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Peter J. F. Harris
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1 Introduction

Carbon in its miscellaneous forms has been used in art and technology since prehistoric times (1.1–1.4). Some of the earliest cave paintings, at Lascaux, Altamira and elsewhere, were produced using a mixture of charcoal and soot. Charcoal, graphite and carbon black (a pure form of soot) have been used as drawing, writing and printing materials ever since: photocopier toner is largely composed of carbon black. Coal and charcoal, of course, have been used as fuels for millennia, and charcoal played an important role in what might be considered humankind's first technology, the smelting and working of metals. Charcoal was used in this way right up to the eighteenth century, when it began to be replaced by coke, a development which helped to stimulate the Industrial Revolution. With the development of the electrical industry in the late nineteenth century, a demand developed for graphite. The American Edward Acheson is credited with producing the first synthetic graphite in 1896. In the twentieth century, the importance of activated carbon in purifying air and water supplies grew steadily, and the invention of carbon fibres in the 1950s provided engineers with a new lightweight, ultra-strong material. Diamonds, like graphite, have been known since antiquity, but until quite recently were only used decoratively. The development of a commercial synthetic method at General Electric in the 1950s opened the way for the industrial use of diamonds.

The history of carbon science is littered with illustrious names. Antoine Lavoisier, in a famous experiment in 1772, proved that diamonds are a form of carbon by demonstrating that they produce nothing but carbon dioxide on combustion. Carl Wilhelm Scheele carried out a similar experiment with graphite in 1779; before that time graphite had been thought to be a form of lead. Humphrey Davy and Michael Faraday carried out extensive studies of combustion at the Royal Institution. Davy correctly ascribed the yellow incandescence of a flame to glowing carbon particles, while Faraday, in his famous series of lectures on ‘The chemical history of a candle’, used a burning candle as the starting point for a wide-ranging dissertation on natural philosophy (1.5). The structure of diamond was one of the first to be solved using X-ray diffraction, by William and Lawrence Bragg in 1913 (1.6), while nine years later John D. Bernal solved the structure of graphite (1.7). In 1951 Rosalind Franklin demonstrated the distinction between graphitizing and non-graphitizing carbons (1.8, 1.9), and at about the same time Kathleen Lonsdale made important contributions to the study of diamonds, both natural and synthetic (e.g. 1.10).

By the early 1980s, however, carbon science was widely considered to be a mature discipline, unlikely to yield any major surprises, let alone Nobel Prizes. That the situation is so different today is due, in large measure, to the synthesis in 1985 by Harry Kroto of

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the University of Sussex and Richard Smalley of Rice University, and their colleagues, of the first all-carbon molecule, buckminsterfullerene (1.11). It was this discovery which led to the synthesis of fullerene-related carbon nanotubes and which made carbon science suddenly so fashionable.

1.1 Buckminsterfullerene

Neither Kroto nor Smalley were traditional carbon scientists, but both had a strong interest in synthesizing carbon clusters. Kroto's interest arose from a long standing fascination with the chemical species that are found in the interstellar medium. He believed that small carbon clusters or molecules might be responsible for some of the unexplained features in the spectra recorded by astronomers. Smalley's motivation was more down to earth. For many years he had been working on the synthesis of inorganic clusters using laser-vaporization, with the aim of producing new semiconductors or catalysts. Carbon clusters produced in a similar way might also have valuable properties.

The now-famous series of experiments involved vaporizing graphite using a Nd:YAG laser. The distribution of carbon clusters in the gas-phase was then determined using mass spectrometry. This produced an extremely striking result. In the distribution of gas-phase carbon clusters, detected by mass spectrometry, clusters containing 60 carbon atoms were by far the dominant species. This dominance became even more marked under conditions that maximized 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 realized that a closed cluster containing precisely 60 carbon atoms would have a structure of unique stability and symmetry, as shown in Fig. 1.1. The unwieldy name which they gave to this structure, buckminsterfullerene, honoured the visionary designer of geodesic domes, Richard Buckminster Fuller. The discovery of C_{60}, announced in *Nature* in November 1985 (1.11), had an enormous impact (1.12–1.15).

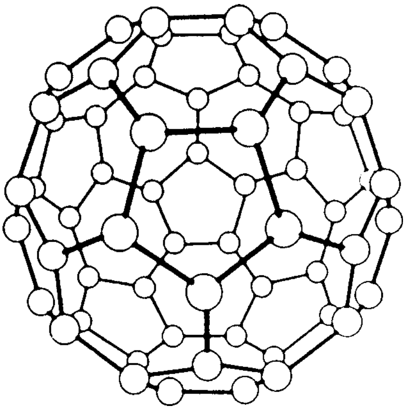

Fig. 1.1 C_{60}: buckminsterfullerene.

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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. 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 vaporize graphite, again in an atmosphere of helium, and collected the soot which settled on the walls of the vessel (1.16). 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 are perhaps the most important fruits of this research.

1.2 Fullerene-related carbon nanotubes

Sumio Iijima, an electron microscopist then working at the NEC laboratories in Japan, was fascinated by the Krätschmer–Huffman *Nature* paper. Ten years earlier he had used transmission electron microscopy to study soot formed in a very similar arc-evaporation apparatus to that used by Krätschmer and Huffman (1.17, 1.18). He found that the soot contained a variety of novel carbon architectures including tightly curved, closed nanoparticles and extended hollow needles. 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, 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 (1.19), prompted fullerene scientists the world over to look again at the used graphite cathodes, previously discarded as junk.

A typical sample of the nanotube-containing cathodic soot is shown at moderate magnification in Fig. 1.2(a). As can be seen, the nanotubes are accompanied by other material, including nanoparticles (hollow, fullerene-related structures) and some disordered carbon. The nanotubes range in length from a few tens of nm to several μm, and in outer diameter from about 2.5 to 30 nm. At high resolution the individual layers making up the concentric tubes can be imaged directly, as in Fig. 1.2(b).

Virtually all of the tubes produced using the arc-evaporation method are closed at both ends with caps which contain pentagonal carbon rings. The structural relationship between nanotubes and fullerenes can be illustrated by considering the two 'archetypal' carbon nanotubes that 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

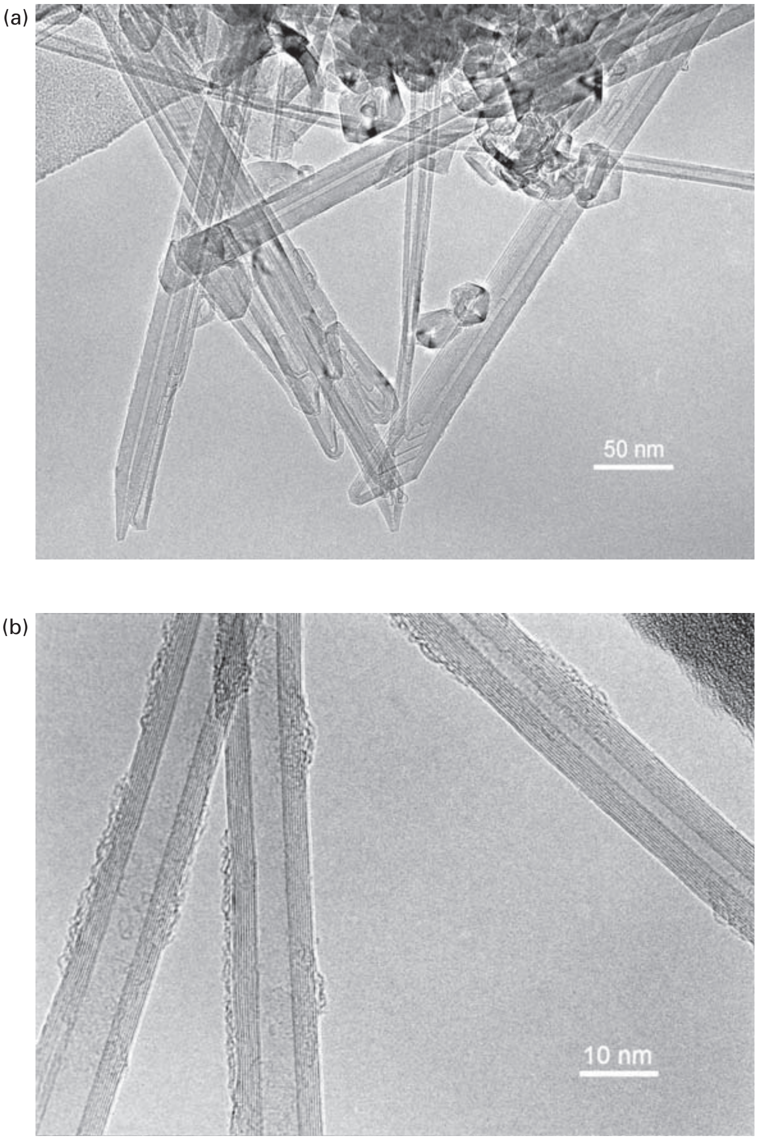

Fig. 1.2 (a) A TEM image of multiwalled carbon nanotubes produced by arc-evaporation. (b) A higher magnification image of individual tubes.

the zig zag nanotube shown in Fig. 1.3(a), while bisecting C_{60} along one of the five-fold axes produces the armchair nanotube shown in Fig. 1.3(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 around the tube axis (see Chapter 3). In practice, the caps are rarely hemispherical in shape, but can have a variety of morphologies; a typical example is shown in Fig. 1.4. More complex cap structures are often observed, owing to the presence of heptagonal as well as pentagonal carbon rings (1.21).

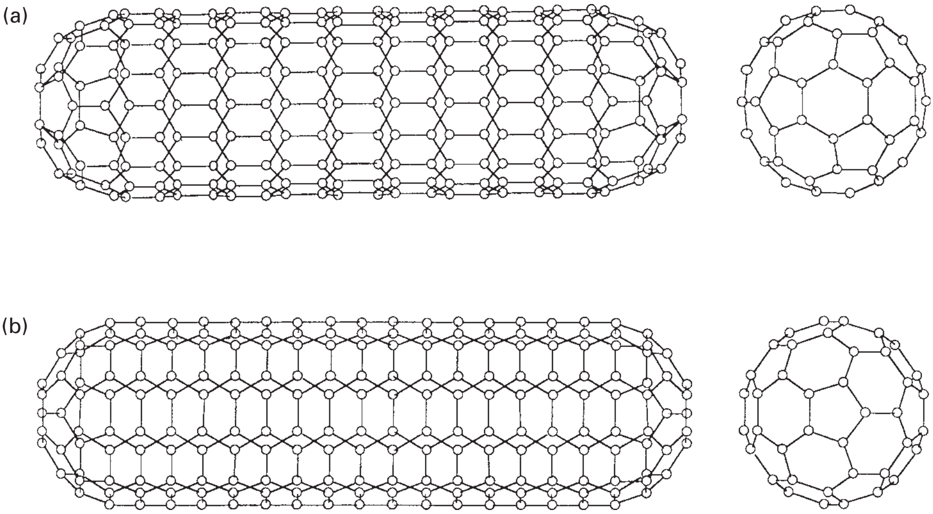

Fig. 1.3 Drawings of the two nanotubes that can be capped by one-half of a C_{60} molecule (1.20). (a) Zig zag (9, 0) structure, (b) armchair (5, 5) structure (see Chapter 5 for an explanation of the indices).

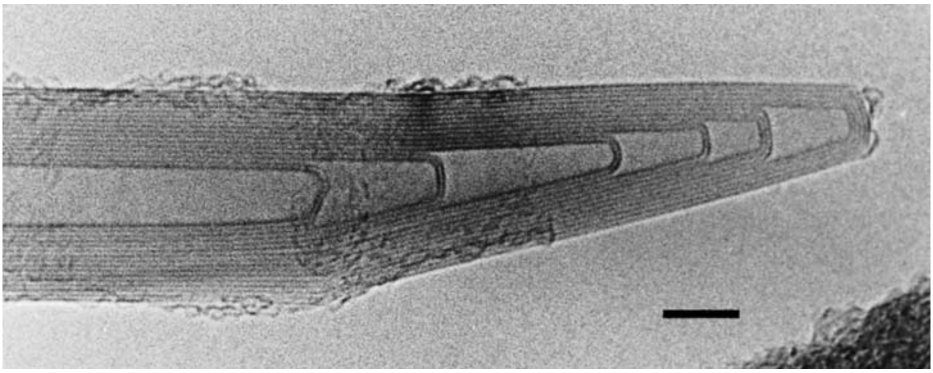

Fig. 1.4 An image of a typical multiwalled nanotube cap. Scale bar 5 nm.

1.3 Single- and double-walled nanotubes

Nanotubes of the kind described by Iijima in 1991 invariably contain more than one graphitic layer, 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 (1.22, 1.23). This proved to be an extremely important development, since the single-walled tubes appeared to have structures that approximate to those of the 'ideal' nanotubes shown in Fig. 1.3. They proved to have extraordinary properties, and today there are more papers published on single-walled tubes than on their multiwalled counterparts. An important advance came in 1996 when Smalley's group described the synthesis of single-walled

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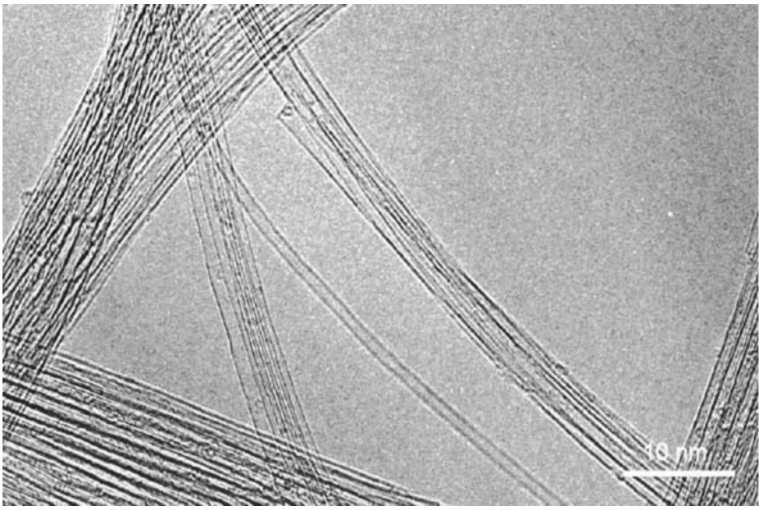

Fig. 1.5 A typical image of single-walled nanotubes. Courtesy Kazu Suenaga.

tubes using laser-vaporization (1.24). They can also be made catalytically, as discussed below. A typical image of single-walled nanotubes (SWNTs) is shown in Fig. 1.5. It can be seen that the appearance is quite different from that of samples of multiwalled nanotubes (MWNTs). The individual tubes have very small diameters (typically ~1 nm), and are often curved rather than straight. They also have a tendency to form bundles or ‘ropes’. Methods for producing double-walled carbon nanotubes (DWNTs) in high yield using arc-evaporation have also now been developed (1.25).

1.4 Catalytically produced carbon nanotubes

The production of filamentous carbon by catalysis had been known long before Iijima’s discovery of fullerene-related carbon nanotubes. As early as 1890, P. and L. Schultzenberger observed the formation of filamentous carbon during experiments involving the passage of cyanogen over red-hot porcelain (1.26). Work in the 1950s established that filaments could be produced by the interaction of a wide range of hydrocarbons and other gases with metals, the most effective of which were iron, cobalt and nickel. Probably the first electron micrographs showing tubular carbon filaments appeared in a 1952 paper by Radushkevich and Lukyanovich in the *Russian Journal of Physical Chemistry* (1.27). Serious research into the catalytic formation of carbon filaments began in the 1970s when it was appreciated that filament growth could constitute a serious problem in the operation of nuclear reactors, and in certain chemical processes. The most extensive programme of research was carried out in the 1970s by Terry Baker and his colleagues at the United Kingdom Atomic Energy Authority’s laboratories at Harwell, and later in the USA (e.g. 1.28). This group were concerned with filamentous carbon growth in the cooling circuits of gas-cooled nuclear reactors. Thus, Baker’s work was primarily motivated by the need to avoid filamentous carbon growth in these cooling pipes. A few workers, however, recognized that it might be possible to produce useful carbon nanofibres by catalysis. Notable among these was Morinobu Endo of Shinshu University in Japan, who proposed in 1988 (1.29) that catalytic carbon nanotubes could represent an alternative to conventional carbon fibres, which are produced by pyrolysing strands of polymer or pitch.

Following Iijima's paper in 1991, interest in catalytically produced carbon nanotubes exploded. As well as multiwalled nanotubes, single-walled and double-walled tubes can now also be produced by catalysis (e.g. 1.30, 1.31). The production of nanotubes catalytically is attractive for many reasons. Perhaps most importantly, it is much more amenable to scale-up than arc-evaporation. A number of processes have now been developed for the bulk synthesis of single-walled tubes using catalysis (e.g. 1.32, 1.33). Catalytic methods also allow the controlled growth of tubes on substrates, for applications in display technology and other areas. The main drawback is that, at least for multiwalled nanotubes, the quality of tubes produced in this way is poorer than for those produced by arc-evaporation.

1.5 Who discovered carbon nanotubes?

If carbon nanotubes have been known since the 1950s, if not earlier, why is Iijima's work considered so important? And who, in fact, should be credited with discovering carbon nanotubes? This has often been debated at nanotube conferences, and in the literature (1.34, 1.35), and the uncertainty surrounding the question of who actually discovered nanotubes probably explains why no Nobel Prizes have yet been awarded in this area. In discussing this topic, some researchers have attempted to downplay the importance of Iijima's work. It has even been stated that Iijima simply took better micrographs than anyone else! In the view of the present author this is wrong. Iijima's 1991 work is undoubtedly responsible for the current explosion of interest in carbon nanotubes, and for good reason. The nanotubes he prepared were far more perfect than those that had been previously produced catalytically, and differed from them in being all-carbon structures, closed at both ends, and not 'contaminated' with catalyst particles. Moreover, all the evidence suggests that arc-produced tubes have superior properties to catalytically-grown ones. This apparently remains the case even after the catalytic tubes have been annealed in an attempt to remove the defects (see Section 7.1.2). Thus it can be argued that fullerene-related carbon nanotubes are different in kind from catalytically produced tubes. It is important to note, however, that this distinction only seems to apply to multiwalled tubes. Tubes with one or two layers seem to have similar properties no matter how they are produced.

If we accept, then, that fullerene-related carbon nanotubes are a different species from catalytically produced tubes, is there evidence that the fullerene-related variety were known before 1991? The answer is yes, although the potential importance of these structures was not recognized. 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 Krätschmer–Huffman technique

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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 Fig. 5(a) in his 1980 *Journal of Microscopy* paper (1.17), 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 structures resembling 'Iijima-type' multiwalled nanotubes scattered throughout the pre-1991 carbon literature. In some cases these structures might be contaminants on the carbon films used to support the samples (1.36). It has also been claimed that an image in a 1976 paper by Agnes Oberlin and colleagues contains an image of a single-walled tube (Fig. 11 of ref. 1.37). While this may be true, the authors did not recognize its significance at the time.

Work by theoreticians 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 (1.38). Two groups of American theorists, one at the Naval Research Laboratory, Washington DC (1.39), and one at the Massachusetts Institute of Technology (1.40) submitted papers on the electronic properties of fullerene tubes just a few weeks before Iijima's paper appeared in *Nature*. Last, but not least, the highly imaginative British chemist David Jones, under his pen-name Daedalus, ruminated about rolled-up tubes of graphite in The *New Scientist* in 1986 (1.41).

1.6 Carbon nanotube research

Interest in carbon nanotubes, which took off following the publication of Iijima's 1991 paper, continues to grow. This can be seen in the rise in the annual total of papers on nanotubes, up from 886 in 2000 to 5406 in 2007 (Fig. 1.6). During the same period the number of papers on fullerenes has remained fairly static at about 700 per year. The contrast between the number of papers on carbon nanotubes and the number on fullerenes of course reflects the far greater potential for practical applications of nanotubes. Despite the continuing growth of interest in carbon nanotubes, however, there are signs that the number of major breakthroughs in the field is falling. Thus, in 2007 there was just one paper on carbon nanotubes in *Nature* and two in *Science*, compared with nine and ten respectively in 1999. As far as the origin of papers is concerned, the United States leads the way, as might be expected, with 27% of the total of carbon nanotube papers published in 2007. Perhaps surprisingly, this is closely followed by China, with 26%, demonstrating a major investment in carbon science and nanotechnology in that country. About 10% of nanotube papers originated in Japan and 7% from South Korea. Of the European countries, Germany contributed about 6% of the total, the United Kingdom about 5% and France 4%.

Perhaps the largest volume of research into nanotubes has been devoted to their electronic properties. The theoretical work that pre-dated Iijima's discovery has already

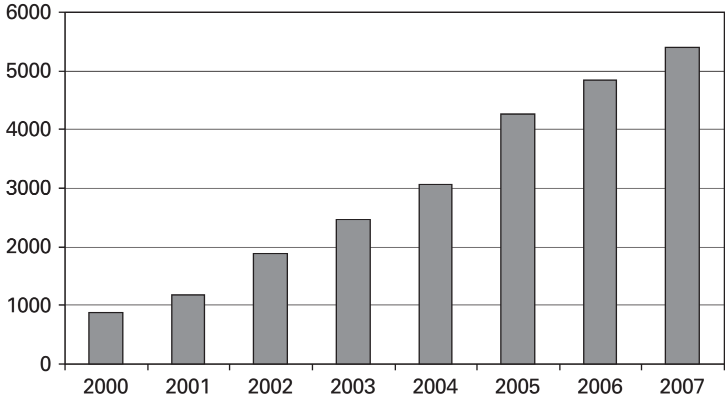

Fig. 1.6 The number of papers on carbon nanotubes published annually, from 2000 to 2007. Data from ISI Web of Knowledge.

been mentioned. A short time after the publication of Iijima's 1991 letter in *Nature*, theoretical studies appeared which demonstrated that the electronic properties of nanotubes were a function of both tube structure and diameter. These remarkable predictions stimulated huge interest, but attempting to determine the electronic properties of nanotubes experimentally presented great difficulties. By the late 1990s, however, studies were appearing which confirmed these predictions, and the first nanotube-based electronic devices began to be produced. The *Science* cover picture shown in Fig. 1.7(a) accompanied a 2001 article on nanotube logic circuits by Cees Dekker of Delft University of Technology and colleagues (see p. 167). The second major area of carbon nanotube research has revolved around their mechanical properties. Again, theory came slightly ahead of experiment, but ingenious measurements using electron microscopy and scanning probe microscopy soon confirmed the theoretical predictions: carbon nanotubes are the stiffest and strongest fibres known. These properties, coupled with their low density, mean that carbon nanotubes are the only fibres suitable for producing a 'space elevator', an Earth-to-space cable first proposed by Arthur C. Clarke (1.42), as illustrated in Fig. 1.7(b). On a more down-to-earth level, the outstanding mechanical properties of carbon nanotubes are beginning to find applications in a whole range of areas, from sports equipment to automobiles. In such applications it is almost always necessary to encapsulate the tubes in a matrix, and the production of carbon nanotube composites is becoming a major field in itself. As well as their electronic and mechanical properties, many other aspects of carbon nanotubes have captivated researchers, and, as will become clear in this book, nanotube research has developed in an amazingly wide range of directions. Some aspects of carbon nanotube research have even begun to impinge on popular culture. While Arthur C. Clarke was unaware of nanotubes when he speculated about space elevators, contemporary science fiction writers are alive to the possibilities offered by these new materials. Thus, in *Rollback* by Robert J. Sawyer (1.43) there is a glistening carbon nanotube tower called the Spire of Hope, while *River of Gods* by Ian McDonald (1.44) features a 'no-maintenance domestic scale carbon nanotube solar power generator', although how this actually works is not specified.

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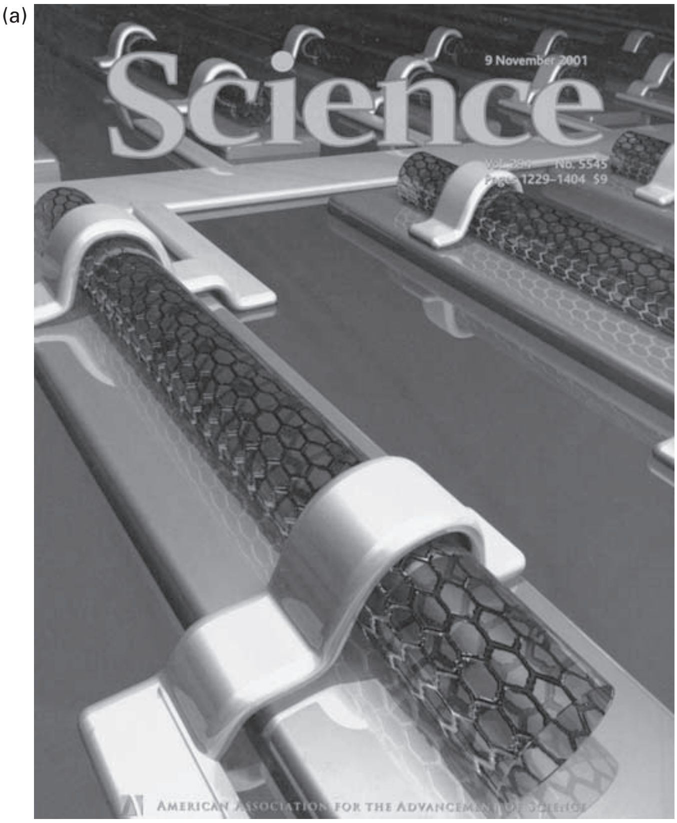

Fig. 1.7 Carbon nanotube cover art. (a) *Science*, 9 November 2001 issue, showing a nanotube-based electronic circuit. (b) *American Scientist*, July–August 1997 issue, with an illustration of a nanotube space elevator.

1.7 Scope of the book

The next two chapters cover the synthesis of carbon nanotubes. Chapter 2 is concerned with non-catalytic methods, primarily arc-evaporation and laser-vaporization, while catalytic synthesis is discussed in Chapter 3. Methods of purifying nanotubes and of processing them into defined forms and arrangements are covered in the following chapter. In Chapter 5, theoretical approaches to the analysis of nanotube structure are outlined, and experimental observations described. One of the major growth points of nanotube science, namely research into their electronic properties, is considered in Chapter 6, while other physical properties, including mechanical, are discussed in the following chapter. Chapter 8, entitled 'Chemistry and biology of nanotubes' covers the chemical and biomolecular functionalization of carbon nanotubes and their interaction with biological systems. Chapters 9–11 discuss the incorporation of nanotubes into polymer and other matrices; the filling of nanotubes with foreign materials and the production and properties of heterogeneous nanotubes; and the use of nanotubes in