Synthesis of Horn-Like BN Derived from Thorn-Like $Ca_2B_2O_5 \cdot H_2O$

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Boron nitride (BN) with horn-like morphology was synthesized by the reaction of thorn-like $Ca_2B_2O_5 \cdot H_2O$ and ammonia at 950 °C for 10 h. XRD, SEM, TEM, and HRTEM were used for characterization. Possible reaction and growth mechanisms were also discussed.

There has been growing interest in materials with specific morphologies in recent years because of the expectation of novel properties.[1] The discoveries of fullerene, nanotubes, and hollow spheres as new forms of matter in the nanoscale range have opened a new challenging field in solid-state physics, chemistry, and materials science owing to their potential applications.

Boron nitride nanotubes have received considerable attention because of advantageous properties such as chemical inertness, extreme hardness, high thermal conductivity, transparency, and electrically insulating performance.[2] Recently, several studies have been reported on BN nanomaterials such as BN nanotubes,[3] BN nanocapsules,[1] and BN nanoparticles,[4] which are prospected to be useful as electronic devices, high heat-resistance semiconductors, and insulator lubricants. Recently, needle-like, hollow spherical, whisker-like, and horn-like boron nitrides have been synthesized.[5–11] However, nano horn-like BN with a high yield and purity synthesized by a method like ours has not been reported yet.

In this paper, BN with horn-like morphology was synthesized by the reaction of thorn-like $Ca_2B_2O_5 \cdot H_2O$ and ammonia. A thermal decomposition evaporation growth mechanism was proposed to interpret the formation of horn-like nano BN.

Analytical pure grade $Ca(OH)_2$ (mass fraction ≥95.0%) and H_3BO_3 (mass fraction ≥99.5%) powders of about 150–300 mesh (50–100 μm) were used without purification. In a typical procedure, 7.42 g of $Ca(OH)_2$, 6.19 g of H_3BO_3, and 400 mL of distilled water were put into a stainless autoclave of 600 mL capacity, then the autoclave was sealed tightly, and heated at 90 °C for 24 h. After cooling to room temperature, the product was washed several times with distilled water and absolute ethanol. 9.59 g gray $Ca_2B_2O_5 \cdot H_2O$ powders were obtained after being dried under vacuum at 80 °C for 12 h. The yield of $Ca_2B_2O_5 \cdot H_2O$ based on calcium was 95.86 wt %. Then 2.30 g $Ca_2B_2O_5 \cdot H_2O$ powders, placed in an alumina boat, were heated to 950 °C at 6 °C min^{-1} in the center of a horizontal tubular furnace for 10 h in an ammonia flowing gas at 0.2–0.4 L min^{-1} at ambient pressure. After cooling to room temperature, the product was washed with 5 M hydrochloric acid, ethanol, and distilled water sequentially. 0.51 g gray BN were obtained after drying under vacuum at 80 °C for 24 h. The yield of BN based on boron was 89.25 wt %.

The obtained samples were characterized by X-ray powder diffraction (XRD) on a Shimadzu XD-5A X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5406$ Å). Fourier transform infrared (FTIR) spectra were obtained using a Nicolet 6700 spectrometer by using pressed KBr disks. Scanning electron microscopy (SEM) was conducted using a Hitachi S-3400N scanning electron microscope. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were performed on a JEOL JEM-2100F transmission electron microscope.

Figure 1a shows the XRD pattern of the $Ca_2B_2O_5 \cdot H_2O$ sample. The lattice constants are $a = 6.702$, $b = 5.419$, and $c = 3.558$ Å, which are close to the reported values of monoclinic phase $Ca_2B_2O_5 \cdot H_2O$ ($a = 6.722$, $b = 5.437$, $c = 3.555$ Å) (PCPDF card# 51-1530). No noticeable peaks of impurities were detected. The SEM image showed in Figure 1b exhibits thorn-like morphology.

The SEM, TEM, and HRTEM images of as-prepared BN are shown in Figure 2. The BN sample exhibits uniform horn-like

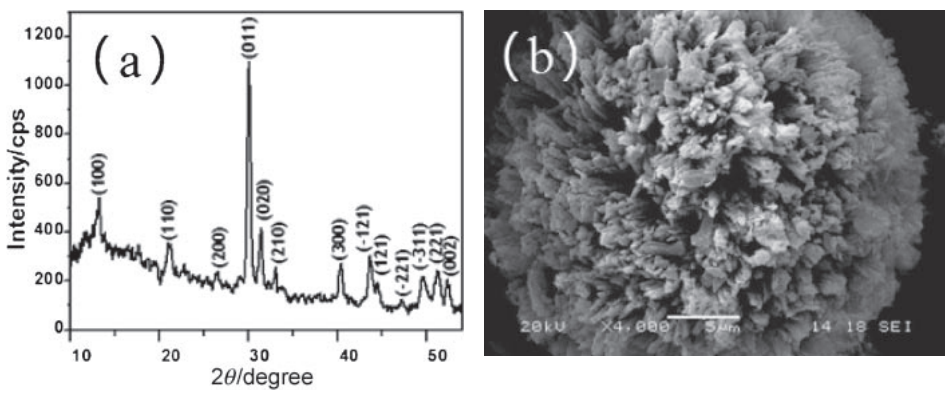

Figure 1. XRD pattern and SEM image of the thorn-like $Ca_2B_2O_5 \cdot H_2O$ sample. Scale bar (b) 5 μm.

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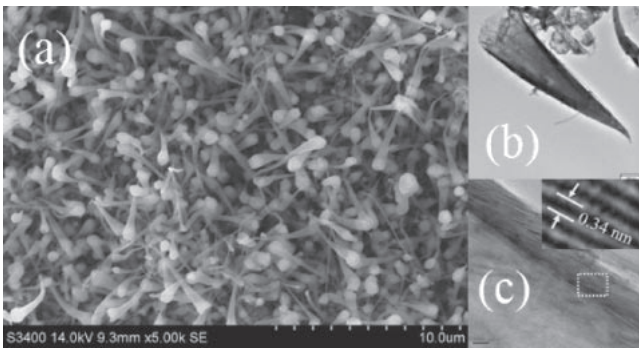

Figure 2. Typical SEM (a), TEM (b), and HRTEM (c) images of the as-prepared horn-like BN sample. Scale bar (a) 10.0 μm, (b) 400 nm, and (c) 10 nm.

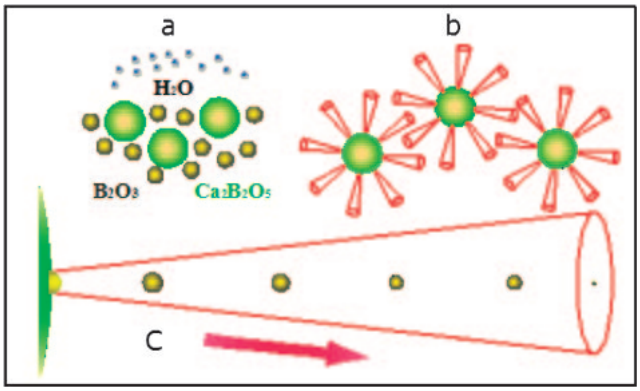

Figure 4. Illustrations of the growth process of horn-like BN.

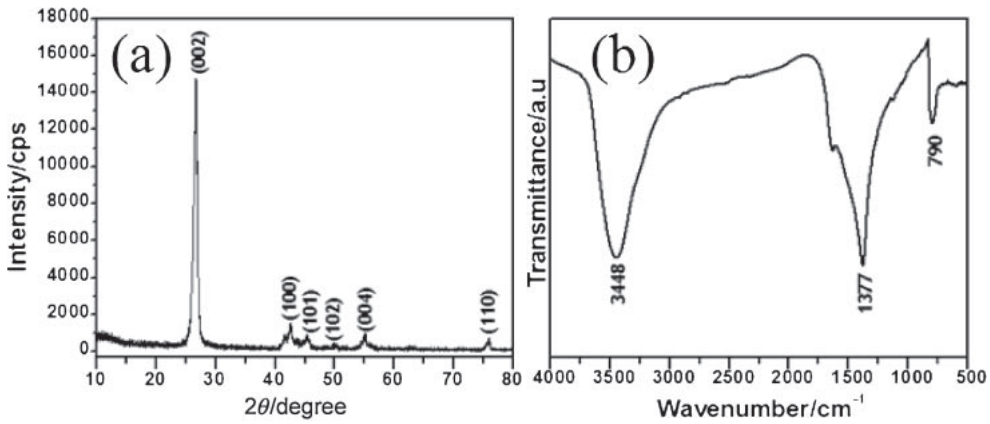

Figure 3. XRD pattern (a) and FTIR spectrum (b) of the horn-like BN sample.

morphology with high yield and purity. The average length and cone angle can be estimated to be 4 μm and 25° (Figures 2a and 2b). HRTEM further showed the product is multiwalled BN (Figure 2c).The BN sample also clearly exhibited fringes with an average interlayer distance about 0.34 nm (see insert image denoted by a frame in Figure 2c), which corresponds to the typical d_{002} spacing in a hexagonal BN.

Figure 3a shows the XRD pattern of the BN sample. The lattice constants are $a = 2.518$ Å and $c = 6.675$ Å, which are close to the reported value of h-BN ($a = 2.502$ and $c = 6.660$ Å) (PCPDF card# 45-0895). No noticeable peaks of impurities can be detected in the XRD pattern. Figure 3b gives the FTIR spectrum of the BN sample at room temperature. A strong and broad peak at 1377 cm^{-1} and a relative weak peak appear at 790 cm^{-1}. These peaks are usually assigned to hexagonal BN (h-BN),[12] which is assigned to the B–N stretching vibrations and B–N–B bending vibrations, respectively. The broad absorption peak at 3448 cm^{-1} is due to water absorbed on the sample after the experiment.

A thermal decomposition evaporation growth mechanism is proposed. In the reactive procedures, when the temperature reaches 400 °C, bulk $Ca_2B_2O_5 \cdot H_2O$ loses crystal water and generates $Ca_2B_2O_5$ clusters concurrently.[13] With the temperature increasing, $Ca_2B_2O_5$ clusters further decompose into liquid B_2O_3 droplets and CaO (Figure 4a). Due to heat generated from the reactions, the liquid B_2O_3 droplets evaporate out from the $Ca_2B_2O_5$ clusters. The out-evaporated droplets transformed into B_2O_3 gas while moving. The farther the out-evaporated droplets separated from $Ca_2B_2O_5$ clusters, the larger volume occupied by B_2O_3 gas. The final shape of B_2O_3 gas generated from one droplet of liquid B_2O_3 looks like a horn. Figure 4b shows many BN horns generated around $Ca_2B_2O_5$ clusters and Figure 4c describes the growth process of one horn-like BN. Liquid B_2O_3 droplets do not react with ammonia due to B_2O_3 gas isolating ammonia. BN grows along with the moving liquid B_2O_3 droplets from the contact surface of B_2O_3 gas and ammonia. Until the B_2O_3 liquid droplet transforms into B_2O_3 gas completely, BN stops growing and one horn-like BN forms, the shape of which is the same as the volume occupied by B_2O_3 gas generated from one droplet of liquid B_2O_3.

A series of contrast experiments were further carried out in order to study the effects of thorn-like $Ca_2B_2O_5 \cdot H_2O$ on the formation of horn-like BN. The following results were obtained: When $Ca_2B_2O_5$, CaO, and milled thorn-like $Ca_2B_2O_5 \cdot H_2O$ were used solely instead of thorn-like $Ca_2B_2O_5 \cdot H_2O$, horn-like BN was hardly observed under TEM observation. Therefore, it is likely that thorn-like $Ca_2B_2O_5 \cdot H_2O$ played a dominant role in the synthesis of horn-like BN.

In summary, horn-like h-BN with an average length 4 μm and cone angle 25° was synthesized successfully. Thorn-like $Ca_2B_2O_5 \cdot H_2O$ played a dominant role in the synthesis of horn-like BN. A thermal decomposition evaporation growth mechanism was proposed to interpret the formation of horn-like BN.

References

1 T. Oku, M. Kuno, H. Kitahara, I. Narita, *Int. J. Inorg. Mater.* **2001**, *3*, 597.

2 H. Kitahara, T. Oku, *J. Ceram. Proc. Res.* **2004**, *5*, 89.

3 T. Oku, I. Narita, A. Nishiwaki, *Mater. Manuf. Processes* **2004**, *19*, 1215.

4 D. Golberg, Y. Bando, O. Stéphan, K. Kurashima, *Appl. Phys. Lett.* **1998**, *73*, 2441.

5 L. Shi, Y. Gu, L. Chen, Y. Qian, Z. Yang, J. Ma, *J. Solid State Chem.* **2004**, *177*, 721.

6 L. Xu, Y. Peng, Z. Meng, D. Wang, W. Zhang, Y. Qian, *Chem. Phys. Lett.* **2003**, *381*, 74.

7 L. Chen, Y. Gu, L. Shi, Z. Yang, J. Ma, Y. Qian, *Solid State Commun.* **2004**, *130*, 537.

8 X. Wang, Y. Xie, Q. Guo, *Chem. Commun.* **2003**, 2688.

9 P. Cai, Z. Yang, L. Chen, L. Shi, A. Zhao, Y. Gu, Y. Qian, *Chem. Lett.* **2005**, *34*, 252.

10 A. Nishiwaki, T. Oku, *Diamond Relat. Mater.* **2005**, *14*, 1183.

11 A. Nishiwaki, T. Oku, *J. Eur. Ceram. Soc.* **2006**, *26*, 435.

12 Y. Wada, Y. K. Yap, M. Yoshimura, Y. Mori, T. Sasaki, *Diamond Relat. Mater.* **2000**, *9*, 620.

13 L. Bao, Z.-H. Xu, R. Li, X. Li, *Nano Lett.* **2010**, *10*, 255.