Synthesis of ultraviolet luminescent turbostratic boron nitride powders via a novel low-temperature, low-cost, and high-yield chemical route

Qixun Guo[a,b], Yi Xie[a,b,*], Chengqi Yi[b], Lei Zhu[b], Peng Gao[b]

[a]School of Chemical & Materials Engineering, Southern YangTze University, Wuxi, Jiangsu 214036, P. R. China
[b]Nanomaterials and Nanochemistry, Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China

Abstract

A novel chemical route has been established for the synthesis of ultraviolet luminescent turbostratic boron nitride (t-BN) powders, by the reaction of NH_4BF_4 with $NaNH_2$ at 320 °C for 10 h, and the yield is as high as 90%. The synthesized brown–yellow samples were characterized by XRD, XPS, FT-IR, SAED, and HRTEM, which matched with t-BN. The electronic and optical properties of the product were investigated by PL and UV absorption. UV spectra revealed that the product has two obvious band gaps ($\sim$5.8 and 4.6 eV) and PL spectra showed that it has an ultraviolet emission at 337 nm ($\lambda_{ex} = 260$ nm). SEM image indicated that the particle size of the synthesized t-BN is mainly in the range of 1–10 μm. The renascent BF_3 and Na_3N intermediates are believed to be responsible for the growth of t-BN under mild conditions.

1. Introduction

Boron nitride (BN) is one of the most appealing materials due to its fascinating properties and applications [1–3]. It has four polymorphs with well-defined crystallographic structures, including two low-density graphite-like phases (hexagonal h-BN and rhombohedral r-BN) and two high-density diamond-like phases (cubic c-BN and wurtzite w-BN) [2]. In addition, BN has partially disordered phases, for example turbostratic boron nitride (t-BN). The two-dimensional layers in this turbostratic phase are stacked roughly parallel to each other but show random rotation and translation about the layer normal [4]. Suppose partially disordered t-BN

becomes ordered more and more, it will finally transform into fully ordered h-BN, which consists of two-dimensional layers of hexagonally linked sp^2 hybridized B–N bonds, arranged in (aa′aa′aa′..) [2]. Turbostratic phase can be transformed into cubic phase by shock compression and it was regarded as the most likely intermediate phase via which shock-induced phase transformation of r-BN to c-BN proceeded under relatively low-shock pressures ($<$ 50 GPa) [5]. Shore et al. prepared tubular forms of the partially ordered t-BN by heating amorphous BN to 1100 °C [6,7].

Traditionally, high-temperature, high-pressure, or vapor deposition technologies were prerequisites to the synthesis of t-BN [1,4,6–9]. Kaner et al. obtained t-BN via a rapid solid-state-precursor synthetic route at about 850 °C within a few seconds [8]. By HR-TEM, Horiuchi et al. observed the formation of a semispiral structure of t-BN under high pressure (7.7 GPa) and high temperature (1800 °C) [9]. For the sake of practicality,

*Corresponding author. School of Chemical & Materials Engineering, Southern YangTze University, Wuxi, Jiangsu 214036, P. R. China. Fax: +865513603987.

E-mail address: yxielab@ustc.edu.cn (Y. Xie).

developing low-temperature, low-cost, and high-yield synthetic routes to BN is urgently expected. Recently, some efforts have been made to synthesize BN at relatively low temperatures (400–500 °C) by using energetical molecule BBr_3 as the boron source [10,11]. However, it is well known that boron trihalides are very expensive and dangerous reagents and hydrolyze rapidly in air, which is not suitable for the large-scale synthesis of BN.

Herein, we report a novel chemical route to synthesize ultraviolet luminescent t-BN powders at low temperature (320 °C), from commercially available low-cost starting materials, NH_4BF_4 and $NaNH_2$. The reaction scheme can be formulated as follows:

$$NH_4BF_4 + 4NaNH_2 \rightarrow t\text{-}BN + 4NaF + 4NH_3. \qquad (1)$$

It is well known that alkali metal amides are strong bases and they have significant applications in chemical synthesis [12–14]. Ionic nitrides can be prepared from amide salts by the loss of ammonia on heating [15], which enlighten us transform $NaNH_2$ to Na_3N by heating. It was reported that NH_4BF_4 would decompose and yield BF_3 and NH_3 when heated in inert gas [16,17]. The renascent Na_3N and BF_3 are excellent sources of nitrogen and boron, respectively, due to their high reactivity.

2. Experiment

All of the manipulations were performed in a glove box with flowing nitrogen gas. In a typical procedure, 1.04 g NH_4BF_4 and 1.70 g $NaNH_2$ were loaded into a 60-mL stainless steel autoclave. The autoclave was sealed and heated from room temperature to 320 °C with the speed of 10 °C/min in a furnace, and then it was maintained at 320 °C for 10 h. After that, the autoclave was cooled to room temperature naturally and then was opened carefully in a drafty place (**Caution**: *the produced NH_3 gas is an eye and nose irritant; do not stare and smell closely!*). The products were washed two times with ethanol, then washed several times with distilled water, and again washed two times with ethanol. After that, the products were dried in vacuum at 60–70 °C for several hours. Finally, about 0.23 g brown yellow powders were obtained for characterization.

Powder XRD pattern was collected with a 2θ range from 10° to 70° with the scan speed of about 2°(2θ)/ min on a Phillips X'Pert SUPER powder X-ray diffractometer with $CuK\alpha$ radiation ($\lambda = 1.5418$ Å), using a silicon wafer as the underlay. SEM image was recorded on a JEOL JSM-6700F SEM, in which the powders were directly deposited onto copper discs. SAED pattern and HRTEM image were recorded on a JEOL-2010 TEM at an acceleration voltage of 200 kV. The sample was deposited from ethanol suspensions of the product onto

amorphous carbon-coated copper grids. XPS was recorded on an ESCALab MKII instrument with $MgK\alpha$ radiation as the exciting source. Ion beam cleaning was not performed before the XPS analysis because previous studies have shown that this high-energy process results in preferential nitrogen loss and changes in nitrogen chemical environment. FT-IR was recorded with a Nicolet Model 759 Fourier transform infrared spectrometer, in transmission mode in a KBr pellet. UV–vis spectrum was obtained from powders suspended in ethanol using a Shimadzu UV–visible Recording Spectrophotometer (UV-240). Photoluminescence spectrum of dry powders was recorded with a HITACHI-850 Fluorescence Spectrophotometer.

3. Results and discussion

XRD pattern (Fig. 1) of the synthesized sample is matched closely with that described in the literatures for t-BN [4,18]. The intense 0 0 2 diffraction at $2\theta = 26.1°$ ($d = 3.41$ Å) with FWHM $\approx 3.5°$ indicates the presence of layered structures in the synthesized t-BN. A less intense, broad peak at $2\theta = 43.1°$ ($d = 2.10$ Å) with FWHM $\approx 3.8°$ corresponds to the (10) diffraction (unresolved (100) and (101) diffractions for h-BN) [7]. Because of its randomness and partially disordered properties, t-BN doesn't have an accurate crystal structure, and its lattice constants are usually determined by reference to h-BN. The lattice constants of the obtained t-BN were $c = 6.82$ Å and $a = 2.42$ Å, which is very similar to the reported data in the literature [18].

The high-resolution XPS spectra (Fig. 2) in the B1 s and N1 s regions show symmetry peaks at about 189.85 and 397.60 eV, respectively (C1s reference: 284.40 eV). These binding energies were in good agreement with those of bulk BN in the literature [19]. The atomic ratio
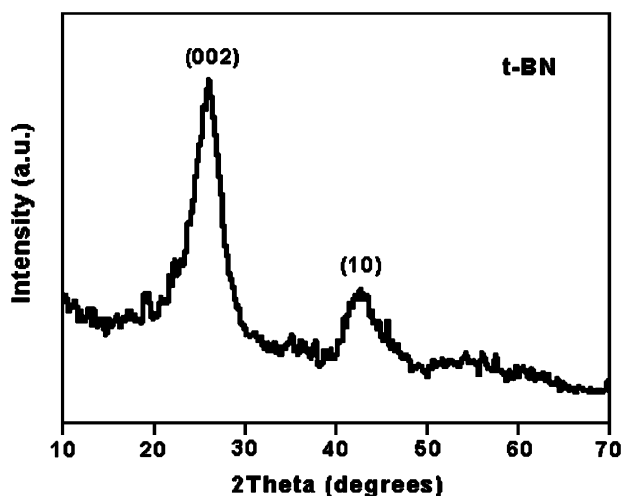

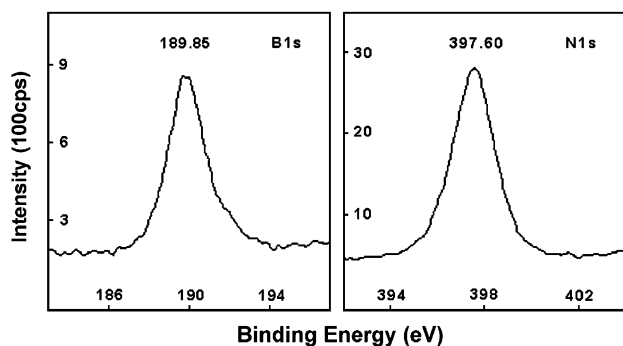Fig. 1. XRD pattern of the sample.

Fig. 2. High-resolution XPS spectra of the sample in the B1s and N1s regions.

Fig. 3. FT-IR spectrum of the sample.

Fig. 4. UV absorption spectrum (a) and PL spectrum (b) of the sample.

of B–N was about 1.04:1 through the quantification of the B1s and N1s peaks (S.F.: B, 0.13; N, 0.42), which was in good agreement with the BN stoichiometry. Besides B and N; O, C, and trace Fe and F were also detected. The atomic ratio B:N:O:C:Fe:F on the surface of the sample was 38.1:36.7:15.5: 5.8: 2.7: 1.1. It should be noted that trace Na was not detected but trace F was detected, which implied that trace B–F bonds existed on the surface of the sample. The peaks for O1s can be attributed to O_2 and H_2O molecules adsorbed on the surface of the sample.

Two strong characteristic absorption bands positioned near 1400 and 800 cm^{-1} were observed in FT-IR spectrum (Fig. 3), which is similar to the reported IR data of t-BN [7]. The band near 1400 cm^{-1} should result from the in-plane B–N TO models of the sp^2-bonded BN, while the band at about 800 cm^{-1} could be attributed to the B–N–B bonding vibration out of the plane [10]. The broad absorption band near 3400 cm^{-1} can be attributed to the stretching vibrations of residual O−H and N−H groups [7]. It was reported that B–F groups had a very strong absorption in the range of 1050–1150 cm^{-1} [20], so the weak absorption near 1100 cm^{-1} can be attributed to the residual B–F groups, which is also supported by the XPS result of the existence of trace B–F bonds.

UV absorption spectrum and PL spectrum were used to investigate the band gap energy (E_g) of the synthesized t-BN. Despite the fact that h-BN is the best-studied polymorph of BN, no agreement concerning its E_g has been obtained so far. The measured E_g values of h-BN are widely dispersed in the range between 3.6 and 7.1 eV, according to the data available in the literature [21]. Herein, we report our measured E_g values of t-BN. UV absorption spectrum (Fig. 4a) shows two intense absorption bands near 216 and 271 nm, which correspond to the two estimated E_g values of ~5.8 and 4.6 eV, respectively. These E_g values are comparable to the reported E_g data of BN in the literatures cited by Solozhenko et al., which were also measured by absorption spectra [21]. Our obtained t-BN shows two
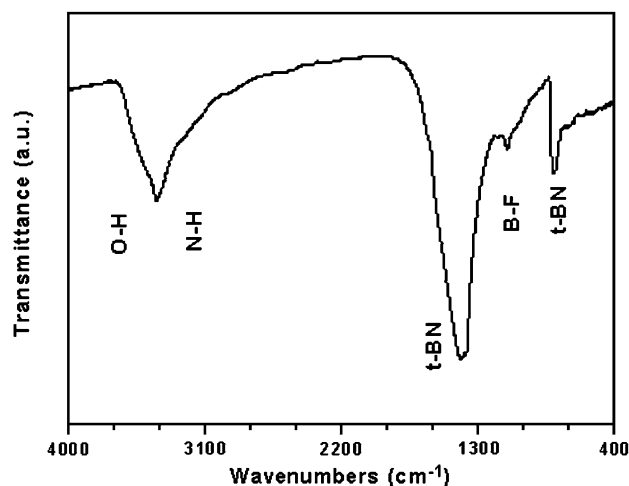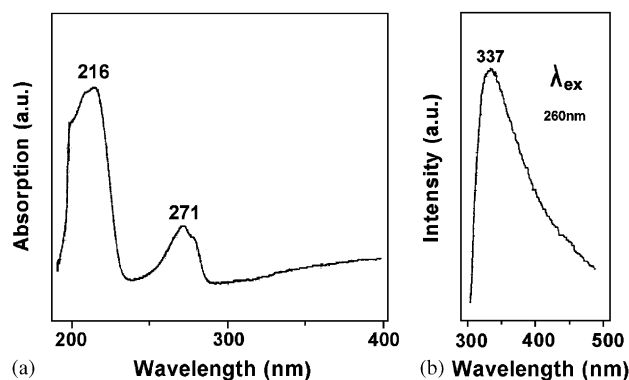
absorption bandgaps, one stronger and the other weaker. The weaker one may be associated with the existence of minor N–H group in the synthesized t-BN. PL spectrum (Fig. 4b) showed one intense broad emission band at $\lambda_{em} = 331$ nm in the range of 300–500 nm when t-BN was excited by ultraviolet light with $\lambda_{ex} = 260$ nm. The corresponding E_g value is ~3.8 eV, which is close to the E_g values of ~3.7 and ~4.0 eV determined by laser-induced fluorescence measurement [18,21]. This PL spectrum is very similar to the reported luminescence data of t-BN ($\lambda_{em} = 340$ nm) in the literature [18], which supports the conclusion that our synthesized BN is t-BN. It should be noted that the reported colors of most t-BN samples were off-white or dark, while our samples were brown yellow, which suggests that the as-prepared products may possess interesting electronic and optical properties.

SEM image (Fig. 5) of the synthesized t-BN powders shows that the particle size is mainly in the range of 1–10 μm. TEM image (not shown here) of the sample indicates that the synthesized t-BN had an irregular
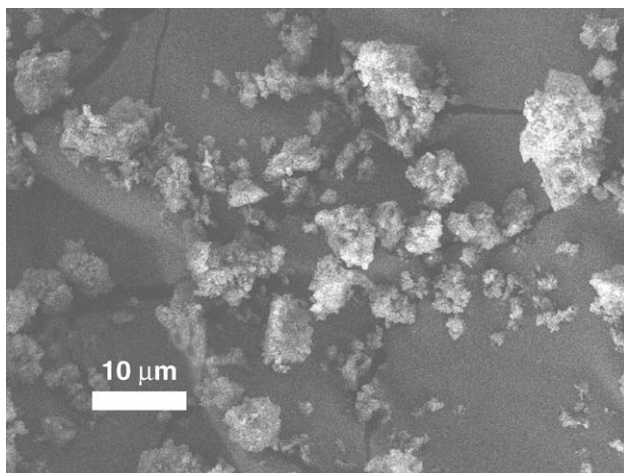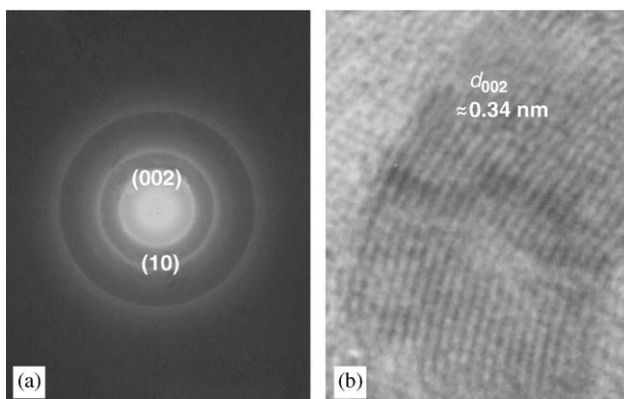
Fig. 5. SEM image of the sample.

Fig. 6. SAED pattern (a) and HRTEM image (b) of the sample.

filmy morphology with curly edges. The diffraction rings in the SAED pattern (Fig. 6a) can be indexed as the (002) and (10) reflections by reference to the XRD pattern of hexagonal boron nitride (h-BN) [7,22]. HRTEM image (Fig. 6b) indicates that the microstructure of the t-BN is characterized by the curly layered structure, which again supports that the synthesized BN is t-BN. The lattice spacing in HRTEM image was measured to be ~0.34 nm, which is close to the value of the (002) spacing (~0.33 nm) of h-BN.

4. Conclusions

In summary, we described a novel chemical route to the low temperature, low-cost, and high-yield synthesis of ultraviolet luminescent t-BN powders by the reaction of NH_4BF_4 with $NaNH_2$. This ultraviolet luminescent t-BN, synthesized reproducibly in large quantities under mild conditions, provides researchers with an opportunity to expediently investigate its electrical and optical characteristics and structure transformations in detail. The renascent BF_3 and Na_3N intermediates are believed to be responsible for the growth of t-BN under mild conditions. Our reaction strategy will give researchers a new guideline for the chemical synthesis of nitrides and borides under mild conditions.

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