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# Formation and atomic structure of boron nitride nanotubes with a cup-stacked structure

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**Abstract**

Boron nitride (BN) nanotubes were synthesized by annealing $Fe_4N$/B powder at 1000 °C for 1 h in a nitrogen gas atmosphere, and large amounts of BN nanotubes with a cup-stacked structure were obtained after a purification process. The atomic structures of the cup-stacked BN nanotubes were investigated by high-resolution electron microscopy as well as molecular mechanics calculations, and compared with double walled BN nanotubes. The present results indicate that the cup-stacked structure with a cone angle of 20° is more stable than the structure with an angle of 38° and ordinary nanotube structures.


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*Keywords:* A. Boron nitride (BN); A. Fe; A. Nanowire; B. Chemical synthesis

## 1. Introduction

In addition to various carbon nanomaterials [1–3], several studies have been reported on boron nitride (BN) nanomaterials such as BN nanotubes [4–6], nanocapsules [7,8], nanoparticles [9,10], nanocables [11,12] and clusters [6,13]. They are expected to be useful as electronic devices, high heat resistance semiconductors, insulators and lubricants because they provide a wide energy gap (∼6 eV), direct transition band structure and excellent protection against oxidation and wear. $H_2$ gas storage in boron nitride (BN) nanomaterials has also been reported [14]. Although BN nanohorns [15,16] as a novel type of BN nanotube have been reported from High-Resolution Electron Microscopy (HREM) images, there are still few reports on the atomic structure and stability of BN nanotubes with a cup-stacked structure [17].

The purpose of the present work is to investigate the atomic structure and stability of BN nanotubes with a cup-stacked structure. HREM, which is a powerful method for atomic structure analysis [18,19], was carried out. Molecular mechanics calculations were also performed to investigate the stability of the cup-stacked BN nanotubes, which are potential nanoscale devices.

## 2. Experimental procedures

$Fe_4N$ (99%, Kojundo Chemical Laboratory (KCL) Co. Ltd., Saitama, Japan) and boron (B) powders (99%, KCL) were used as raw materials [20]. Their particle sizes were about 50 and 45 μm, respectively. After the $Fe_4N$ and B (weight ratio WR = 1:1) were mixed by a triturator, the samples were set on an alumina boat and annealed in the furnace. The furnace was programmed to heat at 6 °C/min from ambient to 1000 °C and hold for 1 h and then it was cooled at 3 °C/min to ambient temperature. The nitrogen pressure was 0.10 MPa, and the gas flow was 100 sccm (standard cubic centimeters per minute).

As-produced soot synthesized from $Fe_4N$/B via the above method was purified by the following steps. The as-produced soot were poured into 4 M HCl solution and stirred for 4 h at a room temperature. The green color of the solution provides an indication of the dissolution of Fe ions. After HCl treatment,

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the samples were poured into 1 M $HNO_3$ solution and stirred for 30 h at 50 °C. The yellow color of the solution provides an indication of the dissolution of boron. After both acid treatments, the solution was filtered and rinsed with deionized water until the pH of the filtrate became neutral and dried. Then the samples were poured into pyridine to eliminate bulk BN, and high purity BN nanotubes with a cup-stacked structure were obtained by collecting the supernatant.

To observe the morphology of the samples, Transmission Electron Microscopy (TEM) and HREM observation were performed with a 300 kV electron microscope (JEM-3000F). For image processing of the observed HREM images, Digital Micrograph software (Gatan, CA, USA) was used. The digital images were masked, and fast Fourier transformed. Basic structure models for BN nanotubes with a cup-stacked structure were constructed by CS Chem3D (CambridgeSoft, MA, USA). For stability calculations, structural optimization of the BN nanotubes with a cup-stacked structure was performed using molecular mechanics calculations (MM2 force field). Molecular mechanics is an empirical method that neglects explicit treatment of electrons; hence energy predictions tend to be meaningless as absolute quantities, and are generally useful only for comparative studies. However, due to the complexity of the system and the number of atoms involved, especially for cup-stacked structures, using an empirical force field is the only feasible and reasonable approach currently available.

In order to compare observed images with calculated ones, HREM images were calculated by the multi-slice method using MacTempas software (Total Resolution, CA, USA). The parameters used in the calculations were as follows: accelerating voltages = 300 kV, radius of the objective apertures = 5.9 $nm^{-1}$, spherical aberration $C_s$ = 0.6 mm, spread of focus $\Delta$ = 8 nm, semi-angle of divergence $a$ = 0.55 mrad, under defocus values $\Delta f = -10$ to $-90$ nm, unit cell (onecluster) = $5.0 \times 5.0 \times 12.0$ $nm^3$, crystal thickness (unit cell thickness, 16 slices) $t = 5.0$ nm, space group $P1$ and assumed temperature factors of 0.02 $nm^2$.

## 3. Results and discussion

Fig. 1(a) shows a TEM image of BN nanotubes with a cup-stacked structure after the purification process. Diameters and lengths of the BN nanotubes are in the range of 40–100 nm and 5–10 μm, respectively. Fe nanoparticles and bulk BN were eliminated during the process. An enlarged image of one of the BN nanotubes is shown in Fig. 1(b), which shows a cup-stacked structure as indicated by lines of BN {002}. Fig. 1(c) is an electron diffraction pattern of Fig. 1(b). 002 reflections of BN are splitting in Fig. 1(c), which indicates that the BN nanotube has a cup-stacked structure, and the cone angle between the BN layers at both nanotube walls is ∼20°. Most of the BN nanotubes (∼90%) have this cup-stacked structure with a cone angle of ∼20°, but normal structures with a cone angle of 0° were sometimes observed (∼10%).

A HREM image of the edge of the nanotube side wall in Fig. 1(b) is shown in Fig. 2(a), and a cup-stacked structure was observed. Edge structures are observed as indicated by

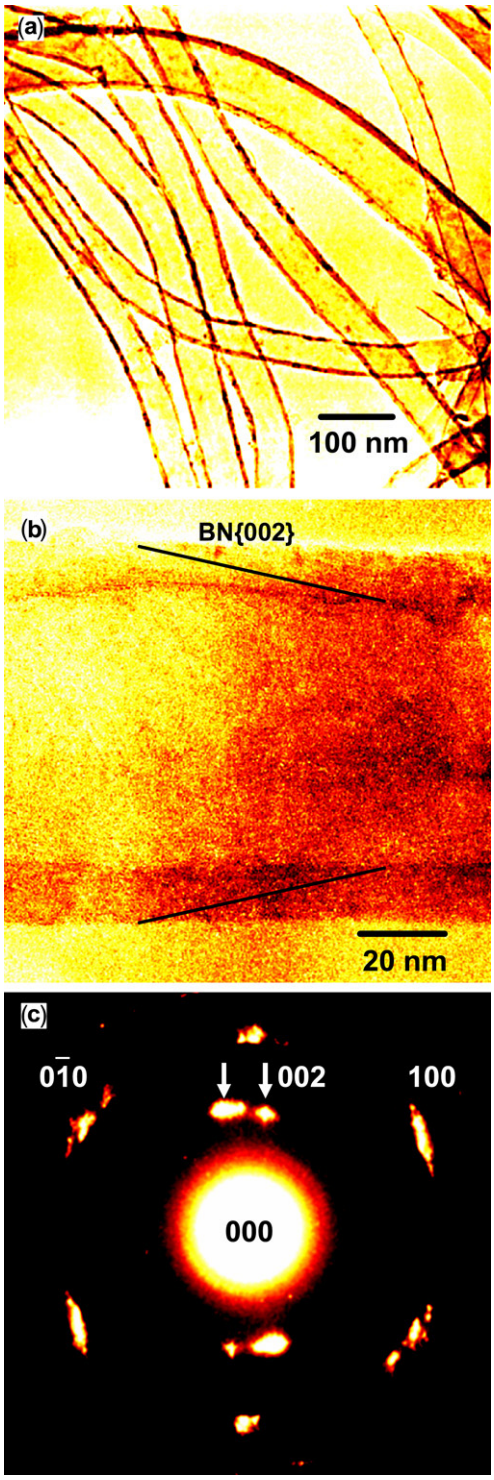


Fig. 1. (a) TEM image of BN nanotubes. (b) Enlarged image of BN nanotube. (c) Electron diffraction pattern of (b).

arrows, and the BN {002} planes are inclined compared to the nanotube axis ($z$-axis). Fig. 2(b) is a processed HREM image after Fourier filtering of the nanotube center of Fig. 1(b), and hexagonal arrangements of white dots are observed, which would correspond to six-membered rings of BN. From these observations, a model for the BN cup-structure was proposed, which consists only of hexagonal BN rings, as shown in Fig. 2(c) and (d).

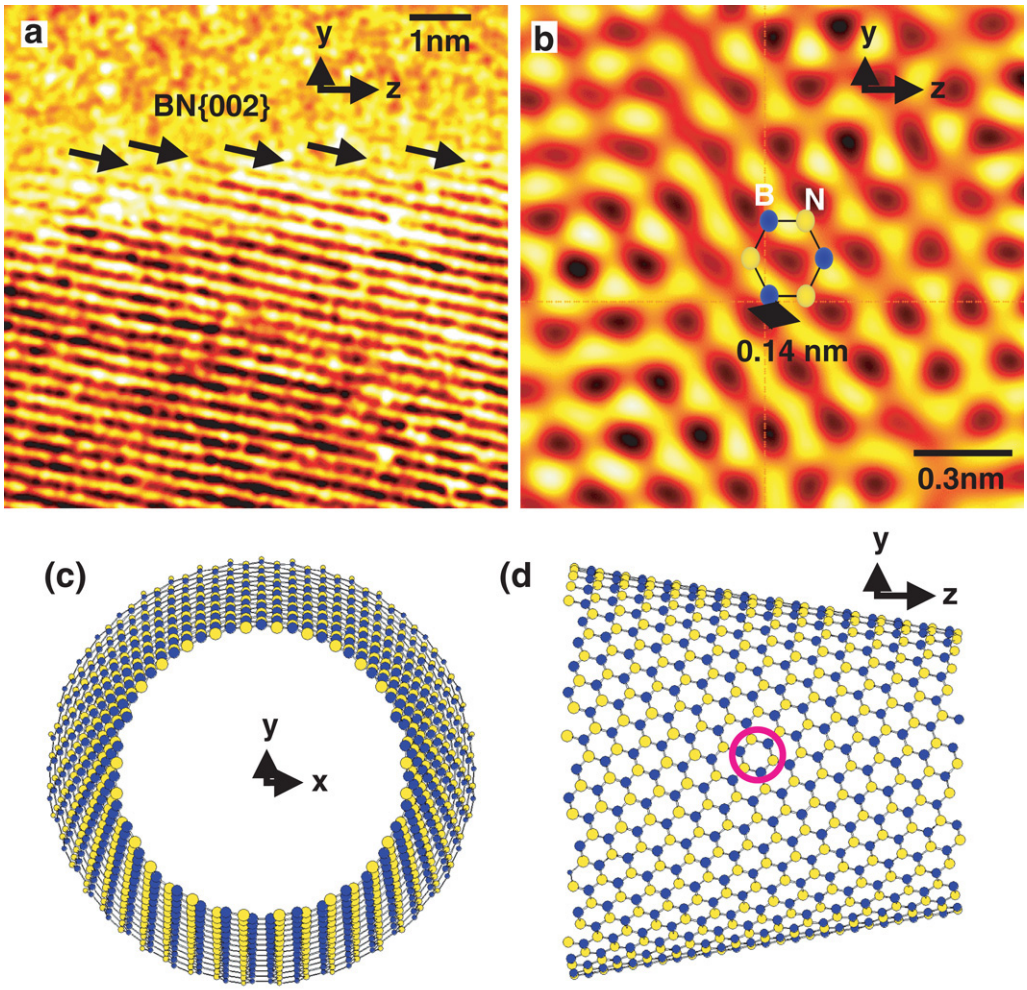


Fig. 2. (a) HREM image of edge of the BN nanotube wall in Fig. 1(b). (b) Processed HREM image after Fourier filtering of the nanotube center of Fig. 1(b). Proposed model of the BN cup structure projected along (c) the $z$-axis (nanotube axis) and (d) the $x$-axis.

Table 1
Empirical total energies of various BN nanotubes by molecular mechanics calculations

| | $B_{273}N_{273}$ | $B_{390}N_{390}$ | $B_{273}N_{273}@B_{390}N_{390}$ | $B_{264}N_{264}$ | $B_{384}N_{384}$ | $B_{264}N_{264}@B_{384}N_{384}$ |
|---|---|---|---|---|---|---|
| Structure type | Zigzag-type | | | Armchair-type | | |
| Outer diameter (nm) | 2.3 | | 2.3 | 2.2 | | 2.2 |
| Inner diameter (nm) | 1.6 | | 1.6 | 1.5 | | 1.5 |
| Number of layers | 1 | 1 | 2 | 1 | 1 | 2 |
| Total energy (kcal/mol) | 459.2 | 701.5 | 556.0 | 466.6 | 693.2 | 779.3 |
| Total energy (kcal/mol atom) | 0.841 | 0.899 | 0.419 | 0.883 | 0.902 | 0.601 |

In order to investigate the stability of the cup-stacked structure, four types of nanotube were considered, as shown in Figs. 3 and 4. Fig. 3(a) and (b) show atomic structure models of double-walled BN nanotubes with zigzag-type and armchair-type structures, respectively. Atomic structure models of four-layered, cup-stacked BN nanotubes with different cone angles are shown in Fig. 4. These structures are summarized in Tables 1 and 2. Total energies of these four-type structures indicates that BN multi-layered nanotubes with and without a cup-stacked structure could be stabilized by stacking hexagonal BN networks. The distance between BN layers in nanotubes with a cup-stacked structure was found in a HREM image to be ∼0.35 nm, and the basic structure model was constructed based on this observation. Geometrical optimizations at the molecular mechanics level result in interlayer distances of ∼0.38 nm. Comparing the empirical total energies for all considered structures, a cup-stacked structure ($B_{2240}N_{2240}$) with cone angle of 20° was found to be the lowest in energy, which indicates the high stability of this structure.

Based on the structure model of a cup-stacked $B_{2240}N_{2240}$ nanotube of Fig. 4(a), an image calculation was carried out as shown in Fig. 5(a). Enlarged calculated HREM images of the edge and center of the BN nanotube in Fig. 5(a) are shown in Fig. 5(b) and (c), respectively. These calculated images agree with the experimental data of Fig. 2(a) and (b), respectively.

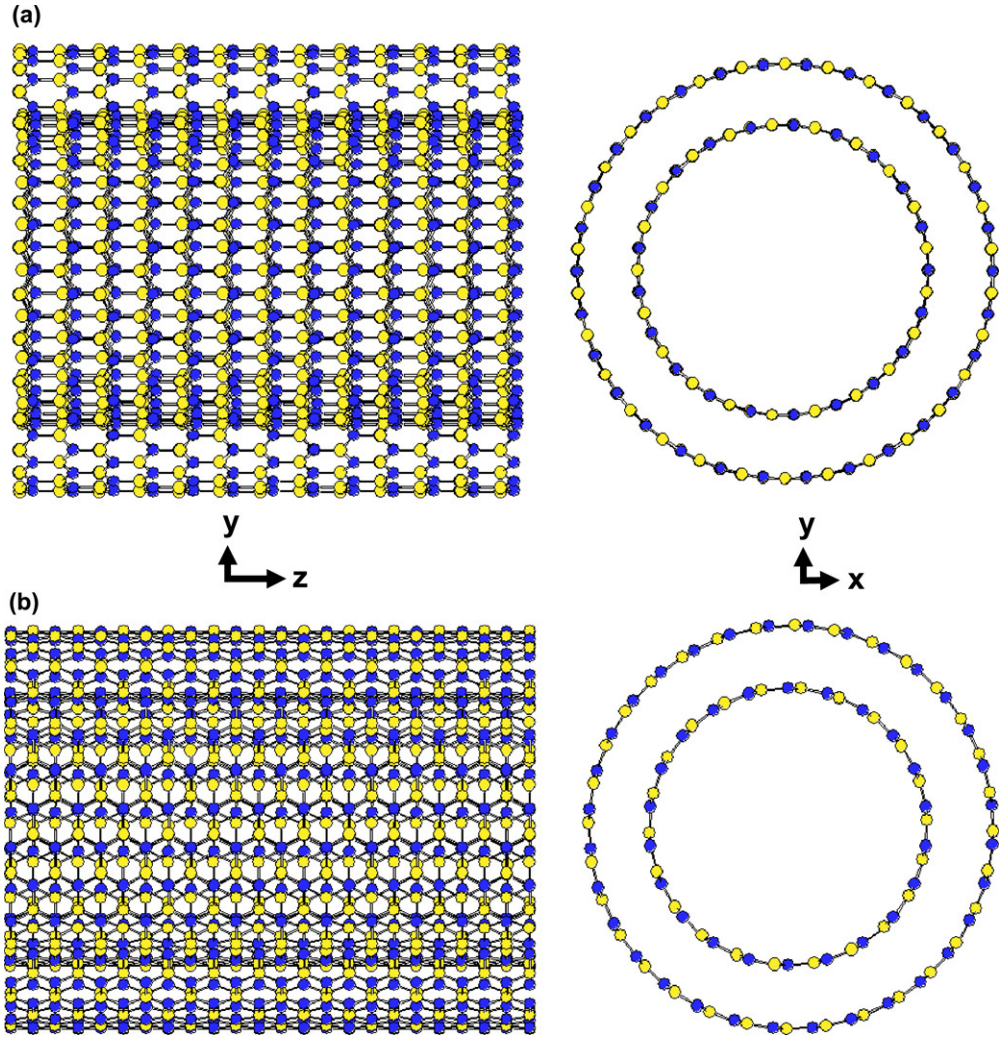


Fig. 3. Atomic structure models of double-walled BN nanotubes with (a) zigzag-type and (b) armchair-type structures.

Table 2
Empirical total energies of various BN nanotubes with a cup-stacked structure by molecular mechanics calculations

| | $B_{560}N_{560}$ | $B_{1120}N_{1120}$ | $B_{2240}N_{2240}$ | $B_{494}N_{494}$ | $B_{988}N_{988}$ | $B_{1976}N_{1976}$ |
|---|---|---|---|---|---|---|
| Cone angle (°) | 20 | 20 | 20 | 36 | 36 | 36 |
| Outer diameter (nm) | 3.4 | 3.4 | 3.4 | 4.2 | 4.2 | 4.2 |
| Inner diameter (nm) | 2.4 | 2.4 | 2.4 | 2.4 | 2.4 | 2.4 |
| Number of layers | 1 | 2 | 4 | 1 | 2 | 4 |
| Total energy (kcal/mol) | 31.46 | −287.9 | −936.4 | 895.1 | 1269 | 2062 |
| Total energy (kcal/mol atom) | 0.028 | −0.129 | −0.209 | 0.906 | 0.642 | 0.522 |

Cup-stacked carbon nanotubes with Pt nanoparticles in the inner surface of the hollow core have been reported [21]. The BN nanotubes with cup-stacked structures in the present work would also be a candidate for atomic and gas storage, as well as carbon nanotubes. Cone angles of BN cup-stacks were measured to be ∼20°, which agreed well with that of the model in Fig. 3(a). Although atomic structure models for BN nanotubes with a cup-stacked structure have been proposed from HREM observation and molecular mechanics calculations [16], the cone angles were ∼36°, and they had bamboo-type structures. In the present work, there is no bamboo-type structure, which was removed during the purification process, and a more stable cup-stacked structure with a cone angle of 20° was formed.

Cone angles of carbon nanotubes with a cup-stacked structure were reported to be in the range of 45°–80° [21]. The present cup-stacked BN nanotubes have a different cone angle due to the different stacking of BN layers along the *c*-axis (B–N–B–N…) from carbon layers.

## 4. Conclusion

Cup-stacked BN nanotubes were synthesized by annealing $Fe_4N$/B powder at 1000 °C for 1 h in a nitrogen gas

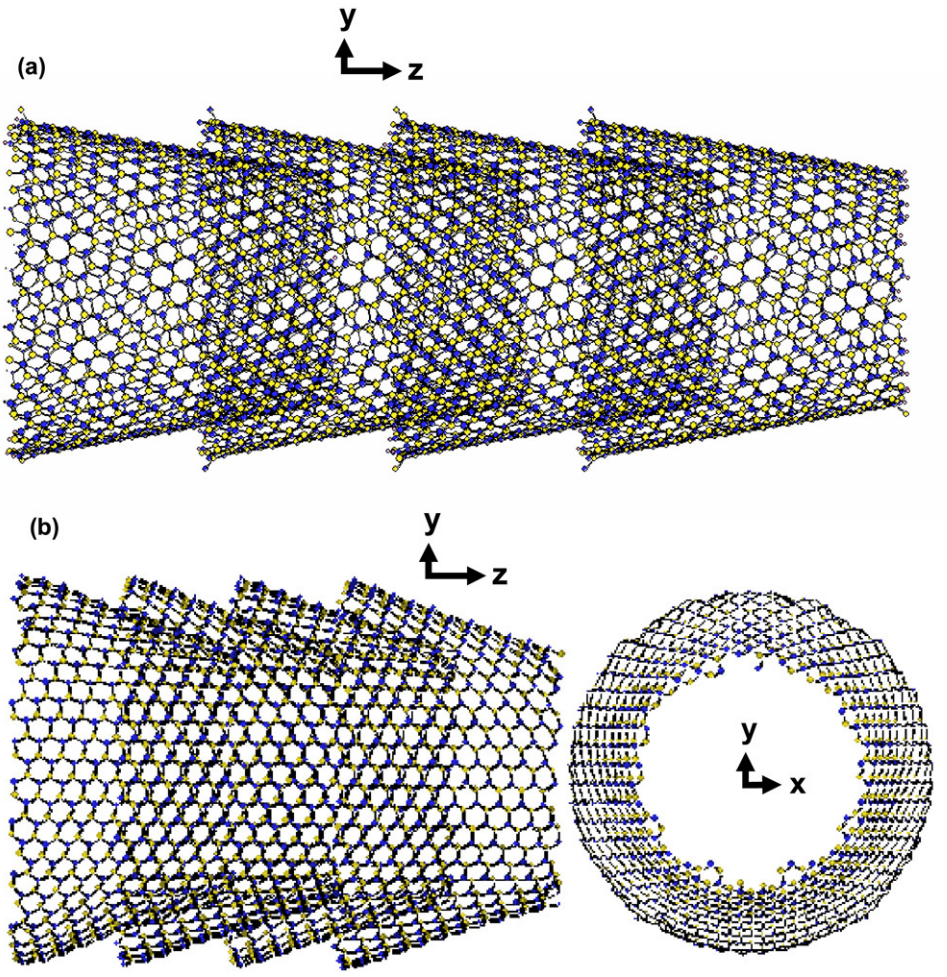


Fig. 4. Atomic structure models of four-layered, cup-stacked BN nanotubes. Cone angles are (a) 20° and (b) 36°.

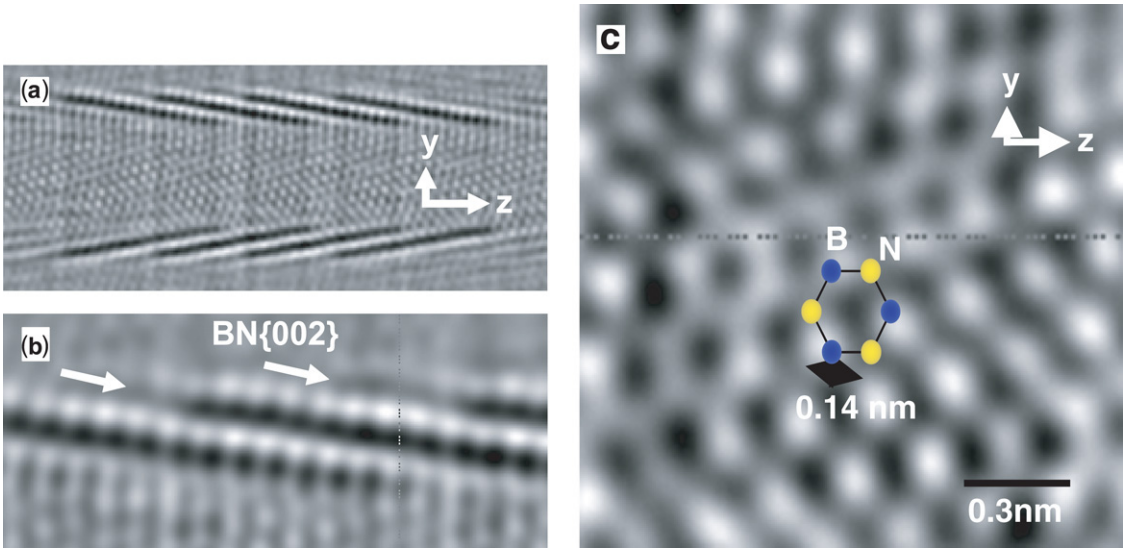


Fig. 5. (a) Calculated HREM image of four-layered, cup-stacked BN nanotube at defocus values of −40 nm. Enlarged image of (b) edge and (c) center of BN nanotube in (a).

atmosphere after a purification process. The atomic structure model of the cup-stacked BN nanotubes was proposed from HREM analysis and molecular mechanics calculations. Image simulations based on the proposed structure model agreed with experimental data. Compared to double walled BN nanotubes and other types of cup-stacked structures, the present cup-

stacked structure with cone angle of 20° is proposed to be more stable. These unique structures would be suitable materials for gas storage, nanoelectronics devices and extreme environmental materials with excellent protection against oxidation and wear.

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