

Boron Nitride Nanotube Peapods

A. Zettl, J. Cumings, Wei-qiang Han, and W. Mickelson

*Department of Physics, University of California at Berkeley, and Materials Sciences Division,
Lawrence Berkeley National Laboratory, Berkeley California, 94720 U.S.A.*

Abstract. We demonstrate that boron nitride (BN) nanotubes can be filled "peapod" fashion with C_{60} molecules. Filling small-diameter BN nanotubes results in a linear chain of C_{60} molecules in the interior, while filling large diameter BN nanotubes leads to nanorods of crystalline C_{60} in the interior. Electron beam damage can be used to fuse the encapsulated C_{60} molecules into carbon nanotubes, leading to carbon nanotubes encased within insulating BN nanotubes. BN nanotubes can also be synthesized with mobile magnetic nanocrystals within their core.

INTRODUCTION

BN nanotubes[1,2] share many of the unusual structural properties of carbon nanotubes[3]. They have comparable (nm-scale) diameters and high aspect ratios, and can be produced in single-wall, exclusively double-wall[4], and multi-wall form. The mechanical properties are exceptional. However, the electrical properties of BN nanotubes are very different from those of carbon nanotubes. While carbon tubes come in three basic forms (metallic, small-gap semiconductor, and modest-gap semiconductor) depending on diameter and chirality, to a first approximation BN nanotubes are electrically uniform with an energy gap of about 4-5 eV independent of wall number, diameter, or chirality. For low applied electric fields BN nanotubes are thus essentially insulating. BN nanotubes form near-ideal geometrical structures for confining other atomic, molecular, or nanocrystalline species whose structural, mechanical, magnetic, electrical, and optical properties are of interest, either individually or in "crystalline" arrays. The insulating properties of the BN "host" can facilitate electrical measurements of the filled species.

We demonstrate that BN nanotubes can be filled "peapod style" with C_{60} fullerenes and other, larger, nanoparticles including those with potentially important magnetic properties. These larger nanoparticles are mobile within the BN nanotube interior.

BN NANOTUBE/ C_{60} PEAPODS

Double-wall BN nanotubes were synthesized using a method similar to that described previously[4]. As-synthesized BN nanotube material was heated in air at 800°C for 20 minutes to open the tips of the nanotubes. The air-annealed samples (gray in color) were then sealed in an evacuated (10^{-6} Torr) quartz ampoule together with C_{60} powder in approximately a 5:1 C_{60} :BN mass ratio, and heated at 630°C for 48 hours. The

CP633, *Structural and Electronic Properties of Molecular Nanostructures*, edited by H. Kuzmany et al.
© 2002 American Institute of Physics 0-7354-0088-1/02/\$19.00

resulting material, black in color, was sonicated in isopropanol and deposited on a holey-carbon grid for TEM analysis.

Fig. 1 shows a TEM image of two parallel double-wall BN nanotubes treated with C_{60} . The "upper" of the two tubes has an inner diameter of approximately 2nm. The interior of this tube is well resolved and clearly shows a linear chain of C_{60} molecules, in close analogy to carbon nanotube/ C_{60} peapod structures previously observed[5-8]. In the BN nanotube of Fig. 1, the C_{60} molecules have a mean (apparent, i.e. plane projected) center-to-center spacing of .890nm and a standard deviation of 0.099nm (with one anomalous minimum of .711nm and one anomalous maximum of 0.1099nm). In carbon peapods[6], TEM images indicate an approximate C_{60} center-to-center spacing of 1.0nm, which could be evidence that in BN nanotubes the C_{60} molecules are under more "pressure" than in carbon nanotubes. Another possibility is that in the BN nanotubes of Fig. 1 (which have a slightly larger inner diameter than typical single-wall carbon nanotubes) the C_{60} 's are arranged in a vertical zig-zag arrangement, which in projection would lead to a smaller *apparent* center-to-center distance. However, in this case we would expect to see some evidence for a horizontal (in-plane) zig-zag pattern, which we do not see.

We have also found that concentrated electron beam irradiation can cause the C_{60} molecules within a BN nanotube to coalesce into a single-wall carbon nanotube, yielding a (possibly conducting) carbon nanotube housed within an insulating BN nanotube protective sheath. This configuration has obvious applications potential and has distinct advantages over complementary observations[8] of temperature-induced fusings of C_{60} molecules in carbon nanotube peapods where the electrical conductivity of the outer tube cannot be reliably controlled. In the BN case, the outer protective coaxial cable "sheath" is guaranteed to be an insulator.

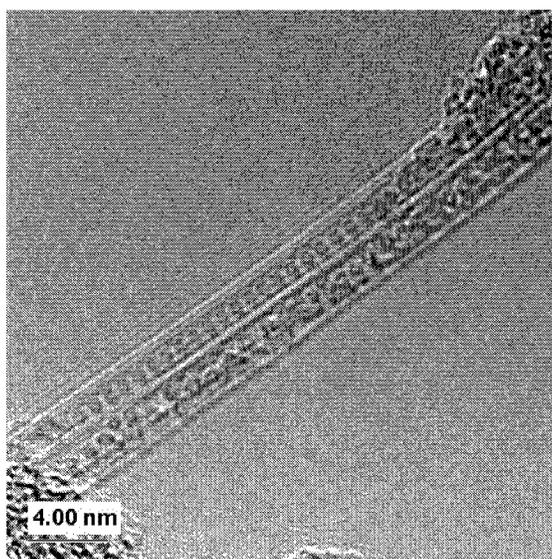


FIGURE 1. High resolution TEM image of BN nanotube peapods. In the upper of the two double-wall BN nanotubes shown, a linear chain of C_{60} 's is clearly resolved within the nanotube core. The average (plane projected) C_{60} - C_{60} center-to-center distance is 0.890nm.

Large inner diameter double-wall BN nanotubes can also be filled with C_{60} , using the same procedure described above. Fig. 2 shows a double-wall BN nanotube with inner diameter 4.15nm, whose interior has been completely filled with C_{60} molecules. Interestingly, the C_{60} s in this case form not just a one dimensional chain, but rather a rod-shaped "quasi-3-D" crystal, i.e. nanocrystalline rod or nanowire. It is not yet known if this nanowire has the same crystal structure as bulk C_{60} . The additional "space" in the larger diameter BN nanotubes suggests that the C_{60} in these nanotube/ C_{60} peapods could be readily doped with alkali metals or other charge transfer or mechanical spacing entities. Also, the insulating nature of the surrounding BN suggests that external gating[9] would be effective in inducing charges in the C_{60} nanowire region, leading perhaps to unusual conductivity (or superconductivity) effects.

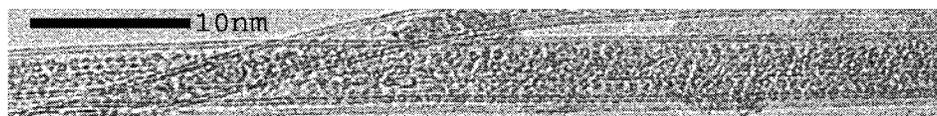


FIGURE 2. High resolution TEM image of 4nm inner diameter BN nanotube peapod. C_{60} 's fill the entire interior space of the nanotube and there constitute a crystalline C_{60} nanorod (i.e. nanowire).

NANOCRYSTAL DYNAMICS WITHIN BN NANOTUBES

We have synthesized multiwall BN nanotubes containing mobile foreign nanocrystals. In some cases, these structures can be produced in a single growth process, i.e. the nanotubes and nanocrystals are produced together in effectively one synthesis step. As an example, we describe BN nanotubes containing solid near-spherical iron nanocrystals; the composite structure was produced in one step from a carbon nanotube precursor. Multiwall carbon nanotubes (CNTs) were first synthesized via thermal chemical vapor deposition (CVD) using $FeO_x-Al_2O_3$ composite nanoparticles as a catalyst. After CVD growth the catalyst nanoparticle are frequently found inside the CNTs. B_2O_3 was then reacted with the CNTs under a N_2 atmosphere at 1600 °C for 30 minutes, effectively transforming the carbon nanotubes into BN nanotubes[10,11]. Interestingly, the transformation retains the catalyst particles within the multiwall nanotube, often yielding a high-quality multiwall BN nanotube filled with several near-spherical nanocrystals.

Fig. 3 shows a TEM image of a multiwall BN nanotube filled with several iron nanocrystals ranging in diameter from 1nm to 2nm. Under typical TEM operating conditions, the BN nanotubes and the nanocrystals acquire excess electrical charge; with sufficient charging, the charge repulsion between nanocrystals can be made to dominate magnetic dipole attractive interactions. Under continuous irradiation (200keV electrons) the nanocrystals display a highly agitated motion within the nanotube. The dynamics represent a competition between thermal, magnetic, and

charging energies. This system opens up exciting possibilities in the study of dimensionally confined nanoparticle interactions and phase transitions.

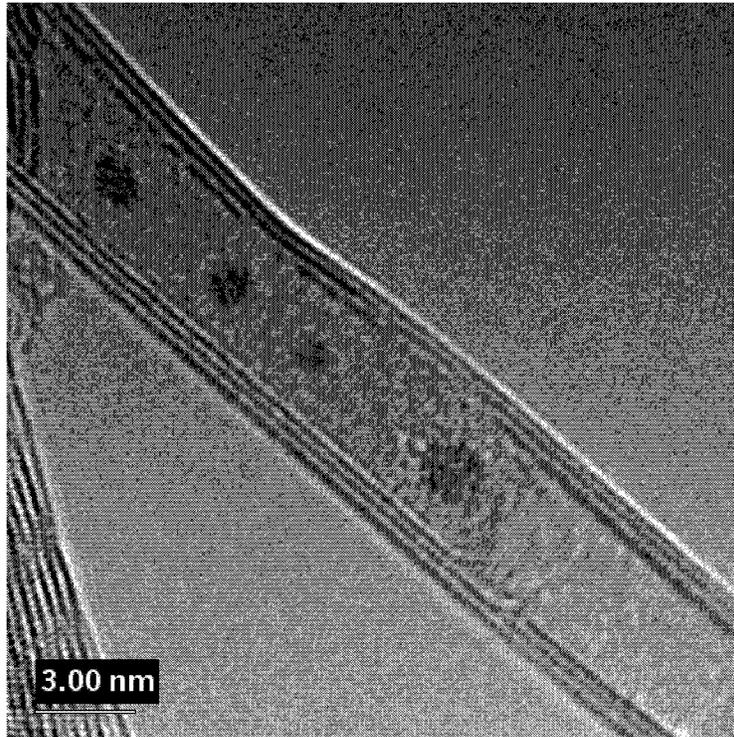


FIGURE 3. High resolution TEM image of multiwall BN nanotube containing four iron nanocrystals. The nanocrystals are highly mobile within the tube, and can be released from the tube in a one-by-one fashion.

We have also found that, using the concentrated electron beam from the TEM, it is possible to locally weaken and rupture the walls of the BN nanotube. This allows the interior nanocrystals to escape, one-by-one in a more or less controlled fashion, through the nanotube opening into the surrounding environment, both changing the nanocrystal concentration within the tube volume as well as providing a very local digital source of desired nanocrystals.

ACKNOWLEDGMENTS

This work was supported in part by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. JC Acknowledges support from an IBM Fellowship.

REFERENCES

1. Rubio, A., Corkill, J., and Cohen, M.L., *Phys. Rev. B.* **49**, 5081 (1994)
2. Chopra, N.P., Luyken, R.J., Cherrey, K., Crespi, V.H., Cohen, M.L., Louie, S.G., and Zettl, A. *Science* **269**, 966 (1995)
3. Iijima, S. *Nature* **354**, 56 (1991)
4. Cumings, J., and Zettl, A. *Chem. Phys. Lett.* **316**, 211 (2000)
5. Smith, B.W., Monthioux, M., and Luzzi, D.E. *Nature* **396**, 323-324 (1998)
6. Burteaux, B., Claye, A., Smith, B.W., Monthioux, M., Luzzi, D.E., and Fischer, J.E., *Chem. Phys. Lett.* **310**, 21-24 (1999)
7. Smith, B.W., Monthioux, M., and Luzzi, D.E., *Chem. Phys. Lett.* **315**, 31-36 (1999)
8. Smith, B.W., and Luzzi, D.E., *Chem. Phys. Lett.* **321**, 169-174 (2000)
9. Schoen, J.H., Kloc, Ch., Haddon, R.C., and Batlogg, B. *Science* **288**, 656-658 (2000)
10. Han, W.Q., Bando, Y., Kurashima, K., and Sato, T. *Appl. Phys. Lett.*, **73**, 3805(1998)
11. Golberg, D., and Bando, Y. *Appl. Phys. Lett.*, **79**, 415 (2001)