10. A New Direction: Nanotubes

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10.1 Introduction

The recent discovery of various stoichiometries of $B_xC_yN_z$ nanotubes provides an interesting application for the formalism covered in the previous chapters. A nanotube can be described as a long thin strip, cut out of a single atomic plane of material, rolled to form a cylinder with a diameter of nanometer scale and a length on the order of microns. This chapter will discuss the discovery of tubes of various layered materials, give a theoretical formulation of the cylindrical nanostructures, show some experimental work done on the mechanical behavior of carbon tubes and provide possible applications of this material in the future.

10.2 Discovery

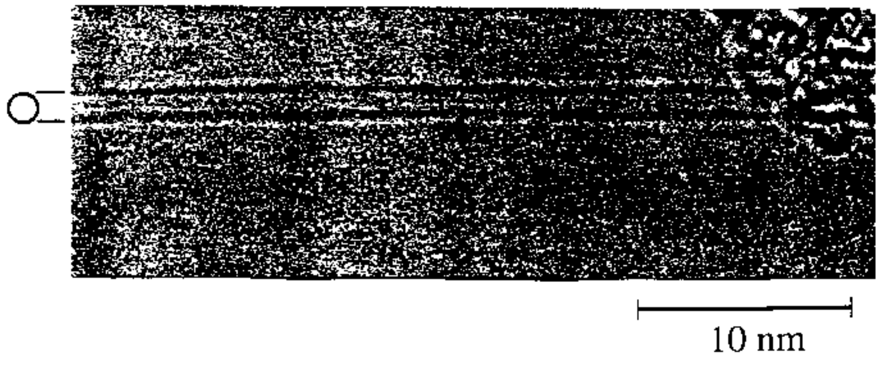

Fig. 10.1. Transmission electron micrograph of a single-wall carbon nanotube. Line drawing shows the cross section of the structure.

Carbon nanotubes ($x = 0, y = 1, z = 0$) were first discovered by Iijima (1991) while performing transmission electron microscopy (TEM) on a fullerene sample taken from the chamber where C_{60} is produced. Fig. 10.1 is a micrograph for both single and multi-walled tube growth have been successful, including vapor condensation (Ge and Sattler 1993), laser ablation (Guo et al 1995) and electrolytic method (Hsu et al 1995).

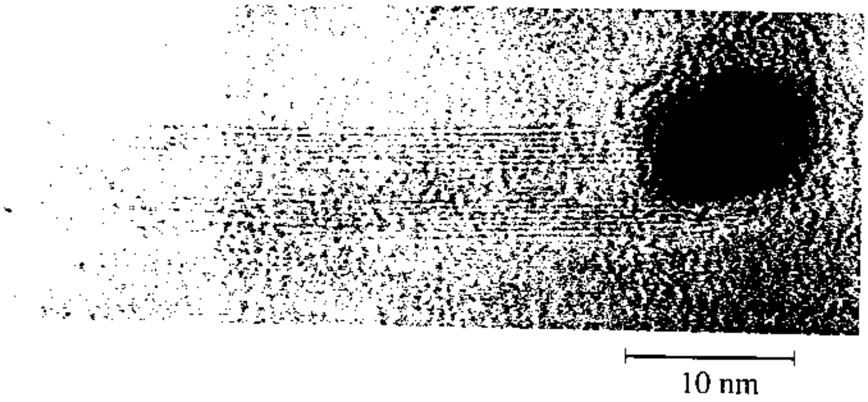

Fig. 10.4. TEM image of multi-wall BN nanotube produces by arcing a BN-filled tungsten electrode. The metal particle seen at the end is believed to help nucleate or terminate tube growth.

Weng-Sieh et al (1995) and Stephan et al (1994) synthesized tubes with $x = 1$, $y = 2$, $z = 1$ stoichiometry of boron, carbon, and nitrogen, namely BC_2N. Most recently boron nitride ($x = 1$, $y = 0$, $z = 1$) nanotubes have been discovered both multi-walled (Chopra et al 1995b) and single-walled (Loiseau et al 1996). All varieties of $B_xC_yN_z$ nanotubes which exist so far have been formed in the arc-discharge chamber using different materials and operating conditions. Fig. 10.4 (Chopra et al 1995b) shows a multi-walled BN nanotube produced by using a BN filled tungsten electrode; tubes synthesized by this method can have a metal particle at the tip which is believed to aid in nucleation or termination of BN tube growth.

10.3 Theory

The theoretical approach to nanotubes begins with defining indices relative to the lattice vectors on the hexagonal plane from which the tubes are formed. Fig. 10.5 shows the simplest hexagonal lattice made from a homogeneous material, simulating the case for carbon. The other, more complicated, materials will have bigger unit cells but can be treated with a similar approach because they are also planar, hexagonal materials in bulk. However, for the sake of simplicity, we consider the case where each vertex is occupied by the same kind of atom, for example carbon atoms in graphite. A tube is formed

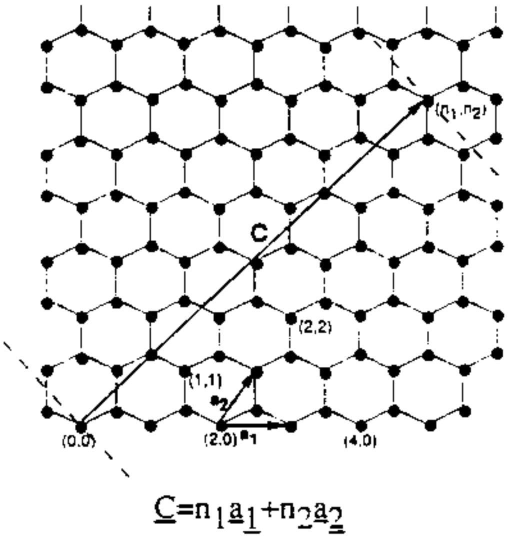

Fig. 10.5. Hexagonal network of atoms defined by indices relative to the lattice vectors. By cutting a strip (dashed line in figure) of this hexagonal sheet and mapping the origin to some (n_1, n_2), a tube is formed, uniquely defined by its circumference vector, $\mathbf{C}$.

by defining a particular circumference vector $\mathbf{C} = n_1\,\mathbf{a}_1 + n_2\,\mathbf{a}_2$ where n_1 and n_2 are integers and $\mathbf{a}_1$ and $\mathbf{a}_2$ are the unit vectors (the same notation as used by Saito et al (1992)); having defined the width of the strip with $\mathbf{C}$, we can form the tube by mapping the origin to the point (n_1, n_2) and the corresponding points down the length of the tube. Thus tubes will have several different chiralities, depending on the circumference vector, $\mathbf{C}$, as seen in the examples of Fig. 10.6a-c.

Calculations of the density of states for carbon nanotubes indicate that the electrical properties of the tubes will range from semi-conducting to metallic depending on the chirality and the diameter of the tube (Saito et al 1992). Miyamoto et al (1994) have performed similar calculation of the electrical properties for BC_2N tubes and have found that they also range from semi-conducting to metallic like carbon nanotubes, but all BN nanotubes are predicted to be semi-conducting independent of their chirality and diameter (Blase et al 1994).

10.4 Mechanical Behavior

The unique size of these nanostructures leads to interesting questions about their mechanical behavior. Can the tubes be treated as continuos hollow

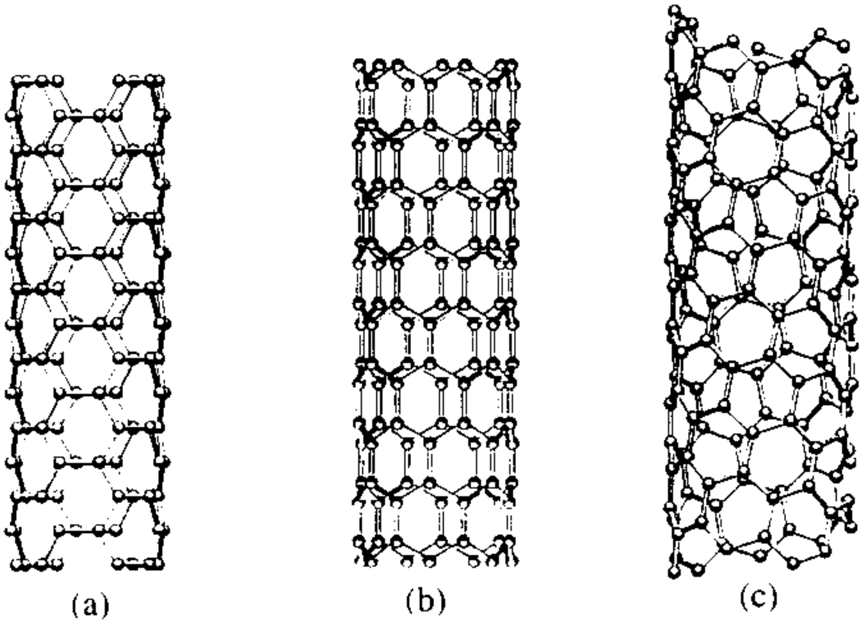

Fig. 10.6. Theoretical examples of tubes with different chiralities. (a) (4,4) armchair chirality tube (b) (8,0) zigzag tube (c) (7,2) tube. The names for the chiralities come from the arrangement of atoms at the cross-sectional edge of the tube as seen in the figure. (Courtesy of Vincent H. Crespi)

cylindrical structures or does their nanometer size call for a more discrete treatment? A doublet mechanical analysis of the mechanical properties of nanotubes has the potential to answer such a question. Meanwhile, energetics and Hamiltonian formulation predicts that carbon nanotubes will be 30 times stiffer than a steel rod of the same dimension (Ouverney et al 1992).

Much of the experimental work carried out on nanotubes has concentrated on carbon nanotubes. Analysis of high resolution TEM micrographs of some of these structures reveals defects in the cylindrical shape of the tube. Hiura et al (1994) found tube cross-sections that were slightly elliptical, and Ruoff et al (1993) have seen tubes with deformed walls which locally change the inner diameter by a small amount. Tubes with localized kinks and bends have also been observed in carbon nanotubes (Endo et al 1993, Despres et al 1995). We expect, then, in following with analogies of hollow cylindrical structures, to see nanotubes which have totally collapsed. Indeed, such structures have been observed and characterized for carbon nanotubes and an example is given in Fig. 10.7 (Chopra et al 1995a). On initial inspection collapsed carbon nanotubes resemble a ribbon-like structure with two distinct regions: a flat region where the wide part of the flattened tube is in the image plane and a twist region where the wide region is perpendicular to the imaging plane. High resolution TEM images of these two regions reveal the following: when the flat part is in the imaging plane two parallel sets of equal-numbered lattice fringes, separated by a gap are observed; and when the width of the ribbon is perpendicular to the image plane the same total number of lattice fringes are seen but with no gap. These features are characterized in the insets in Fig. 10.7 in order to give a clear representation of the geometries. Careful analysis of the structure including an in situ rotation study proved that the projected diameter of the collapsed structure changed as the sample was rotated in contrast to the conventional inflated tube where, as expected, the projection did not change with rotation of the sample.

10.5 Applications

The study of nanotubes is of interest to a variety of researchers from different fields mainly because of the potentially wide reaching effect these structures could have on various areas of technology. The most exciting and realizable potential from the electronics industry is to look at single-wall nanotubes, some of which are predicted to being metallic, as nanowires. The forefront of the microchip industry produces micron scale circuitry; nanotubes boast the ability to reduce the scale by a factor of a thousand. In fact, due to the semiconducting nature of BN nanotubes, theoretically, it is possible to dope with different substances to achieve p-type and n-type doping leading to the eventual revolutionary idea of having whole circuits on single nanotubes.

Also the predicted high strength, high flexibility of these nanostructures makes them candidates for building blocks of extremely strong, versatile ma-

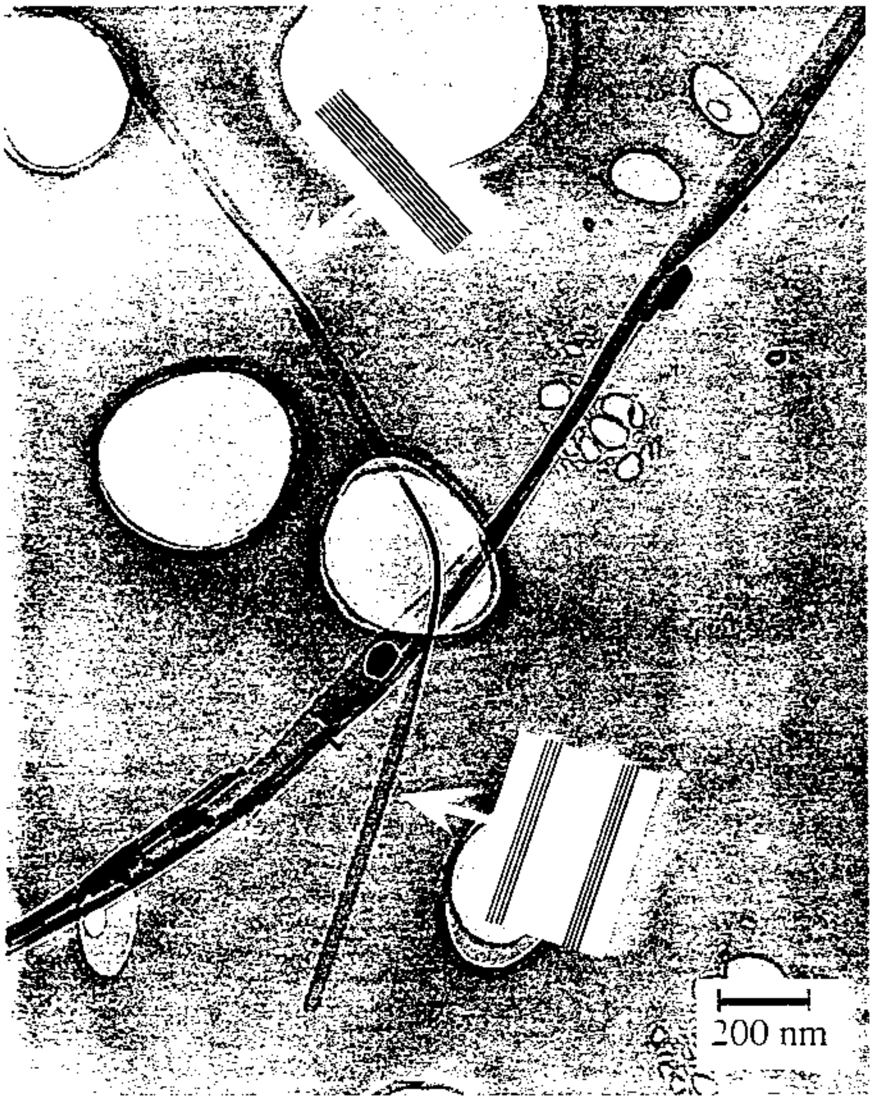

Fig. 10.7. TEM micrograph of a collapsed carbon nanotube. The insets (not to scale) emphasize the unique features of a flattened multi-wall nanotube. This ribbon-like structure has two distinct regions: a flat part, as illustrated in the lower inset, has an equal number of lattice fringes on either side of the gap, while the twist part has the same total number of lattice fringes but no gap (top inset).

terials. Presently graphite fibers are widely used in industry for their high performance; carbon nanotubes with their mostly defect free, crystalline walls are likely to be a vast improvement upon them.