

- are not excluded by our data, the orientational constraints imposed on the ligand by the docking site suppresses trajectories with small θ at the transition state.
32. L. J. Rothberg, M. Roberson, T. M. Jedju, *Proc. SPIE* **1599**, 309 (1991).
 33. Corrections to the measured ratio $\Delta A^\perp/\Delta A^\parallel$ due to fractional photolysis of an optically thin sample have been proposed previously (22, 39). We go one step further and calculate the correction for fractional photolysis in an optically thick sample, which, under our experimental conditions, is nearly twice that predicted for an optically thin sample. The validity of this correction has been verified experimentally.
 34. B. Locke, T. Lian, R. M. Hochstrasser, *Chem. Phys.* **190**, 155 (1995).

35. Microperoxidase is a water-soluble heme-peptide (pH 7) formed by enzymatic digestion of cytochrome c oxidase. One face of the heme is exposed to solvent while the other is in contact with and covalently bound to the peptide through a histidine linkage. The electronic spectra of microperoxidase-CO and MbCO are similar, suggesting that the electronic environment of microperoxidase models that of Mb.
36. K. A. Jongeward *et al.*, *J. Am. Chem. Soc.* **110**, 380 (1988).
37. Oxygen rebinds biexponentially with its slow phase approximately 2 orders of magnitude faster than what we measure for CO rebinding.
38. P. A. Anfinrud, M. Lim, T. A. Jackson, *Proc. SPIE* **2138**, 107 (1994).
39. P. A. Hansen, J. N. Moore, R. M. Hochstrasser, *Chem. Phys.* **131**, 49 (1989).

40. C. W. F. T. Pistorius and P. C. Haarhoff, *J. Chem. Phys.* **31**, 1439 (1959).
41. A. K. Churg and M. W. Makinen, *ibid.* **68**, 1913 (1978); W. A. Eaton and J. Hofrichter, *Methods Enzymol.* **76**, 175 (1981).
42. X. Cheng and B. P. Schoenborn, *J. Mol. Biol.* **220**, 381 (1991).
43. K. Moffat, personal communication.
44. This work is supported in part by NIH grant DK45306, the National Science Foundation Young Investigators Program, the Beckman Foundation, and the Mitsubishi Kasei Corporation. We thank J. S. Olson for generously supplying the Mb.

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Boron Nitride Nanotubes

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The successful synthesis of pure boron nitride (BN) nanotubes is reported here. Multiwalled tubes with inner diameters on the order of 1 to 3 nanometers and with lengths up to 200 nanometers were produced in a carbon-free plasma discharge between a BN-packed tungsten rod and a cooled copper electrode. Electron energy-loss spectroscopy on individual tubes yielded B:N ratios of approximately 1, which is consistent with theoretical predictions of stable BN tube structures.

The discovery of carbon nanotubes in 1991 (1) has generated intense experimental and theoretical interest in such structures. Theoretical studies of carbon tubes suggest that their electrical properties will range from metallic to semiconducting, depending on the tube diameter and chirality (2, 3). This leads to a diverse spectrum of properties, but it is also highly complex from an applications point of view, as the tube chirality and diameter are impossible to control with the use of present synthesis methods. Most carbon nanotubes observed are composed of multiple coaxial tubes, with the spacing between tube walls being approximately the graphite interplanar distance. The properties of a multiwalled carbon nanotube are expected to be even more complex, because they will depend sensitively on the detailed geometry of each constituent tube.

Authors of a recent tight-binding calculation have proposed that nanotubes might also be formed from hexagonal boron nitride (BN) (4). Local density approximation and quasi-particle calculations indicate that BN tubes are semiconducting with a gap of roughly 5.5 eV [versus 5.8 eV (5) for bulk hexagonal BN] and that the gap is nearly independent of tube diameter, chirality, and the number of tube walls (6). The calculated

uniform electronic properties of BN tubes contrast sharply with the heterogeneity of carbon tubes [and other carbon-containing tubes such as those formed from BC_2N (7) and BC_3 (8)] and suggest that BN tubes may have significant advantages for applications. Although previous studies have demonstrated the existence of BN filaments with diameters on the order of 100 nm (9), as well as carbon-containing nanotubes with the stoichiometry of BC_2N (10, 11) and BC_3 (10), pure BN nanotubes have not been reported. We describe here the synthesis and stoichiometric characterization of multiwalled BN nanotubes.

Boron nitride nanotubes were synthe-

sized in a plasma arc discharge apparatus similar to that used for carbon fullerene production (12). To avoid the possibility of carbon contamination, no graphite components were used in the synthesis. The insulating nature of bulk BN prevents the use of a pure BN electrode. Instead, a pressed rod of hexagonal BN 3.17 mm in diameter was inserted into a hollow tungsten electrode with an outer diameter of 6.3 mm, forming a compound anode. The cathode consisted of a rapidly cooled pure copper electrode. During discharge, the environmental helium gas was maintained at 650 torr and the dc current was ramped from 50 to 140 A to maintain a constant potential drop of 30 V between the electrodes. A dark gray soot deposited on the copper cathode, in contrast to the case of carbon tube growth, in which typically a more cohesive cylindrical deposit with a hard crustlike shell forms on the cathode. After the arcing was complete, pieces of solidified tungsten were found spattered inside the chamber, indicating that the temperature at the anode during synthesis exceeded 3700 K, the melting point of tungsten.

Characterization of the cathodic deposit was accomplished with transmission electron microscopy (TEM) with the use of a JEOL JEM 200CX electron micro-

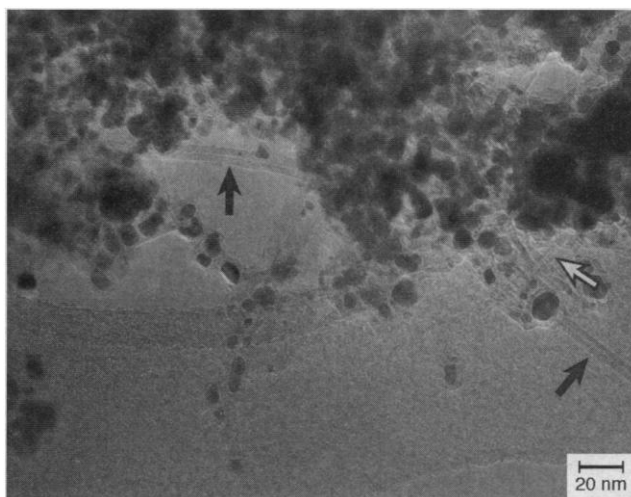


Fig. 1. TEM image of a BN soot sample on an amorphous support grid. Dark arrows point out one long BN multiwalled nanotube. The light arrow identifies another nanotube.

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scope with 200-keV accelerating voltage. Portions of the gray soot were deposited onto holey carbon grids and analyzed under phase-contrast imaging conditions.

Figure 1 shows a typical TEM image taken over a large area of the support grid. Numerous structures of distinct and contrasting morphologies are apparent. The large amorphous band covering nearly the entire lower half of the image is a portion of the support grid. The dark clusters scattered throughout the upper half of the image are tentatively identified as tungsten. Figure 1 clearly shows structures that appear to be multiwalled nanotubes, with inner diameters on the order of 1 to 3 nm, outer diameters on the order of 6 to 8 nm, and lengths exceeding 200 nm. The two dark arrows in Fig. 1 identify one such tube, which extends beyond the left and right borders of the image. The light arrow in Fig. 1 identifies another multiwalled tube of apparently shorter length.

Figure 2 shows a high-resolution TEM image of a portion of an observed nanotube. This and other similar images exhibit sharp lattice fringes indicating that the walls of the tubes are well ordered with an interlayer distance of ~ 3.3 Å, which is consistent with the interplanar distance of 3.33 Å in bulk hexagonal BN (13). The particular tube shown in Fig. 2 has eight walls; similar tubes with wall numbers ranging from seven to nine have been observed.

A careful study of the ends of BN nanotubes reveals an interesting feature. Every end that we have observed contains a dense particle, possibly tungsten (or a tungsten compound with boron and nitrogen) whose diameter is comparable to the outer BN tube diameter. The end of a typical BN nanotube is shown in detail in Fig. 3. We note that the fullerene-like capping or other cappings seen in carbon nanotubes, all of

which involve pentagons, are not observed in BN structures. The formation of pentagons in a pure BN system would necessitate the creation of B-B or N-N bonds, which are unfavorable compared with B-N bonds, and thus there is frustration in capping a BN nanotube. Nature seems to solve this problem by using a small metal cluster, as seen in Fig. 3. The presence of many metal particles wrapped in layers of planar BN, as evident in Fig. 1, suggests a possible scenario for BN tube nucleation and growth. We speculate that in a high-curvature region of a covered particle, the outer layers of the BN coating may pull away from the innermost layer (as the layer-layer interaction in BN is rather weak) and grow outward to form a tube. Given this scenario, the tube growth is also likely to terminate when a metal particle collides with the open end of a growing tube and attaches to the dangling bonds, particularly if the metal forms stable nitrides and borides, as tungsten does.

Determination of the stoichiometry of individual tubes is possible with the use of electron energy-loss spectroscopy (EELS) inside the TEM. We have done EELS studies on portions of tubes suspended over holes in the carbon support grid. A

characteristic tube energy-loss spectrum is shown in Fig. 4. Two distinct absorption features are revealed, one beginning at 188 eV and another at 401 eV. These correspond to the known K-edge onsets for boron and nitrogen, respectively. The fine structure in the spectrum reveals the hexagonal bonding between boron and nitrogen (14). Noteworthy is the absence of any feature at 284 eV, the K-edge absorption for carbon. Quantification analysis of the tube EELS spectrum gives a B:N ratio of 1.14, which is consistent with a stoichiometry of BN (due to uncertainties in baseline corrections, the given B:N ratio has an estimated error of 20%).

Previously predicted tubes of the sp^2 bonded hexagonal BN sheet material have now been successfully synthesized. Because of their predicted uniformly semiconducting behavior, BN tubes provide interesting possibilities for potential device applications. The existence of carbon and BN nanotubes, along with the recent discovery of MoS_2 (15), BC_2N (10, 11), and BC_3 (10) tubes suggest that the tubular structure may be stable for other layered materials. Thus, the method we have described for the synthesis of BN tubes may be a technique useful for the production of tubes from other novel materials with varying electrical properties.

REFERENCES AND NOTES

1. S. Iijima, *Nature* **354**, 56 (1991).
2. N. Hamada, S.-i. Sawada, A. Oshiyama, *Phys. Rev. Lett.* **68**, 1579 (1992).
3. R. Saito, M. Fujita, G. Dresselhaus, M. S. Dresselhaus, *Phys. Rev. B* **46**, 1804 (1992).
4. A. Rubio, J. Corkill, M. L. Cohen, *ibid.* **49**, 5081 (1994).
5. A. Zunger, A. Katzir, A. Halperin, *ibid.* **13**, 5560 (1976).
6. X. Blase, A. Rubio, S. G. Louie, M. L. Cohen, *Europhys. Lett.* **28**, 335 (1994).
7. Y. Miyamoto, A. Rubio, M. L. Cohen, S. G. Louie, *Phys. Rev. B* **50**, 4976 (1994).
8. Y. Miyamoto, A. Rubio, S. G. Louie, M. L. Cohen, *ibid.*, p. 18360.
9. P. Gleize *et al.*, *J. Mat. Sci. Lett.* **13**, 1413 (1994).
10. Z. Weng-Sieh *et al.*, *Phys. Rev. B* **51**, 11229 (1995).
11. O. Stephan *et al.*, *Science* **266**, 1683 (1994).
12. W. Kratschmer, L. D. Lamb, K. Fostiropoulos, D. R. Huffman, *Nature* **347**, 354 (1990).
13. R. S. Pease, *Acta Crystallogr.* **5**, 356 (1952).
14. L. Reimer, *Transmission Electron Microscopy*, P. W. Hawkes, Eds. (Springer-Verlag, Heidelberg, Germany, 1993), vol. 36.
15. Y. Feldman, E. Wasserman, D. J. Srolovitz, R. Tenne, *Science* **267**, 222 (1995).
16. We thank C. Echer and M. O'Keefe of the National Center for Electron Microscopy, Lawrence Berkeley Laboratory, for helpful interactions. Supported by NSF grants DMR-9404755 and DMR-9120269, and by the director of the Office of Energy Research, Office of Basic Energy Services, Materials Science Division of the U.S. Department of Energy under contract DE-AC03-76SF00098. N.G.C. acknowledges support from a Department of Education Graduate Fellowship.

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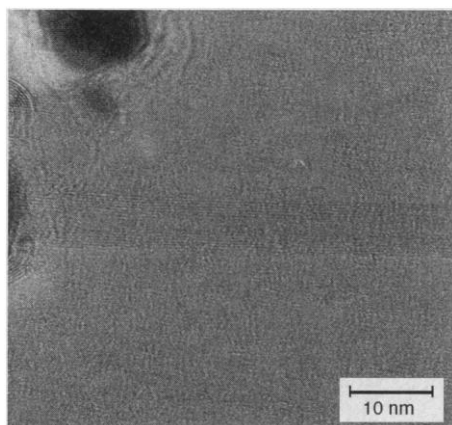


Fig. 2. High-resolution TEM image of a BN nanotube. The image shows a clear signature of a tube with an equal number of lattice fringes on either side of a hollow; this particular tube has eight walls.

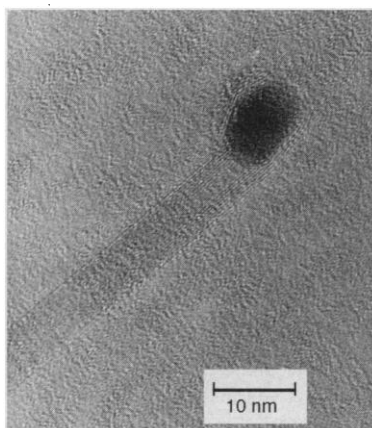


Fig. 3. High-resolution TEM micrograph of the capping of a BN nanotube. A dense metal particle is present at the tube end.

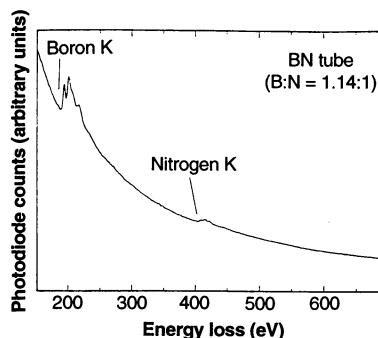


Fig. 4. EELS spectrum of a BN nanotube. The composition of the tube is boron and nitrogen with a B:N ratio of ~ 1 .