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LETTERS

Square, Pentagon, and Heptagon Rings at BN Nanotube Tips

Yahachi Saito* and Masatomo Maida

Department of Electrical and Electronic Engineering, Mie University, Tsu 514-8507, Japan

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Nanotubes of hexagonal boron nitride (*h*-BN) have been synthesized by arc discharge between ZrB_2 electrodes in a nitrogen atmosphere. A new morphology of BN nanotubes at their tips, exhibiting a "triangular flag" like shape, was observed by transmission electron microscopy. This morphology suggests the presence of energetically unfavorable odd-membered rings (e.g., pentagons and heptagons) in addition to favorable even-membered rings (e.g., squares).

Introduction

The discovery of carbon nanotubes[1] in 1991 has stimulated intense experimental and theoretical studies concerning structures based on hexagon networks. Single-wall nanotubes[2−4] and multiwall nanotubes are separately produced under different conditions. Tips of carbon nanotubes are closed by introducing pentagons into the hexagonal network, six pentagons for each tip. Heptagons, which bring about negative curvatures, can also be introduced together with additional pentagons. The presence of pairs of heptagons and pentagons is responsible for peculiar tube morphologies such as "bill"-shaped tips,[5] semitoroidal tips,[6] and helical tubes.[7]

Hexagonal boron nitride (*h*-BN) is layered material with a structure of graphite type in which planar networks of BN-hexagons are stacked regularly. Recently, *h*-BN has been shown to form closed concentric-shell nanotubes.[8−10] Tips of BN tubes exhibited a morphology characteristic of hexagonal BN networks, i.e., a flat tip with right angle corners, which was brought about by the introduction of three squares (four-membered rings) into the hexagon network.[9,10] In the present study, we observed a new morphology of BN nanotubes at their tips, which suggests the presence of less-favorable odd-membered rings (e.g., pentagon and heptagon).

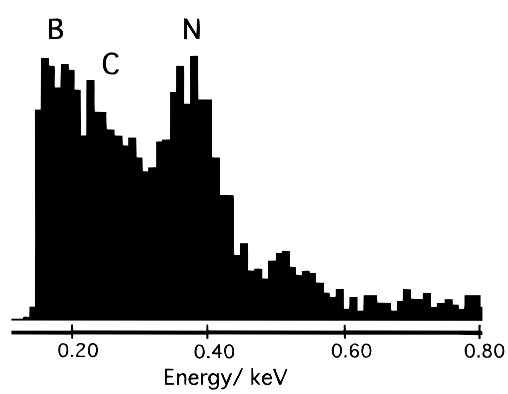

Figure 1. EDX spectrum of the soot material containing BN nanotubes. Signals from carbon are due to a sample-supporting film which is made of amorphous carbon.

Experimental Section

BN nanotubes were synthesized by evaporating zirconium diboride (ZrB_2) by electric arc discharge in an N_2 atmosphere. Sources of boron and nitrogen for producing BN nanotubes were the ZrB_2 rods and the N_2 gas, respectively. Details of the synthesis method have been described elsewhere.[11] Briefly, the ZrB_2 rods had a square cross-section of 6×6 mm^2 and a length of 40 mm. The pressure of N_2 gas (purity 99.999%) in the reactor chamber was 100, 500, and 700 Torr. The discharge

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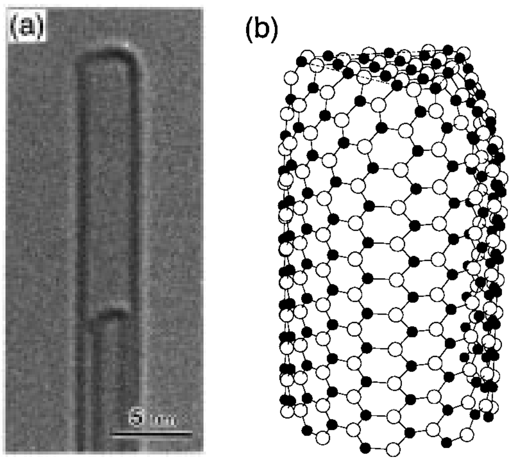

Figure 2. (a) TEM image of a tip of BN nanotube exhibiting a flat end. This tip morphology, being brought about by introducing three square (B_2N_2) rings into the BN hexagonal network, is characteristic of BN nanotubes. (b) Schematic drawing of the structure model for the flat-end BN tubes. Black circles and open circles represent boron and carbon atoms, respectively.

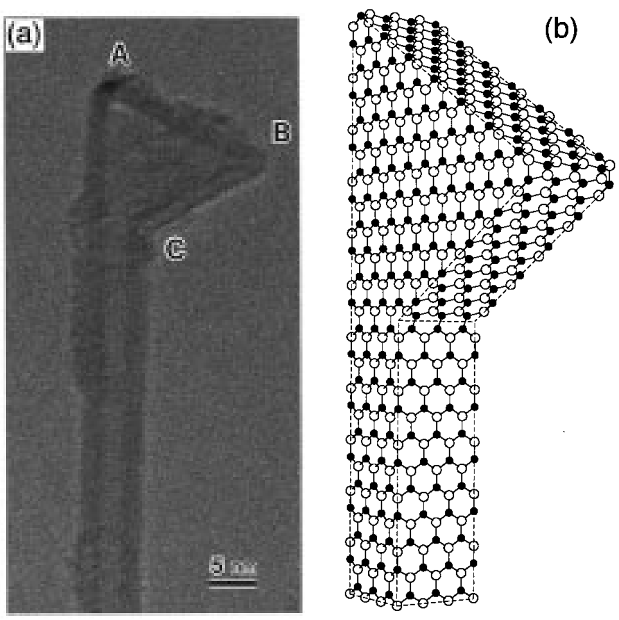

Figure 3. "Triangular flag"-shaped termination of a BN nanotube. (a) TEM image. (b) Schematic drawing of the structure model. Four B_2N_2 squares and two B_3N_4 (or B_4N_3) heptagons are introduced into the hexagonal network.

current was 50 A, and the voltage was about 20 V. The arc gap between the electrodes was kept constant, 1−2 mm. After an arcing for about 3 min, dark bluish-gray soot was obtained on the chamber walls and on the water-cooled cathode surface. The collected soot was examined by a transmission electron microscope (TEM) equipped with an energy-dispersive X-ray (EDX) analyzer.

Results and Discussion

Figure 1 shows an EDX spectrum obtained from the soot-containing tubular material. Peaks due to boron and nitrogen give nearly equal intensities, suggesting a composition ratio of B:N ≈ 1:1. A small hump between the peaks of B and N is due to carbon, originating from a sample-supporting film (holey carbon film).

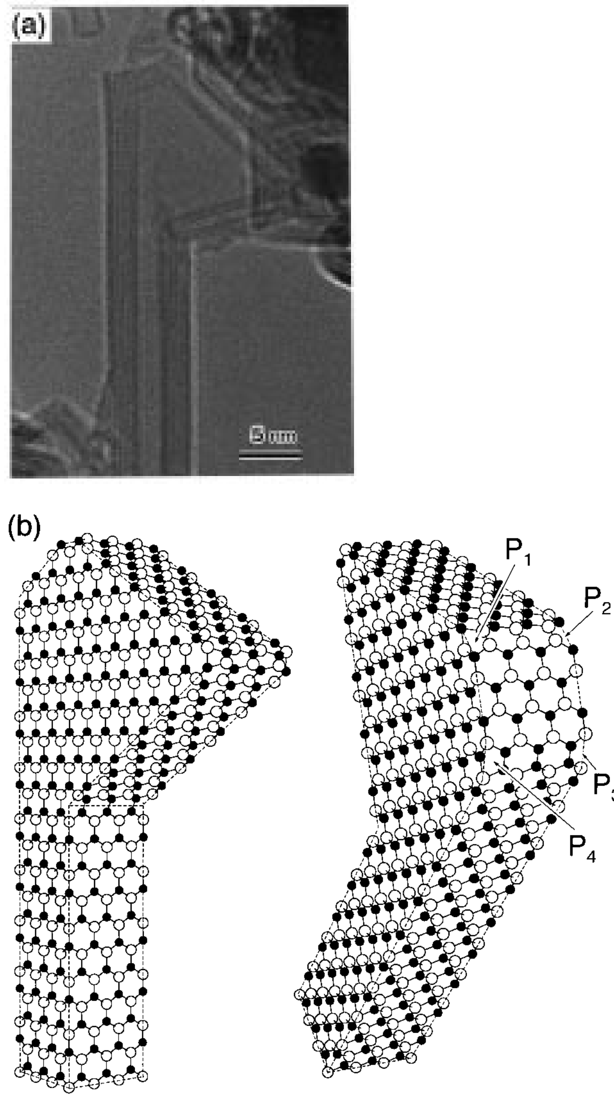

Figure 4. Truncated "triangular flag"-shaped termination of a BN nanotube. (a) TEM image. (b) Schematic drawing of the structure model, viewed from two different directions. Two B_2N_2 squares in Figure 3 are replace with four pentagons. Thus, the tip contains two squares, four pentagons, and two heptagons.

Most of BN nanotubes produced were multilayer tubes with the diameter from 3 to 30 nm and the length on the order of 100 nm. The number of layers were typically in a range between 2 and 10, being rather small compared with that for carbon nanotubes. Single-wall BN nanotubes were also produced as a minor product.[11]

Tips of BN nanotubes possess characteristic shapes, being distinguished from carbon nanotubes. A flat tip with right-angle corners, as shown in Figure 2, is the most common morphology for hexagonal BN networks, as already revealed.[9,10] The right-angle termination results from the presence of four-membered rings (B_2N_2 squares) at the tip, instead of five-membered rings as shown in Figure 2b. Even-numbered rings (e.g., squares, hexagons, and octagons) preserve energetically favorable B−N bonds, while odd-numbered rings (e.g., pentagons) introduce unfavorable B−B (or N−N) bonds.

In the present study we found a tip morphology, which suggests the presence of odd-numbered rings as shown in Figures 3 and 4. The tip shown in Figure 3a exhibits a "triangular flag" like shape. The inner angles at the corners A and B are, respectively, 62 ± 2° and 57 ± 2°, and the outer angle at C is 119 ± 2°. In measuring the corner angles, the rotation angle of the nanotube relative to the incident electron beam was not taken into account. These angle values, which are approximately 60° for A and B and 120° for C, can be realized by placing two squares (four-membered rings) at the acute corners (A and B) and one heptagon at the base of the triangular flag (C), as illustrated in a schematic model (Figure 3b). One square introduces a $+2\pi/3$ disclination in the hexagonal BN network, while one heptagon introduces a $-\pi/3$ disclination. We recall that a set of disclinations, with angles adding up to 2π, is required to close one end of a tube. The structure model shown in Figure 3b satisfies this requirement because the rear face also contains two squares and one heptagon at its corners in a similar way. It should be noted that an array of B−B (or N−N) bonds are formed along the line connecting two heptagons.

Triangular flags with one corner being truncated were also observed, as shown in Figure 4. This shape is derived by truncating the corner “A” of the triangular flag of Figure 3. A structure model of the truncated flag is shown in Figure 4b. Two square rings (on the front and the rear faces) at the corner “A” in Figure 3b are replaced with four pentagons (P_1-P_4), i.e., one square is split into two pentagons. Since the total disclination is preserved after this replacement, the tip of this truncated flag is also completely closed by a BN hexagon network. For this truncated tip, two more lines of B−B (or N−N) bonds are added between adjacent pentagons. In Figure 4b, pairs of like atoms are placed along the two lines P_1-P_2 and P_3-P_4. However, there is another way to place the two lines of like atom pairs, i.e., pairs of like atoms can be placed along the lines P_2-P_3 and P_4-P_1 instead of the lines P_1-P_2 and P_3-P_4. At present, we cannot distinguish between the two ways placing the lines of unfavorable B−B (or N−N) bonds.

The present discovery of odd-membered rings in BN networks exhibits the diverse topology of this heteronetworks. Energy consideration of such structures, which we have not discussed, is a future subject to develop our understanding of the structures of BN networks.

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