A Low-temperature Coreduction Route to Boron Nitride Flakes and Hollow Spheres

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Boron nitride flakes and hollow spheres were synthesized by coreduction of NH_4Cl and BBr_3 using sodium as reductant. X-ray powder diffraction (XRD) pattern could be indexed as hexagonal BN. The X-ray photoelectron spectra (XPS) were used to determine the composition ratio, which is B:N = 1:1.05. The transmission electron microscopy (TEM) images showed flake-like and hollow spherical morphology.

There has been growing interest in materials with specific morphologies because of the expectation of novel properties in recently years.[1,2] The discoveries of fullerene, nanotubes, hollow spheres as new form of matter in the nanoscale range have opened a new challenging field in solid state physics, chemistry, and materials science owing to their potential applications.[1,3]

Boron nitride (BN) has received considerable attention because of its advantageous properties such as chemical inertness, extreme hardness, high thermal conductivity, transparency, and electrically insulating performance. It has great potential application in refractory, lubricants, and cutting tools.[4–6] Various methods were reported for synthesis of boron nitride, such as the direct reaction of boron and nitrogen, the carbothermic reduction of boron oxide and so on.[7,8] Recently, Yang et al.[9,10] synthesized nanocrystalline cubic BN by pulsed laser-induced liquid–solid interfacial reaction; Tang et al.[11] reported that large-scale BN submicron spherical particles could be synthesized by chemical vapor deposition; Xu et al.[12] synthesized BN nano-bubes by co-pyrolysis NH_4BF_4, KBH_4, and NaN_3 at 450 °C.

Herein, we report a low-temperature route to BN flakes and hollow spheres by coreduction of ammonium chloride (NH4Cl) and boron tribromide (BBr_3) using metallic sodium as reductant. The reaction can be described as follows:

$$BBr_3 + NH_4Cl + 4Na \xrightarrow{350\,°C} BN + 3NaBr + NaCl + 2H_2$$
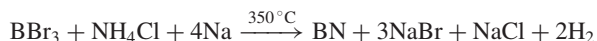
In this reaction, nascent nitrogen and boron are generated in the reaction of NH_4Cl and BBr_3 by metallic sodium, and they combine to form hexagonal BN.

All the manipulations were carried out in a dry glove box with Ar flowing. In the typical process, NH_4Cl (0.01 mol), BBr_3 (0.01 mol), and sodium (0.04 mol) were placed into a stainless steel autoclave with a quartz liner. Then the autoclave was sealed and heated at 350 °C for 6 h, followed by cooling to room temperature on standing. The product in the quartz liner was washed with distilled water and absolute ethanol for several times to remove the impurities. The final product was vacuum-dried at 80 °C for 4 h. White powders were obtained.

X-ray powder diffraction (XRD) measurement was carried out on a Rigaku Dmax-γA X-ray diffractometer with Cu Kα 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. X-ray photoelectron spectra (XPS) were recorded on a VGESCALAB MKII X-ray photoelectron spectrometer, using nonmonochromatized Mg Kα X-rays as the excitation source. Fourier transformation infrared spectroscopy (FTIR) spectra were obtained using a Shimadzu IR-400 spectrometer by using pressed KBr disks.

The XRD pattern of the as-prepared BN sample is shown Figure 1. All of the four peaks at d spacings of 3.354, 2.177, 1.671, 1.252 Å can be indexed as hexagonal BN ((002), (100), (004), (110)). The lattice constants are $a = 2.506$ and $c = 6.623$ Å, close to $a = 2.503$ and $c = 6.661$ Å (JCPDS card# 73-2095). No impurities such as B_2O_3 can be detected in the XRD pattern.

Figure 2 shows the XPS spectrum of the as-prepared h-BN sample. It indicates that the sample surface consists of nitrogen and boron, with binding energies of N1s, and B1s at 397.9 and 190.4 eV, respectively. The B1s peak at 190.4 eV and the N1s peak at 397.9 eV indicate BN, in good agreement with those in the literature.[13] Quantification of B1s and N1s peaks gives an average B:N atomic ratio of 1:1.05, close to that of BN.
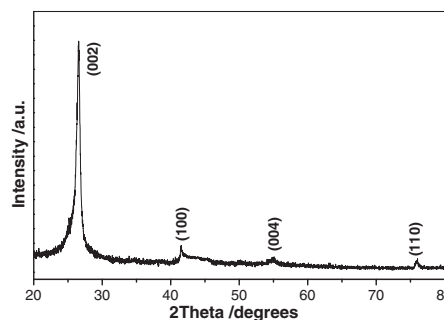

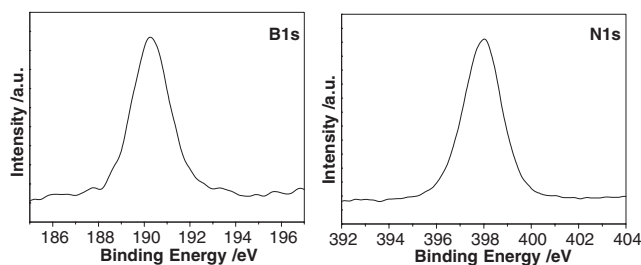**Figure 1.** XRD pattern of the BN sample.

Figure 2. XPS spectra of the BN sample.

The FTIR spectrum of the sample at room temperature is shown in Figure 3. Two strong characteristic peaks locate at 1382 and 816 cm^{-1}, which can be attributed to the in-plane B–

N stretching vibrations and out-of-plane B–N–B bending vibrations, respectively.[14,15] The broad absorption peak at 3421 cm^{-1}
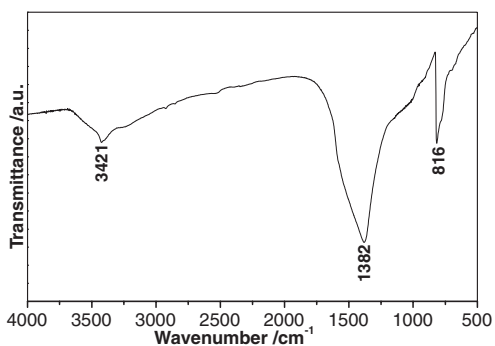

Figure 3. FTIR spectrum of the BN sample.

may be due to the moisture absorbed on the surface of the sample.

The TEM images and selected area electron diffraction (SAED) patterns of as-prepared BN are shown in Figure 4. From Figure 4a it can be seen that the sample consists of flake-like morphology. The corresponding SAED pattern (Figure 4b) of BN flakes is consistent with the single crystalline nature. In Figure 4c, the sample consists hollow spheres of 50–200 nm in diameter and the shell thickness of approximately 10–20 nm. The strong contrast between the dark edge and the light center exhibits its hollow nature. The SAED pattern (Figure 4d) of a single BN hollow sphere shows two clear diffraction rings corresponding to the (100), (110) crystal planes of hexagonal BN. This result suggests that the shells of BN hollow spheres are
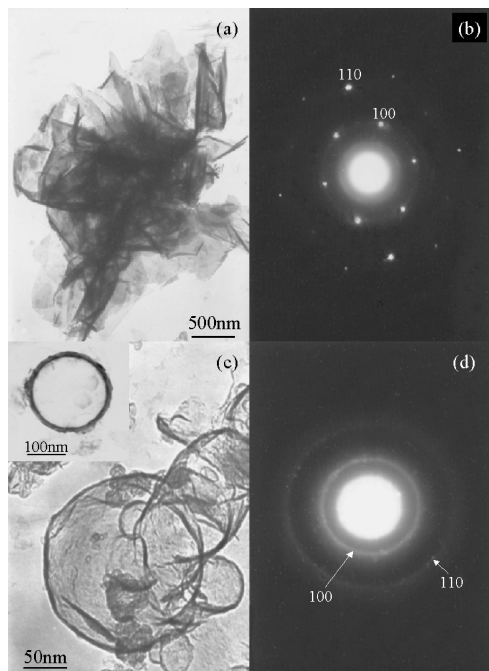

Figure 4. TEM images and SAED patterns of the BN sample: (a) flakes; (b) the corresponding SAED pattern of the BN flakes; (c) hollow spheres and a single hollow sphere (inset); (d) the corresponding SAED pattern of the BN hollow sphere.

constructed by BN polycrystals.

According to free energy calculations, the above BN synthetic reaction is thermodynamically spontaneous and highly exothermic ($\Delta G = -1220.2$ kJmol^{-1} and $\Delta H = -1246.2$ kJmol^{-1}). A great deal of heat generates during the reaction process and results in an instantaneous local high temperature, which favors the synthesis of hexagonal BN.

The formation mechanism of BN hollow spheres is proposed. In this reaction system, metallic sodium droplets, which form owing to reaction heat generated from the exothermic reaction, may act as templates to form BN hollow spheres. When the reaction temperature reaches 350 °C, NH$_4$Cl (bp 337.8 °C) and BBr$_3$ (bp 90 °C) begin to vaporize and react with sodium (mp 97.8 °C). Because of the strongly exothermic reaction, the local temperature near the surface of sodium is very high and the sodium vaporizes to form many small droplets. Subsequently, the coreduction reaction takes place on the surface of the sodium droplets, which is a key step and may result in the formation of BN shell on the sodium core. As the reaction continues, the amount of sodium becomes depleted and the shell gradually thickens, resulting finally in hollow sphere with a polycrystalline shell. In order to understand the formation mechanism of BN hollow spheres, further studies are underway.

In summary, we have succeeded in synthesizing hexagonal BN flakes and hollow spheres of 50–200 nm in diameter by coreduction of NH$_4$Cl and BBr$_3$ using metallic sodium as reductant at 350 °C. The hollow spheres formation mechanism of metallic sodium droplets acting as templates is proposed.

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