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Synthesis, characterization and properties of novel BN nanocages from a single-source precursor

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Abstract

In this Letter, we report the synthesis of hexagonal crystalline BN powders with novel cage-like structures from a single-source precursor NH_4BF_4 at 400–600 °C for 12 h. The obtained samples are characterized by XRD, XPS, TEM and HRTEM. Experiments reveal that the as-prepared BN powders exist in multiwall nanocages with dimensions from about 20 to 200 nm and have very good anti-oxidation properties at high temperatures.

1. Introduction

Boron nitride (BN) is a structural analog of carbon, existing in cubic (diamond-like), hexagonal (graphite-like), turbostratic, and amorphous forms [1]. These structure characteristics offer BN various properties, such as supreme hardness (for cubic BN), low density (for hexagonal BN), high temperature stability, high thermal conductivity, high melting point, low dielectric constant and chemical inertness. Boron nitride has found wide applications in many areas. For instance, it can be used as cutting tools, grinding abrasive, refractory, lubricants, electronic devices, electrical insulators and so on [2–4].

Since the discoveries of carbon fullerenes and nanotubes [5,6], boron nitride has attracted intensive interests of researchers. Based on its structural similarity to carbon, BN was expected to have fullerene and nanotube morphologies, too. In fact, various synthesis methods have been reported for the preparation of boron nitride, such as arc discharge [7], electron-beam irradiation [8], chemical vapor deposition (CVD) [9], laser ablation [10], pyrolysis method [11,12] and some other methods [13–15]. Up to now, besides particles, BN powders with tube-like [7,15], sphere-like [16], wire-like [17], cocoon-like [18], tassel-like and tree-like shapes [19] have been achieved.

Inspired by the previous researches [20,21], in this Letter, we report a simple single-source precursor approach to synthesize hexagonal crystalline BN powders with novel cage-like structures. The reaction was carried out in an autoclave via the pyrolysis of NH_4BF_4 in metallic Na flux in a temperature range of 400–600 °C.

Compared to the previous methods, this simple route has the following advantages: (1) both B and N sources from a single cheap safe precursor NH_4BF_4; (2) without using rigorous synthesis conditions or complicated apparatus or air-sensitive or toxic reagents (BBr_3, Li_3N, NaN_3, $NaNH_2$, etc.). The obtained BN nanocages exhibit very good anti-oxidation properties at high temperatures.

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2. Experimental

The reagents NH_4BF_4 and metallic Na were of analytical purity from Shanghai Chemicals Company. In a typical procedure, 3.0 g NH_4BF_4 and 3.0 g granular metallic Na (excessive) were put in a stainless steel autoclave of 50 mL capacity. The autoclave was sealed and heated in an electric furnace at 400–600 °C for 12 h, then cooled to room temperature naturally. The product was washed first with absolute alcohol to remove the excessive Na, then, rinsed with distilled water to remove the residual NaF and some other impurities. After being dried in vacuum at 70 °C for 4 h, a white powder product was obtained.

X-ray powder diffraction (XRD) patterns were recorded on a Japan Rigaku Dmax-γA X-ray diffractometer with Cu Kα radiation ($\lambda = 1.54178$ Å). The transmission electron microscopy (TEM) images were taken with a Hitachi H-800 transmission electron microscope. The high-resolution transmission electron microscopy (HRTEM) observation and the selected area electron diffraction (SAED) pattern were performed with a 200 kV electron microscope on JEOL-2010. X-ray photoelectron spectroscopy (XPS) measurements were performed on a VGESCALAB MKII X-ray photoelectron spectrometer with an exciting source of Mg Kα = 1253.6 eV. Thermogravimetric analysis (TGA) was carried on a Shimadzu TGA-50H thermogravimeter analyzer and the sample was heated from room temperature to 1000 °C at a rate of 10 °C/min in a steady flow of air.

3. Results and discussion

The composition and crystallinity of the as-synthesized BN samples were examined by XRD. The XRD patterns of the obtained products are shown in Fig. 1. Fig. 1a–c are the XRD patterns of samples A–C, which were prepared at 400, 500 and 600 °C, respectively, for 12 h. It can be seen that with increasing reaction temperature the crystallization of the BN samples becomes better. At 400 and 500 °C, the (1 0 0) and (1 0 1) peaks still overlap (see Fig. 1a,b), indicating the existence of an incompletely ordered h-BN structure [22]. The (1 0 0) and (1 0 1) peaks begin to split at 600 °C (see Fig. 1c). All the reflections of sample C can be indexed as hexagonal BN with lattice constants of $a = 2.5022$ Å and $c = 6.6675$ Å, which are close to the reported values of h-BN ($a = 2.50399$ Å, $c = 6.6612$ Å, JCPDS card, No. 73-2095). No noticeable peaks of impurities are observed in the XRD patterns. From the XRD patterns, the prominence of the (0 0 2) plane can be observed, which may indicates the existence of well-stacked layered structures in the hexagonal BN samples [23,24].

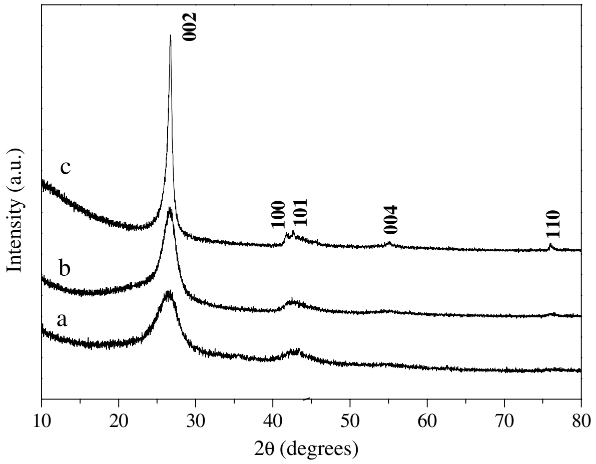

Fig. 1. XRD patterns of the prepared samples. (a) Sample A: prepared at 400 °C, 12 h; (b) Sample B: prepared at 500 °C, 12 h; (c) Sample C: prepared at 600 °C, 12 h.

Fig. 2 displays the TEM and HRTEM morphologies of sample C, which was prepared at 600 °C for 12 h. It can be seen that the obtained sample exists in nanocages (Fig. 2a). Most of the cages are box-like, which, to our knowledge, has not been reported for BN yet and some are hollow sphere-like. The dimensions of the cages range from about 20 to 200 nm and the thickness of the wall range from about 4 to 10 nm. Fig. 2b is the high-resolution TEM images of sample C. The corresponding selected area electron diffraction (SAED) patterns of sample C (inset in Fig. 2b) indicate that the product is crystallized. From the patterns, the reflections of (0 0 2) and (1 0 1) of hexagonal BN crystallites can be observed. Fig. 2c is the HRTEM images of the box-like nanocage (marked by arrow 1 in Fig. 2b). Fig. 2d shows the HRTEM images of two connected cages sharing the same wall (marked by arrow 2 in Fig. 2b), which is quite common in the TEM image (see Fig. 2a) and probably happens when the two cages grow side by side. The walls of the nanocages consist of 12–16 layers, but the wall shared by two cages may have more layers. The fringe spacing is about 0.33 nm, which is close to the interplanar spacing of the (0 0 2) lattice planes of h-BN.

Fig. 3 gives the XPS spectra of Sample C. The C1s line of carbon contamination appears at 284.75 eV and all binding energies are corrected accordingly. The survey spectrum of sample C (Fig. 3a) indicates the presence of B and N elements, and 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 binding energies centered at 398.30 eV for N1s (Fig. 3b) and 190.70 eV for B1s (Fig. 3c) are in good agreement with the reported values of bulk BN [25]. Quantification of B1s and N1s peaks gives

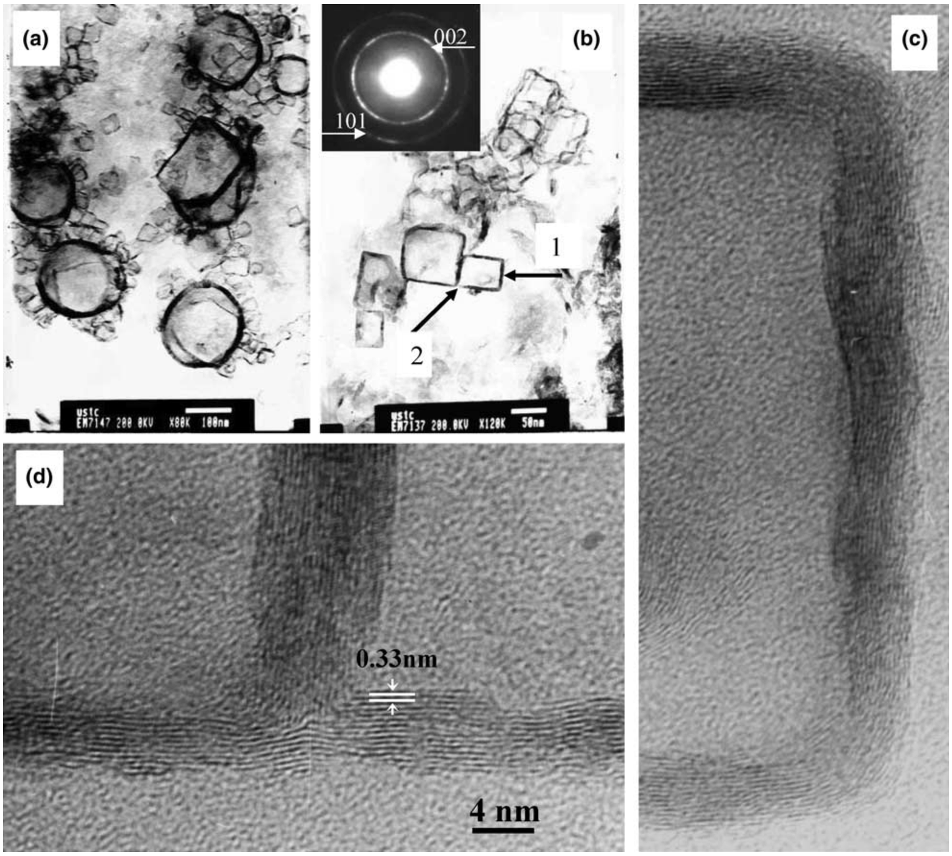

Fig. 2. TEM and HRTEM images of sample C. (a) TEM images of nanocages of sample C: prepared at 600 °C, 12 h. (b) High-resolution TEM images of sample C. Inset: the corresponding SAED pattern of the h-BN powder. (c) HRTEM images of the box-like nanocage (marked by arrow 1 in Fig. 2b). (d) HRTEM images of two connected cages sharing the same wall (marked by arrow 2 in Fig. 2b).

average B:N atomic ratio of 0.998:1, which closely agrees with the stoichiometric composition of BN.

The oxidation behavior of the BN sample (sample C) was investigated at the temperatures below 1000 °C by TGA, as shown in Fig. 4. Below 700 °C, the weight gain almost has not changed, which proves that the BN sample has very good anti-oxidation properties at high temperatures. 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. Nitrogen oxides are carried away by air. The weight gain from 700 to 1000 °C is 31.69%, which is less than the theoretical weight gain (40.31%) from BN to B_2O_3. It can be explained that around 1000 °C B_2O_3 begins to evaporate [26], which counteracts the weight gain from the oxidation of BN. The excellent anti-oxidation properties will make BN nanocage powders particularly useful for high temperature applications.

As to the reaction mechanism, we consider that at the reaction temperature, NH_4BF_4 firstly decomposes into BF_3, NH_3 and HF.

$$NH_4BF_4 = BF_3 + NH_3 + HF \tag{1}$$

The freshly produced BF_3 and NH_3 will react with each other to form BN. In metallic Na flux, the process can be expressed in following equations:

$$BF_3 + NH_3 + HF + 4Na = BN + 4NaF + 2H_2 \tag{2}$$

$$\text{In total,}\ NH_4BF_4 + 4Na = BN + 4NaF + 2H_2 \tag{3}$$

The formation of cubic NaF was confirmed by the XRD analysis of the intermediate product (omitted here), which did not undergo the washing with absolute alcohol and distilled water at all.

In the process, the use of metallic Na is in favor of forming BN at lower temperature, because the reaction of HF with Na is thermodynamically spontaneous and exothermic and the reaction heat could produce higher local reaction temperatures. For comparison, without use of Na, we heated NH_4BF_4 in the autoclave at 600 °C for 12 h and no BN was obtained.

As to the formation of the special BN nanocage structures, we think that boron nitride with hexagonal structure is similar to graphite and the cell parameters of h-BN (a = 2.5022 Å and c = 6.6675 Å) are close to those of graphite (a = 2.464 Å, c = 6.708 Å). Like graphite, it tends to form sp^2-like bonded layer-structure. According

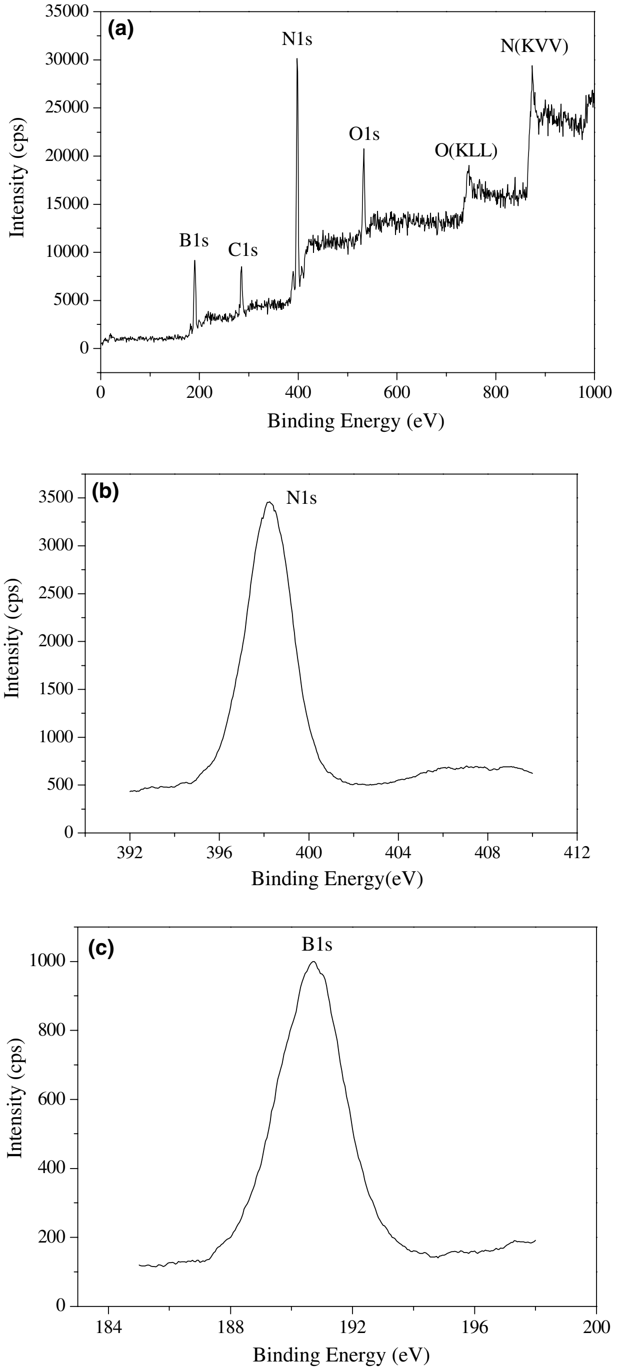

Fig. 3. XPS spectra of the h-BN sample prepared at 600 °C, 12 h: (a) survey spectrum; (b) N1s region; (c) B1s region.

to Terrones and co-workers [27], an ordered arrangement of some specific defects with a hexagonal lattice would lead to closed cage structures. In this work, the high temperature and high pressure coming from H_2 in the sealed autoclave may provide a kind of metastable growth condition under which specific topological defects would form. Therefore, the lamellar h-BN structures tend to close up to minimize their surface energy.

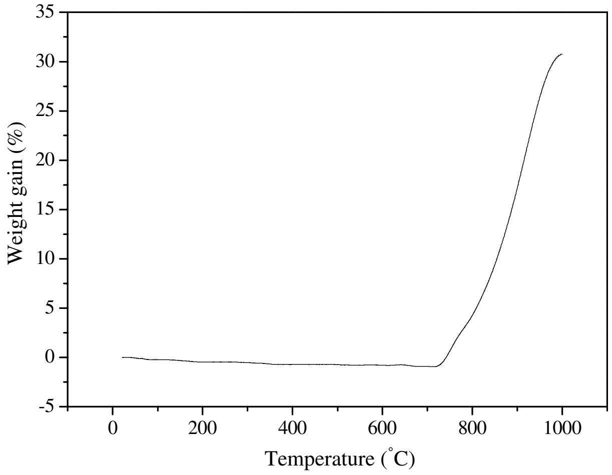

Fig. 4. TGA curve of the h-BN sample prepared at 600 °C, 12 h.

On the other hand, we speculate that during the reaction process, cubic NaF crystals form first, which exist in cube-like solids (NaF melting point: 995 °C [28]) in the system and probably play the role of templates. Later, h-BN layers form outside the NaF cube-like templates to yield a core-shell structure. Through the post-treatment of washing, the NaF solids in the core part are dissolved and BN nanocages are obtained. With the aid of the NaF cube-like templates, the novel BN nanocages with nearly 90° bend box-like structure arise. However, further investigation is necessary to understand the exact mechanism of forming the box-like BN nanocages.

4. Conclusions

Box-like BN nanocages were successfully prepared via a single-source precursor reaction in an autoclave in the temperature range of 400–600 °C. The sizes of the cages range from about 20 to 200 nm with multiwalls and the thickness of the wall range from about 4 to 10 nm. The as-prepared BN sample displays excellent anti-oxidation properties at high temperatures. So they might be advantageous to be used as high temperature materials as well as to find other potential applications. In addition, this simple single-source precursor approach might be extended to synthesis of other compounds.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2005.02.041.

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