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A room-temperature approach to boron nitride hollow spheres

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Abstract

Boron nitride hollow spheres were synthesized by the reaction of BBr₃ and NaNH₂ at room temperature; X-ray powder diffraction pattern could be indexed as hexagonal BN with the lattice constants of a = 2.482 and c = 6.701 Å; high-resolution transmission electron microscopy image showed the hollow spheres consisted of BN nanoparticles, with diameter between 80 and 300 nm; a possible formation mechanism of BN hollow spheres was discussed. © 2004 Elsevier Ltd. All rights reserved.

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1. Introduction

In recent years there has been increasing interest in materials with specific nanomorphologies because of the expectation of novel properties. Among them, the nanoscale hollow spheres are useful in many areas. They can serve as extremely small containers for encapsulation, delivery of drugs, development of artificial cells, and protection of biologically active agents because of their low density, large specific surface area, and interesting optical properties [1-4]. Various hollow spheres including carbon, polymers, metals, and inorganic oxides have been synthesized by using spherical templates such as polystyrene beads [5-7]. Several other methods have also been developed to fabricate hollow spheres, such as coaxial nozzle techniques, microemulsion, reverse microemulsion, self-organization, and template-interface methods [8,9].

Boron nitride (BN) is well known for its advantageous properties such as high temperature stability, large thermal conductivity, high mechanical strength, extreme hardness, corrosion resistance, and oxidation resistance. These properties make BN an interesting material for many applications such as refractory, lubricants, grinding, optical coatings, ceramic composites and so on [10,11].

Traditional, boron nitride has been synthesized by various high-temperature routes, such as the combination of boron with nitrogen [12], the carbothermic reduction of boron oxide [13]. Recently, Hao et al. [14] prepared nanocrystalline cubic BN by reacting LiN₃ with BBr₃ at low-temperature benzene conditions; Xu et al. [15] synthesized BN nanobubes by co-pyrolysis NH₄BF₄, KBH₄, and NaN₃ at 450 °C; Tang et al. [16] reported that large-scale BN sub-micron spherical particles could be synthesized by chemical vapor deposition.

Herein, we provide an approach to prepare BN hollow sphere at room temperature, using boron tribromide (BBr_3) as the boron source and sodium amide ($NaNH_2$) as nitrogen. The whole process can be formulated as follows:

$$BBr_3 + NaNH_2 \xrightarrow{25} BN + NaBr + 2HBr$$

25.00

2. Experimental procedure

All the manipulations were carried out in a dry glove box with Ar flowing. All the reagents used were of analyticalgrade purity. In a typical procedure, $NaNH_2$ (0.02 mol) was added into a crucible and then BBr₃ (0.02 mol) was dripped

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into the crucible at room temperature (25 °C), when the BBr₃ was added, NaNH₂ immediately reacted with BBr₃. The product was washed with distilled water and absolute ethanol for several times to remove the impurities. The final product was vacuum-dried at 60 °C for 4 h.

X-ray powder diffraction (XRD) pattern was carried out on a Rigaku Dmax- γ A X-ray diffractometer with Cu K α radiation ($\lambda = 1.54178$ Å). The morphology of nanocrystalline BN was examined from transmission electron microscopy (TEM) images taken with a Hitachi H-800 transmission electron microscope. High-resolution transmission electron microscope. High-resolution transmission electron microscopy (HRTEM) image was recorded on a JEOL-2010 TEM at an acceleration voltage of 200 kV. Fourier transformation infrared spectroscopy (FTIR) spectra were obtained using a Shimadzu IR-400 spectrometer by using pressed KBr disks. 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.

3. Results and discussion

Fig. 1 shows the XRD pattern of the samples. All of the four peaks at *d*-spacings of 3.379, 2.153, 2.059, 1.677 Å can be indexed as hexagonal BN ((002), (100), (101), (004)). The lattice constants are a = 2.482 and c = 6.701 Å, close to a = 2.503 and c = 6.661 Å (JCPDS card# 73-2095). No impurities such as B₂O₃ can be detected in the XRD pattern. The broadening nature of the XRD peaks indicates that the particle size of the samples is within nanometer scale.

Fig. 2 shows the FTIR spectra of the sample. Two strong characteristic peaks locate at 1379 and 802 cm⁻¹, respectively. The absorption band at 1379 cm⁻¹ is identified with the B–N stretching vibrations, and the absorption band at 802 cm⁻¹ can be attributed to the B–N–B bending vibrations [17,18]. The broad absorption peak at 3407 cm⁻¹ is due to absorbed water on the sample.

The XPS spectra of the as-prepared h-BN sample are



Fig. 1. XRD pattern of the BN sample.



Fig. 2. FTIR spectra of the BN sample.

shown in Fig. 3. It shows that the sample surface consists of nitrogen and boron, with binding energies of N1s, and B1s at 398.1 and 190.4 eV, respectively. The B1s peak at 190.4 eV and the N1s peak at 398.1 eV indicate BN, in good agreement with those in the literature [19]. The atomic ratio of N:B is 1:1.01, close to that of BN.

The TEM images and selected area electron diffraction (SAED) pattern of as-prepared BN are shown in Fig. 4.



Fig. 3. XPS spectra of the BN sample.





From Fig. 4(a) and (b) it can be seen that there is an obvious contrast between the dark edge and the center of the sample, revealing that the core is hollow. The as-prepared BN spheres have diameter ranging from 80 to 300 nm, with thickness of the shell is about 10-20 nm. The SAED pattern (Fig. 4(c)) of a single BN sphere shows three clear diffraction rings corresponding to the (002), (100), (101) crystal planes of h-BN. This result suggests that the shells of BN hollow spheres are constructed by BN polycrystallines. From the HRTEM image (Fig. 4(d)), it can be seen that the shells of BN spheres are mainly composed of nanoparticles between 2 and 4 nm.

According to free energy calculations, the reaction is thermodynamically spontaneously and highly exothermic $(\Delta G = -322.81 \text{ kJmol}^{-1} \text{ and } \Delta H = -380.32 \text{ kJmol}^{-1})$. A great deal of heat generates during the reaction process and results in an instantaneous local high temperature, which favors the formation of BN hollow spheres. The possible formation process is illustrated in Fig. 5. Strongly exothermic reaction raises the local temperature near the surface and leads BBr₃ (b.p. 90 °C) to vaporize to form many small droplets. Then the reaction can occur on the surface of the BBr₃ droplets in the atmosphere of NaNH₂, which may result in the formation of a BN shell around the BBr₃ core. This is an important step in the synthesis of hollow spheres. With the BBr₃ droplets further reacting with



Fig. 5. The formation mechanism of BN hollow spheres.

NaNH₂, the shell becomes thicker. In this process BBr₃ droplets may serve as a template with the BN shells formed near the liquid–solid interface.

4. Conclusions

We have succeeded in synthesizing h-BN hollow spheres with diameter between 80 and 300 nm by the reaction of NaNH₂ and BBr₃ at room temperature. The HRTEM image shows that the shells of BN spheres are mainly composed of nanoparticles between 2 and 4 nm. A possible mechanism of BBr₃ droplets serving as a template has been proposed.

Acknowledgements

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