

Facile Synthesis and Characterization of Hexagonal Boron Nitride Nanoplates by Two-Step Route

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Large quantities of hexagonal boron nitride (h-BN) nanoplates with hexagonal morphologies have been successfully synthesized by a simple two-step route without using any template or catalyst, including combustion synthesis and then annealing processes. The phase content, morphology, and optical properties of the products have been characterized. It reveals that the obtained products are pure and of high crystallinity. The UVvis absorption spectrum indicates that the h-BN nanoplates have an optical band gap of ~6.07 eV. Strong violet-blue photoluminescence (PL) emission with a broad band ranging from 400 nm to 475 nm has been observed, indicating that the nanoplates as-grown by this simple route are promising for application in nanosize optical devices (LEDs, blue-light source, UV detector, etc.). The phonon lines features are obviously found in the PL spectra, the phonon frequency involved in these transitions is consistent with the B-N E_{2a} vibrational mode, which has been measured by the Raman spectroscopy.

I. Introduction

R $_{\rm ECENTLY,}$ much interest has been focused on nanostructures due to their peculiar, fascinating properties and a wide range of interesting potential applications which, in many cases, shall be more fruitful than for the corresponding bulk counterparts. Since the first report of carbon nanotubes (CNTs) in 1991,¹ theoretical and experimental studies on nanostructures of similar honeycomb-like networks have been stimulated intensely. Isostructural to graphite, hexagonal boron nitride (h-BN) is one of the most important III-V group materials with in-plane trigonal sp^2 bonding, in which B and N atoms substitute for C atoms in a graphitic-like sheet with almost no change in atomic spacing.^{2,3} In comparison to the carbon system, BN is a semiconductor with a wide band gap near 6 eV. Moreover, it possesses excellent mechanical properties and thermal conductivity, and is much more thermally and chemically stable than GaN and AlN; the interesting optical properties of h-BN make it a candidate for new ultraviolet-light-emitting devices.^{4,5} As the main member of BN nanomaterials, BN-nanotubes (BNNTs) have been synthesized and investigated as a potential candidate for a nanosized luminescent material.^{6,7}

The BNNTs were first reported by Chopra *et al.* via an arc-discharge route.⁸ After that, considerable efforts have been devoted to BNNTs through laser heated,⁹ carbothermal synthesis methods,¹⁰ "amide" routes,¹¹ chemical vapor deposition (CVD) synthesis methods,^{12–14} plasma-based¹⁵ and ball-milling techniques,¹⁶ in the past decade. The optical properties of single-walled BNNTs have been directly mea-

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sured by using a UV-vis spectrophotometer and show the existence of electronic transitions between 4.4 and 6.2 eV. Luminescence spectroscopies (photoluminescence, electroluminescence, cathodoluminescence, etc.) have also been employed to investigate the optical properties of BNNTs.^{18,19} In addition to the BN nanotube structure, a variety of h-BN nanomaterials have been synthesized, such as nanocones,²⁰ nanocapsules,²¹ nanohorns,²² nanorods,²³ nanowires,²⁴ core/ shell heterostructures,^{25,26} nanospheres,^{27,28}, hollow nanorib-bons,^{29,30} and nanosheets (BNNSs).^{31–36} Obviously, compared to its sister one-dimensional (1D) BNNTs, the twodimensional (2D) BN nanostructures, such as BNNSs and nannoplates^{37,38} have remained much less explored. And the detailed studies on optical properties of these 2D BN nanostructures have not yet been performed so far, due to limitation of facial fabrication methods adopted. Classical synthesis methods utilize special technologies, such as high-temperature arc plasma,⁸ a laser in a diamond anvil cell at high nitrogen pressure (5–15 GPa),⁹ CVD system,^{12–14,17} most of the methods carried out above were at high temperatures (from 1100°C to 2700°C)^{17,19,21–27}; and moreover, in most as-grown products there contained undesirable impurities (e.g., amorphous B particles and metallic or metal oxide impurities).³ Therefore, for the sake of practicality, developing facile lowcost and large-scale synthetic routes to synthesize 2D h-BN nanomaterials with high purity, high crystallinity, uniform, and fine particle size is urgently expected.

The combustion synthesis method is an effective, low-cost method for production of various industrially useful materials. Significant advantages of this synthesis route include a template and catalyst-free, low-temperature, facile procedure, and high yield. Recently, a number of important break-throughs in this method made it notable for development of new catalysts and functional nanomaterials with properties better than those for similar traditional materials.³⁹ Herein, we report a two-step facile route for growing h-BN nanoplates of bulk quantities with uniform size distribution. This method consists of combustion process and subsequent annealing under nitrogen atmospheric conditions. Significant advantages of the synthesis route include a template-free, low-temperature, facile procedure, and high yield. Detailed structure, morphology, and optical properties of the h-BN nanoplates achieved by this route have been evaluated.

II. Experimental Procedure

The combustion synthesis and annealing processes were used to fabricate the h-BN nanoplates in this work. Boric acid (H₃BO₃, AR, Sinopharm Chemical Reagent Co., Ltd, China), urea ((NH₂)₂CO, AR, Shantou Xilong Chemical Reagent Co., Ltd, China), sodium azide (NaN₃, AR, Tianjing Fucheng Chemical Reagent Co., Ltd, China), and ammonium chloride (NH₄Cl, AR, Sinopharm Chemical Reagent Co., Ltd.) were used as raw materials. In a typical process, H₃BO₃ (0.05 mol), NaN₃ (0.1 mol), NH₄Cl (0.1 mol), and (NH₂)₂CO (0.125 mol) were dissolved in 10mL de-ionized

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The phase identification of samples was carried out by a Rigaku D/Max-2400 X-ray diffractometer with Ni-filtered CuKa radiation. Scanning electron microscopy (SEM) images were taken by a Hitachi S-4800 scanning electron microscopy. Transmission electron microscopy (TEM) studies were carried with a Tecnai G2 F30 instrument operating at 300 kV. Typically, the h-BN nanoplates sample obtained at 1400°C was dispersed in de-ionized water and then was put into the ultrasonic bath for 4 h; the resultant slurry was centrifuged at 3000 rpm for 20 min; precipitate and fractions were removed, and the supernatant containing the h-BN nanoplates was collected for TEM analysis. Raman scattering spectra were obtained at room temperature using a Horiba Jobin Yvon LABRAM-HR800 laser micro-Raman spectrometer with a 532 nm laser. The laser power was about 1 mW, and provided a typical spatial resolution < 1 µm and spectral resolution better than 1 cm^{-1} in peak position. The instrument was calibrated with the peak of Si 520 cm⁻¹. Fourier transform infrared spectroscopy (FTIR) analysis was performed on a Nicolet AVATAR 360 Fourier transform infrared spectra spectrometer in KBr pellets. Diffuse reflectance spectra (DRS) of samples were collected on finely ground samples by an UV-vis spectrophotometer (PE lambda950) using BaSO₄ as a reference in the range of 200-700 nm and the reflection spectra were converted to the absorbance spectra by the Kubelka-Munk method. The photoluminescence (PL) spectra were measured by a FLS-920T fluorescence spectrophotometer with Xe 900 (450W xenon arc lamp) as the light source.

III. Results and Discussion

Figure 1 shows X-ray diffraction (XRD) patterns of the sample prepared by combustion synthesis process and those annealed at 1000°C, 1200°C, 1400°C for 6 h in a tube furnace with a N₂ ambience, respectively. Figure 1(a) is the XRD pattern of the sample prepared after combustion synthesis process, which matches closely with that described in the literature for turbostratic BN (t-BN).⁴⁰⁻⁴² It means that after combustion process the product has t-BN structure. The t-BN is a partially disordered phase of BN, whose structure is formally analogous to that of turbostratic carbon blacks and can be identified as intermediate between the



Fig. 1. XRD patterns of the BN product by combustion synthesis process ignited at 600°C in atmosphere for 10 min (a) and the samples after being annealed in a N_2 atmosphere for 6 h at 1000°C (b), 1200°C (c), and 1400°C (d).

h-BN and amorphous BN. Because of its randomness and partially disordered properties, t-BN does not have an accurate crystal structure, and its lattice constants are usually determined by reference to h-BN. In an X-ray diffraction pattern, t-BN can be indexed on the basis of the diffraction maxima of well-defined h-BN, although some reflections of h-BN alter their shape and other reflections are missing. The most characteristic changes caused by the layer disorder in turbostratic relative to h-BN are seen in a broadening of the (002) reflection at $2\theta = 26.76^{\circ}$, with the appearance of a less intense, broad peak at $2\theta = 42.54^{\circ}$ corresponding to the two-dimensional (10) reflection [merged from the (100) and (101) reflections for h-BN] and the disappearance of higher indexed reflections (004) and (110)above $2\theta = 50^{\circ}$. Figures 1(b)-(d) show XRD patterns of the samples prepared after annealing at 1000°C, 1200°C, and 1400°C for 6 h in a tube furnace with a N_2 ambient, respectively. Figure 1(b) is the XRD pattern of the product heated at 1000°C, which suggests that there is a small quantity of impurity phase associated with the h-BN. The attribution of the small peak near 34° has not been clear now, but may be attributed to the rhombohedral BN (r-BN) phases (104) line (Joint Committee on Powder Diffraction Standards [JCPDS] card 50-1504). Both h-BN and r-BN are layered materials differing in the packing of hexagonal BN-networks only. Upon thermal treatment at 1200°C and above this small peak disappeared, and all the peaks can be assigned as those of h-BN with the lattice parameters of a = 2.4979 Å and c = 6.6504 Å (JCPDS card no. 34-0421). No other crystalline phases can be detected in the patterns, which indicates that under current synthesis conditions the obtained samples has pure hexagonal structure. The intense diffraction peaks denote the high crystallinity of the h-BN obtained, as Fig. 1(d) shown. The (002) peak is intense and sharp (full width at half maximum [FWHM] ~0.48°], indicating that the crystallite size is large in the c-axis direction, indicative of well-stacked layer structures is in the products, which is matched with that illustrated in the SEM image Fig. 2(b).

Figure 2 shows typical SEM images of the as-synthesized samples by combustion [Fig. 2(a)] process and annealed sample at 1400°C for 6 h [Figs. 2(b,c)]. As Fig. 2(a) shows, a large quantity of thin wall structures can be clearly observed in the product synthesized by combustion process, but they have no regular arrangement. After being heated at 1400°C for 6 h, the samples grow into regular vertically aligned nanoplates [Fig. 2(b)], though templates have not been used. From Fig. 2(c), we find some crystalline facets of these nanoplates forming ~120° with a neighboring facet which resembles the in-plane hexagonal arrangement of atoms in h-BN. The size of most as-obtained h-BN nanoplates is in the range of 300–500 nm [Figs. 2(b,c)], and the thickness could be roughly measured to be below 30 nm.

The TEM was used to further analyze the structures of the obtained samples. Figure 3 shows the TEM images of the h-BN nanoplates dispersion sample obtained using the ultrasonic bath for 4 h in de-ionized water. Figure 3(a) is the low-magnification TEM image of the samples. The h-BN nanoplates are almost transparent indicative of their small thickness, but their thicknesses cannot be accurately deduced from the image. Notably the lateral sizes of the nanoplates become smaller compared to pristine ones that are observed by SEM [Figs. 2(b,c)] because the sonication is able to peel and cut nanoparticles induced by interactions between solvent molecules and sheets surfaces and by the ultrasonica-tion-assisted hydrolysis.⁴³ Figure 3(b) is the selected area electron diffraction (SAED) pattern taken from the region in Fig. 3(a). We find the diffraction spots form into five diffraction rings, which correspond to (002), (100), (101), (004), and (110), which indicate that these nanoplates have high crystallinity. Figures 3(c) and (d) show the high-resolution TEM image (HR-TEM) and the enlarged image of the fragment of the nanoplates. The incident electron beam was



Fig. 2. SEM images of the sample fabricated by combustion synthesis process (a) and the sample annealed in a N_2 atmosphere for 6 h at 1400°C (b, c).



Fig. 3. TEM images of the sample that annealed at 1400°C. Low-magnification image (a). Selected area electron diffraction pattern (b). High-resolution TEM images of the sample at different magnifications (c, d).

along the [002] direction, thus perpendicular to the (002) crystal face. It is well known that h-BN is structurally similar to graphite in nature, except for the different stacking sequences of atomic planes. Highly crystallized graphite possesses a Bernal (AB) stacking sequence, while h-BN is stacked with the B atoms above and beneath the corresponding N atoms. From Fig. 3(c) highly ordered alternating dots (lattice fringes) can be clearly observed. The periodicity between each two neighboring white dots is 0.22 nm. This value is equal to the (100) lattice constant of h-BN, which is consistent with that measured from the XRD pattern (Fig. 1). The hexagonal atomic arrangement of the nanoplates can be seen from the HR-TEM image in Fig. 3(d), the distance between two neighboring dots in the hexagon reveals that the spacing between B and N atoms is ~1.43 Å, which is quite close to the well-known length of a B-N bond of 1.44 Å.

Raman and FTIR spectroscopy, in which phonons are excited by inelastic scattering of light or light absorption, respectively, are convenient tools to investigate the phonon features and phase purity of samples. Figure 4 shows the high-frequency Raman spectrum of the products. As it is known, only two characteristic Raman active B–N vibrational modes, the in-phase E_{2g} mode (50 cm⁻¹) and counter-phase E_{2g} mode (1367 cm⁻¹), exist for h-BN.⁴⁴ The low-frequency rigid-layer mode in any of the prepared samples is not observable due to strong electronic scattering and a broad luminescence background. As shown in Fig. 4, a dominant sharp Raman peak at 1369cm⁻¹ has been found, which corresponds to counter-phase BN vibrational mode (E_{2g}) within BN sheets. The peak of as-prepared h-BN nanoplates is up-shifted about 2 cm⁻¹ compared with the well-known one (1367 cm⁻¹) of bulky h-BN. The FWHM of the peak is ~20cm⁻¹, which is wider than that observed in h-BN single crystals obtained by



Fig. 4. Raman spectrum of the sample annealed at 1400°C.



Fig. 5. FTIR spectrum of the sample annealed at 1400°C.

high-pressure and high-temperature synthesis $(9.1 \text{ cm}^{-1})^5$ and that observed in pure BNNTs $(13 \text{ cm}^{-1})^{.17}$ An up-shift and broadening of the E_{2g} mode are typical for small h-BN crystallites.⁴⁴ However, this value is smaller than that of the pyrolytic BN (~30 cm⁻¹)⁴⁵ and the BNNTs (27 cm⁻¹) synthesized at $1200^{\circ}C^{46}$; and is close to the BN nanosheets prepared by microwave plasma chemical vapor deposition (MPCVD) (~19 cm⁻¹).³⁴ It suggests that quality of the nanoplates from this simple route is relatively good.

More information of the lattice vibrations and composition can be gained through FTIR characterization. Figure 5 shows the typical FTIR spectrum of the products, in which two strong characteristic peaks positioned at 1378 and 811 cm⁻¹ are observed. The broad peak at 1378 cm⁻¹ is ascribed to the E_{1u} (B–N stretching vibration mode perpendicular to the *c*-axis) modes of h-BN; while the absorption band of the sharper, weaker peak at 811 cm⁻¹ could be attributed to the A_{2u} (B–N–B bending vibration mode parallel to the *c*-axis).⁴⁷ The peak around 3428 cm⁻¹ can be attributed to the water molecules absorbed on the surface of the samples. No obvious absorption peaks associated with the starting materials and carbon are observed.

To investigate the optical properties of the products for potential applications in UV–blue light emitters, UV detector, etc., the UV–vis absorption and PL spectra of the samples have been measured, shown in Figs. 6, 7 and 8. From UV–vis absorption spectrum (Fig. 6), three absorption lines are observed, which are approximately located at 204, 225, and 278 nm. The absorption line centered at 204 nm corresponds to a band gap of ~6.07 eV for these h-BN nanoplates. This energy is smaller than the reported one (centered at 6.15 eV) for h-BN micron sized crystals.⁷ The low-energy lines at ~225 nm (~5.50 eV) and 278 nm (4.45 eV) have been observed in single-walled⁷ and multiwalled BNNTs^{48,49} and were further assigned, respectively, to impurity-levels and near-edge excitonic absorption. These two lines were not present in the optical absorption spectra



Fig. 6. UV-vis spectrum of as-prepared sample annealed at 1400°C.



Fig. 7. Excitation PL spectrum ($\lambda_{em} = 406$ nm) of the sample annealed at 1400°C.



Fig. 8. Emission PL spectrum ($\lambda_{ex} = 313$ nm) of the sample annealed at 1400°C. The inset shows the phonon replica energies plotted against the number of phonons emitted.

of bulk h-BN materials and, therefore, were attributed to the rolling up of h-BN sheets.⁷ The presence of these two lines in our work indicates that optical absorption transitions at 4.45 and 5.5 eV are not intrinsic characteristic of BN-nanotubes, single-wall or multi-wall. Though the nature of these two peaks is not clear, until now, one preferred suggestion is the presence of defects in the BN-network, such as vacancies and impurities.⁵⁰ Based on first-principal quantumchemical calculations on the stability and electronic structure of self-interstitials and vacancies in h-BN structures, the

boron and nitrogen interstitials and the nitrogen vacancy have low formation energy suggesting that they are likely to occur in BN thin films.⁵¹ The vacancies introduce additional states into the gap and alter the optical properties of BN material.⁵² Hence, appearance of these two low-energy peaks in the optical absorption spectrum of the samples is indicative of existence of two kinds of defects, which is more likely to be attributed to vacancies and carbon substitutions in BN network.5

Figures 7 and 8 show representative example of excitation and emission spectra measured for the synthesized h-BN nanoplates at room temperature. The excitation spectrum contains seven UV peaks, which are divided into three sets named A, B, and C. Excitation set B, which at 289 (4.29 eV), 301 (4.12 eV), and 313 (3.96 eV) nm, could be assigned to the deep-level transitions of BO⁻ ion from the ground state $(^{1}\Sigma^{+})$ to the first excited state $(^{2}\Sigma^{+})$; excitation set A at 267 nm (4.64 eV) might be related to the second excited state of BO⁻ ion.⁵³ It is still difficult to identify the origin of the peaks of set C at 345 (3.59 eV), 362 (3.42 eV), and 380 (3.26 eV) nm. One possibility is that the excitations are caused by B or N vacancy-type defect-trapped states.^{18,29} As shown in Fig. 8, it displays intense emission between 400 and 475 nm, and tails off toward low energy, when excited at 313 nm, the maximum excitation. The broad emission band is structured and composed of three peaks centered at 406 (3.05 eV), 430 (2.88 eV), and 459 (2.70 eV) nm, respectively. The spacing among the three observed peaks is found regular. We therefore attribute the peaks at 430 (2.88 eV) and 459 (2.70 eV) nm to the phonon replicas of the band at 406 nm (3.05 eV), with respective 1 and 2 emitted phonons. The plot of the energy of each peak against the number of phonons is given in the inset of Fig. 8. The slope of the lin-ear dependence is 0.17 eV (1370 cm⁻¹) per phonon, which is in good agreement with the B–N E_{2g} vibrational mode phonon frequency (1369 cm⁻¹) of the h-BN nanoplates measured by Raman spectroscopy as shown in Fig. 4. The origin of the emission band is probably due to the deep levels presumably associated with O impurities, B, and N vacancies,54-57 and further investigation will be carried out in future work.

IV. Conclusion

Large quantities of h-BN nanoplates with hexagonal morphologies have been successfully prepared by a facile template- and catalyst- free two-step method, which was carried out at comparatively low-temperature and under normal pressure conditions. The XRD patterns, Raman, and FTIR spectra show that the products are pure and have high crystallinity. From SEM images, the synthesized nanoplates have diameters of 300-500 nm and the thickness is below 30 nm. Optical properties have been systematically investigated via UV-vis absorption spectrometry and PL spectrometry. The UV-vis absorption spectrum indicates that the samples have a band gap of ~ 6.07 eV; the presence of the two low-energy lines at ~225 nm (~5.50 eV) and at 278 nm (4.45 eV) in our work indicates that optical absorption transitions at 4.45 and 5.5 eV are not intrinsic characteristics of BN-nanotubes, single-wall or multi-wall. Strong violet-blue PL emission with a broad band ranging from 400 to 475 nm has been observed in PL spectrum, indicating that the h-BN nanoplates as-grown by this simple route are highly promising for application in nanosize optical devices (LEDs, blue-light source, UV detector, etc.). The phonon replica features are obvious in the photoluminescence spectroscopy.

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