.10), prompted fullerene scientists the world over to look again at the used graphite cathodes, previously discarded as junk.

1.2 Characteristics of multiwalled nanotubes

A typical sample of the nanotube-containing cathodic soot is shown at moderate magnification in Fig. 1.3(a). As can be seen, the nanotubes are accompanied by other material, including nanoparticles (hollow, fullerene-related struc-

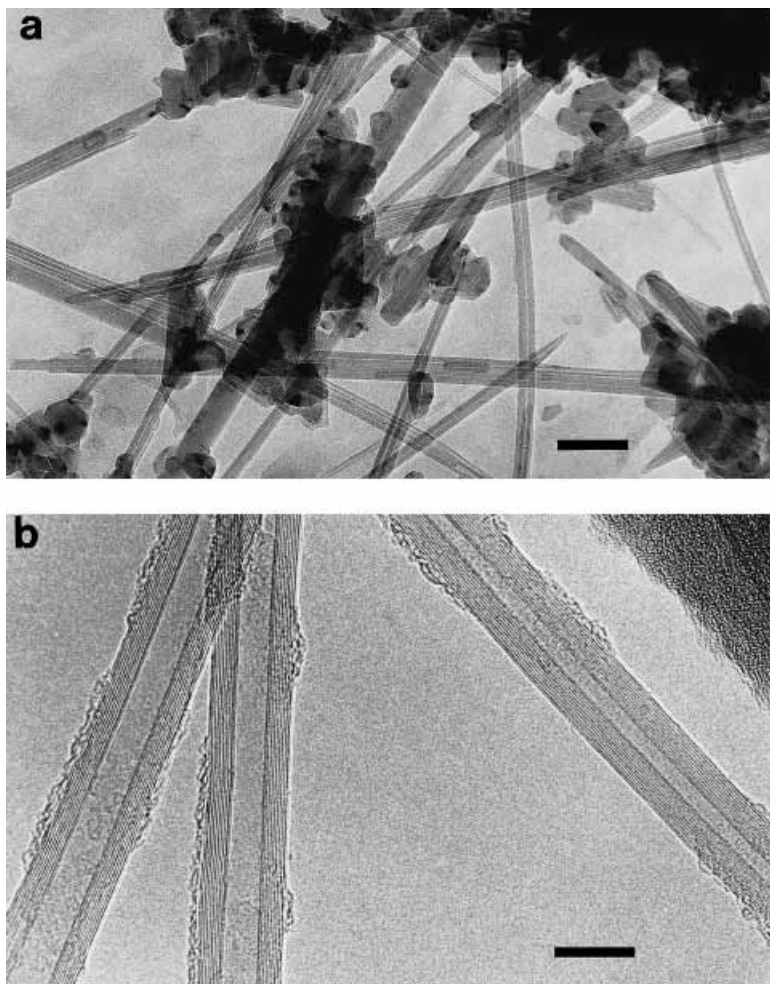


Fig. 1.3. (a) TEM image of nanotube-containing soot. Scale bar 100 nm. (b) Higher magnification image of individual tubes. Scale bar 10 nm.

tures) and some disordered carbon. The nanotubes range in length from a few tens of nanometres to several micrometres, and in outer diameter from about 2.5 nm to 30 nm. At high resolution the individual layers making up the concentric tubes can be imaged directly, as in Fig. 1.3(b). It is quite frequently observed that the central cavity of a nanotube is traversed by graphitic layers, effectively capping one or more of the inner tubes and reducing the total number of layers in the tube. An example is shown in Fig. 1.4, where a single layer forms a cap across the central tube, reducing the number of concentric layers from six to five.

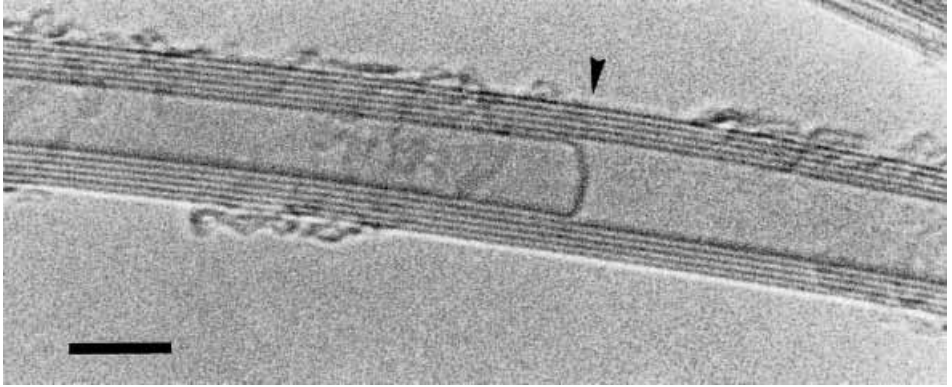


Fig. 1.4. High resolution image of multiwalled nanotube with 'internal cap'. Scale bar 5 nm.

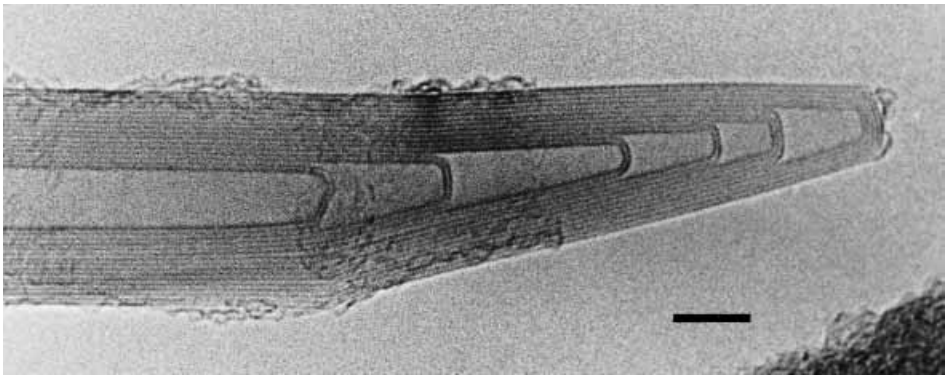


Fig. 1.5. Image of typical multiwalled nanotube cap. Scale bar 5 nm.

As mentioned above, virtually all of the tubes are closed at both ends with caps which contain pentagonal carbon rings. In practice, the caps are rarely hemispherical in shape, but can have a variety of morphologies; a typical example is shown in Fig. 1.5. More complex cap structures are often observed, owing to the presence of heptagonal as well as pentagonal carbon rings (1.11). Iijima has often illustrated the role played by pentagonal and heptagonal rings in nanotube caps by referring to the art of Japanese basket-work, of the kind shown in Fig. 1.6, where non-hexagonal rings play a similar topological role. Structures analogous to those of carbon nanotubes also occur among viruses (see Chapter 3), and, perhaps inevitably, among the architectural designs of Buckminster Fuller (Fig. 1.7).



Fig. 1.6. Japanese bamboo vase which incorporates pentagonal and heptagonal rings. Courtesy Prof. Eiji Osawa.

1.3 Single-walled nanotubes

Nanotubes of the kind described by Iijima in 1991 invariably contain at least two graphitic layers, and generally have inner diameters of around 4 nm. In 1993, Iijima and Toshinari Ichihashi of NEC, and Donald Bethune and colleagues of the IBM Almaden Research Center in California independently reported the synthesis of *single-walled* nanotubes (1.13, 1.14). This proved to be an extremely important development, since the single-walled tubes appeared to have structures which approximate to those of the ‘ideal’ nanotubes shown in Fig. 1.2. Moreover, the single-walled tubes were completely novel. While multiwalled graphitic tubules, produced by catalysis, had been known for many years before the discovery of fullerene-related nanotubes (see next section), nothing like single-walled carbon nanotubes had been observed before. An early image of a single-walled nanotube (SWNT) sample is shown in Fig. 1.8(a). It can be seen that the appearance is quite different to that of samples of multiwalled nanotubes (MWNT). The individual tubes have very small diameters (typically ~ 1 nm), and are curled and looped rather than straight. In this image, the tubes are contaminated with amorphous carbon and catalytic particles; subsequent work has enabled much purer samples to be produced. A higher magnification image of some individual tubes is shown in Fig. 1.8(b).

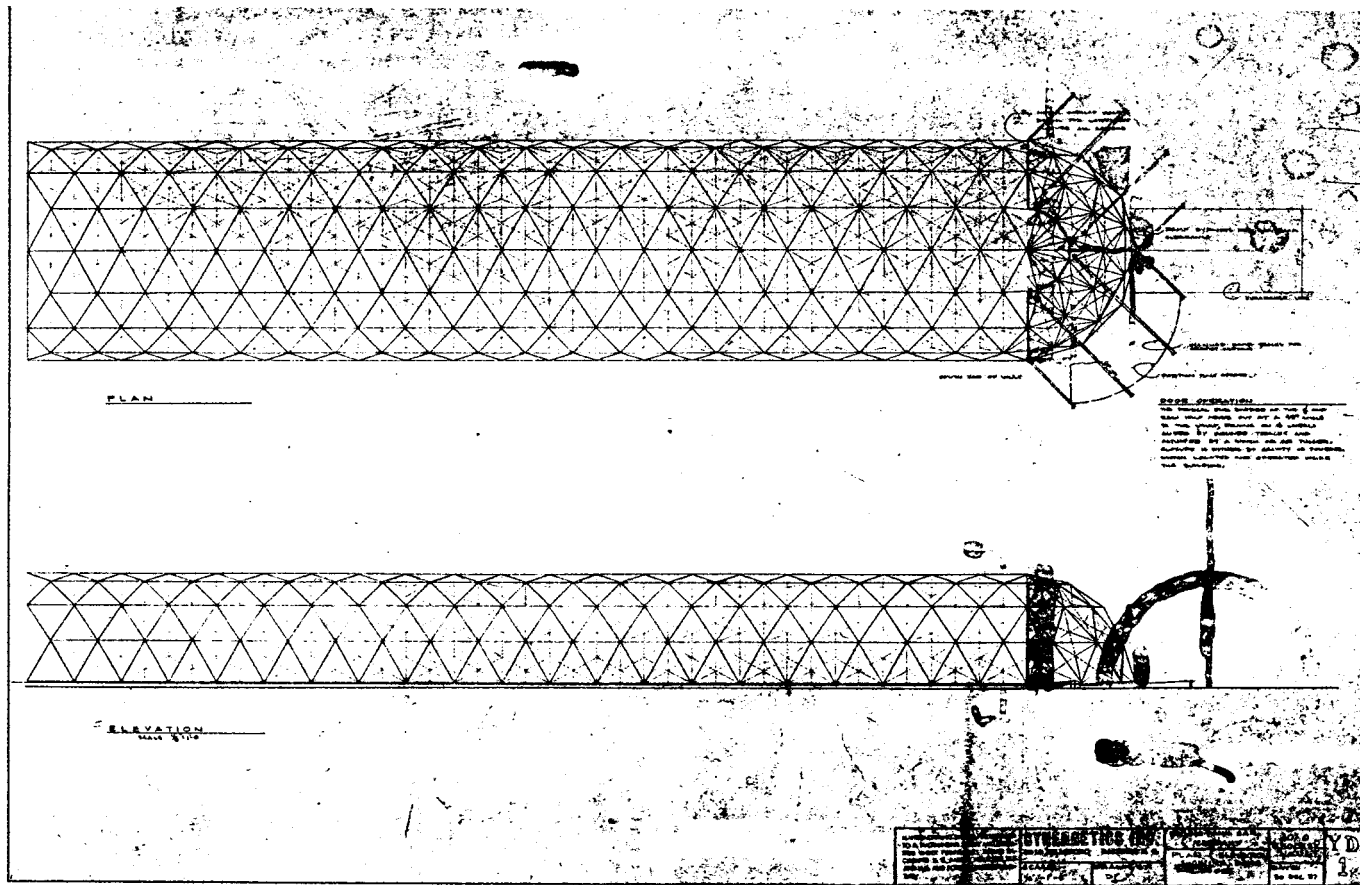


Fig. 1.7. The original 'buckytube'? Buckminster Fuller's design for the entrance pavilion of the Union Tank Car Company dome, Baton Rouge, Louisiana (1.12).

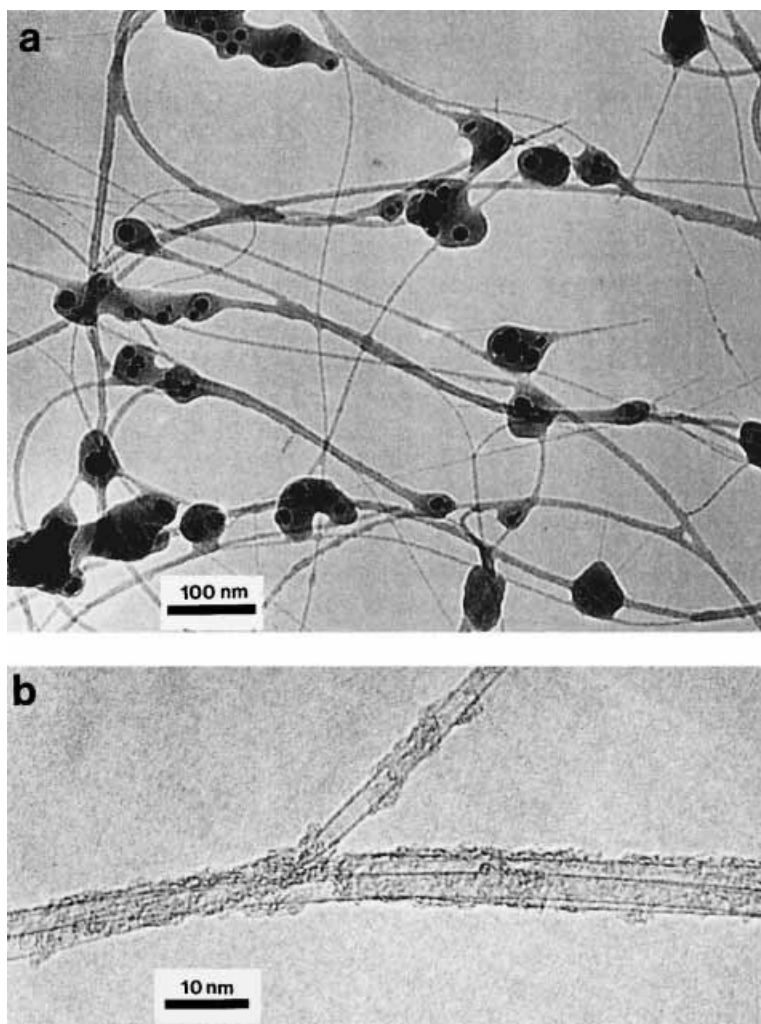


Fig. 1.8. Typical sample of single-walled nanotubes. (a) General area, showing tubes coated with amorphous carbon. Catalytic metal particles can also be seen (courtesy Donald Bethune). (b) Higher magnification image of individual tubes (1.15).

An alternative method of preparing single-walled nanotubes was described by Smalley's group in 1996 (1.16). Like the original method of preparing C_{60} , this involved the laser-vaporisation of graphite, and resulted in a high yield of single-walled tubes with unusually uniform diameters. These highly uniform tubes had a greater tendency to form aligned bundles than those prepared using arc-evaporation, and led Smalley to christen the bundles nanotube 'ropes'. Initial experiments indicated that the rope samples contained a very high proportion of nanotubes with a specific armchair structure. This created

considerable excitement (1.17), since one of the problems with nanotube samples up to that point was the wide range of different structures present. Subsequent work has suggested that the rope samples may be less homogeneous than originally thought. Nevertheless, the synthesis of nanotube ropes gave an important boost to nanotube research, and some of the most impressive work has been carried out on these samples.

1.4 Pre-1991 evidence for carbon nanotubes

The discovery of carbon nanotubes was immediately recognised as an important event, and prompted the question: why were they not discovered many years ago? The same question has frequently been asked about buckminsterfullerene itself. All of the techniques required to prepare and characterise these materials have been available for decades, so why did we have to wait so long? In the case of carbon nanotubes, part of the answer seems to be that they *were* seen previously, but simply not recognised as a new and important form of carbon. From a historical point of view it is of interest to review the pre-1991 evidence for the existence of ‘buckytubes’, but this should not be seen as diminishing the importance of Iijima’s work, which was the first to appreciate fully the nature and importance of these structures.

A letter in *Nature* in October 1992 claimed that nanotubes had been observed as early as 1953 (1.18). The writer described thread-like carbon structures obtained from the reaction of CO and Fe_3O_4 at 450°C , which he suggested were ‘similar, if not identical’ to carbon nanotubes. This illustrates the care which must be taken in assessing claims of prior discovery in this area. Fine tubules of carbon produced by catalytic methods have been known for many years, but these have a much less perfect structure than the fullerene-related tubes, as discussed in Chapters 2 and 3. The tubes are not closed with fullerene-like caps, but usually have a metal particle attached to one end. Although there has been a substantial amount of research on carbon tubules produced by catalysis (e.g. 1.19), these imperfect structures do not lend themselves to the range of potential applications which seem possible for fullerene-related nanotubes.

A number of authors have also pointed out the similarities between carbon nanotubes and graphite whiskers, the highly perfect form of carbon fibres which were first prepared by Roger Bacon in 1960 (1.20). It is certainly true that the technique used to produce whiskers, which involves a DC carbon arc, seems very close to the arc-evaporation method of nanotube synthesis. However, there are major differences between graphite whiskers and carbon nanotubes, not least the fact that whiskers are far larger: typically about $5\ \mu\text{m}$

in diameter and up to 3 cm in length. There are also structural differences: whiskers are scroll-like, while nanotubes are believed to have Russian-doll like structures (see Chapter 6 for further details on whiskers).

If catalytically produced tubes and graphite whiskers can be dismissed, what is the evidence that *genuine* carbon nanotubes were observed prior to 1991? To begin, there are Iijima's studies of carbon films carried out in the late 1970s and early 1980s, which were mentioned above. For this work he prepared specimens of arc-evaporated carbon using an apparatus of the type commonly employed to make carbon support films for electron microscopy. The method he used would have differed slightly (but significantly) from the Krättschmer–Huffman technique in that the chamber would have been evacuated rather than filled with a small pressure of helium. The resulting films were largely amorphous, but contained small, partially graphitized regions which contained some unusual structures. These structures included discrete graphitic particles apparently made up of concentric closed shells, tightly curved around a central cavity. One of these structures, reproduced as Figure 5(a) in his 1980 *Journal of Microscopy* paper (1.8), is clearly a nanotube, and Iijima confirmed its tubular nature using tilting experiments. But he did not explore these structures in detail, and suggested that the curved layers were probably due to sp^3 bonding, rather than, as we now believe, the presence of pentagonal rings.

There are other examples of nanotube-like structures scattered throughout the pre-1991 carbon literature (see, for instance, Fig. 10 in Ref. (1.21)). In some cases these structures might be contaminants on the carbon films used to support the samples (see p. 34). Evidence for the existence of elongated fullerene-like structures also came from high resolution electron microscopy studies of C_{60} crystals. In one of the first such studies, published in July 1991 (1.22), Su Wang and Peter Buseck of Arizona State University reported that fullerite crystals contained closed carbon cages both smaller and larger than C_{60} . The larger fullerenes had the projected shapes of elongated ellipsoids, which were estimated to contain roughly 130 carbon atoms. It is possible that such structures arose from the coalescence of adjacent C_{60} or C_{70} molecules in the crystal.

Work by other authors also anticipated the discovery of carbon nanotubes. For example, Patrick Fowler of Exeter University described theoretical studies of small cylindrical fullerene molecules in early 1990 (1.23). Two groups of American theoreticians, one at the Naval Research Laboratory, Washington DC (1.24), and one at the Massachusetts Institute of Technology (1.25) submitted papers on the electronic properties of fullerene tubes just a few weeks before Iijima's paper appeared in *Nature*. Finally, the highly imaginative

British chemist David Jones, under his pen-name Daedalus, also ruminated about rolled-up tubes of graphite in the *New Scientist* in 1986 (1.26). He suggested that molecules of this type might behave as extremely viscous supercritical gases at room temperature, which could be useful in calming the atmosphere at violent public demonstrations. Although this particular prophecy did not prove accurate, Daedalus has an excellent record in the field of fullerene research. In the 1960s he had predicted the existence of spherical carbon molecules, anticipating the discovery of fullerenes by nearly 20 years.

1.5 Nanotube research

The method for producing nanotubes described by Iijima in 1991 gave relatively poor yields, making further research into their structure and properties difficult. A significant advance came in July 1992 when Thomas Ebbesen and Pulickel Ajayan, working at the same Japanese laboratory as Iijima, described a method for making gram quantities of nanotubes (1.27). Again, this was a serendipitous discovery: Ebbesen and Ajayan had been trying to make fullerene derivatives when they found that increasing the pressure of helium in the arc-evaporation chamber dramatically improved the yield of nanotubes formed in the cathodic soot. The availability of nanotubes in bulk gave an enormous boost to the pace of research worldwide.

One area which attracted early interest was the idea of using carbon nanotubes and nanoparticles as ‘molecular containers’. A landmark in this field was the demonstration, by Ajayan and Iijima, that nanotubes could be filled with molten lead, and thus be used as moulds for ‘nanowires’ (1.28). Subsequently, more controlled methods of opening and filling nanotubes have been developed, enabling a wide range of materials, including biological ones, to be placed inside. The resulting opened or filled tubes might have fascinating properties, with possible applications in catalysis, or as biological sensors. Filled carbon nanoparticles may also have important applications, in areas as diverse as magnetic recording and nuclear medicine.

Perhaps the largest volume of research into nanotubes has been devoted to their electronic properties. The theoretical work which pre-dated Iijima’s discovery has already been mentioned. A short time after the publication of Iijima’s 1991 letter in *Nature*, two other papers appeared on the electronic structure of carbon nanotubes (1.29, 1.30). The MIT group, and Noriaki Hamada and colleagues from Iijima’s laboratory in Tsukuba, carried out band structure calculations on narrow tubes using a tight-binding model, and demonstrated that electronic properties were a function of both tube structure and diameter. These remarkable predictions stimulated a great deal of interest,

but attempting to determine the electronic properties of nanotubes experimentally presented great difficulties. Since 1996, however, experimental measurements have been carried out on individual nanotubes, which appear to confirm the theoretical predictions. These results have prompted speculation that nanotubes might become components of future nanoelectronic devices.

Determining the mechanical properties of carbon nanotubes also presented formidable difficulties, but once again experimentalists have proved equal to the challenge. Measurements carried out using transmission electron microscopy and atomic force microscopy have demonstrated that the mechanical characteristics of carbon nanotubes may be just as exceptional as their electronic properties. As a result, there is growing interest in using nanotubes in composite materials.

A variety of other possible applications of nanotubes are currently exciting interest. For example, a number of groups are exploring the idea of using nanotubes as tips for scanning probe microscopy. With their elongated shapes, pointed caps and high stiffness, nanotubes would appear to be ideally suited for this purpose, and initial experiments in this area have produced some extremely impressive results. Nanotubes have also been shown to have useful field emission properties, which might lead to their being used in flat-panel displays. Overall, the volume of nanotube research is growing at an astonishing rate, and commercial applications will surely not be far behind.

1.6 Organisation of the book

The chapter which follows considers the various methods for synthesising nanotubes, including catalytically produced and single-walled tubes, and summarises current thinking on growth mechanisms. Methods of purifying, aligning and processing nanotubes are also covered. In Chapter 3, theoretical approaches to the analysis of nanotube structure are outlined, and experimental observations described. The structures of carbon nanoparticles and nanocones are also discussed. Chapter 4, entitled 'The physics of nanotubes', is primarily concerned with the electronic properties of carbon nanotubes, but also considers magnetic, optical and vibrational properties of nanotubes, as well as experimental studies of nanotubes as field emitters. Methods of opening and filling carbon nanotubes and nanoparticles are described in Chapter 5, together with the possible uses of these filled nanocapsules. Theoretical and experimental work on the mechanical properties of nanotubes, and nanotube-containing composites are discussed in Chapter 6.

Chapter 7 covers inorganic analogues of fullerenes and nanotubes. Curved and tubular inorganic crystals have been known for many years, but there has

been renewed interest in such structures since the discovery of 'inorganic fullerenes' based on dichalcogenides by Israeli workers in 1992. Fullerene-like structures containing boron and nitrogen are also discussed in this chapter. In Chapter 8 a discussion is given of spheroidal forms of carbon. The first part of the chapter is concerned with the recently discovered fullerene-like structures known as 'onions', and this is followed by a brief survey of more well established spheroidal carbon structures including soot and carbon black particles. The evidence that these structures contain fullerene-like elements is reviewed. Finally, Chapter 9 considers some possible future directions in which nanotube science might develop.

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