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One convenient synthesis route to boron nitride nanotube

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Abstract

We describe one convenient synthesis route to boron nitride (BN) nanotube by the reaction of boron powder, iron oxide, and ammonium chloride at 600 °C for 12 h. Characterized by XRD, FTIR, XPS, TEM and SAED, the composition and morphology of the products are confirmed. The possible reaction mechanism is also discussed.

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Keywords: A. Boron nitride; A. Nanotube; B. Synthesis

1. Introduction

Boron nitride (BN) has received considerable attention due to its advantageous properties such as extreme hardness, high thermal conductivity, chemical inertness, transparency and electrically insulating performance [1,2]. These properties make BN an interesting material for many applications such as lubricants, protective and optical coatings, advanced ceramic composites, and mold release liners [3].

Up to now, there have been a series of reports on BN synthesis, such as the carbothermic reduction of boron oxide [4], the direct reaction of boron and nitrogen, pyrolysis of $(HBNH)_3$ [5], direct nitriding of boron acid with ammonia gas [6] or heating the mixture of boron and iron oxide in a flowing ammonia gas at 1300 °C [7]. Recently, Shi et al. reported that BN nanocrystalline could be synthesized by nitriding of MgB_2 with NH_4Cl and NH_4Cl–NaN_3, respectively [8].

Here, we report a convenient chemical route to synthesize BN nanotube employed ammonium chloride as nitrogen source. The reaction is carried out in an autoclave at 600 °C.

2. Experimental procedure

All the reagents used were of analytical-grade purity (purchased from Shanghai Chem. Co.). The manipulations were carried out in a dry glove box filled with N_2. In a typical procedure, an appropriate amount of B powder (0.02 mol), Fe_2O_3 (0.01 mol) and excess NH_4Cl (0.1 mol) were put into a stainless autoclave of 50 ml capacity, then the autoclave was sealed tightly, heated at 600 °C for 12 h, then cooled to room temperature naturally. The products were washed with hydrochloric acid (1 M) and distilled water to remove impurities. Then, the gray products were dried in a vacuum at 65 °C for 4 h.

The obtained samples were characterized by X-ray powder diffraction (XRD) on a Rigaku Dmax-γA X-ray

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diffractometer with Cu K_α radiation ($\lambda = 1.54178$ Å). The morphology of BN nanotube 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 non-monochromatized Mg K_α X-rays as the excitation source. Raman spectrum was performed at ambient temperature on a Spex 1403 Raman spectrometer with an argon ion laser at an excitation wavelength of 514.5 nm. Fourier transformation infrared spectroscopy (FTIR) spectra were obtained using a Shimadzu IR-400 spectrometer by using pressed KBr disks.

3. Results and discussion

Fig. 1 gives the FTIR spectra of the BN nanotube samples at room temperature. Two strong peaks around 1382 and 784 cm^{-1} could be observed clearly, which is assigned to the B–N stretching vibrations and B–N–B bending vibrations, respectively. The broad absorbed absorption peak at 3391 cm^{-1} is due to water absorbed on the sample.

Fig. 2 shows the XRD pattern of the sample. All reflections can be indexed as hexagonal BN with lattice constants $a = 2.497$ and $c = 6.685$ Å, which are close to the reported values of h-BN ($a = 2.510$ Å, $c = 6.690$ Å) (JCPDS No. 85-1068). No noticeable peaks of impurities such as Fe_2O_3 and B can be detected in the XRD pattern. The broadening nature of the XRD peaks indicates that the particles size of the samples is within nanometer scale.

The Raman spectrum of the samples is shown in Fig. 3. An active vibration band at about 1368.5 cm^{-1} is correspond to the E_{2g} symmetric vibration mode of BN [9]. Coinciding with that of the XRD and IR analysis, the as-prepared products are h-BN.

The XPS spectra of the as-prepared h-BN sample are shown in Fig. 4, in which the B1s and N1s core-level regions are examined. It shows that the sample surface consists of nitrogen and boron, with binding energies of N1s, and B1s at 398.7 and 191.5 eV, respectively. The N1s peak at 398.7 eV and B1s peak at 191.5 eV indicate BN, in good agreement with those in the literature [10]. The qualification of the peak intensities reveals that the atomic ratio of B–N is 1.02:1.00, which agrees well with the chemical stoichiometric relation between B and N.

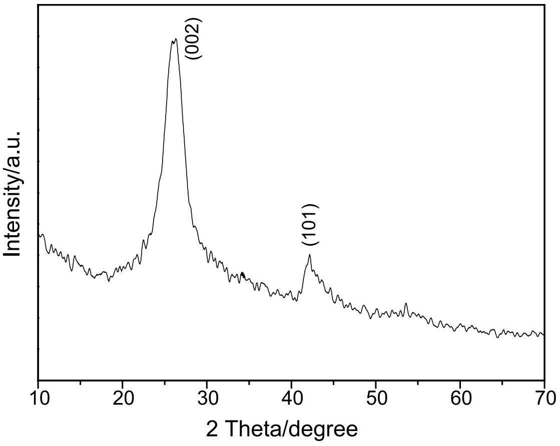

Fig. 2. XRD pattern of BN nanotube sample.

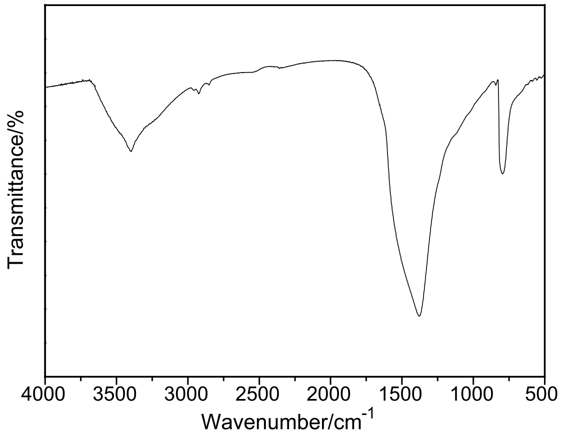

Fig. 1. FTIR spectra of BN nanotube sample.

Fig. 5 show the tubular morphologies of the as-prepared BN products. In Fig. 5(a), we find that most of the BN nanotubes are flexible and tend to bend. Most of them have lengths of up to several micrometers. Based on the observation of TEM, the estimated yield of BN nanotubes is 50%. Fig. 5(b) shows a typical nanotube. It has inner diameters of 100 nm and wall thickness of 10 nm. We can also observe that the nanotube has two obvious open ends [indicated by the arrow in Fig. 5(b)]. Typical one is characterized by its selected area electron diffraction pattern [SAED]. The SAED pattern of one BN nanotube [inset in Fig. 5(b)] is characteristic of a BN nanotube with a

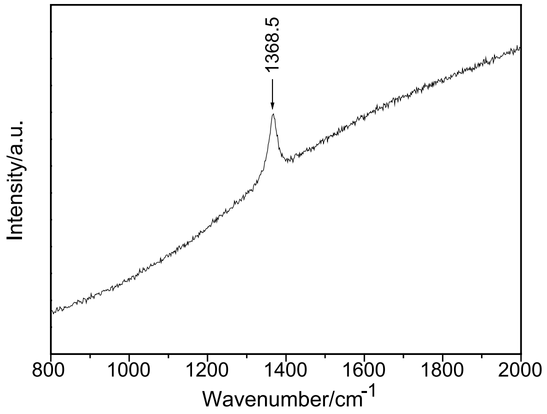

Fig. 3. Raman spectrum of the samples.

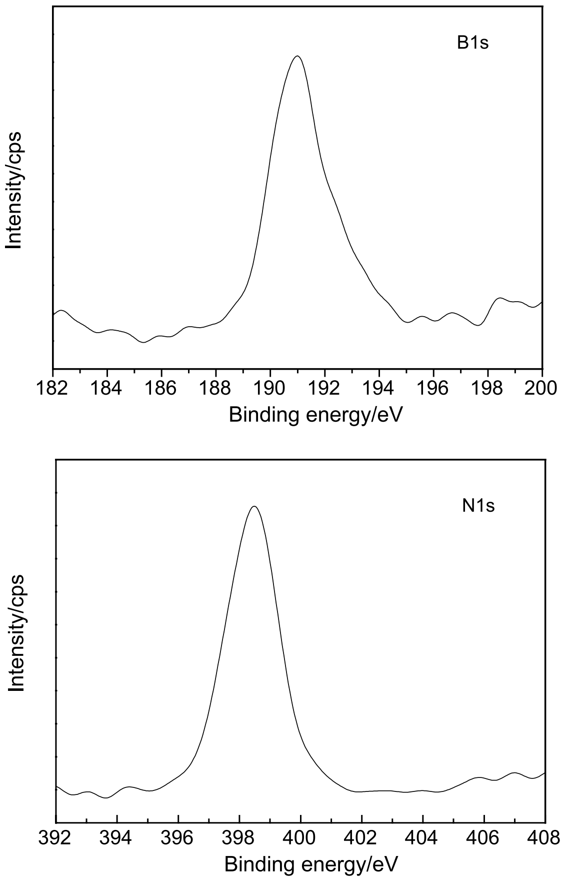

Fig. 4. XPS spectra of BN nanotube sample.

hexagonal BN crystalline (JCPDS 85-1068) structure. The rings in the pattern correspond to (002), (100) and (110).

The possible reaction mechanism of BN is proposed. To study the effects of the Fe_2O_3 on the formation of BN, another contrast experiment was carried out with the procedure similar to that mentioned in the experimental section, in which NH_4Cl, B powder served as the reactants. There was no BN obtained. Supported by the above result, we speculate that Fe_2O_3 plays a role of catalyst and oxidant. In the present route, redox reaction is taken place between elemental B and Fe_2O_3 to produce B_2O_2. At the same time, with the temperature increasing, NH_4Cl begins to decompose resulting NH_3, which contributes nitrogen source. The product BN occurs from the resultants followed between B_2O_2 and NH_3 [11].

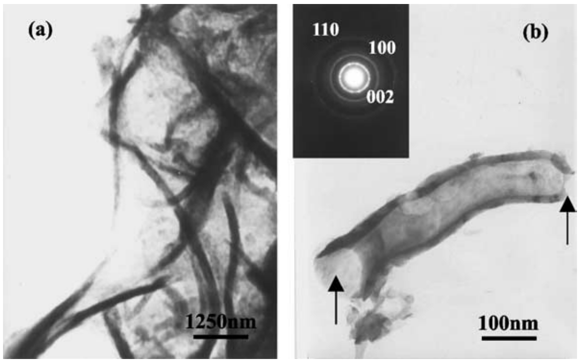

Fig. 5. TEM images showing: (a) several BN nanotubes; (b) a typical BN nanotube, (inset) SAED pattern on the BN nanotube.

4. Conclusions

In summary, BN nanotubes, with inner diameters of 100 nm, wall thickness of 10 nm and length up to several micrometers are successfully synthesized using boron and ammonium chloride as the reactants by the aid of iron oxide at a temperature of 600 °C for 12 h. The product is characterized with XRD, FTIR, XPS, Raman spectrum and TEM.

Acknowledgements

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