# 1 Overview of carbon nanotubes

*Nature is the origin of all things.*

## 1.1 Introduction

*Carbon is an old but new material*. It has been used for centuries going back to antiquity, but yet many new crystalline forms of carbon have only recently been experimentally discovered in the last few decades. These newer crystalline forms include buckyballs, carbon nanotubes (CNTs), and graphene, where the latter two are illustrated in Figure 1.1. Furthermore, carbon nanotubes come in two major flavors, the single-wall and multi-wall varieties, as shown in Figure 1.1a and b respectively. The newer forms of carbon have significantly contrasting properties compared with the older forms of carbon, which are graphite and diamond.[1] In particular, they share in common a hexagonal lattice or arrangement of carbon atoms. In addition, CNTs and graphene occupy a reduced amount of space compared with their older siblings; hence, they are often referred to as reduced-dimensional or low-dimensional solids or nanomaterials for short. To give a comparative (order of magnitude) idea of the critical size scales of these nanomaterials, nanotubes are about 10 000 times thinner than human hair, and graphene is about 300 000 times thinner than a sheet of paper. The typical diameter of nanotubes range from about 1 to 100 nm, and graphene ideally has the thickness of a single atomic layer (~3.4 Å). Fundamentally, it is the combination of the reduced dimensions and the different lattice structure that leads to the fascinating properties unique to nanotubes and graphene.

The fascinating electronic properties are the main subject matter of this textbook. While both nanotubes and graphene will be formally studied, the primary focus will be on CNTs. This is because nanotubes have been actively studied since 1991, affording a relatively greater wealth of understanding compared with graphene, which have only recently enjoyed intense scrutiny (since 2005). The excitement and accumulated knowledge regarding nanotubes can be seen in the number of related articles published in the international journals of three major disciplines

[1] Quite fascinatingly, carbon produces the most esthetically beautiful of materials, diamond, and also arguably the ugliest of materials, graphite (the stuff found in pencils).

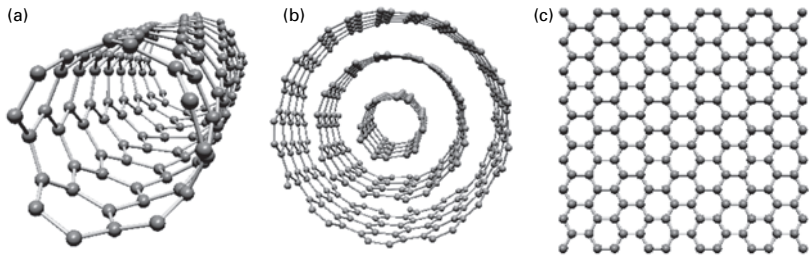


**Fig. 1.1** Ball-and-stick models of CNTs and graphene: (a) single-wall nanotube, (b) multi-wall nanotube with three shells, and (c) graphene, which is a single sheet of graphite. The balls (spheres) represent the carbon atoms and the sticks (lines) stand for the bonds between carbon atoms.

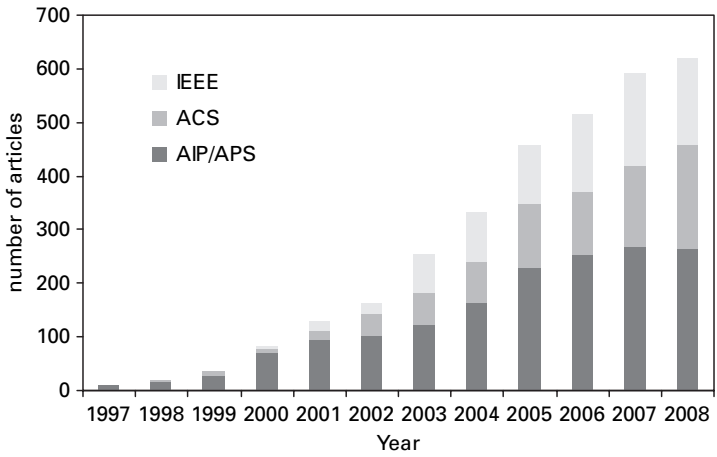


**Fig. 1.2** Increase in the number of articles in the major international journals with the phrase "carbon nanotube" in the title. AIP/APS stands for the journals of the American Institute of Physics and American Physical Society respectively. ACS is the acronym for the journals of the American Chemical Society, and IEEE represents the journals of the Institute of Electrical and Electronic Engineers.

(physics, chemistry, and electrical engineering), which is reflected in Figure 1.2. Indeed, CNTs have enjoyed a somewhat exponential interest over the past decade, and the current gradual saturation in publications is a sign of the maturity of understanding about their properties. Accordingly, many diverse and novel applications have been explored, as can be seen in Figure 1.3, which is an indicator of the growing applications of CNTs.

This chapter will present a broad historical perspective on CNTs and a brief discussion of the common synthesis and characterization methods. It concludes with a note about non-CNT so that the reader is not left with the impression than only carbon atoms can form nanotubes. The discussion in this chapter is simply an

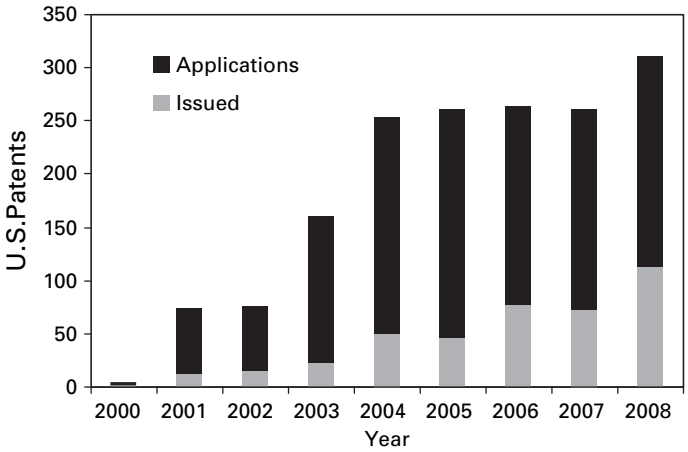


**Fig. 1.3** United States patents issued and patent applications containing the phrase "carbon nanotube" in the patent abstract. In a sense, this is an indicator of the growing interest in applications of CNTs.

overview and is not required for any of the subsequent chapters. For an advanced technical overview from a different perspective, readers are encouraged to read some of the recent comprehensive reviews on CNTs, such as the one by Avouris *et al.*[2]

## 1.2 An abbreviated zigzag history of CNTs

The developments leading to the *discovery* of CNTs, or perhaps more fittingly their *accidental synthesis*, followed a somewhat jagged path of experimental research. Before proceeding any further, the reader should keep in mind that natural deposits of CNTs may well exist in some as yet undiscovered location(s). However, these locations (if they exist) have not been found, or at least no one has been actively searching for them. Moreover, the production of nanotubes may have similarly existed through some inadvertent process for a long time. A case in point is an interesting article by Indian scientists reporting on the synthesis of CNTs from oxidation of specially prepared carbon soot popularly known as *kajal* in South Asia, a substance that has been used as an eye-makeup as far back as the eighth century BC.[3] Within our scientific context, the historical discussion here will be limited to synthetic or man-made nanotubes that have clearly been identified by undeniable

[2] Ph. Avouris, Z. Chen and V. Perebeinos, Carbon-based electronics. *Nat. Nanotechnol.*, **2** (2007) 605–15.

[3] P. Dubey, D. Muthukumaran, S. Dash, R. Mukhopadhyay and S. Sarkar, Synthesis and characterization of water-soluble carbon nanotubes from mustard soot. *Pramana*, **65** (2005) 687–97.

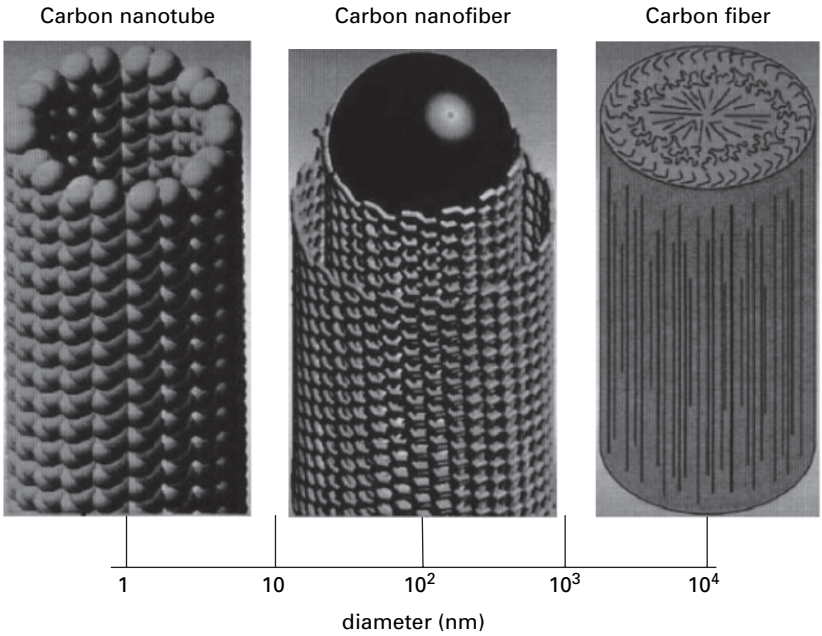


**Fig. 1.4** Illustrative morphology and range of typical diameters for different filamental carbon.

evidence. The origins of these CNTs are ultimately rooted and intertwined with developments of their siblings, carbon nanofibers and fibers which are hair-like filaments. All three slender structures, namely nanotubes, nanofibers and fibers, can be categorized as filamental carbon for short, with dimensions and morphologies illustrated in Figure 1.4.

Historically, the intentional synthesis of carbon fibers can be traced back to the time of Thomas Edison and the beginnings of electrical lighting (late 1800s), when this material enjoyed a growing application as filaments in the commercially successful incandescent light bulb. Indeed, a US patent was issued in 1889 to two British scientists documenting the detailed synthesis of carbon filaments or fibers by what is now known as the chemical vapor deposition (CVD) method. The first page of the patent is shown in Figure 1.5.

Remarkably, the patented CVD recipe, which employs iron to catalyze the thermal decomposition of a mixture of hydrogen and hydrocarbon gases (methane and ethylene are mentioned in the patent as preferable) leading to the growth of carbon fibers, remains the most popular method of synthesizing nanofibers and nanotubes even after a century's worth of research in carbon materials. Some of the highlights in the patent schematic (all labels refer to Figure 1.5) include a gas outlet (labeled $k$) to bake out and evacuate any moisture/steam in the chamber before growth and an inlet ($c$) to allow the flow of the gases through a small opening ($b^x$) for subsequent carbon synthesis at high temperatures. The carbon fibers grow from

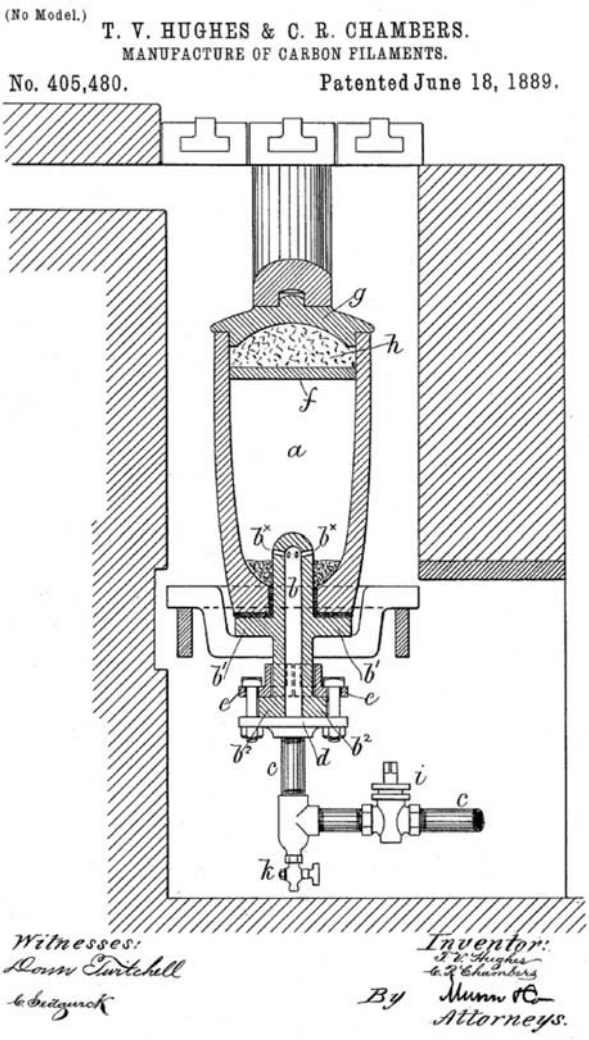


**Fig. 1.5** Patent drawing of Hughes and Chambers for the invention of a catalytic high-temperature technique for growing carbon fibers or filaments in a CVD chamber under atmospheric conditions.

the bottom and the walls of the iron crucible to fill the ~5-inch tall chamber and were mentioned to be of low electrical resistance and high density. At the time, the role of iron as a catalyst was not recognized in the patent. Now we know that iron is a particularly efficient catalyst for filamentary carbon synthesis from methane. A sequence of clay-like layers ($f$ /$h$) is used to trap the gaseous by-products which are removed after synthesis. Essentially the same procedure is employed today for the basic CVD synthesis of nanotubes, typically employing a quartz chamber and patterned iron nanoparticles on a substrate for localized directed growth of CNTs.

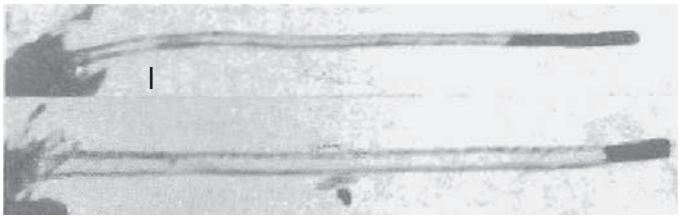

**Fig. 1.6** TEM images of what appears to be multi-wall CNTs. Adapted from the 1952 article by Radushkevich and Lukyanovich.[5] The upper and lower multi-wall CNTs have diameters of 50 nm and 100 nm respectively.

With the development of the electron microscope in the 1930s, scientists had a new, extremely useful (and expensive) tool to play with. They immediately began to take a close look at the structure of nature at length scales that had been previously inaccessible.[4] In 1952, Russian scientists reported intriguing transmission electron microscope (TEM) images of filamental carbon structures synthesized from the iron-catalyzed decomposition of carbon monoxide at temperatures in the range of 400–700 °C.[5] The TEM images (Figure 1.6) are believed to be the first to show what appears to be (what we now call) multi-wall nanotubes among the other filamental and amorphous carbon products described in the article. They recognized the catalytic properties of iron in facilitating the growth of tubular carbon, and also discussed the initial formation of iron carbide at the base of the tubes followed by the subsequent growth of carbon filaments, a theory which is widely accepted today. Perhaps partly due to *cold war* difficulties in rapidly disseminating new knowledge at that time, British materials researchers (apparently unaware of the Russian article) independently announced similar filamental observations resulting from thermal decomposition of carbon monoxide in the presence of iron a year later.[6] Their work appears to have been motivated by the need to understand the degradation of ceramic bricks used in blast furnaces. Blast-furnaces are furnaces used for the production of industrial metals such as iron, and bricks are traditionally used in the furnace lining. The deposition of amorphous and filamental carbon on the bricks is entirely undesirable in a blast furnace because it compromises the material integrity of the bricks, resulting in a serious reliability issue. This had been a major problem they were investigating. They also speculated that carbon filaments likely accumulate in domestic chimneys, because

[4] Optical microscopes can provide a magnification up to about 1000 times, while electron microscopes can offer a magnification of about a million times, corresponding to sub-nanometer resolution.

[5] L. V. Radushkevich and V. M. Lukyanovich, O strukture ugleroda, obrazujucegosja pri termiceskom razlozenii okisi ugleroda na zeleznom kontakte (On the structure of carbon formed by the thermal decomposition of carbon monoxide to the contact with iron). *Zh. Fis. Khim. (Russ. J. Phys. Chem.)*, **26** (1952) 88–95.

[6] W. R. Davis, R. J. Slawson and G. R. Rigby, An unusual form of carbon. *Nature*, **171** (1953) 756.

similar processes occur. Accordingly, it is certainly plausible that the unintentional production of carbon fibers and tubes may have been going on for a very long time, say for at least as long as chimneys have been around. This is another reason why we prefer to focus on the scientific investigations of carbon morphologies.

Inspired by the reports from the Russian and British researchers, Hofer *et al.* followed up on the suggestion from the former that similar carbon filaments might be produced using cobalt or nickel catalysts instead of iron. In 1955, they were successful in reproducing the synthesis of carbon filaments from carbon monoxide using either cobalt or nickel catalysts.[7]

So far, the electron microscope had been an indispensable tool for elucidating the morphology of the different carbon filaments and for bringing their general structural properties to light, leading to a renewal in scientific interest. However, no industrial application had been developed at that time, as tungsten had largely replaced carbon as filaments in the lighting industry by 1910.[8] Fortunately, all this changed by the 1960s, largely due to the pioneering work of Roger Bacon, an American scientist who was then with the National Carbon Company, a fitting name for a corporation devoted to applications of carbon materials. While studying the properties of graphite in an arc-discharge furnace under extreme conditions (close to its triple point, temperature ~3900 K, pressure ~92 atm), he discovered the formation of carbon nanofibers with somewhat different (but similar) morphology than had been previously observed.[9] The reported TEM images seem to show that the carbon nanofibers are composed of concentric cylindrical layers of carbon similar to a multi-wall nanotube but with a length-dependent diameter ranging from sub-micrometers to over 5 μm, leading Roger Bacon to propose a scroll model for the morphology for the fibers. Subsequent work by others has also shown that nanofibers can have a morphology similar to a stack of cones (or a stack of paper cups),[10] which is close to the structure of a paper scroll (see Figure 1.7).

Roger Bacon was able to optimize the growth conditions to yield high-performance polycrystalline carbon fibers with outstanding mechanical properties (Young's modulus ~700 GPa, tensile strength ~20 GPa) which were notably much superior to steel (Young's modulus ~200 GPa, tensile strength ~1–2 GPa), while retaining room-temperature resistivity (~65 μΩ cm) comparable to that of crystalline graphite.[9] In the following decade significant progress was made in commercializing carbon fiber technology. For example, around 1970 several high-profile review and news articles had been published that discussed the comparative

[7] L. J. E. Hofer, E. Sterling and J. T. McCartney, Structure of the carbon deposited from carbon monoxide on iron, cobalt and nickel. *J. Phys. Chem.*, **59** (1955) 1153–5.

[8] Remarkably, more than a century, later, tungsten continues to be the ubiquitous choice for filaments in incandescent light bulbs.

[9] R. Bacon, Growth, structure, and properties of graphite whiskers, *J. Appl. Phys.*, **31** (1960) 283–90.

[10] A case in point is: M. Endo *et al.*, Pyrolytic carbon nanotubes from vapor-grown carbon fibers, *Carbon*, **33** (1995) 873–81.

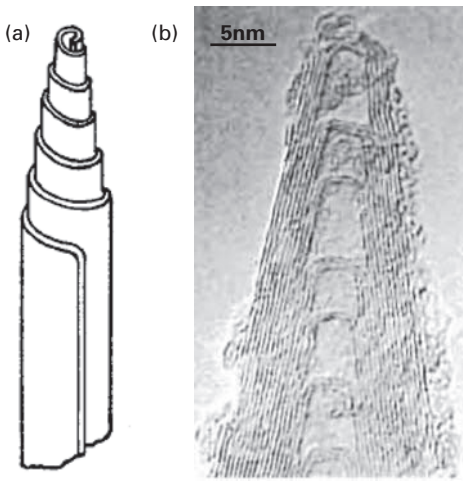


**Fig. 1.7** Morphology of carbon nanofibers. (a) Scroll model proposed by Roger Bacon. Reprinted with permission from Ref. 9. Copyright (1960), American Institute of Physics. (b) High-resolution TEM image of a nanofiber showing a hollow cone-like structure with multiple walls. Adapted from Endo *et al.*[10] Copyright (1995), with permission from Elsevier.

benefits of carbon fibers and the new emerging applications.[11] If we consider the late 1800s as the birth of carbon fibers driven by light-bulb applications, then the 1960s can be seen as the *first renaissance* (a second one will be mentioned later) for fiber technology driven by new applications. The new applications were grounded on taking advantage of the mechanical (strength, stiffness, lightness) and high-temperature properties of the fibers to manufacture composites (reinforced plastics, metals, glass, etc.) with tailor-made engineered performance for a variety of industries, including vehicle parts and engines for the aerospace, space, and automotive industries. Making filamental carbon was once again big business with commercial ramifications. To tap their full commercial potential, much of the subsequent development over the next few decades was in lower cost, higher volume production of carbon fibers.

Along this line, Morinobu Endo, then a graduate student in Japan, started working on different recipes to synthesize lower cost carbon fibers in the early 1970s. At that time, owing to the growing commercialization, a wide variety of manufacturing techniques had been developed. In France as a visiting scholar, he was exploring the growth of carbon fibers on a substrate, based on thermal decomposition of a gas mixture of benzene and hydrogen, when by chance he observed both single-wall and multi-wall CNT (Figure 1.8). This was a total accidental rediscovery of

[11] See: New Materials make their mark. *Nature*, **219** (1968) 875; R. W. Chan and B. Harris, Newer forms of carbon and their uses. *Nature*, **221** (1969) 132–41; and R. Jeffries, Prospects for carbon fibres. *Nature*, **232** (1971) 304–7.

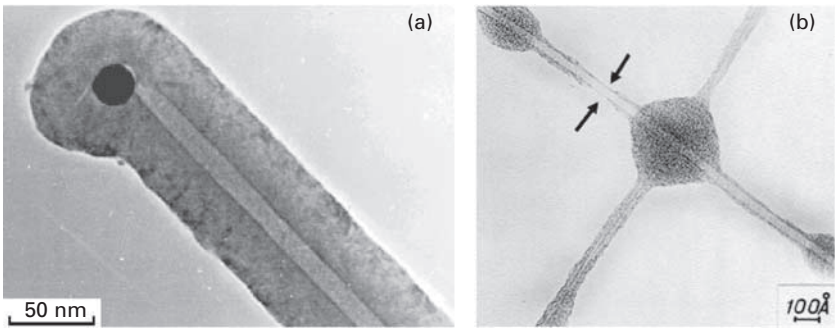


**Fig. 1.8** Electron microscope images of multi-wall and single-wall hollow tubes recorded in 1976. (a) A thick nanotube with a hollow core corresponding to a multi-wall CNT with diameter of ~70 nm. (b) The arrows are pointing to a section of a hollow tube with a single shell with diameter of ~4 nm. Courtesy of Morinobu Endo. Reprinted from Ref. 13. Copyright (1976), with permission from Elsevier.

hollow carbon tubes brought about by a practical desire to hasten the cleaning of the substrate for later reuse, so as to increase the throughput of the CVD system. This is very much similar to baking cake in a pan in an oven. After baking, the pan has to be cleaned for subsequent baking runs. If the cleaning takes too long, one can imagine then that only so many baking runs are possible in a given time. Morinobu Endo was keen on reducing the time for cleaning the substrate (typically consumed about two and a half days) in order to increase the number of experiments he could run. By simply cleaning the blackened substrate with sandpaper, he afterwards noticed the growth (at 1100 °C) of what he termed hollow tubes (which we now call CNTs) facilitated by the catalytic iron particles unknowingly left behind from the sandpaper on the substrate.[12] Apparently unaware of the prior work of Raduskevich and Lukyanovich,[5] Endo and coworkers performed detailed studies elucidating the role of the iron as a catalyst, the crystalline structure of the hollow tubes and their long concentric shells, and even reported the first recorded image of a hollow tube with a single shell (see Figure 1.8b).[13] The single-wall CNT was a momentary curiosity and was all but forgotten shortly after because interest then was in carbon fibers which were increasingly well developed for use in the several industries employing composite materials. There was no study of the non-mechanical properties of the CNTs, such as their electrical, optical, and sensor properties, that might have shed light on new, interesting applications. That had to wait for the second renaissance in filamental carbon science about 15 years later.

[12] He was greatly inspired by his French supervisor (Professor Agnes Oberlin) to "see what is really there, not what you would like to see."

[13] A. Oberlin, M. Endo and T. Koyama, Filamentous growth of carbon through benzene decomposition. *J. Cryst. Growth*, **32** (1976) 335–49.

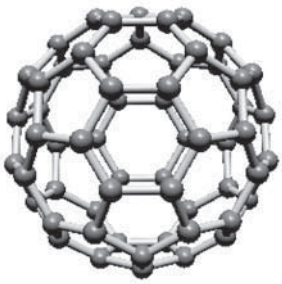

**Fig. 1.9** Ball-and-stick model of $C_{60}$ or buckyball. The balls (spheres) represent the carbon atoms and the sticks (lines) stand for the bonds between carbon atoms.

A major breakthrough occurred in 1985 with the *experimental discovery* of a zero-dimensional (relatively speaking, compared with larger forms of carbon) allotrope of carbon named $C_{60}$ (or *buckyball* or *buckminsterfullerene* after Richard Buckminster "Bucky" Fuller, the American architect famous for geodesic domes) by the discoverers Kroto, Curl, Smalley, and coworkers at Rice University in Texas.[14] This discovery was completely by chance, as the chemists were performing experiments to simulate the conditions of carbon nucleation and formation in giant stars (much larger than the Sun) and interstellar space. In the course of these experiments they managed to observe $C_{60}$, which resembles a soccer ball. Indeed, in the landmark article, the authors showed an image of a soccer ball (notably pointing out it was on Texas grass) to illustrate the structure of $C_{60}$. A ball-and-stick model is shown in Figure 1.9. This discovery renewed focus on low-dimensional crystalline allotropes of carbon, and speculation about the possibility of single-wall CNTs had been swirling by the late 1980s (the previously reported images of single-wall and multi-wall hollow tubes had largely remained unnoticed).[15]

By 1990 there was a great deal of excitement, and at the Fall 1990 MRS (Materials Research Society) meeting in Boston, Kroto strongly urged Iijima (an electron microscope expert at NEC laboratories with a long history in carbon research) to work on buckyballs. Immediately, Iijima started conducting experiments aimed at elucidating the growth mechanism of buckyballs using an arc-discharge method common to fullerene synthesis. Within a year, by serendipity he noticed elongated hollow structures in the carbon soot which were multi-wall CNTs, including a double-wall nanotube where the walls can be clearly seen (Figure 1.10).[16]

[14] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl and R. E. Smalley, $C_{60}$: Buckminsterfullerene. *Nature*, **318** (1985) 162–3. Kroto, Curl, and Smalley subsequently won the Nobel Prize in Chemistry in 1996. The Nobel Prize is limited to a maximum of three recipients; as such, the then graduate student co-authors (Heath and O'Brien) did not participate in the award.

[15] M. S. Dresselhaus, G. Dresselhaus, and Ph. Avouris (editors), *Carbon Nanotubes: Synthesis, Structure, Properties, and Applications* (Springer-Verlag, 2001), Chapter 1.

[16] S. Iijima, Helical microtubules of graphitic carbon. *Nature*, **354** (1991) 56–8.