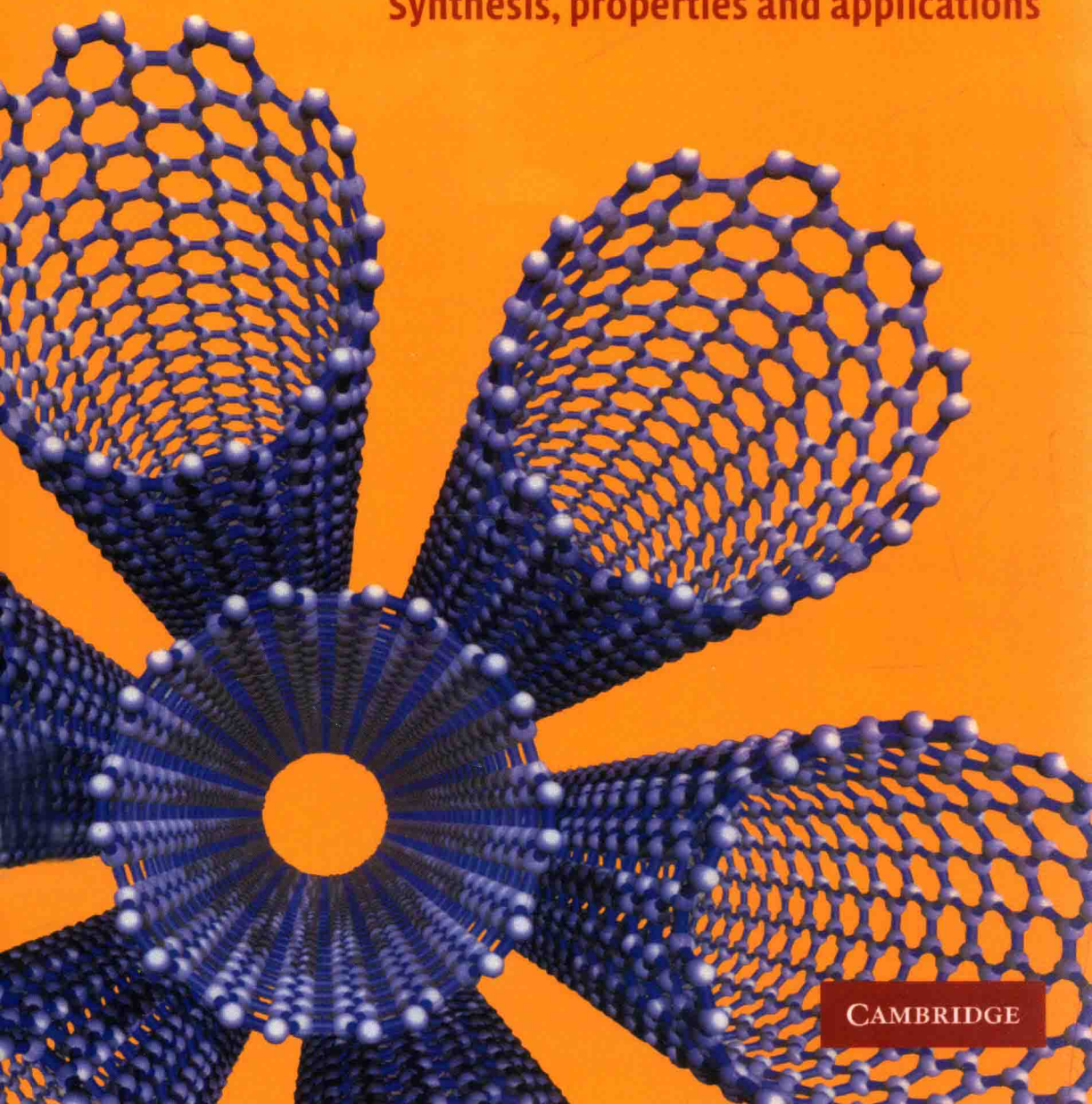Peter J. F. Harris

Carbon Nanotube Science

Synthesis, properties and applications

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Carbon Nanotube Science

Synthesis, Properties and Applications

Carbon nanotubes represent one of the most exciting research areas in modern science. These molecular-scale carbon tubes are the stiffest and strongest fibres known, with remarkable electronic properties, and potential applications in medicine, sensing devices and a wide range of other fields. Cutting through the plethora of information available, *Carbon Nanotube Science* is the most concise, accessible book for the field, presenting the basic knowledge graduates and researchers need to know.

Based on the successful *Carbon Nanotubes and Related Structures*, this new book focuses solely on carbon nanotubes, covering the major advances made in recent years in this rapidly developing field. Chapters focus on electronic properties, chemical and biomolecular functionalization, nanotube composites and nanotube-based probes and sensors. The book begins with a comprehensive and up-to-date discussion of synthesis, purification and processing methods. With its full coverage of the state of the art in this active research field, this book will appeal to researchers in a broad range of disciplines, including nanotechnology, engineering, materials science, chemistry and physics.

Peter J F Harris is Manager of the Centre for Advanced Microscopy at the University of Reading, where he is involved in a wide range of projects in both the physical and biological sciences. His personal research interests mainly involve the application of high-resolution TEM to carbon materials. He is a member of the Editorial Advisory Boards both for the *Journal of Physics: Condensed Matter* and *Carbon*.

Preface

This book was originally conceived as a second edition of my earlier work *Carbon nanotubes and related structures: new materials for the twenty-first century* (Cambridge University Press, 1999). However, the field has expanded rapidly since 1999, and the tale grew in the telling, to the point where I realized I had essentially written a new book. The new title reflects this, as well as the fact that most of the material concerned with 'related structures' has been omitted: the book now focuses almost entirely on carbon nanotubes themselves. As with the first book, I have benefited enormously from the freely given assistance of colleagues from around the world, many of whom have also provided copies of images and preprints. The following list almost certainly fails to include all who have helped me, so I apologize for any omissions. I also stress that any errors which remain in the book are my responsibility alone.

I wish to thank: Pulickel Ajayan, Lizzie Brown, Marko Burghard, Hui-Ming Cheng, Hongjie Dai, Walt De Heer, Cees Dekker, Chris Ewels, John Gallop, Jason Hafner, Michael Holzinger, Martin Hulman, Kaili Jiang, Hiromichi Kataura, Ian Kinloch, Ralph Krupke, Alan Lau, Cheol Jin Lee, Jannik Meyer, Geoff Mitchell, Pasha Nikolaev, Henk Postma, Zhifeng Ren, Daniel Resasco, Andrew Rinzler, Milo Shaffer, Wenhui Song, Kazu Suenaga, Sander Tans, Kenneth Teo, Edman Tsang, Daniel Ugarte, Bruce Weisman and Karen Winey.

I would also like to thank Cambridge University Press for their encouragement and patience.

Most importantly, I want to thank my wife, Elaine, and daughters Katy and Laura for their continuing love and support.

Peter Harris,
Twyford, November 2008

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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

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).
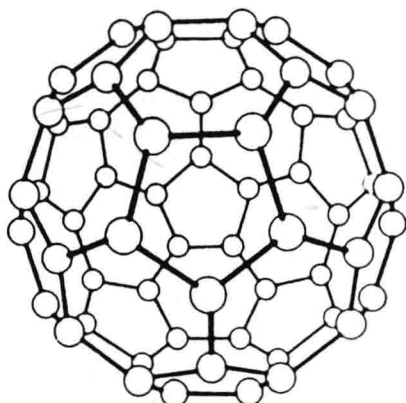

Fig. 1.1 C_{60}: buckminsterfullerene.

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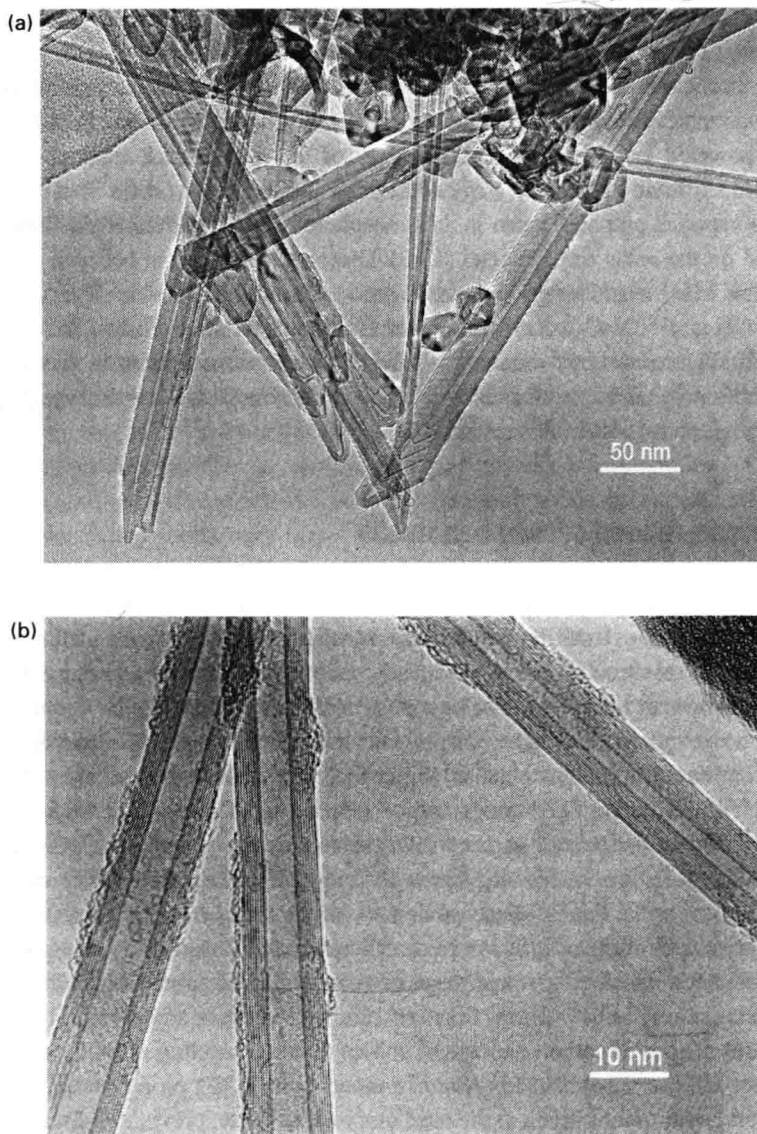
Fig. 1.2   (a) A TEM image of multiwalled carbon nanotubes produced by arc-evaporation. (b) A higher magnification image of individual tubes.

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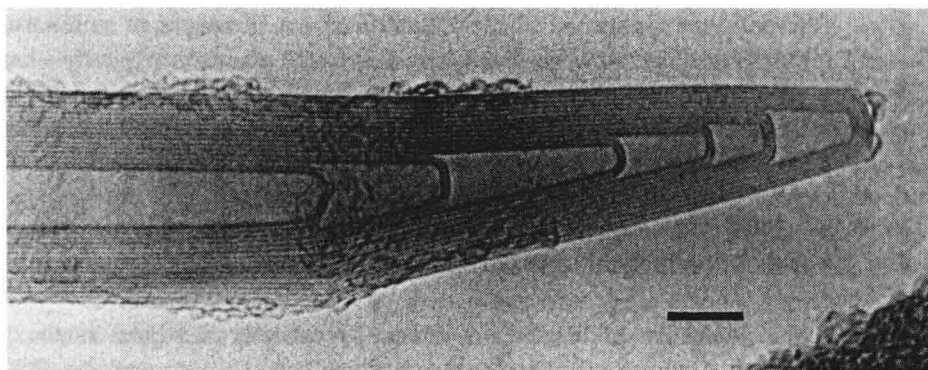
Fig. 1.4   An image of a typical multiwalled nanotube cap. Scale bar 5 nm.

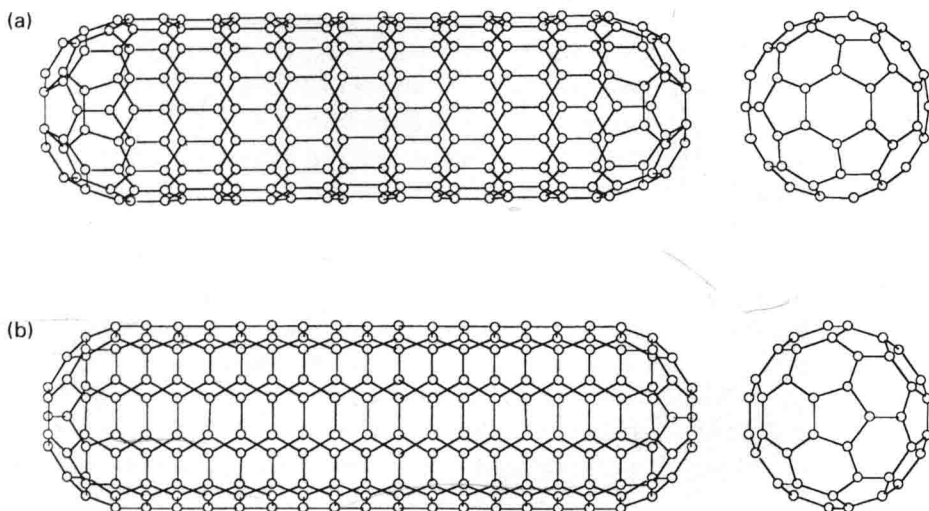## 1.3   Single- and double-walled nanotubes

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

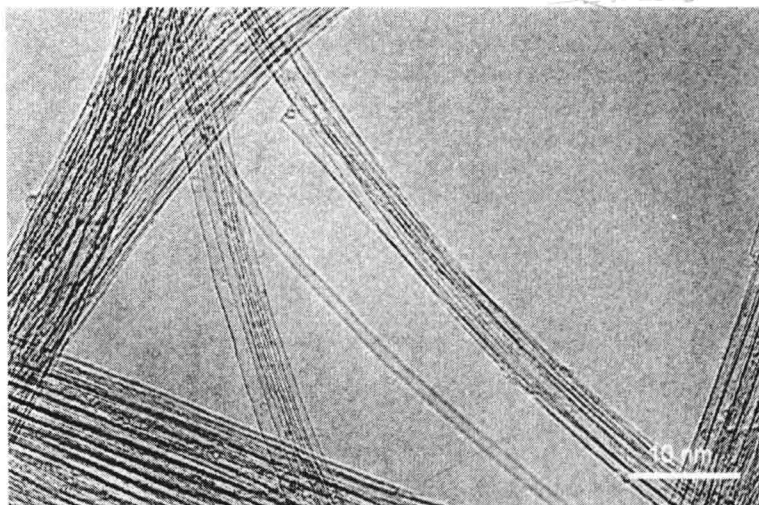**Fig. 1.5**   A typical image of single-walled nanotubes. Courtesy Kazu Suenaga.

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