

A Facile Continuous Production of Hexagonal Boron Nitride Powders

Laiping Zhang,¹ Yunle Gu,^{*1} Chunxiao Ge,² and Jisheng Chang²

¹*School of Material Science and Engineering, Wuhan Institute of Technology, Wuhan 430073, P. R. China*

²*Weifang Bangde Special Material Co., Ltd., Weifang 262400, P. R. China*

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An intermediate-frequency furnace was used for continuous production of hexagonal boron nitride (h-BN) by heating a mixture of $C_3N_6H_6$ and H_3BO_3 in a flowing nitrogen gas at 1800–1950 °C. The products were examined by XRD, Raman, FTIR, and SEM. The results indicate the as-synthesized products are h-BN flakes with a purity of 98.73 wt %. A possible reaction mechanism is discussed.

Hexagonal boron nitride (h-BN) is a material which has received considerable attention due to its excellent properties such as distinguishable chemical stability, high thermal conductivity, high-temperature oxidation resistance, and high neutron absorption.¹ It is widely used in the chemical, ceramics, refractories, electronic, electrical, and nuclear industries and other areas. It is also used to synthesize superhard cubic BN as raw material.^{2–4}

Mainly, three routes by using $Na_2B_4O_7 \cdot 10H_2O/NH_4Cl/NH_3$, $Na_2B_4O_7 \cdot 10H_2O/(NH_2)_2CO/NH_3$, and $B_2O_3/Ca_3(PO_4)_2/NH_3$ are suitable for extensive industrial production.⁵ By these methods, their manufacturing processes are complicated. Moreover, substantial by-products and waste residue would be produced during the production process, and the purity of h-BN is not high. In recent years, the $C_3H_6N_6/H_3BO_3$ synthetic process has been found to have clear advantages over others in large-scale production. However, it is still difficult to obtain successively bulk quantity h-BN with uniform morphology reliably using the standard production process.

Herein, we report an intermediate-frequency furnace (IMF) for continuously synthesizing bulk h-BN by heating a mixture of $C_3N_6H_6$ and H_3BO_3 in a flowing nitrogen gas at 1800–1950 °C. IMF can be easy to operate and has many advantages, such as good heat uniformity, high efficiency, and lower cost than electrically heated furnaces. The whole process consists of only three main steps, i.e., mixing the raw materials, reacting in IMF, and shearing the crude product into fine powders.

An IMF (300–1000 Hz, Weifang Jinhuaxin Electric Furnace Manufacturing Co., Ltd.) with a graphite tube was used for the synthesis in this study. The graphite tube has an outer diameter of 160 mm and a length of 2.5 m. The temperature control apparatus was EURO THERM 818 controller with a precision of 1 °C.

The reagents, melamine ($C_3N_6H_6$) and boric acid (H_3BO_3) were commercial chemicals and about 50–150 mesh powders. In a typical procedure, 226 kg of $C_3N_6H_6$ and 250 kg of H_3BO_3 (molar ratio $C_3N_6H_6:H_3BO_3 = 1:2.25$) were well mixed in a blender mixer. The mixture was loaded on graphite boats (8.5 kg/boat) and then placed into the IMF, as shown in Figure 1. The reaction process was carried out under a N_2 atmosphere at a flow rate of 5–8 $L \cdot min^{-1}$ at 1800–1950 °C. The entrance of N_2 must be set in the side of the exit of graphite

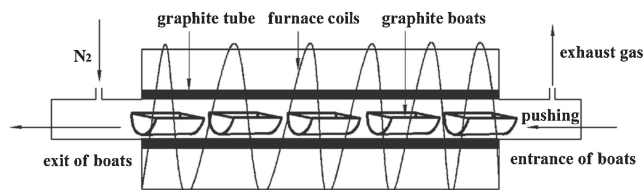


Figure 1. Schematic illustration for the fabrication of h-BN.

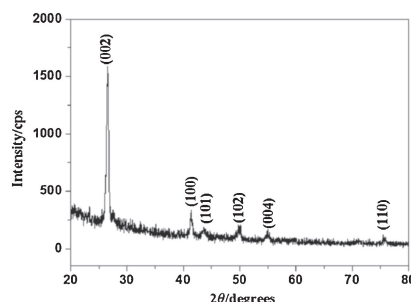


Figure 2. XRD pattern of the as-synthesized sample.

boats. This avoids polluting the products by exhaust gas and improves the purity of products. Every about 20 to 30 min, graphite boats were pushed out and into the furnace. It achieved continuous synthesis of bulk h-BN repeating the above “pushing in and out” process until the batch was completed. After crushing the whole raw products, 98.6 kg of h-BN powders were obtained. The high yield was up to 98.54% based on boron.

The as-synthesized products were comprehensively characterized using X-ray diffraction (XRD, Shimadzu XD-5A, $CuK\alpha$), scanning electron microscopy (SEM, JSM-5510LV), Raman spectroscopy (Nicolet DXR micro Raman system with Nd:YAG laser at excitation of 532 nm.), and Fourier transform infrared spectroscopy (FTIR, Nicolet 6700). The content of nitrogen in as-synthesized products was determined by neutralization titration.⁶

Figure 2 shows the XRD pattern of the as-synthesized sample. All diffraction peaks in this pattern can be indexed to h-BN with lattice parameters of $a = 0.2515$ nm and $c = 0.6789$ nm, which agree with those listed in the JCPDS Card (No. 73-2095) $a = 0.2504$ nm and $c = 0.6661$ nm. The d spacing of the diffraction peaks at 3.3532, 2.1831, 2.0732, 1.8233, 1.6705, and 1.2568 Å can be indexed as the planes (002), (100), (101), (102), (004), and (110) of h-BN, respectively. No other crystalline impurities, such as boron carbide, were detected. The XRD analysis reveals that the as-grown product is pure h-BN.

The as-synthesized h-BN sample was also characterized by Raman and FTIR spectroscopy. A sharp Raman peak at about 1354 cm^{-1} can be detected in Figure 3a, which corresponds to

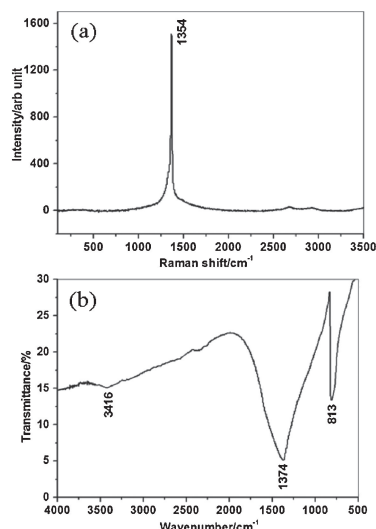
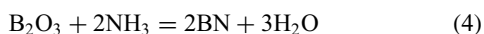
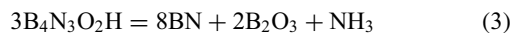
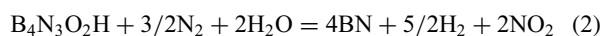
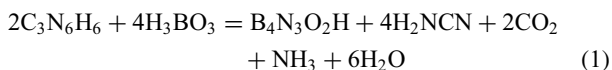


Figure 3. Raman (a) and FTIR (b) spectra of the as-synthesized sample.

the E_{2g} in-plane vibration mode of the h-BN networks.⁷ The wide-scan FTIR spectrum in the range of 500 to 4000 cm^{-1} is shown in Figure 3b. Two absorption bands centered around 813 and 1374 cm^{-1} are due to the in-plane B–N transverse optical phonon modes and the B–N–B out-plane vibration,^{8,9} respectively. The other band at about 3416 cm^{-1} could be attributed to the O–H bonds due to the absorbed water. The Raman and FTIR spectra also indicate that no other impurities in the products, such as free carbon and carbide. The content of nitrogen is 55.71 wt % by neutralization titration, and the purity of h-BN can be calculated as 98.73 wt %.

Figure 4a represents SEM image of a few very small h-BN particles, showing clearly the formation of h-BN flakes. It also displays a large quantity of h-BN flakes aggregated together. Figure 4b is a typical SEM view of the as-synthesized h-BN. These h-BN flakes have a diameter in the range of 0.5–5 μm and an average thickness of about 250 nm.

The overall reactions of pure h-BN synthesized in the present work are probably described by eq 1–4.



As shown in eq 1, the precursor $\text{B}_4\text{N}_3\text{O}_2\text{H}$ may be formed from the raw materials $\text{C}_3\text{N}_6\text{H}_6$ and H_3BO_3 at about 800 $^\circ\text{C}$, releasing lots of gaseous H_2NCN , CO_2 , NH_3 , and H_2O .¹⁰ Then, BN can be grown from the precursor $\text{B}_4\text{N}_3\text{O}_2\text{H}$ with the assistance of N_2 at experimental temperature 1800–1950 $^\circ\text{C}$ (eq 2). Meanwhile, some $\text{B}_4\text{N}_3\text{O}_2\text{H}$ was directly decomposed and generated BN, B_2O_3 , and NH_3 (eq 3). And a small amount of h-BN may be produced simultaneously from the newly produced B_2O_3 and

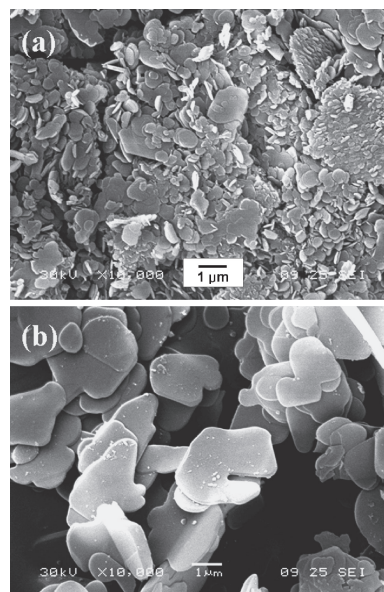


Figure 4. (a) SEM image of a few very small h-BN particles and (b) a typical SEM image of the as-synthesized h-BN sample. Scale bar: (a) 1 μm , (b) 1 μm .

NH_3 again (eq 4). During the synthesis, the large amount of releasing H_2O , H_2 , CO_2 , NH_3 , and NO_2 gases have an important role in isolating the crystalline particles to form homogeneously fine powders.

In conclusion, bulk h-BN has been continuously synthesized from $\text{C}_3\text{N}_6\text{H}_6$ and H_3BO_3 under flowing nitrogen atmosphere at 1800–1950 $^\circ\text{C}$ in an intermediate-frequency furnace. The high yield of h-BN was up to 98.54%. The products were pure h-BN flakes with diameters between 0.5 to 5 μm and an average thickness of about 250 nm. This is an inexpensive and feasible technology suitable for industrial scale production.

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