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Research News

Non-Carbon Nanotubes**

By Alex Zettl*

1. Introduction

Shortly after the discovery of a method to mass-produce C_{60} and related fullerene molecules,[1] it was found that the same arc-discharge plasma method produces near-perfect carbon tubules of nanometer-scale diameter.[2] The aspect ratios are impressive and tubes exceeding 20 μm in length are not uncommon. On a microscopic scale, the structure of a carbon nanotube is exceedingly simple: it resembles a sheet of sp^2-bonded carbon (graphite) rolled into a seamless tube. Because of the inherent strength of the in-plane carbon–carbon bond in graphite, nanotubes are expected to be exceptionally strong in the axial direction, forming perhaps the "ultimate" high-strength, lightweight, flexible fiber.

The electronic properties of carbon nanotubes are complex. The predicted electrical conductivity of the tubes depends sensitively on the tube diameter and chirality.[3] For a non-chiral tube, a traversal of the bond structure around the belly of the tube leads to a closed circle. For a chiral tube, a similar traversal leads to a helical path. Non-chiral and chiral tubes have predicted conductivities ranging from highly conducting (metallic) to semiconducting.

Although "single-wall" carbon nanotubes have been produced,[4] usually the tubes grow as "multi-walled" structures consisting of several to many coaxial tubes each just fitting inside the next (the distance between walls is typically the van der Waals separation observed in graphite). The individual tubes that form a given multi-walled unit necessarily have different diameters (and possibly also random chiralities).

The unusual geometry, mechanical characteristics, and electrical conduction properties may make carbon nanotubes suitable for applications ranging from field-emission sources and nanoscale electronic devices to molecular filters, mechanical/electronic property enhancers in composite materials, and high strength high temperature fibers.

The successful synthesis of carbon nanotubes with shelled walls, each wall having a graphite-sheet-like structure, suggests the possibility of synthesizing single- and multi-walled nanotubes based on other layered materials.

2. Novel Nanotubes

Graphite has numerous close and distant structural relatives, many of which could, in principle, be the rootstock of new fullerene-like and nanotube structures. Particularly favorable candidates are boron-nitride-containing compounds and transition-metal dichalcogenides. Indeed, significant progress has been made in the prediction and synthesis of novel non-carbon-containing nanotubes derived from these compounds. In some cases the theoretical models indicate that non-carbon nanotubes may have electronic properties far superior to those attainable with conventional pure carbon nanotubes.

Tenne and co-workers[5,6] have used relatively low-temperature ($\sim 1000\,^{\circ}C$) techniques to synthesize fullerene-like structures based on MX_2 compounds (M = transition metal; X = chalcogen). In the case of tungsten disulfide (WS_2), small cylindrical structures are generated when tungsten films deposited on quartz substrates are annealed in H_2S in a reducing atmosphere.[5] For the synthesis of molybdenum disulfide (MoS_2) tubes, MoO_{3-x} and H_2S are reacted in a reducing atmosphere, yielding nanotubes of micrometer length and diameters on the order of 30 nm.[6]

Nanotubes containing boron and nitrogen perhaps together with carbon (general formula $B_xC_yN_z$) have been the most extensively studied. Original theoretical studies by Cohen and co-workers[7] predicted that pure boron-nitride (BN) tubes should be energetically stable. Electronic band structure calculations[8] show that BN nanotubes are wide gap semiconductors with a gap value ~ 5.5 eV. Interestingly, and in sharp contrast to pure carbon nanotubes, this gap value is *independent* of the radius and chirality of the tube. Hence any BN nanotube, single- or multi-walled, should have this uniform gap value. Another unique feature of BN nanotubes is that the lowest lying "interlayer" conduction band is nearly-free-electron-like, with a maximum charge density ~ 2 Å interior of the innermost tube wall.[8] This implies that, upon moderate doping of the BN tube wall fabric, the BN tube will contain a highly conducting electron gas within its interior. Figure 1 shows a central axis interior view of a predicted BN nanotube.

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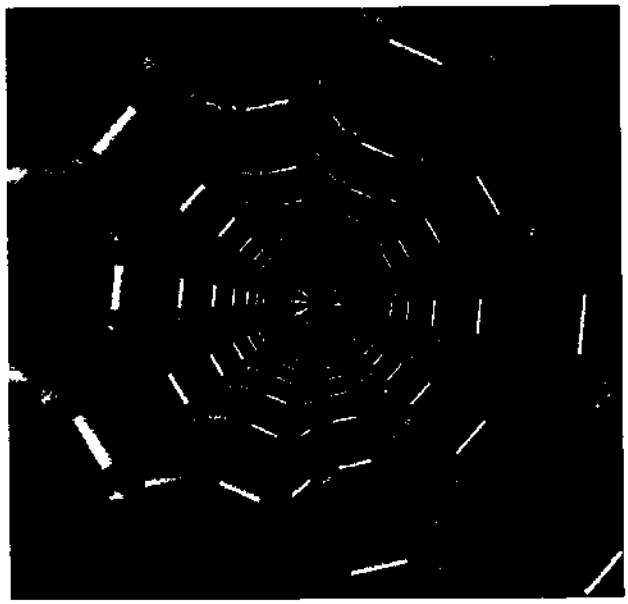

Fig. 1. Central axis view of predicted BN nanotube. Larger (red) atoms are boron; smaller (dark gray) atoms are nitrogen. This particular tube has no chirality. Image courtesy of Dr. Vincent Crespi.

Several experimental investigations have been made into the formation of tube-like boron-nitride structures. Heating amorphous BN at 1100 °C leads to large diameter ($\sim 3\,\mu$m) hollow tubes with a turbostratic (non-crystalline) form.[9] Heating ZrB_2 in B_2H_6 and NH_3 (or N_2), again at 1100 °C, produces tubular boron-nitride filaments somewhat analogous to carbon fibers.[10] The successful synthesis of pure crystalline BN nanotubes was recently reported by Chopra et al.[11] This synthesis used a high-temperature arc plasma similar to that used in conventional carbon nanotube production. A tungsten rod loaded with pressed hexagonal BN was arced against a cooled copper cathode, resulting in numerous multi-walled boron-nitride nanotubes (typical diameter 8 nm) with a B:N ratio of ~ 1, consistent with theoretical predictions. The inter-wall spacing of the BN nanotubes is 3.3 Å, in agreement with the inter-plane distance of 3.33 Å in bulk hexagonal BN. Interestingly, the visible ends of the BN nanotubes contain a dense metal particle, suggesting that tungsten helps to catalyze and or terminate BN nanotube growth. Figure 2 shows a transmission electron micrograph of an 8-walled BN nanotube.

Other stable stoichiometries of $B_xC_yN_z$ nanotubes have been predicted and experimentally investigated, in particular

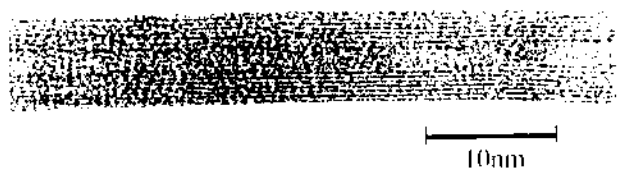

Fig. 2. Transmission electron micrograph of multi-walled crystalline BN nanotube.

BC_3 and BC_2N. The electronic structure of these tubes is diverse. Concentric BC_3 tubes are predicted to be metallic.[12] Different isomers of BC_2N nanotubes are proposed.[13] Figure 3 shows two types of BC_2N tubes; type I tubes range from being metallic to semiconducting, depending on chirality and diameter. Type II tubes, on the other

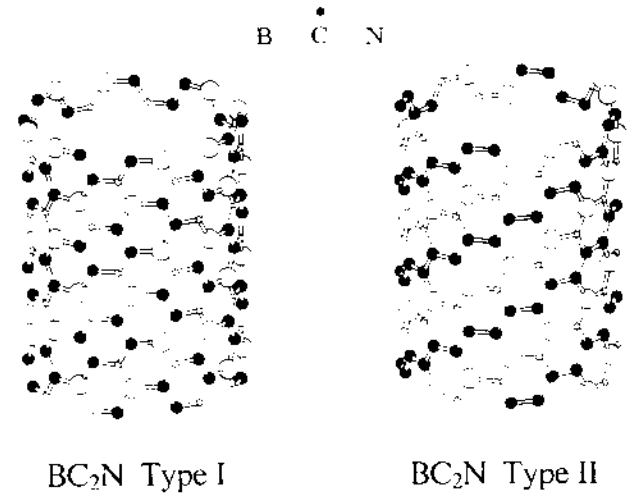

Fig. 3. Two different isomers of BC_2N nanotubes. Type II BC_2N nanotubes form "nanocoils". Adapted from ref. [12].

hand, are all semiconducting with a gap value 1.28 eV. Interestingly, the tube wall fabric of type II BC_2N nanotubes is calculated to be anisotropic. This implies that if current were to be injected into the end of a (doped) type II BC_2N tube, the current would trace out a helical path (note the barber-pole stripes of carbon carbon bonds around the tube body). This constitutes the smallest possible solenoid, a "nanocoil".[13] Such a nanocoil could have electronic applications including miniature inductors, transformers, receivers, and magnetic storage. It is anticipated that in the random synthesis of BC_2N nanotubes, type II tubes will dominate.

BC_3 and BC_2N nanotubes have been successfully synthesized. Zettl and co-workers[14] used high temperature arc-discharge methods (employing a composite graphite/BN source rod) to produce BC_3 and BC_2N nanotubes. The stoichiometry of individual nanotubes was determined with electron energy loss spectroscopy, and in some cases tubes with sharp concentration gradients along their long axis were observed. This suggests the interesting possibility of on-tube devices (pn junctions, Schottky barriers, etc.). The doping of carbon nanotubes with boron and nitrogen has been reported by Stephan et al.[15] where evidence for BC_2N nanotube structure is again found.

3. Conclusions

Nanotube formation is not limited to carbon; it appears to be a general feature of layered materials. Several new classes of nanotubes have been predicted and synthesized.

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Different synthesis routes appear to be viable. Although the stoichiometries of synthesized $B_xC_yN_z$ nanotubes have been determined, no detailed structural or electronic transport measurements have been performed. The theoretical predictions, such as the type II BC_2N nanocoil, point to rich and enticing research and applications opportunities.

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