Formation and atomic structures of boron nitride nanohorns

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Abstract

Boron nitride (BN) nanohorns were synthesized by an arc-melting method, and atomic structure models for BN nanohorns with tetragonal BN rings were proposed from high-resolution electron microscopy. Stability and electronic structures of the BN nanohorns were investigated by molecular orbital/mechanics calculations. The calculation showed that multiwalled BN nanohorns would be stabilized by stacking of BN nanohorns. The energy gap of BN nanohorn was calculated to be 0.8 eV, which is lower compared to those of BN clusters and nanotubes.

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1. Introduction

Carbon-based nanocage structures, such as fullerene clusters, nanotubes, nanopolyhedra, cones, cubes and onions, have great potential for studying materials of low dimensions in an isolated environment [1–3]. Especially, carbon nanohorns are expected as catalyst electrode materials for next-generation fuel cells, which separate hydrogen and electrons from methanol [4–14]. Boron nitride (BN) nanostructured materials with a bandgap energy of ~6 eV and non-magnetism are also expected to show various electronic, optical and magnetic properties such as Coulomb blockade, photoluminescence, and supermagnetism [3,15]. Recently, several studies have been reported on BN nanomaterials such as BN nanotubes [16–19], BN nanocapsules [3,15,18], BN nanoparticles [20,21] and BN clusters [3,15,22,23], which are expected to be useful as electronic devices, high heat-resistance semi-conductors and insulator lubricants.

Some BN nanostructure clusters have been predicted theoretically, and BN clusters with sizes of ~1 nm were observed [3,22] by high-resolution electron microscopy (HREM). BN nanocones were also reported, which would be a one of the candidates for hydrogen storage materials [24–26]. However, there are still few reports on electronic structures and stability of BN nanohorns [27].

The purpose of the present work is to synthesize BN nanohorns by using the arc-melting method, and to investigate the atomic structures and electronic states of BN nanohorns by HREM and molecular orbital and molecular mechanics calculations. To synthesize BN nanohorns with hollow structures, YB₆ powder was selected for arc-melting, which is a useful catalysis for BN nanotubes synthesis. The present study will give us a guideline for designing and synthesis of the BN nanohorns, which are expected as future nanoscale devices.

2. Experimental procedures

The YB₆ powder (4.0 g, 99.6%, Kojundo Chemical Lab Co., Ltd) was set on a copper mold in an electric-arc furnace, which was evacuated down to 1.0×10⁻³ Pa [28]. After introducing a mixed gas of Ar (0.025 MPa) and N₂ (0.025 MPa), arc-melting was applied to the samples at an accelerating voltage of 200 V and an arc current of 125 A for 10 s. Arc-melting was performed with a vacuum arc-melting furnace (NEV-AD03, Nisshin Engineering Co., Ltd). Samples for HREM observation were prepared by dispersing the materials on holey carbon grids. HREM
observation was performed with a 300 kV electron microscope (JEM-3000F).

Basic structure models for BN nanohorns were constructed by CS Chem3D (CambridgeSoft). For energy calculations, structural optimization of the BN nanohorns was performed by the semi-empirical molecular orbital calculations (PM5) using a program of MOPAC2002 in WinMOPAC 3.5 Professional (Fujitsu Ltd) and molecular mechanics calculation (MM2). For the prediction of energy levels and density of states for the BN nanohorns, molecular orbital calculation using the DV-Xα method was carried out for the optimized structure.

3. Results and discussion

Fig. 1(a) is a HREM image of BN nanohorns synthesized by an arc-melting method. Enlarged HREM images of BN nanohorns with seven and eight BN layers are shown in Fig. 1(b) and (c), respectively. (002) layers of BN are clearly observed. Since the distortion of an apex of BN nanohorn is very large, the structure may not be completely perfect, which results in the vague contrast at the apex. From the results of HREM observation in Fig. 1, structure models for BN nanohorns were proposed, as shown in Fig. 2. Structure models of Fig. 2(a) and (b)

![Image](image1.png)

![Image](image2.png)

Fig. 2. Structure models for BN nanohorns. Tetragonal BN rings are introduced for model (a).

|                  | B_{31}N_{31} | B_{34}N_{34} |
|------------------|--------------|--------------|
| Number of tetragonal BN rings | 2            | 0            |
| Heat of formation (J/mol)       | −4305        | −4619        |
| Heat of formation (J/mol atom)  | −69.45       | −67.91       |

Table 1
Heats of formation of BN nanohorns by molecular orbital calculations

![Image](image3.png)
are B$_{31}$N$_{31}$ and B$_{34}$N$_{34}$ nanohorns, respectively. Tetragonal BN rings are introduced for a model in Fig. 2(a). The structure model in Fig. 2(b) consists only of hexagonal BN rings.

Heats of formation for B$_{31}$N$_{31}$ and B$_{34}$N$_{34}$ nanohorns were investigated by molecular orbital calculation, as listed in Table 1. In the present work, the unit of ‘J/mol’ was defined as energy to generate 6.02×10$^{23}$ nanohorns. Since

Fig. 3. (a) Energy level diagram and (b) density of states for BN nanohorn.

Fig. 4. Atomic structure model of BN nanohorn extended along z-axis of Fig. 2(a). (a)–(c) is viewed from z-, x- and y-axes, respectively.
the number of atoms in the model of Fig. 2(a) is different from that of Fig. 2(b), the heats of formation were divided by total atom numbers for comparison. Comparing $B_{31}N_{31}$ to $B_{34}N_{34}$ nanohorns, $B_{31}N_{31}$ nanohorn shows a lower energy per mol atom than that of $B_{34}N_{34}$ nanohorn. Tip structure of $B_{34}N_{34}$ nanohorns is equivalent to the previously reported one [24]. In the present work the $B_{31}N_{31}$ nanohorn showed more stable structure from molecular orbital calculation. The angle of BN nanohorn in Fig. 1 is $\sim 35^\circ$, and the angle of structure model in Fig. 2(a) is in the range of 35–43$^\circ$, which are consistent with the HREM image of Fig. 1.

Electronic structures of $B_{31}N_{31}$ nanohorn, which has a lower energy per mol atom than $B_{34}N_{34}$, were investigated for the optimized structure, as shown in Fig. 3(a) and (b). Energy level diagram of $B_{31}N_{31}$ nanohorn shows a narrow energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), as shown in Fig. 3(a). The HOMO–LUMO gap of $B_{31}N_{31}$ nanohorn was calculated to be 0.80 eV.

Fig. 4 is atomic structure model of $B_{150}N_{150}$ nanohorn extended along $z$-axis of Fig. 2(a). Fig. 4(a)–(c) is along $z$-, $x$- and $y$-axes, respectively. Fig. 5(a) and (b) is double and eight-fold walled BN nanohorns based on the structure.
model of Fig. 4, respectively. Total energies of $B_{150}N_{150}$, $B_{300}N_{300}$ and $B_{1200}N_{1200}$ nanohorns calculated by molecular mechanics calculation are listed in Table 2. Distance between BN layers of nanohorn in a HREM image was measured to be $\approx 0.35$ nm, and the basic structure model was constructed based on it. After molecular mechanics calculation, the layer distances were optimized as $\approx 0.36$ nm.

BN nanohorns of Fig. 1(b) and (c) are synthesized at the same time as shown in Fig. 1(a). The apex angle of nanohorns of Fig. 1(b) is different form that of Fig. 1(c), which would be due to the different observation direction of the BN nanohorn. The value of apex angle changes by the observation direction as shown in Fig. 2. Heat of formation of $B_{31}N_{31}$ nanohorn in Fig. 2(a) shows lower energy than that of $B_{31}N_{31}$ nanohorn in Fig. 2(b), as shown in Table 1. In addition, both boron and nitrogen atoms at the tip of BN nanohorn in Fig. 2(b) have three B–N single bonds, which would provide instability. Tetragonal BN rings are introduced for the model of Fig. 2(a), which is different from the model of Fig. 2(b) consisting only of hexagonal BN rings and from the model of carbon nanohorns with pentagonal carbon rings. An energy gap calculated based on the atomic structure model of Fig. 2(a) shows lower value (0.80 eV) compared to that of BN nanotubes or BN fullerences (5 eV). The band gap was reduced for BN nanohorns, and various new applicable fields are expected by combining the BN nanohorns with BN nanotubes or BN fullerences. Total energies per mol atom of BN nanohorns were reduced by nanohorns with BN nanotubes or BN fullerenes. Total energy (J/mol atom) 4.065 3.013 2.149

4. Conclusions

BN nanohorns with a hollow structure were synthesized by an arc-melting of YB$_6$ powder in N$_2$/Ar mixture gas. Atomic structure models for BN nanohorns with tetragonal BN rings are proposed from HREM observation and molecular orbital calculations. An energy gap of BN nanohorn was calculated to be 0.80 eV, which is lower compared to those of BN nanotubes and BN fullerences. Multilayered structures with tetragonal BN ring networks would be stabilized by stacking BN nanohorns. Applications of BN nanohorns in the present work for gas storage and extreme environmental materials are expected.

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Table 2

| Number of nanohorn layers | $B_{150}N_{150}$ | $B_{300}N_{300}$ | $B_{1200}N_{1200}$ |
|---------------------------|------------------|------------------|-------------------|
| Total energy (J/mol)      | 1220             | 1808             | 5159              |
| Total energy (J/mol atom) | 4.065            | 3.013            | 2.149             |

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