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Fabrication and characterization of hollow spherical boron nitride powders

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Abstract

Hollow spherical boron nitride powders with diameters ranging from 100 nm to a few micrometers were prepared by Co-pyrolysis of NH_4BF_4 and KBH_4 with zinc powder at 600 °C The roles of each reactant played in this experiment and the possible formation mechanism was discussed.

1. Introduction

Owing to their useful properties and their growing importance in industry, inorganic nanoparticles of generally spherical or onion-like shape have been of great interest to the broad scientific community for decades [1]. These nanoparticles include metal chalcogenides [2], metal oxides [3], silica [4], carbon [5], boron nitride (BN) [6] and so on. Among these materials, BN is one of the most important III–V compounds, which has many promising applications in a wide range of areas, for example, it can be used as lubricants, protective and optical coatings, advanced ceramic composites, and mold release liners [7,8].

Up to now, BN powders with tube-like [9], sphere-like [6], wire-like [10], cocoon-like [11], tassel-like and tree-like shapes [12] have been synthesized. Among these morphologies, spherical BN powders have attracted increasing attention because they may permit higher filler loadings than platelet morphology in standard thermoset polymers and improved composite processing characteristics [6], and the random orientation of crystallites in spherical shapes should diminish the anisotropic properties typical of BN [13]. There have been some reports on how to synthesize solid spherical BN particles, for example, the reaction of BCl_3 and gaseous ammonia at low temperature [14]; Spray pyrolysis of poly(borazinylamine) precursor dissolved in liquid ammonia [13]; Aerosol-assisted vapor deposition method [15]; the method combining chemical vapor deposition and pyrolysis of trimethoxyborane under ammonia atmosphere [6].

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Though solid spherical BN powders have been produced with large yields and/or with high purity by the above methods, there are few reports about the preparation of BN hollow spheres. In this Letter, we report a simple method to fabricate BN hollow spheres with diameters ranging from 100 nm to a few micrometers by Co-pyrolysis of NH_4BF_4 and KBH_4 with zinc powder at 600 °C. This report is a further progress of our previous work [16].

2. Experimental

In order to minimize oxygen contamination, all the manipulations were carried out in a N_2 flowing glove box. In a typical experiment procedure, NH_4BF_4 (0.033 mol), KBH_4 (0.020 mol) and Zn powder (0.034 mol, 99.999%) were mixed and loaded into a 20-ml stainless steel autoclave. The autoclave was sealed and put into an electric furnace at 500 °C, then the temperature of the furnace was increased to 600 °C in 10 min and maintained at 600 °C for 36 h. After that the autoclave was allowed to cool to room temperature naturally and was carefully opened. The product in the autoclave was collected and washed with diluted hydrochloric acid and distilled water several times. Then it was filtered and dried in a vacuum at 70 °C for 3 h. The final product in white color was collected for characterization.

Taking our previous work into consideration, the overall reaction involved in this experiment could be tentatively written as follows [17,18]:

$$2NH_4BF_4 + 2KBH_4 + 3Zn = 2BN + 3ZnF_2 + 2KF + 5H_2 + B_2H_6$$

X-ray powder diffraction (XRD) pattern of the products was recorded on a Philips X'pert diffractometer with Cu $K\alpha_1$ radiation ($\lambda = 1.54178$ Å). Raman spectrum was obtained on a Ramalog 6 (Spex). X-ray photoelectron spectroscopy (XPS) measurements were performed on a VGESCALAB MKII X-ray photoelectron spectrometer. The morphology of the products were examined by scanning electron microscope (SEM) using an X-650 microanalyzer. Transmission electron microscopy (TEM) was operated on a Hitachi H-800 microscope. High-resolution TEM study was carried out in a JEOL 2010 microscope. A Gatan-2000 spectrometer (attached on a JEM-2010F TEM) was used for parallel detection of electron energy loss spectra (EELS). The samples used for characterization were dispersed in absolute ethanol and were ultrasonicated before SEM, TEM, HRTEM and EELS analyses.

3. Results and discussion

A typical XRD pattern of the as-prepared products is shown in Fig. 1. It contains two diffraction peaks at about $2\theta = 25.5°$ and 42.5°, which can be assigned to the (0 0 2) and (1 0 0) reflections of hexagonal BN. The broadness of the two peaks indicates the existence of partial disordering structures in the samples [6]. Raman spectrum of the samples (Fig. 2) shows an active vibrational band at about 1370 cm^{-1}, which corresponds to the typical frequency observed in h-BN. It was due to the E_{2g} symmetric vibration mode in h-BN (B–N in plane atomic displacement) [19,20]. This result coincides with that of the XRD analysis, indicating the as-prepared products were h-BN.

XPS spectra of the samples shown in Fig. 3 indicate that the binding energies centered at about 190.37 eV for B1s (Fig. 3b) and 398.10 eV for N1s (Fig. 3c) are in agreement with the values of bulk BN in literature [21]. Quantification of B1s and N1s peaks gives average B:N atomic ratio of

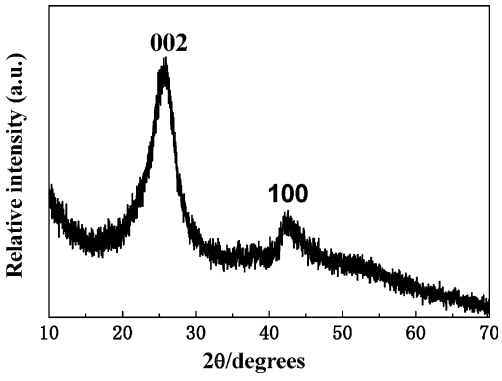

Fig. 1. Typical XRD pattern of the products.

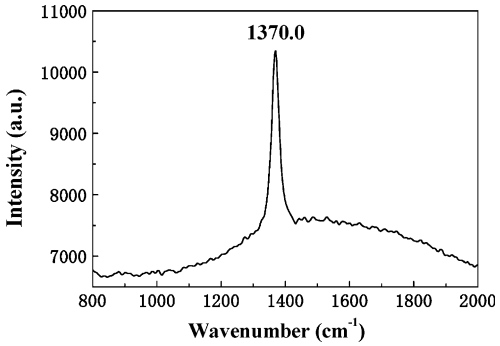

Fig. 2. Typical Raman spectrum of the samples.

approximate 1.04:1.00, which corresponds to the stoichiometric composition of BN.

SEM and TEM observation indicated that the samples were composed of hollow BN spheres, turbostratic h-BN [22] and BN nanotubes. The yields of the three components, based on statistical analyses of the SEM and TEM images, were in the range of 35–40%, 55–60%, 1–5%, respectively. The coexisting turbostratic BN may contribute greatly to the broadening of both the XRD pattern (Fig. 1) and the Raman spectrum (Fig. 2) [23]. Figs. 4a and b show representative SEM and TEM images of the as-prepared BN spheres. It can be seen that they are hollow and are nearly perfect round. The BN hollow spheres have diameters ranging from 100 nm to a few micrometers. A magnified TEM image of a large BN sphere was shown in Fig. 4c. Its selected area electron diffraction (SAED) pattern was shown in Fig. 4d, which can be indexed as 0 0 2, 1 0 0, and 1 1 0 diffraction, respectively. Fig. 4e shows a HRTEM image of part of the shell of a BN hollow sphere, the average distance between the neighboring fringes is about 0.34 nm, which corresponds to the 0 0 2 d-spacing of h-BN. The HRTEM image shows that the BN hollow spheres were well-crystallized. EELS analyses (Fig. 5) indicate that the as-obtained BN hollow spheres were of relatively high purity [24].

It is evident from Fig. 4a that many micrometer BN hollow spheres were broken, which may indicate that the micrometer spheres are less stable compared with the nanoscale ones. It is thought that the drag and shear forces acted on the hollow BN spheres when they were sonicated should be

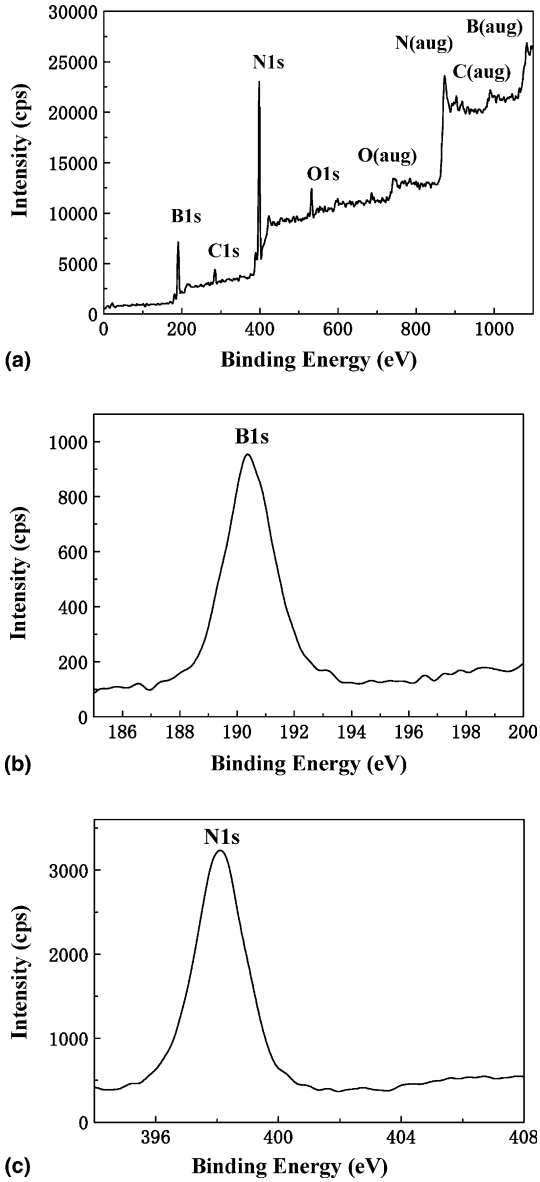

Fig. 3. XPS spectra of the as-prepared BN: (a) survey spectrum, (b) B1s, (c) N1s.

partly responsible for the breakage of these spheres [25], but the exact reason is not known.

In our previous work, we have systematically studied the reactions between NH_4BF_4, KBH_4, NaN_3, elemental Fe and Zn under the reported experimental conditions (see Table 1 of [16]), and have found the best reaction parameters to pro-

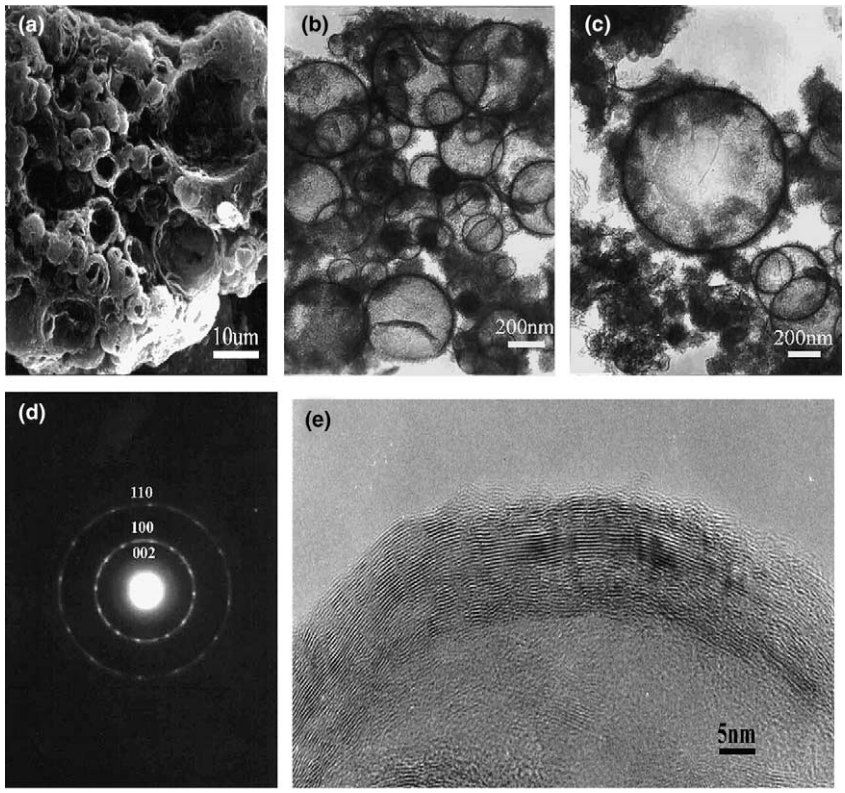

Fig. 4. Representative SEM and TEM images of the as-prepared BN hollow spheres: (a) SEM image, (b) TEM image, (c) and (d) a magnified TEM image of a large sphere and its SAED pattern, (e) HRTEM image of part of the shell of a BN hollow sphere.

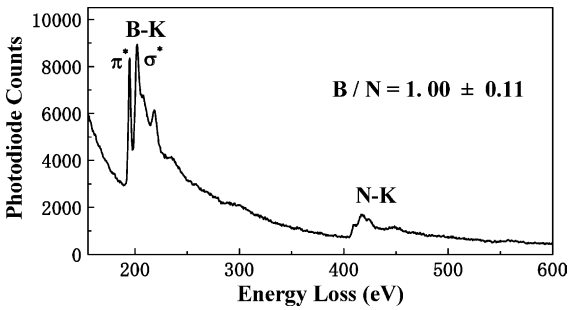

Fig. 5. Typical EELS spectrum of BN hollow spheres.

duce BN nanotubes with relatively high yield. But the reactions listed in Table 1 of [16] always give mixtures of BN nanotubes and BN hollow spheres (or cages). In order to increase the yield and percentage of BN hollow spheres, we have re-done the experiments shown in Table 1 of [16] under adjusted reaction conditions, and have found that the reaction between NH_4BF_4, KBH_4 and Zn with a fast initial increasing speed of reaction temperature (compared with the increasing speed of reaction temperature in [16]) can give the highest yield of BN hollow spheres and in the meantime the lowest yield of BN nanotubes. Different to the production of BN nanotubes, it was found that the addition of NaN_3 and/or Fe powder has no good effect on the yield and content of BN hollow spheres. The yield and percentage of BN hollow spheres were reduced when KBH_4 was substituted by NaN_3 and/or Zn was replaced by Fe powder. A worth noting phenomenon is that the yields of BN hollow spheres seem to increase along with the increasing addition of Zn powder, but when the spare space of the autoclave was all filled with Zn powder, the yield would decrease. Under the present experimental condition, the highest yield of hollow BN spheres was obtained when 0.18–0.20 mol Zn powder was added. This result may be

related with the corresponding change of pressure in the autoclave, however, the exact reason is presently not known. It was also found that the yield of BN hollow spheres depends much on the initial increasing speed of reaction temperature. Quick initial increasing speed of reaction temperature (see Section 2) usually gave relatively higher yield of BN hollow spheres. However, when the autoclave was heated directly at 600 °C (means a much faster increasing speed of reaction temperature), the yield of hollow BN spheres would be very low. Terrones and co-workers [26–29] have ever suggested that an ordered arrangement of some specific ring defects within a hexagonal lattice would lead to closed cage structures. Thus, the production of BN hollow spheres may as well demand specific topological defects under the present experimental conditions. And these defects may be produced in a narrow temperature range and under proper vapor pressure in our experiment [30]. This point of view may tentatively explain the phenomenon that a relatively fast initial increasing speed of reaction temperature would lead to a high yield of BN hollow spheres, and when the increasing speed was too high (means the autoclave was directly heated at 600 °C), the yield of BN hollow spheres would decrease. However, the exact reason is presently unknown.

As for the roles of each reactant played in the present experiment, we considered that NH_4BF_4 not only acts as nitrogen source but also acts as a boron source, because no BN hollow spheres could be observed when NH_4BF_4 was replaced by NH_4F or NH_4Cl while other reaction conditions remained unchanged. As only a little amount of BN hollow spheres could be obtained without the addition of KBH_4, it was thought that KBH_4 might also act as a boron source, and in the meantime as a reductant. Considering our previous work [16], Zn powder may play a catalytic role in this experiment, because no BN hollow spheres could be observed when Zn powder was absent. Of course, it might also be a reductant.

Previous to this report, spherulitic BN have been synthesized by pyrolysis of borazine [31]. Borazine was considered to undergo ring cleavage and polymerization process to yield liquid and gaseous intermediates with different molecular weights. The intermediates enriched with active N–H and B–H bonds appeared to release hydrogen and aggregate to coalesce to form BN. The overall process was considered to facilitate the formation of spherulitic morphology [31]. The authors thus speculated that a similar process might also occur in the formation of the present hollow BN spheres in our experiment. Because NH_4BF_4 and KBH_4 may decompose into small molecules enriched with active N–H, B–H and B–F bonds at temperatures higher than 500 °C [17,18], these molecules may then release hydrogen or hydrogen fluoride and undergo similar coalescing process to produce hollow spherical BN, however, the exact formation mechanism still needs further research.

4. Conclusions

A Co-pyrolysis method using NH_4BF_4 and KBH_4 as reactants and Zn powder as catalyst was developed to prepare hollow spherical BN at 600 °C. These hollow spheres were well-crystallized and have diameters ranging from 100 nm to a few micrometers. The roles of each reactants played in this experiment and the possible formation mechanism were discussed.

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