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Atomic structures of bamboo-type boron nitride nanotubes with cup-stacked structures

Takeo Oku*, Ichihito Narita, Atsushi Nishiwaki

Institute of Scientific and Industrial Research, Osaka University, Mihogaoka 8-1, Ibaraki, Osaka 567-0047, Japan

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Abstract

Bamboo-type boron nitride (BN) nanotubes with cup-stacked structures were produced by annealing of Fe_4N and boron particles at 1000 °C for 5 h in nitrogen atmosphere. The iron nitride particles were reduced to α-Fe. Atomic structure models and the formation mechanism were proposed from the results of high-resolution electron microscopy (HREM), image simulations and molecular mechanics calculations. The nanotube structures would be stabilized by stacking of BN cup-layers.

Keywords: Powders-solid state reaction; Electron microscopy; Microstructure; Nitrides

1. Introduction

Various 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.[1–5] Recently, carbon nanotubes with a cup-stacked structure[6–11] and nanohorns[12–14] as a novel type of carbon nanotubes have been reported by high-resolution electron microscopy (HREM). 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.[3,5] Recently, several studies have been reported on BN nanomaterials, such as BN nanotubes,[15–17] BN nanocapsules[3,5,18] and BN nanoparticles.[19,20] Although BN nanohorns[21,22] as a novel type of BN nanotubes were also reported by HREM image, there are still few reports on atomic structures and stability of BN nanotubes with a cup-stacked structure.[21]

The purpose of the present work is to synthesize BN nanotubes with a cup-stacked structure, and to investigate the atomic structures by HREM and molecular mechanics calculations. HREM is a powerful method for direct structure analysis on an atomic scale.[23,24] The present study will give us a guideline for designing and synthesis of the BN nanotubes with a cup-stacked structure, which are expected as future nanoscale devices.

2. Experimental procedures

Fe_4N and B powders were selected as starting materials. Their particle sizes were about 50 μm and 45 μm in diameters, respectively. After the Fe_4N and B (weight ratio = 1:1) were mixed by a triturator, the samples were set on an alumina boat. The samples were annealed at 1000 °C for 5 h in 100 sccm flowing nitrogen (N_2) gas atmosphere, and cooled down to room temperature in the furnace. 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). For image processing of the observed HREM images, Digital Micrograph Software (Gatan Inc., California) 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). For stability calculations, structural optimization of the BN nanotubes with a cup-stacked structure

* Corresponding author. Tel.: +81 6 6879 8521; fax: +81 6 6879 8522.
E-mail address: Oku@sanken.osaka-u.ac.jp (T. Oku).

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was performed by molecular mechanics calculations (MM2). To compare observed images with calculated ones, HREM images were calculated by the multi-slice method using the MacTempas software (Total Resolution, CA, USA). The parameters used in the calculations are 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 $\alpha = 0.55$ mrad, under defocus values $\Delta f = -20$ to -90 nm, unit cell (one cluster) = 5.0 × 5.0 × 7.0 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

Phases of the samples were determined by X-ray diffraction, which showed peaks of hexagonal BN and α-Fe. Large amounts of BN nanotubes were produced, and Fig. 1(a) is a typical low magnification image of BN nanotubes with bamboo-structures. Lengths and widths of BN nanotubes are approximately 5–10 μm and 40–200 nm, respectively. In addition, iron nanoparticles were often observed at the tip of nanotubes, as shown in Fig. 1(b). Enlarged images of a tip and an interface between the Fe nanoparticle and the nanotube are shown in Fig. 1(c) and (d), respectively. In Fig. 1(c), amorphous structures (AM) and lattice fringes of Fe_2B {2 0 0} are observed near the growth point of BN layers. The amorphous structure would be boron-rich phase formed from reaction with Fe_4N. At the interface between the Fe particle and BN nanotube in Fig. 1(d), lattice fringes of Fe {1 1 0} are observed, and the BN {0 0 2} layers are inclined from the nanotube axis indicate by *z*-axis.

A HREM image of the bamboo-type BN nanotube with a cup-stacked structure is shown in Fig. 2(a), and the bamboo structure consists of BN {0 0 2} layers. Enlarged images of both nanotube walls in Fig. 2(a) are shown in Fig. 2(b) and (c). BN {0 0 2} layers are inclined compared to the nanotube axis, and the cone angle between the BN layers at both nanotube walls is ∼36°. An enlarged image of nanotube center in Fig. 2(a) is shown in Fig. 2(d), and a HREM image with clear contrast was processed after Fourier noise filtering as shown in Fig. 2(e), which shows hexagonal arrangements of white dots.

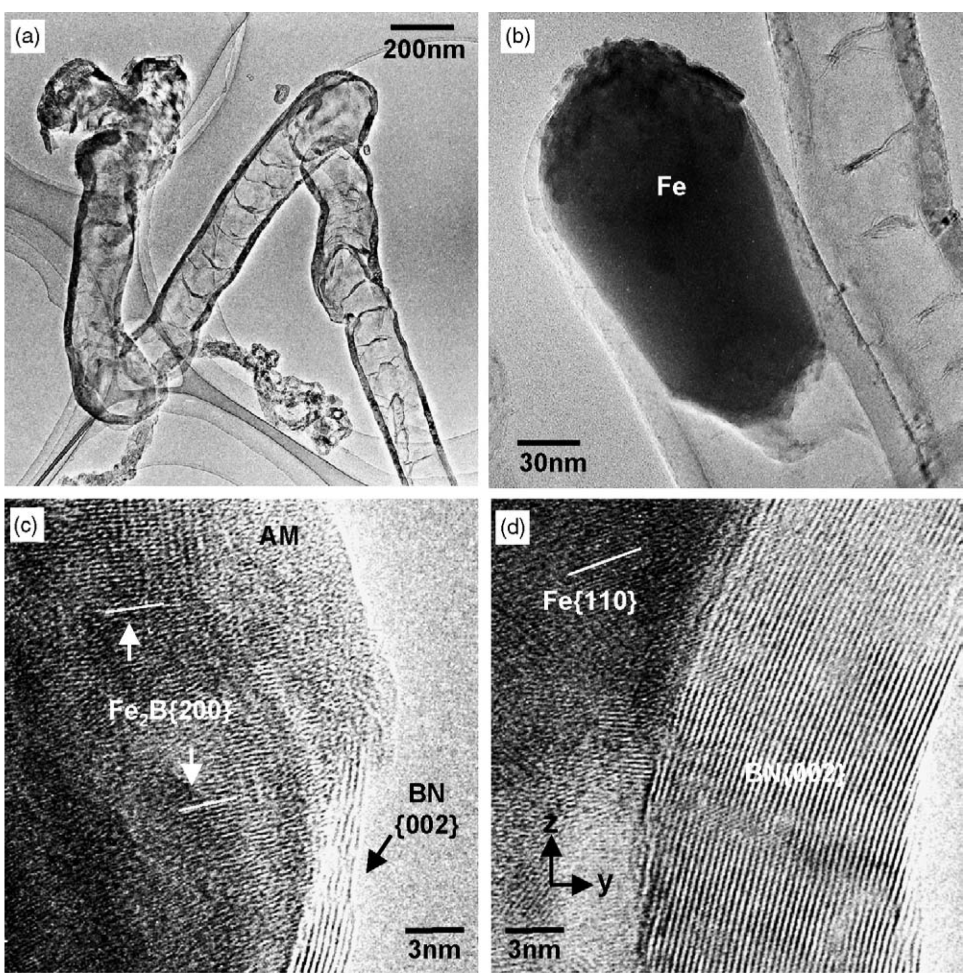

Fig. 1. Low magnification images of (a) BN nanotubes with bamboo-structures and (b) iron nanoparticle at a tip of nanotube. Enlarged images of (c) a tip and (d) an interface between the Fe nanoparticle and the nanotube.

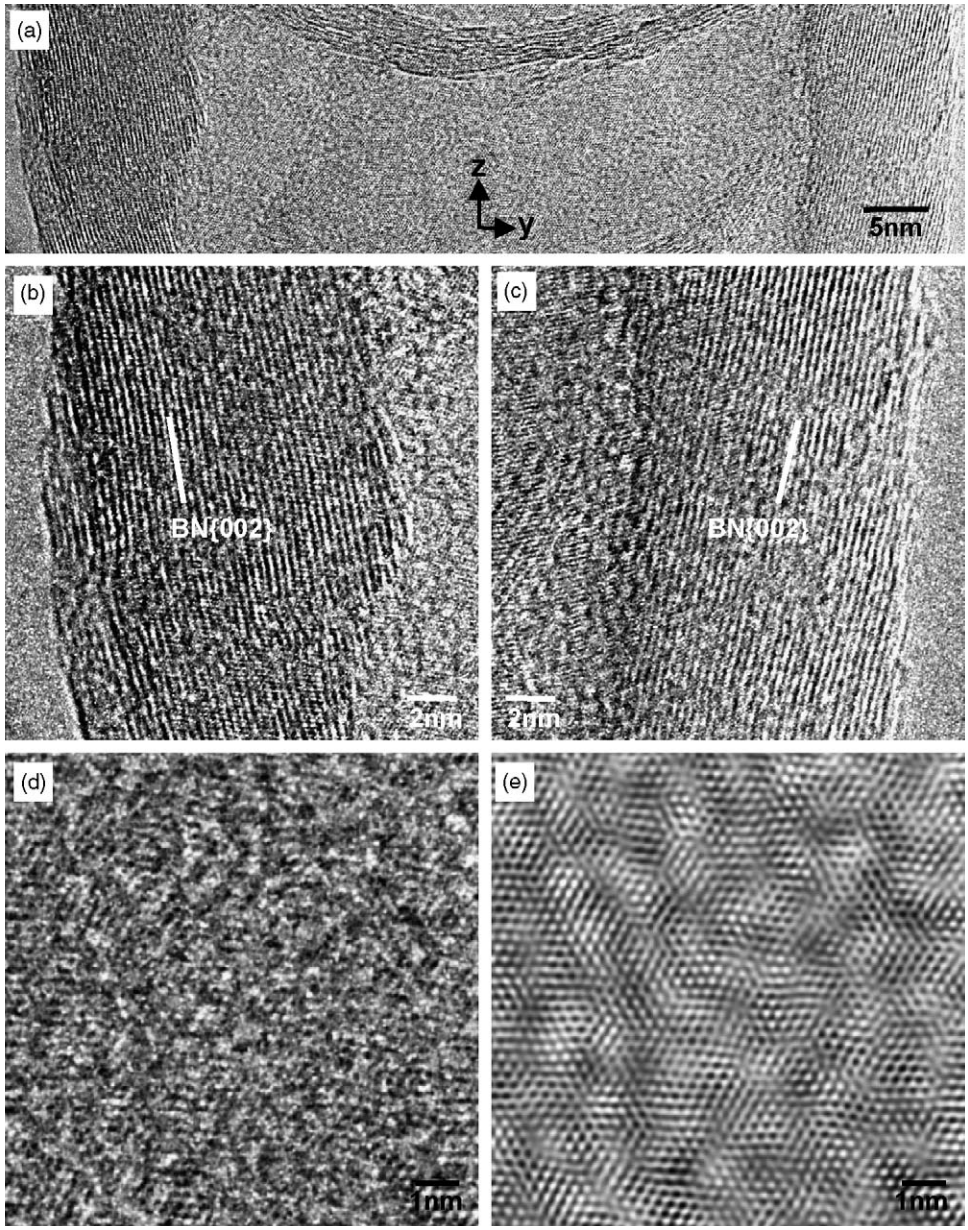

Fig. 2. (a) HREM image of bamboo-type BN nanotube with cup-stacked structures. (b, c) Enlarged images of nanotube wall in (a). (d) Enlarged image of nanotube center in (a). (e) Processed image after Fourier filtering of (d).

Fig. 3 is a proposed structure model for $B_{494}N_{494}$ cup-layer, which consists only of hexagonal BN rings. The nanotube axis is indicated by *z*-axis. A structure model and calculated HREM images of four-fold walled $B_{1976}N_{1976}$ nanotube with a cup-stacked structure are shown in Fig. 4. The calculated image at defocus values in the range of −40 to −60 nm agree with the HREM images in Fig. 2. Total energies of $B_{494}N_{494}$, $B_{988}N_{988}$ and $B_{1976}N_{1976}$ cup-stacked BN layers calculated by molecular mechanics calculation are listed in Table 1. Distance between BN layers of nanotubes with a cup-stacked structure in a HREM image was measured to be ∼0.35 nm, and the basic structure model was constructed based on it. After molecular mechanics calculations, the layer distances were optimized as ∼0.38 nm. In addition, total energies per mol atom of $B_{988}N_{988}$ and $B_{1976}N_{1976}$ were reduced by stacking of $B_{494}N_{494}$ nanotubes with a cup-stacked structure, and it is believed that the structure of BN multi-layered

Table 1
Total energies of BN nanotubes with a cup-stacked structure by molecular mechanics calculation

	$B_{494}N_{494}$	$B_{988}N_{988}$	$B_{1976}N_{1976}$
Number of layers	1	2	4
Total energy (kcal/mol)	895.1	1269	2062
Total energy (kcal/mol atom)	0.906	0.642	0.522

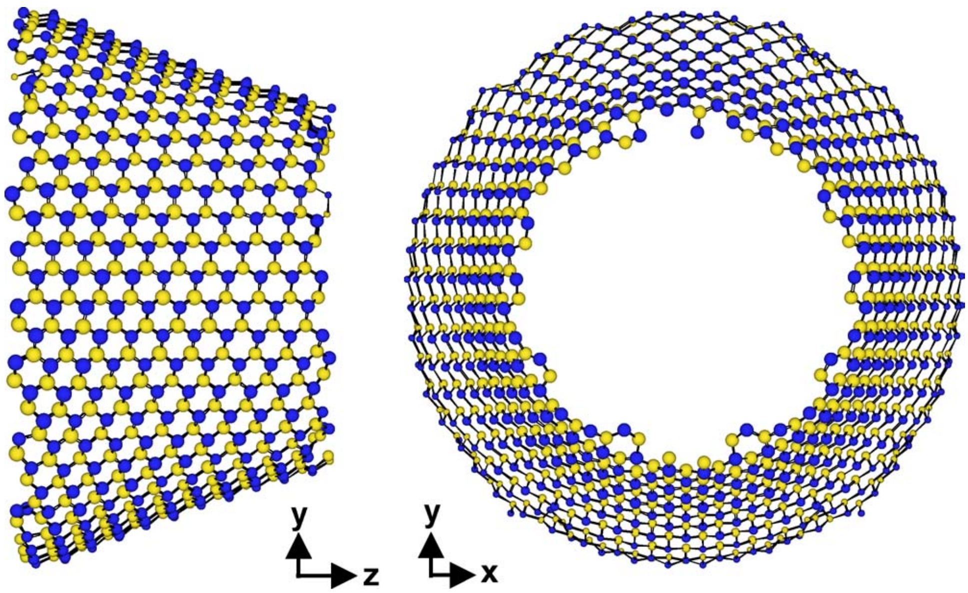

Fig. 3. Structure model for $B_{494}N_{494}$ cup structure.

nanotubes with a cup-stacked structure would be stabilized by stacking hexagonal BN networks.

Cup-stacked carbon nanotubes with Pt nanoparticles in inner surface of the hollow core had been reported.[9] The BN nanotubes with cup-stacked structures in the present work would also be one of the candidates for atomic and gas storage, as well as carbon nanotubes. Cone angles of BN cup-stacks were measured to be ∼36°, which agreed well

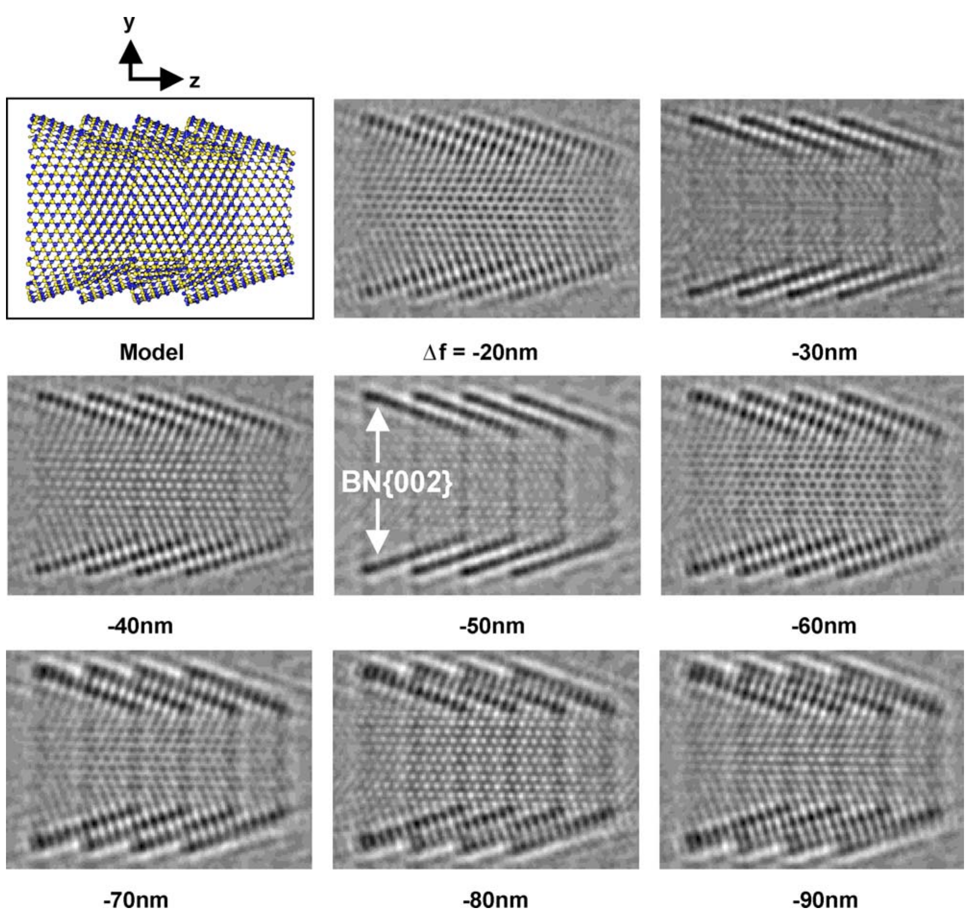

Fig. 4. Calculated HREM images of four-fold walled $B_{1976}N_{1976}$ nanotube with a cup-stacked structure as a function of defocus values.

with that of the model in Fig. 3 (38°). Cone angles of carbon nanotubes with a cup-stacked structure were reported to be in the range of 45–80°.[5,8] The cause of the different cone angles of the present cup-stacked BN nanotubes would be due to the different stacking of BN layers along *c*-axis (B–N–B–N. . .) from carbon layers. The cone angles might also depend on the shape of catalysis particles, as shown in Fig. 1(d).

A small amount of nanocrystalline Fe_2B compounds were observed at the tip of the BN nanotube. Chemical formulas that Fe_4N reacts with B, and generates Fe and BN in our experiments can be proposed as follows:

$$Fe_4N + 3B \rightarrow BN + 2Fe_2B \quad (1)$$

$$2Fe_2B + N_2(g) \rightarrow 2BN + 4Fe \quad (2)$$

Gibb's energy on each formula is calculated as −89.4 and −23.2 kcal for the formulas (1) and (2) at 1000 °C, respectively. These negative values would stand for correctness of the proposed formulas. It is considered that a formation of Fe-B compounds might plays an important role for growth of the BN nanotubes, and that amorphous boron might change to BN and Fe_2B on the surface of the Fe_4N nanoparticles.

When magnetic materials are used as catalysis metals for BN nanotube formation, the magnetic nanoparticles would move around by magnetic field of a coil heater during the reaction process. Then, segments of BN {0 0 2} layers were produced in the tubes, which results in formation of bamboo structures. The interval of the BN layer segments might be related to the amount of iron nanoparticles, and further studies are expected on the control of the bamboo structure.

4. Conclusion

Bamboo-type BN nanotubes with a cup-stacked structure were synthesized from Fe_4N and boron particles. The iron nitride particles were reduced to α-Fe during annealing at 1000 °C for 5 h. Atomic structure models and formation mechanism were proposed from HREM. Image simulations based on the proposed structure models agreed with experimental data, and molecular mechanics calculation showed that the present multilayered structures with hexagonal BN networks would be stabilized by stacking of BN cup-layers. These unique structures would be suitable for H_2 gas storage materials.

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References

1. Kroto, H. W., Heath, J. R., O'Brien, S. C. and Smalley, R. E., C_{60}: Backminsterfullerene. *Nature*, 1985, **318**, 162–163.
2. Iijima, S., Helical microtubles of graphitic carbon. *Nature*, 1991, **354**, 56–58.
3. Oku, T., Kuno, M., Kitahara, H. and Narita, I., Formation, atomic structures and properties of boron nitride and carbon nanocage fullerene materials. *Int. J. Inorg. Mater.*, 2001, **3**, 597–612.
4. Oku, T., Narita, I., Nishiwaki, A. and Koi, N., Atomic structures, electronic states and hydrogen storage of boron nitride nanocage clusters, nanotubes and nanohorns. *Defect Diffus. Forum*, 2004, **226–228**, 113–140.
5. Oku, T., Hirano, T., Kuno, M., Kusunose, T., Niihara, K. and Suganuma, K., Synthesis, atomic structures and properties of carbon and boron nitride fullerene materials. *Mater. Sci. Eng. B*, 2000, **74**, 206–217.
6. Endo, M., Kim, Y. A., Hayashi, T., Fukai, Y., Oshida, K., Terrones, M. *et al.*, Structural characterization of cup-stacked-type nanofibers with an entirely hollow core. *Appl. Phys. Lett.*, 2002, **80**, 1267–1269.
7. Kim, Y. A., Hayashi, T., Fukai, Y., Endo, M., Yanagisawa, T. and Dresselhaus, M. S., Effect of ball milling on morphology of cup-stacked carbon nanotubes. *Chem. Phys. Lett.*, 2002, **355**, 279–284.
8. Shiratori, Y., Hiraoka, H., Takeuchi, Y., Itoh, S. and Yamamoto, M., One-step formation of aligned carbon nanotube field emitters at 400 °C. *Appl. Phys. Lett.*, 2003, **82**, 2485–2487.
9. Endo, M., Kim, Y. A., Hayashi, T., Yanagisawa, T., Muramatsu, H., Ezaka, M. *et al.*, Microstructural changes induced in "stacked cup" carbon nanofibers by heat treatment. *Carbon*, 2003, **41**, 1941–1947.
10. Endo, M., Kim, Y. A., Ezaka, M., Osada, K., Yanagisawa, T., Hayashi, T. *et al.*, Selective and efficient impregnation of metal nanoparticles on cup-stacked-type carbon nanofibers. *Nano Lett.*, 2003, **3**, 723–726.
11. Inagaki, M., Kaneko, K. and Nishizawa, T., Nanocarbons—recent research in Japan. *Carbon*, 2004, **42**, 1401–1417.
12. Iijima, S., Yudasaka, M., Yamada, R., Bandow, S., Suenaga, K., Kokai, F. *et al.*, Nano-aggregates of single-walled graphitic carbon nano-horns. *Chem. Phys. Lett.*, 1999, **309**, 165–170.
13. Bandow, S., Kokai, F., Takahashi, K., Yudasaka, M., Qin, L. C. and Iijima, S., Interlayer spacing anomaly of single-wall carbon nanohorn aggregate. *Chem. Phys. Lett.*, 2000, **321**, 514–519.
14. Bekyarova, E., Kaneko, K., Kasuya, D., Takahashi, K., Kokai, F., Yudasaka, M. *et al.*, Pore structure and adsorption properties of single-walled carbon nanohorn bud-like aggregates treated in different atmospheres. *Physica B*, 2002, **323**, 143–145.
15. Mickelson, W., Aloni, S., Han, W.-Q., Cumings, J. and Zettl, A., Packing C_{60} in boron nitride nanotubes. *Science*, 2003, **300**, 467–469.
16. Golberg, D., Xu, F.-F. and Bando, Y., Filling boron nitride nanotubes with metals. *Appl. Phys. A*, 2003, **76**, 479–485.
17. Oku, T. and Narita, I., Atomic structures and stabilities of zigzag and armchair-type boron nitride nanotubes studied by high-resolution electron microscopy and molecular mechanics calculation. *Diamond Relat. Mater.*, 2004, **13**, 1254–1260.
18. Kitahara, H. and Oku, T., Nanostructures and electronic properties of carbon and boron nitride nanocapsules. *J. Ceram. Process. Res.*, 2004, **5**, 89–93.
19. Oku, T., Hiraga, K., Matsuda, T., Hirai, T. and Hirabayashi, M., Formation and structures of multiply-twinned nanoparticles with fivefold symmetry in chemical vapor deposited boron nitride. *Diamond Relat. Mater.*, 2003, **12**, 1918–1926.
20. Oku, T., Hiraga, K., Matsuda, T., Hirai, T. and Hirabayashi, M., Twin structures of rhombohedral and cubic boron nitride prepared by chemical vapor deposition method. *Diamond Relat. Mater.*, 2003, **12**, 1138–1145.

21. Golberg, D., Rode, A., Bando, Y., Mitome, M., Gamaly, E. and Luter-Davies, B., Boron nitride nanostructures formed by ultra-high-repetition rate laser ablation. *Diamond Relat. Mater.*, 2003, **12**, 1269–1274.
22. Nishiwaki, A., Oku, T. and Narita, I., Formation and atomic structures of boron nitride nanohorns. *Sci. Tech. Adv. Mater.*, 2004, **5**, 629–634.
23. Oku, T., Narita, I. and Nishiwaki, A., Formation, atomic structures and structural optimization of tetrahedral carbon onion. *Diamond Relat. Mater.*, 2004, **13**, 1337–1341.
24. Oku, T., Three-dimensional atomic imaging of Y and $(B_{12})_{13}$ clusters in YB_{56} by HREM and crystallographic image processing. *Sci. Tech. Adv. Mater.*, 2004, **5**, 657–661.