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One simple synthesis route to whisker-like nanocrystalline boron nitride by the reaction of NaBH₄ and NaN₃

Short communication

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Abstract

Nanocrystalline boron nitride (BN) was synthesized via a simple route by the reaction of sodium borohydride with sodium azide in an autoclave at 600 °C. X-ray powder diffraction pattern indicated that the product was hexagonal BN, and the cell constant was a = 2.495 Å, c = 6.687 Å. Transmission electron microscopy image showed that it consisted of whisker-like particles with an average size of 200 nm × 20 nm. The product was also studied by FT-IR, XPS and TGA. It has good thermal stability and oxidation resistance in high temperature.

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1. Introduction

Boron nitride (BN) is often referred to as "white graphite" because it is a lubricious material with the same platy hexagonal structure as carbon graphite. Unlike graphite, BN is a very good electrical insulator. It offers very high thermal conductivity and good thermal shock resistance. BN is stable in inert and reducing atmospheres up to 2800 °C, and in oxidizing atmospheres to 850 °C. Besides these, it has other advantageous properties, such as extreme hardness, chemical inertness, high mechanical strength and low density, high melting point, corrosion resistance, and oxidation resistance [1–3]. Due to these properties, BN becomes an important material. It has great potential applications in refractory, lubricants, protective and optical coatings, electrical insulators, cutting tools, grinding, and abrasive materials, advanced ceramic composites, and mold release liners, electronic devices, electrical insulators and so on [4–6].

Up to now, intensive research works have been carried out on the synthesis of boron nitride (BN) materials. In general, BN can be obtained by direct combination of boron and nitrogen [7] and carbothermal reduction of boric oxide [8]. Moreover, other methods have also been developed to prepare BN. Hirano et al. [9] pyrolyzed (HBNH)₃ at 250–700 °C and 100 MPa and obtained cubic BN by subsequent pyrolysis under 6.5 GPa at 1800 °C. Kusunose [10] reported that BN could be obtained by direct nitriding of boron acid with ammonia gas. Tang et al. [11] synthesized BN by heating the mixture of boron and iron oxide in a flowing ammonia gas at 1300 °C. Rao and Kaner [12] and

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983

Solozhenko et al. [13] prepared crystalline BN powders via a self-propagation route by the reaction of MBF_4 (M = K or Na) with Li₃N and NaN₃.

Recently, hydrothermal or solvothermal method has been reported to prepare BN. Yu et al. [14,15] synthesized boron nitride nanocrystals with high crystalline perfection by a hydrothermal synthesis route. Hao et al. [16] prepared BN nanoparticles by the reaction of Li₃N and BBr₃ at 250–550 °C via the benzene-thermal methods. Shi et al. [17] reported that BN nanocrystalline could be synthesized by nitriding of MgB₂ with NH₄Cl and NH₄Cl–NaN₃, respectively. Cai et al. [18] reported one convenient synthesis route to boron nitride nanotube by the reaction of boron powder, iron oxide, and ammonium chloride at 600 °C in an autoclave. Chen et al. [19] prepared nanocrystalline boron nitride by the reaction of BBr₃ and Mg₃N₂ at 400 °C in an autoclave.

In this paper, nanocrystalline BN has been synthesized via a convenient route by the reaction of sodium borohydride (NaBH₄) and sodium azide (NaN₃) in an autoclave at 600 °C. In this reaction, sodium borohydride is as the boron source and sodium azide is as the nitrogen source.

2. Experimental

All of the manipulations were carried out in a dry glove box with flowing nitrogen gas. Typically, 0.03 mol analytical grade sodium borohydride and 0.035 mol sodium azide (a slight excess amount) were put into a stainless steel autoclave. After sealing under argon atmosphere, the autoclave was heated at 600 °C for 8 h, followed by cooling to room temperature in the furnace. The obtained product from the autoclave was washed with absolute ethanol to remove metallic sodium generated in the reaction. After that, the product was washed several times with distilled water to remove the formed impurities. Finally the product was washed three times with absolute ethanol to remove water. The final product was vacuum-dried at 60 °C for 12 h. Gray powders were obtained.

The obtained sample was analyzed by powder X-ray diffraction (XRD) on a Rigaku Dmax- γ A X-ray diffractometer using Cu K α radiation (wavelength $\lambda = 1.54178$ Å). The morphology of the sample was examined from transmission electron microscopy (TEM) on a Hitachi H-800 transmission electron microscope. X-ray photoelectron spectra (XPS) were recorded on a VGESCALAB MKII X-ray photoelectron spectrometer, using non-monochromatized Mg K α X-rays as the excitation source. Fourier transformation infrared spectroscopy (FT-IR) spectra were obtained using a Shimadzu IR-400 spectrometer by using pressed KBr disks. The thermogravimetric analysis was performed on a thermal analyzer (model: TA-50) below 1000 °C in air and nitrogen gases at a rate of 10 °C min⁻¹ to study its thermal stability and oxidation behavior.

3. Results and discussion

Fig. 1 shows the XRD pattern of the as-prepared sample. There are four obvious diffraction peaks on this pattern. And all these diffraction peaks ((0 0 2), (1 0 0), (1 0 1), (1 0 2), (0 0 4)) at different *d*-spacing can be indexed as hexagonal BN. The refinement gives the cell constants, a = 2.495 Å, c = 6.687 Å, which are consistent with the values



Fig. 1. XRD pattern of the as-prepared sample.



Fig. 2. TEM image and SAED pattern of the as-prepared BN sample.

reported in the literature (a = 2.503 Å, c = 6.661 Å) (JCPDS card no. 73-2095). No evidences of impurities such as B, B₂O₃, can be found in this XRD pattern. The broadening nature of the XRD peaks indicated that the grain sizes of the samples are on a nanometer scale.

The morphology of the prepared BN sample was investigated by transmission electron microscopy (TEM) and selected area transmission electron diffraction (SAED). The TEM image and the SAED pattern are shown in Fig. 2.



Fig. 3. FT-IR spectra of the BN sample.



Fig. 4. XPS spectra of the BN sample.

In figure, the sample shows that it consists of whisker-like particles that have an average diameter of 20 nm and an average length of about 200 nm. These whisker-like particles exhibits slightly agglomerated particle morphology due to the ultrafine size. The SAED pattern of BN samples is inserted in Fig. 2. In this pattern, two obvious diffraction rings can be found. These rings can be indexed as $(0\ 0\ 2)$ and $(1\ 0\ 0)$. And the SAED pattern of the sample can also confirm the crystallinity of BN, in which the diffraction ring diameters again correspond well to the hexagonal BN structure.

Fig. 3 shows the FT-IR spectra of the whisker-like BN sample at room temperature. Two strong peaks around 1379 and 802 cm⁻¹ could be observed clearly for the sample, which are assigned to the B–N stretching vibrations and B–N–B bending vibrations, respectively [20,21]. A weak peak around 3405 cm⁻¹ could be attributed to the moisture absorbed on the surface of the sample.

Further evidence for the formation of BN can be obtained from the XPS of the sample. Fig. 4 shows the results of the XPS spectra. They show that the sample surface consists of nitrogen, boron, carbon and oxygen, with binding energies of N 1s, B 1s, C 1s and O 1s at 398.7, 191.5, 284.40 and 532.40 eV, respectively. The C 1s and O 1s peaks indicate that there exists a small amount of impurity elements such as C and O due to the adsorption of CO_2 , H_2O and O_2 on the surface of the sample. The B 1s peak at 191.5 eV and the N 1s peak at 398.7 eV indicate BN, in good agreement with those in the literature [22]. The quantification of B 1s and N 1s peaks confirmed that the atomic ratio of B:N was 1.01:1, which closely agrees with the stoichiometric composition of BN.

To investigate the thermal stability and the oxidation resistance of the as-prepared nanocrystalline BN, the thermogravimetric analysis (TGA) was carried out at temperatures below 1000 °C under flowing air or nitrogen. Fig. 5 shows the TGA curves of the sample. From the TGA curve (a), heated under flowing air, we can find that the weight of the product has not changed significantly below 600 °C. A slight weight loss indicates that the sample might adsorb a little water on the surface. But the quantity of the adsorbed water is very small. As the temperature keeps on rising from 700 to 1000 °C, there is an obvious weight gain during the process, indicating that the BN sample is oxidized into B_2O_3 and nitrogen oxides. The TGA curve (b) is carried out under flowing nitrogen. We can find that the weight of the product has not changed significantly below 1000 °C except a slight water weight loss on the surface. These indicate that the prepared BN has excellent thermal stability and anti-oxidation property that will make it particularly useful for high temperature applications.

The influences of the reaction temperature and time on the formation of nanocrystalline BN were investigated. An optimum reaction conditions for the formation of nanocrystalline BN was 600 °C for 8 h. If the reaction temperature was lower than 500 °C, the reaction was incomplete and the crystallinity of the as-prepared BN was lower. But if the temperature was above 700 °C, the particles size increased. So the reaction temperature we chose was 600 °C. If the reaction time was shorter than 4 h, the reaction was incomplete and the crystallinity of BN was lower. Varying the reaction time in the range of 5–10 h at 600 °C did not significantly affect the crystallinity and particle size of the as-prepared BN.

In our present route, with the temperature increasing, excessive NaN₃ decomposed (decomposition point: 300 $^{\circ}$ C) generating N₂ and molten Na (melting point: 98 $^{\circ}$ C) based on the overall equation (Eq. (1)) [23]. During the



Fig. 5. TGA curves of the as-prepared BN sample.

decomposition process, nitrogen atoms may be generated [24]. These nitrogen atoms are regarded as the nitrogen source in synthesizing BN. The NaBH₄ began to decompose with increasing temperature (>500 °C) [25] as expressed in Eq. (4). The newly formed nitrogen atoms are so active that they can react directly with the BH₃ to produce BN and H₂. The excessive molten Na may act as a medium for the transition of nitrogen and electron in the reaction process to control the reaction speed and the particles' size. And the high pressure in the autoclave may help to reduce the reaction temperature. The possible process could be illustrated as follows

$2NaN_3 \rightarrow 3N_2 + 2Na$	(1)
$N_3^- \rightarrow N_2 + N + e + energy$	(2)
$Na^+ + e \rightarrow Na$	(3)
$NaBH_4 \rightarrow BH_3 + NaH$	(4)
$2NaH \rightarrow 2Na + H_2$	(5)
$2BH_3 + 2N \rightarrow 2BN + 3H_2$	(6)
According to the above possible processes, the total reaction can be described as	following

$$NaBH_4 + NaN_3 \rightarrow BN + 2Na + 2H_2 + N_2 \tag{7}$$

4. Conclusion

Nanocrystalline BN has been successfully prepared via a simple route by the reaction of sodium borohydride with sodium azide in an autoclave at 600 °C. The product has the hexagonal BN structure. It consists of whisker-like particles with an average size of 200 nm \times 20 nm. The excessive molten Na may act as a medium for the transition of nitrogen and electron in the reaction process to control the reaction speed and the particles' size. And the high pressure in the autoclave may help to reduce the reaction temperature. The product has good thermal stability and oxidation resistance in the high temperature.

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