

Fabrication and characterization of hexagonal boron nitride powder by a precursor conversion method

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The reaction of melamine ($C_3N_6H_6$) with boric acid (H_3BO_3) by a wet chemical approach afforded precursor, hexagonal boron nitride was then prepared by the heat treatment of the precursor in the air. An investigation of the effects of melamine to boron acid molar ratio, solution concentration, synthesis temperature and time on the synthesis process of boron nitride has been carried out. The FT-IR, XRD, SEM and elemental analyses revealed that the precursor was identified as a supra-molecular adduct formed by intermolecular hydrogen bond, and the morphology of precursor exhibits rod-like crystals and its molecular formula is $C_3N_6H_6 \cdot 2H_3BO_3$. Moreover, the better precursor crystals were synthesized by using the molar ratio of 1 : 2 for melamine and boric acid. The rod-like precursor was treated at 800 °C–1000 °C for 3 h–6 h in the air to afford products which were characterized by XRD, SEM and particle size analyses. The results indicated that the rod-like precursor was treated at 950 °C for 6 h to afford good crystals of h-BN powder with a primary particle size of 15 μm .

Key words: Hexagonal Boron Nitride, Melamine, Fabrication, Characterization, Precursor.

Introduction

Hexagonal boron nitride (h-BN) is a material with a graphite-like structure, which has received considerable attention due to its intriguing properties such as lubricity, hardness, chemical inertness, high thermal conductivity, the capability of hydrogen uptake, low dielectric constant and loss, and has a wide application in industry [1–3]. Traditionally, some processes have been developed for manufacturing h-BN at high temperatures, such as the direct reaction of boron and nitrogen at more than 1200 °C [4], and the carbothermic reduction of boric oxide at more than 1800 °C [5]. However, owing to high reaction temperature, raw materials being mixed non-uniformly and needing the protection of inert gases or ammonia in the traditional synthesis processes, the preparation cost of h-BN is rather high and its application is restricted although these routes are simple and run conveniently. Therefore, other methods were developed for preparing BN, such as chemical vapor deposition [6, 7], precursor methods [8, 9], low temperature route [10, 11] and self-propagation route [12]. It is necessary to develop the lower cost and lower temperature production methods for manufacturing h-BN powders due to increasing consumption of h-BN.

Recently, precursor methods for preparing h-BN have attracted researcher's interests because the syntheses of h-BN can be carried out at low temperatures. However, these methods were carried out in N_2 or ammonia flow

and employed precious raw materials to prepare h-BN. In this paper, we selected melamine and boric acid as raw materials to afford a precursor which was then calcined at less than 1000 °C in air atmosphere to prepare h-BN easily.

Experimental

Preparation of precursor

All the reagents used in this work were of analytical grade purity (purchased from Sinopharm Chemical Reagent Co., Ltd). Melamine and boric acid with various molar ratios of 3 : 1, 2 : 1, 1 : 1, 1 : 2, 1 : 3 and 1 : 4 were put into a suitable volume of deionized water in which overall concentration total dissolved melamine and boric acid is 0.5 mol/L. The mixture was then heated up to 95 °C and stirred to dissolve all melamine and boric acid. The prepared transparent solution was cooled down to room temperature and white precipitate was observed. The product was washed by deionized water and dried in air oven. The boron content of the precursor was measured and suitable raw materials molar ratio was obtained.

Preparation of h-BN powder

The prepared precursor was put in a corundum crucible and then the sample in the corundum crucible was heated in an electric furnace at 800–1000 °C for 6 hrs, cooled to room temperature naturally. In addition, the precursor was calcined at 950 °C for 4–8 hrs and then cooled to room temperature. The obtained products were respectively washed by water and dilute hydrochloric acid solution to remove vitreous boron

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oxide. A white powder product was obtained after being dried in air oven.

Characterization

XRD patterns of precursor and h-BN were collected with 2θ range from 5° to 80° with a scan speed of $10^\circ/\text{min}$ on D/MAX-2400 powder X-ray diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). SEM images were recorded on a JSM6360-LV scanning electron microscope. FT-IR was recorded with a Fourier transform infrared spectrometer by using pressed KBr disks. The determination of the particle size of powders was carried out by particle size distribution analysis (SA-CP3) in which the powder was dispersed in ethylene glycol. TG-DTG was recorded with METTLER-TOLEDO TGA/SDTA851e.

Results and discussion

Effect of melamine to boric acid molar ratio on the synthesis of precursor

The CHN elemental analysis of the precursors synthesized at different melamine to boric acid molar ratios was measured and listed in Table 1. It is noted that the found CHN values of the precursors synthesized at 1 : 2 and 1 : 3 of molar ratios match closely with those calculated according to the formula of $\text{C}_3\text{N}_6\text{H}_6 \cdot 2\text{H}_3\text{BO}_3$ [13, 14]. However, the found CN values of precursor obtained at 3 : 1 molar ratio are higher than those calculated, indicating that surplus melamine precipitated with precursor crystallization. The above results show that the suitable melamine to boric acid molar ratio is 1 : 2.

FT-IR spectroscopy and powder X-ray diffraction of precursor

The IR spectra of melamine and precursor which was prepared at 1 : 2 of melamine to boric acid ratio were shown in Fig. 1. The absorption peaks at 3469.85 cm^{-1} , 3419.70 cm^{-1} , 3330.98 cm^{-1} , 3130.39 cm^{-1} in Fig. 1(a) are due to the anti-symmetric and symmetric stretching vibrations of NH_2 group in melamine. The peaks at 1652.95 cm^{-1} and 1026.11 cm^{-1} in Fig. 1(a) are respectively attributed to the N-H deforming and N-H distorted vibrations. The peaks at 1552.66 cm^{-1} and 813.94 cm^{-1} in Fig. 1(a) can be ascribed to stretching and

deforming vibrations of C = N group in triazine ring.

Fig. 1(b) shows the IR spectrum of precursor in which the peaks at 3469.35 cm^{-1} and 3415.31 cm^{-1} are due to anti-symmetric vibrations of NH_2 group which shift to low wave number compared with those of melamine, indicating the formation of hydrogen bond [15, 16]. The peak at 3197.40 cm^{-1} is the overlap of NH_2 group stretching vibration (3130.39 cm^{-1}) and wide absorption peak (3219 cm^{-1}) of B-OH group. The adsorption at 1579.41 cm^{-1} in Fig. 1(b) is attributed to the vibration of C = N group in triazine, and the absorption peak at 1438.64 cm^{-1} belongs to the anti-symmetric stretching vibration of B-O bond. The N-H distorted vibration (1029.74 cm^{-1}) in precursor shifts to high wave number compared with that (1026.11 cm^{-1}) of melamine due to the formation of hydrogen bond. The peak at 1127.62 cm^{-1} corresponds to B-OH bending vibration. The peaks at 1276.65 cm^{-1} , 1236.39 cm^{-1} , 802.24 cm^{-1} and 649.89 cm^{-1} are resulted from the stretching vibrations of BO_3 group. The vibration adsorptions of triazine, NH_2 , B-OH and BO_3 groups were observed in the precursor, indicating that an adduct between melamine and boric acid was formed.

The XRD patterns of raw materials and the precursor prepared at melamine to boric acid molar ratio of 1 : 2 were shown in Fig. 2. The XRD pattern of precursor is different from those of melamine and boric acid. The precursor is a highly ordered crystal phase according to index lines of Fig. 2(b). The precursor XRD pattern

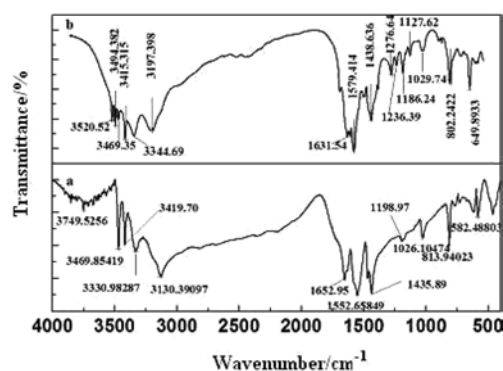


Fig. 1. FT-IR spectra of (a) melamine and (b) the synthetic precursors.

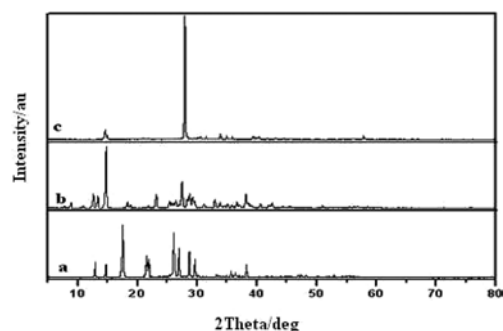


Fig. 2. XRD patterns of the prepared precursor and raw materials: (a) melamine, (b) precursor and (c) boric acid.

Table 1. Elemental analysis of the precursors.

Melamine to boric acid molar ratio	N (%)		C (%)		H (%)	
	Found	calcu- lated	Found	calcu- lated	Found	calcu- lated
3 : 1	64.27	33.63	26.31	14.41	4.76	4.80
1 : 2	34.41	33.63	14.43	14.41	4.74	4.80
1 : 3	34.71	33.63	14.42	14.41	4.77	4.80

indicated that no melamine and boric acid phases were observed in the precursor, indicating that the adduct is not a simple mixture of melamine and boric acid.

SEM images of precursor

The SEM images of precursors synthesized at different melamine to boric acid molar ratios were shown in Fig. 3. The precursor synthesized at 3 : 1 of melamine to boric acid molar ratio exhibits long rod-like crystals with a length of 5–10 μm and a diameter of 0.5 μm (Fig. 3(a)), while the precursors prepared at melamine to boric acid molar ratios of 1 : 2 and 1 : 3 present shorter rod-like crystals with a diameter similar to that of the former precursor (Fig. 3(b) and Fig. 3(c)). The phenomenon illustrates that the raw material molar ratio has an effect on the length to diameter ratio of precursors besides the composition of precursors. The length to diameter ratio of precursor increases with an excess of melamine or boric acid. The smaller length to diameter ratio for the precursor at melamine to boric acid molar ratios of 1 : 2 was observed, which favors the following

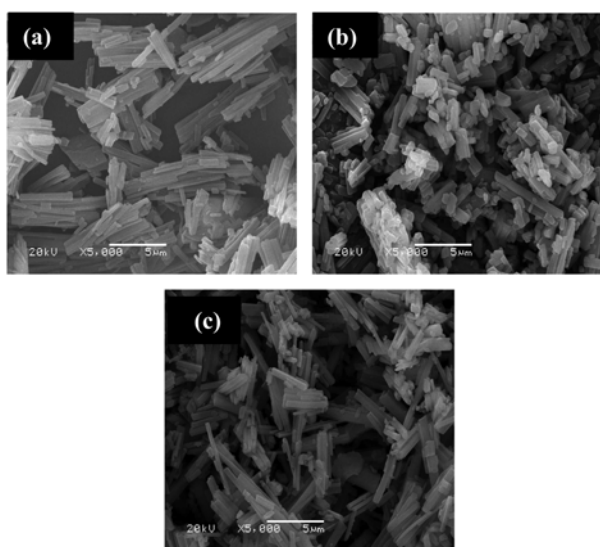


Fig. 3. SEM images of the precursors prepared at different reactant molar ratios.

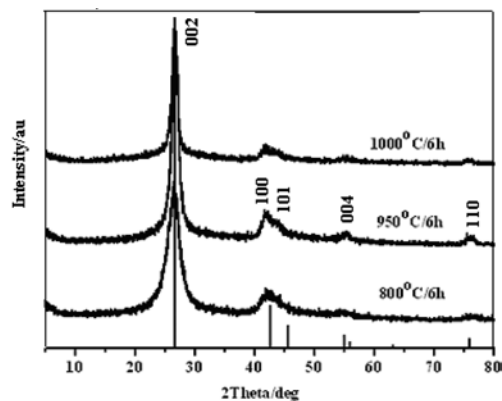


Fig. 4. XRD patterns of the products at different temperatures.

preparation of boron nitride at high temperatures. The formation of different length to diameter ratios can be ascribed to the growth rate and super-saturation of precursors.

Effect of calcining temperature and time on the synthesis of hexagonal boron nitride

The calcining temperature takes an important role in the synthesis of h-BN [17], and suitable temperature favors the formation and growth of boron nitride crystal [18]. The highest calcining temperature in this work was fixed at 1000 $^{\circ}\text{C}$ due to the decomposition of BN above 1000 $^{\circ}\text{C}$ in air atmosphere. The precursor calcination was carried out at 800 $^{\circ}\text{C}$, 950 $^{\circ}\text{C}$ and 1000 $^{\circ}\text{C}$ for 6 h, respectively. Fig. 4 presents the XRD patterns of h-BN obtained by calcining precursors at different temperatures for 6 hrs. The results indicate that the formation of h-BN was observed by calcining precursor at 800 $^{\circ}\text{C}$ for 6 hrs in air atmosphere, and the crystallization of the h-BN products becomes better with increasing temperature from 800 $^{\circ}\text{C}$ to 950 $^{\circ}\text{C}$. However, the (100), (101), (004) and (110) peaks become weaker with further increasing temperature from 950 $^{\circ}\text{C}$ to 1000 $^{\circ}\text{C}$, indicating that the existence of an incompletely ordered h-BN structure at 1000 $^{\circ}\text{C}$ [19].

Table 2 presents the purities of synthesized h-BN samples obtained by calcining precursors at 950 $^{\circ}\text{C}$ for different times. The results revealed that the purities of h-BN samples increase with increasing calcination time. It is noted that the purity of the h-BN samples tends to be a constant over 6 hrs, which illustrates that the chemical equilibrium of the h-BN formation reaction has been reached. Therefore, the suitable calcining time for preparing h-BN is 6 hrs.

FT-IR spectra of h-BN products

The FT-IR spectrum of the leached h-BN powder obtained at 950 $^{\circ}\text{C}$ for 6 hrs is presented in Fig. 5. The strong peak at 1384.81 cm^{-1} belongs to the transverse

Table 2. Purities of the h-BN products prepared at 950 $^{\circ}\text{C}$ for different roasting times.

Time/h	2	3	4	5	6	7	8
h-BN/%	92.22	93.32	92.29	92.75	93.98	94.43	94.01

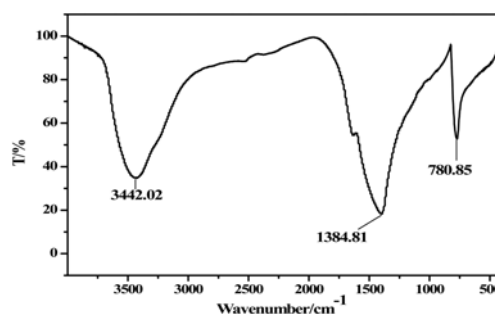


Fig. 5. FT-IR spectrum of h-BN powder.

optical vibration mode of B-N bond and the peak at 780.85 cm^{-1} is attributed to the out of plane bending vibration mode of B-N-B, which are similar to the B-N stretching vibration at 1385 cm^{-1} and B-N-B bending vibration at 795 cm^{-1} previously reported in the literature [20]. The peak at around 3442.02 cm^{-1} could be assigned to the moisture absorbed on the surface of the powder sample.

SEM microscopy and particle size distribution of h-BN powders

The morphologies of the prepared h-BN powders by calcining precursors at different temperatures for 6 hrs were investigated by SEM and depicted in Fig. 6. As illustrated in Fig. 6(a), some rod-like crystals were observed which is similar to the morphology of precursor crystals. However, the rod-like crystals disappeared with increasing calcining temperature. In addition, it is noted that the particle sizes of h-BN powders become smaller with increasing calcining temperature. These phenomena reveal that the formation of h-BN powder by calcining rod-like precursors consists of two competition processes,

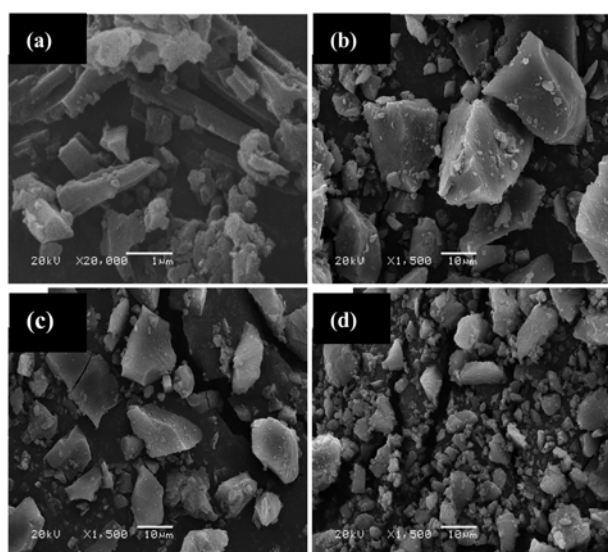


Fig. 6. SEM images of the synthesized h-BN powders at different roasting conditions; (a) 800 °C, (b) 900 °C, (c) 950 °C, and (d) 1000 °C.

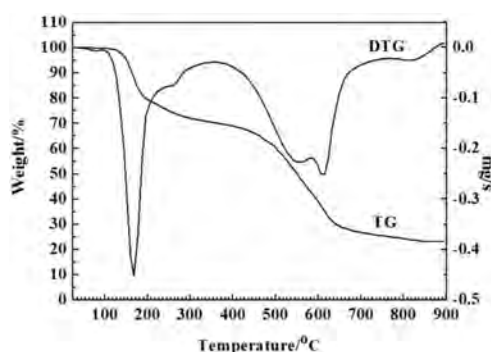


Fig. 7. TG-DTG curves of the precursor.

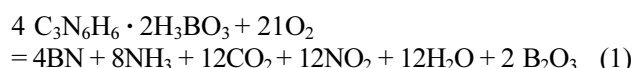
i.e. the agglomeration and cracking of rod-like precursor crystals. The agglomeration of rod-like precursor crystals is predominant process at relatively low temperatures. However, the cracking process of rod-like precursor crystals predominated at higher temperatures in the formation of h-BN powders, leading to affording h-BN powders with a smaller particle size.

The particle size distribution of the prepared h-BN powders was measured by centrifugal particle size analyzer SA-CP3. The analysis result of the prepared h-BN sample at 950 °C for 6 hrs reveals that the particle size of the sample mainly centered between 10 μm and 30 μm and the media size is around 15 μm which matches closely with SEM results.

Reaction mechanism of h-BN powder prepared by calcining precursor

As can be seen in Fig. 7, the precursor begins to lose weight at around 100 °C and an overall weight loss reaches to 28% up to 380 °C due to losing absorbed and structure water in the precursor, and meanwhile a small amount of ammonia was given off. A large amount of oxygen consumption was observed between 350 °C and 400 °C, and a large amount of CO_2 , NO_2 and NH_3 were given off between 400 °C and 700 °C [21]. The above phenomenon indicates that the C-N bonds of triazine were destroyed from 350 °C, C and N reacted with oxygen combined with B or in air to afford CO_2 and NO_2 , and meanwhile NH_2 groups in melamine were also removed between 400 °C and 700 °C. The two peaks of DTG in Fig. 7 resulted from the discharging of CO_2/NO_2 and removing of NH_3 , respectively. The final residue for the pyrolysis of precursor in air is about 23% above 820 °C.

As mentioned above, the process of h-BN formation by calcining precursor can be realized as follows, i.e. boric acid losses structural water to form vitreous B_2O_3 , and then triazine and B-O bonds are gradually destroyed and NH_2 groups of thiotriazinone are removed in NH_3 , C and partial N react with oxygen combined with B or in air to give off CO_2 and NO_2 , finally partial free B and free N combine with each other to form h-BN. The probable overall process can be formulated as follows.



According to the reaction formula, the obtained BN and B_2O_3 account for 23.9% of overall weight of reactants which closely matches with thermal result of 23%.

Conclusions

The rod-like crystals of precursor ($\text{C}_3\text{N}_6\text{H}_6 \cdot 2\text{H}_3\text{BO}_3$) with using melamine and boric acid as raw materials

were prepared by 1 : 2 of melamine to boric acid molar ratio. The dried precursor was treated between 800 °C and 1000 °C in air atmosphere to afford h-BN containing products which was leached by water and acid solution to obtain highly ordered h-BN crystals. The favorable calcining temperature 950 °C and calcining time 6 h were observed and the particle size of obtained h-BN powders under these favorable conditions is about 15 µm. The process of preparing h-BN powder provides an approach to manufacture h-BN crystals in air atmosphere at low temperatures.

References

1. C. Tang, Y. Bando, C. Liu, S. Fan, J. Zhang, X. Ding, and D. Golberg, *J. Phys. Chem. B* 110 (2006) 10354-10357.
2. R. Ma, Y. Bando, H. Zhu, T. Sato, and C. Wu, *J. Am. Chem. Soc.* 124 (2002) 7672-7673.
3. R.T. Paine, C.K. Narula, *Chem. Rev.* 90 (1990) 73-91.
4. J.B. Condon, C.E. Holcombe, D.H. Johnson, and L.M. Steckel, *Inorg. Chem.* 15 (1976) 2173-2179.
5. K.A. Schwetz, A. Lipp, in: W. Gerhartz, et al. (eds.) "Ullmann's Encyclopedia of Industrial Chemistry, Vol. 4" (VCH Weinheim, 1985) p. 295.
6. J.S. Li, C.R. Zhang, B. Li, F. Cao, and S.Q. Wang, *Surf. Coat. Technol.* 205 (2011) 3736-3741.
7. C. Tang, Y. Bando, and D. Golberg, *Chem. Commun.* 23 (2002) 2826-2827.
8. M. Hubacek, M. Ueki, *J. Solid State Chem.* 123 (1996) 215-222.
9. L. Lin, Y. Zheng, Y. Zheng and K. Wei, *Mater. Lett.* 61 (2007) 1735-1737.
10. L. Chen, M. Huang, T. Luo, Y. Gu, L. Shi, Z. Yang, and Y. Qian, *Mater. Lett.* 58 (2004) 3634-3636.
11. Z. Yang, L. Shi, L. Chen, Y. Gu, P. Cai, A. Zhao, and Y. Qian, *Chem. Phys. Lett.* 405 (2005) 229-233.
12. V.L. Solozhenko, V.Z. Turkevich, and G. Will, *J. Am. Ceram. Soc.* 79 (1996) 798-805.
13. A. Roy, A. Choudhury, and C.N.R. Rao, *J. Mol. Struct.* 613 (2002) 61-66.
14. R. Ma, Y. Bando, T. Sato, and K. Kurashima, *Chem. Mater.* 13 (2001) 2965-2971.
15. R.J. Meier, J.R. Maple, and M.J. Hwang, *J. Phys. Chem.* 99 (1995) 5445-5456.
16. J.R. Schneider, B. Schrader, *J. Mol. Struct.* 29 (1975) 1-14.
17. L. Zhao, Y.-J. Zhang, H.-Y. Gong, and D.-L. Zhao, *J. Synth. Cryst.* 39 (2010) 922-925.
18. A.V. Kurdyumov, T.S. Bartnitskaya, and V.I. Lyashenko, *Powder Metall. Met. Ceram.* 44 (2005) 590-5970.
19. B. Yao, L. Liu, and W.H. Su, *J. Appl. Phys.* 96 (2004) 1947-1952.
20. H. Zhang, Y. Chen., J. Ma, H. Tong, J. Yang, D. Ni, H. Hu, and F. Zheng, *J. Alloys Compd.* 509 (2011) 6616-6620.
21. J. Yang, T. Qiu, C. and Shen, *Chin. J. Proc. Eng.* 6 (2006) 466-471.