Synthesis of Whisker-like Boron Nitride by a Diamine Thermal Method

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In this paper we described the synthesis of nanocrystalline boron nitride (BN) with whisker-like morphology by the reaction of boron and diamine hydrate at 550 °C for 10 h. Characterizing by XRD, FTIR, XPS, TEM, the composition and morphology of the product were confirmed.

Boron nitride is an important material, which is widely used because of its advantageous properties such as chemical inertness, extreme hardness, high thermal conductivity, low dielectric constant, and high mechanical strength.[1,2] Up to now, there have been a series of reports on BN synthesis, such as the carbothermic reduction of boron oxide,[3] the direct reaction of boron and nitrogen, pyrolysis of $(HBNH)_3$,[4] direct nitriding of boron acid with ammonia gas.[5] Recently, needle-like and hollow spherical boron nitride powders have been synthesized by reducing the boron source, such as NH_4BF_4, BBr_3, MgB_2 with Zn, NaN_3, Li_3N, or $NaNH_2$, which also serve as nitrogen source.[6–9]

In this paper, we report the synthesis of nanocrystalline boron nitride (BN) with whisker-like morphology by the direct reaction of boron and diamine hydrate. To our knowledge, no reports on such wok are found in the literature.

In a typical procedure, 1.08 g (0.1 mol) of B and excess amount of $N_2H_4 \cdot H_2O$ (25 mL, 85%) were put into a stainless autoclave of 30-mL capacity, then the autoclave was sealed tightly, and heated at 550 °C for 10 h. After cooling to room temperature, the product was washed with several times with diluted sodium hydroxide solution, distilled water and absolute ethanol to remove impurities. Then the gray powders were dried in a vacuum at 65 °C for 4 h.

The obtained sample was characterized by X-ray powder diffraction (XRD) 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 (FTIR) spectra were obtained using a Shimadzu IR-400 spectrometer by using pressed KBr disks.

Figure 1 shows the XRD pattern of the sample. The two main peaks at d spacings of 3.320 and 2.167 Å can be assigned to the (002) and (100) reflections of hexagonal BN with lattice constants $a = 2.527$ and $c = 6.687$ Å, which are close to the reported values of h-BN ($a = 2.504$, $c = 6.656$ Å) (JCPDS No. 34-0421). No noticeable peaks of impurities can be detected in the XRD pattern.

Figure 2 gives the FTIR spectra of the BN sample at room temperature. Two strong peaks around 1394 and 797 cm^{-1} could be observed clearly, which is assigned to the B–N stretching vi-

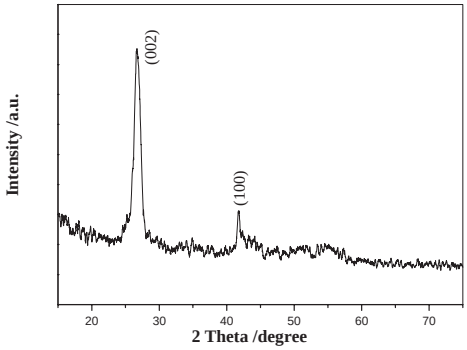

Figure 1. XRD pattern of whisker-like BN sample.

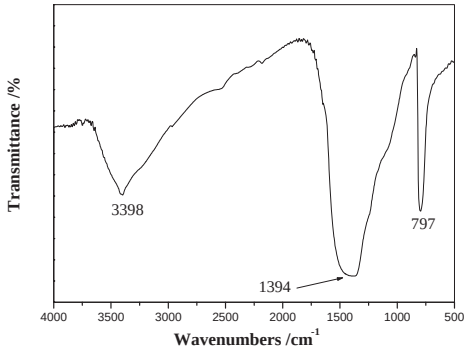

Figure 2. FTIR spectra of whisker-like BN sample.

brations and B–N–B bending vibrations, respectively. The broad absorption peak at 3398 cm^{-1} was due to water absorbed on the sample.

The product purity and element composition were determined by X-ray photoelectron spectroscopy (XPS), and the XPS spectra for BN are shown in Figure 3. The bonding energies obtained in the XPS analysis are standarized for specimen charging using C1s as the reference at 284.6 eV. No peaks of other elements except C, O, B, N, are observed on the survey spectrum. The peaks for O can be attributed to the O_2, CO_2, or H_2O adsorbed on the surface of the sample. The B1s and N1s core-level regions were examined. It is found that the binding energy of B1s is 190.75 eV and N1s 398.60 eV, which is consistent with the reported values for BN.[7] The qualification of the peak intensities reveals that the atomic ratio of B to N is 1.05:1.00, which agrees well with the chemical stoichiometric relation between B and N.

The TEM image and selected area electron diffraction (SAED) pattern of as-prepared BN are shown in Figure 4. It can be seen that the sample exhibits whisker-like morphology. The average length and diameter can be estimated at 100 and 5 nm, the aspect ratio of the whiskers is about 20. On the basis

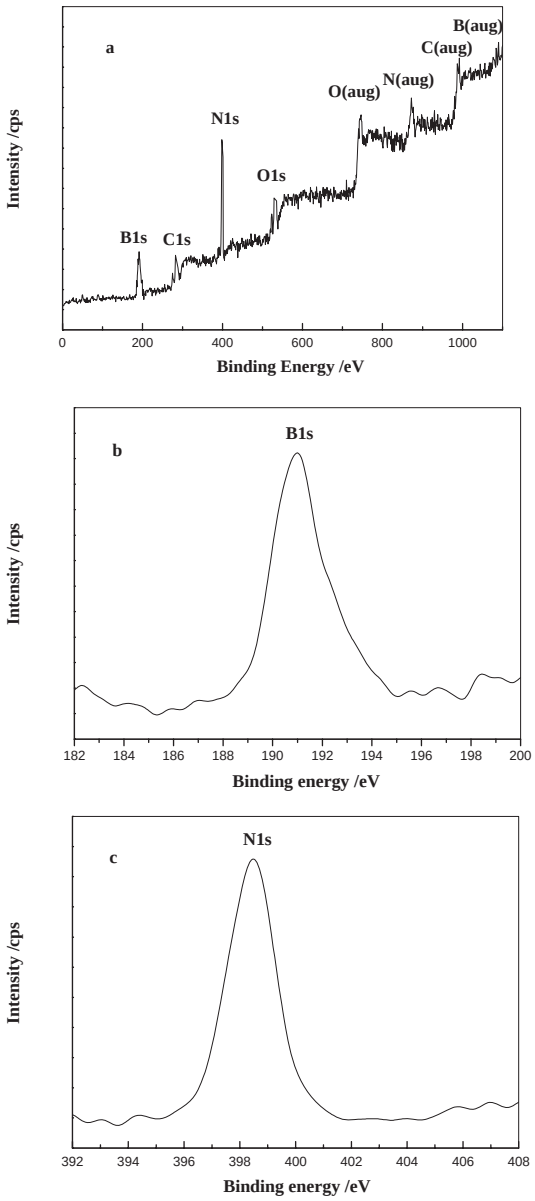

Figure 3. XPS spectra of whisker-like BN sample: (a) survey spectra; (b) B1s region; (c) N1s region.

of the observation of TEM, the yield of the whiskers is 50%. The SAED pattern of BN shows two clear diffraction rings corresponding to the crystal planes of hexagonal BN.

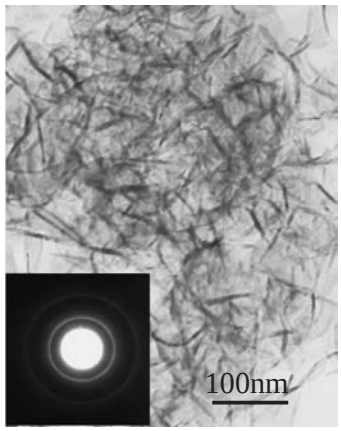

Figure 4. TEM image and SAED pattern (inset) of the BN sample.

In summary, nanocrystalline BN with whisker-like morphology were successfully synthesized using boron and diamine hydrate as the reactants at 550 °C. The product was characterized with XRD, FTIR, XPS, and TEM. XPS analysis gave the chemical formula $B_{1.05}N$.

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