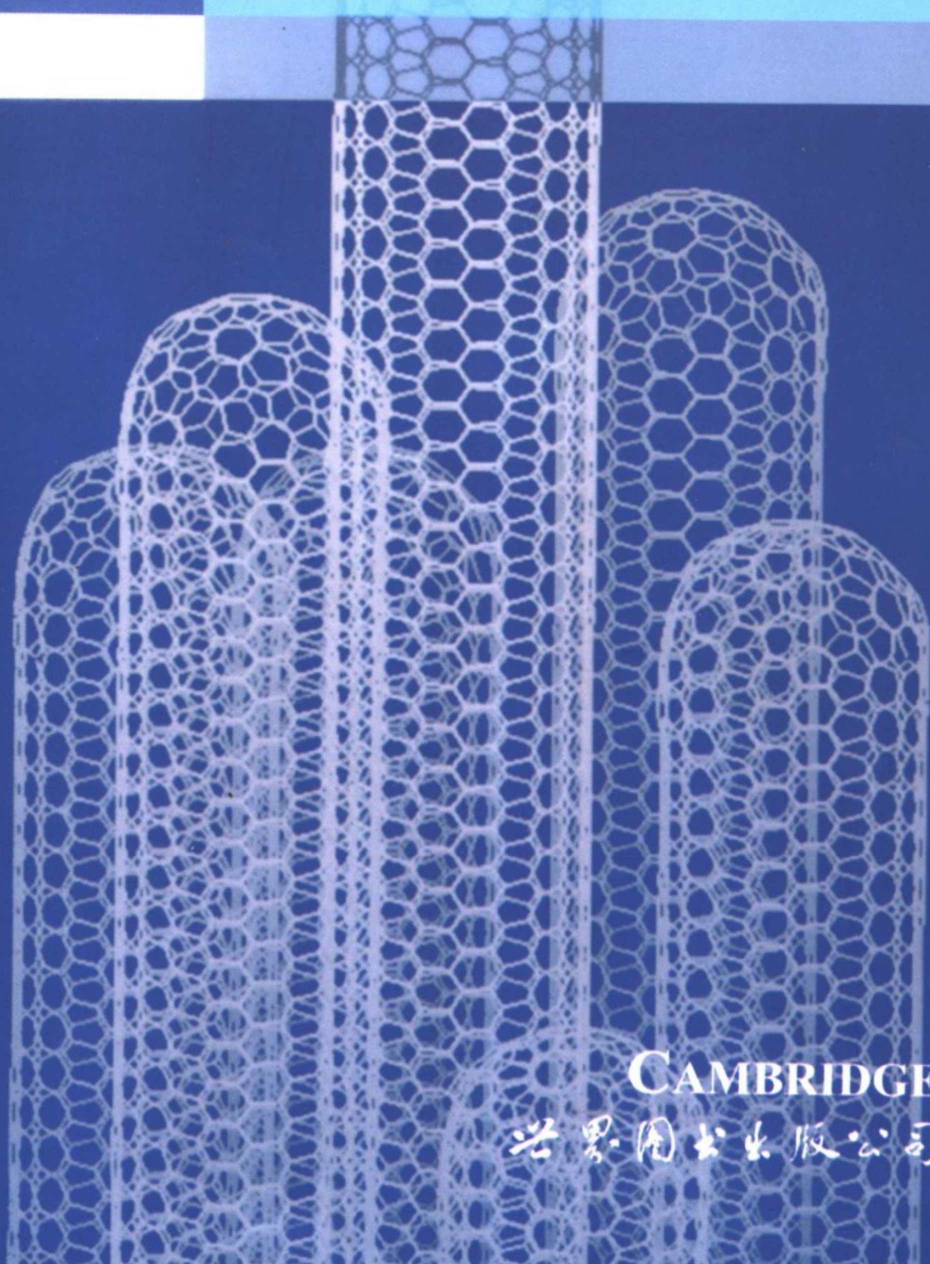
Carbon Nanotubes and Related Structures

New Materials for the Twenty-first Century

Peter J. F. Harris

碳纳米管及其相关结构



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Peter Harris
Twyford

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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

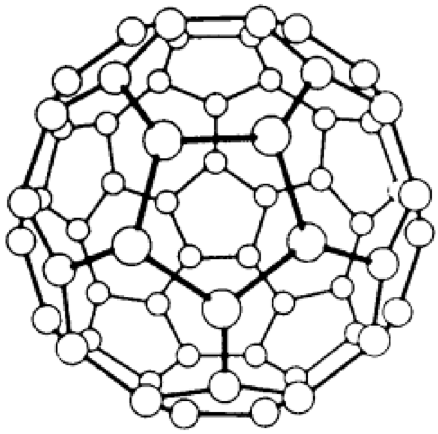

Fig. 1.1. C_{60}: buckminsterfullerene.

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

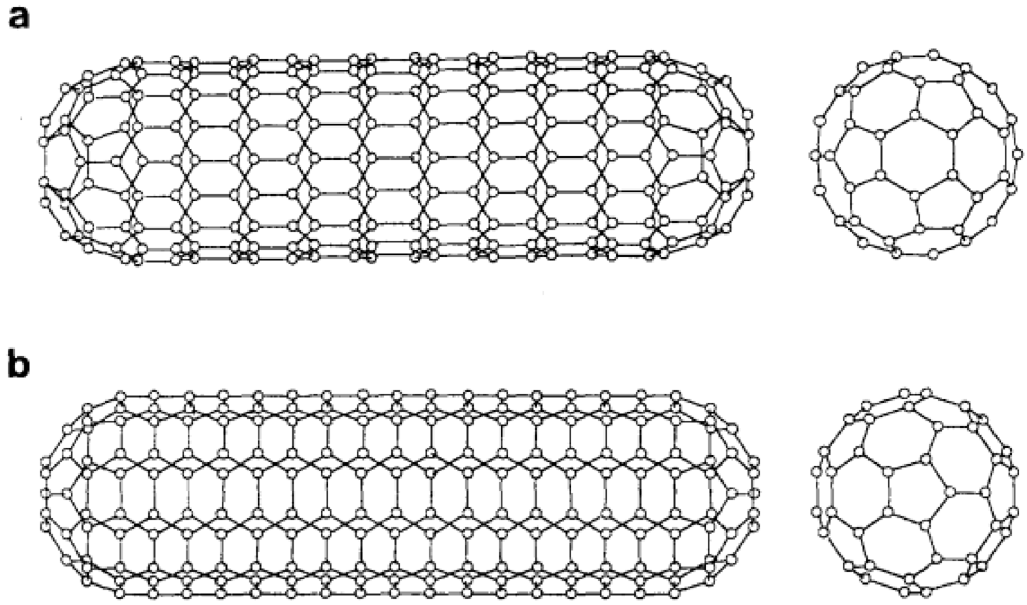

Fig. 1.2. Drawings of the two nanotubes which can be capped by one half of a C_{60} molecule (1.7). (a) Zig-zag (9,0) structure, (b) armchair (5,5) structure (see Chapter 3 for explanation of indices).

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-

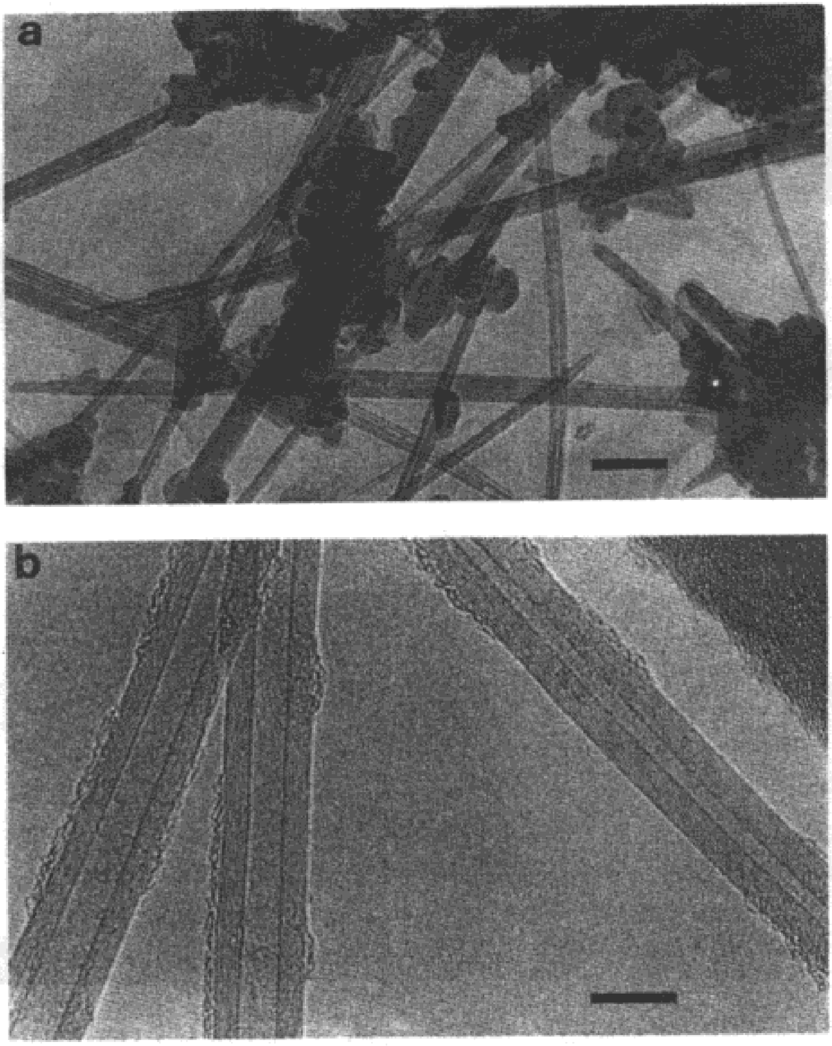

Fig. 1.3. (a) TEM image of nanotube-containing soot. Scale bar 100 nm. (b) Higher magnification image of individual tubes. Scale bar 10 nm.

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.

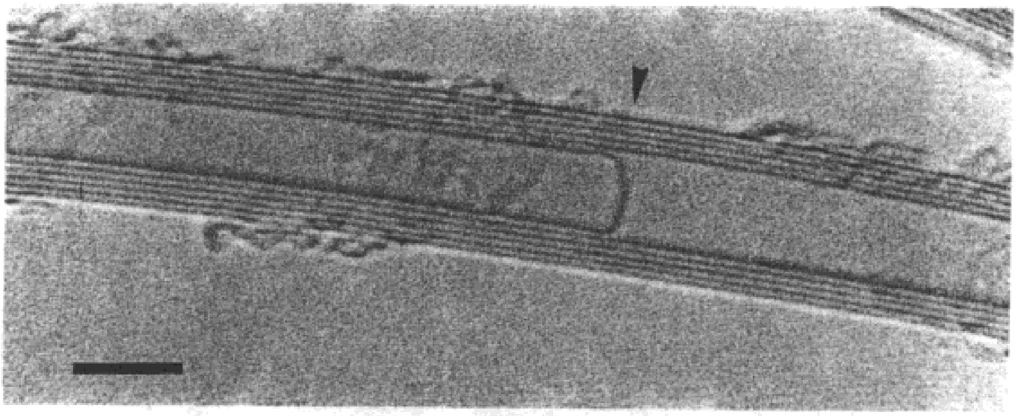

Fig. 1.4. High resolution image of multiwalled nanotube with 'internal cap'. Scale bar 5 nm.

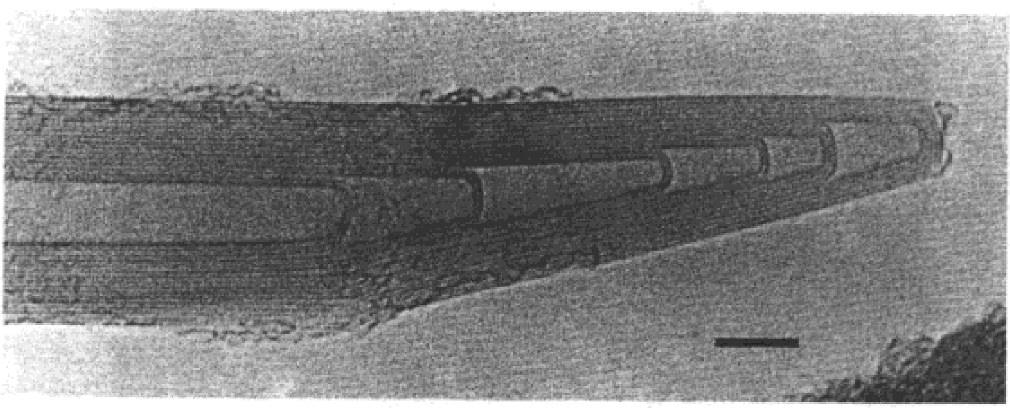

Fig. 1.5. Image of typical multiwalled nanotube cap. Scale bar 5 nm.

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).