New Boron Nitride Whiskers: Showing Strong Ultraviolet and Visible Light Luminescence

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Boron nitride whiskers with a special structure have been synthesized by a thermal reaction process. The as-prepared BN whiskers have a length of tens of micrometers and a mean diameter of 500 nm. High-resolution TEM analysis shows that the as-prepared BN whiskers can be described as a nanofiber-interweaved network. Infrared and electron energy loss spectra reveal that the BN whiskers are composed of both σ-sp^2 and σ-sp^3 chemical bonds. The UV−vis absorption spectrum displays the energy band gap of the BN whiskers and multiple fine absorption peaks of the phonon−electron coupling. Both photoluminescence (PL) and cathodoluminescence (CL) measurements show the specially structured BN emits strong UV and visible luminescences, which is a promising material for deep-blue and UV applications.

Introduction

Boron nitride is one of the important non-oxide materials, and exists in the form of hexagonal BN (HBN), cubic BN (CBN), turbostratic BN (TBN), wurtzitic BN (WBN), rhombohedral BN (RBN), and explosive BN (EBN).[1] HBN and CBN are the two main forms among these boron nitrides. The common characteristics of BN are the high thermal conductivity, high electrical resistivity, and chemical inertness. HBN is a graphite-like material,[2] which has potential applications such as high-temperature crucibles, fibers, coatings, and lubricants. CBN is a diamond-like material, which has the highest band gap among all the known covalently bonded materials so far; therefore, it is a promising material for deep-blue and UV applications.[3]

There is considerable research on electronic and luminescent properties of BN. The measured and calculated values of the HBN band gap energy (E_g) are widely dispersed in the range from 3.6 to 7.1 eV.[4] The band gap energy of CBN is generally affirmed to be larger than 6.4 eV.[5] The luminescence properties of both BN bulk crystals and BN polycrystalline films have been investigated with various methods, such as cathodoluminescence (CL), photoluminescence (PL), thermoluminescence, electroluminescence, and ionoluminescence. The reported results show that CBN has promising optical properties, but the difficulty in preparation limits its application. In this work, we report a new BN, i.e., BN whiskers interweaved by BN nanofibers, which emit a strong ultraviolet and visible luminescence. The structure and properties of the as-prepared BN whiskers have been characterized and discussed in comparison with those of the previously reported BN.

Experimental Section

The BN whiskers were prepared using a B−N−O precursor,[6] which was calcined at 500 °C in air for 2 h and at 800 °C in a nitrogen atmosphere for 1 h. The as-prepared yellow precursor was divided into two portions: one is put into a graphite crucible; the other is on a graphite disk located above the graphite crucible. The graphite crucible containing graphite powders was located below the graphite crucible filled with B−N−O precursor. All the components were enclosed in a graphite susceptor that was held in a flowing N$_2$ atmosphere (1.5 L/min.) An induction furnace was used for heating the susceptor. The temperature of the susceptor was controlled to ensure that B−N−O precursor in the crucible was heated to 1750 °C, the B−N−O precursor on the graphite disk was heated to 1100 °C, and graphite powder was heated to 1500 °C. The N$_2$/H$_2$O stream was managed to pass through graphite powders and the B−N−O precursor. After the process was conducted for about 1.5 h, products were collected on the graphite disk.

The as-prepared product was characterized by X-ray diffraction (XRD), PL, UV−vis absorption, and infrared (IR) spectroscopy. A JEM-3000F (JEOL) high-resolution transmission electron microscope operated at 300 kV was attached to a parallel detection Gatan-666 electron energy loss spectrometer and an energy-dispersive X-ray analyzer. CL spectroscopy was carried out using a high-spatial-resolution and low-energy CL (LE-CL) system and a thermal field emission scanning electron microscope (Hitachi S4200).

Results and Discussion

Thermal decomposition (TD) of melamine diborate produced HBN and TBN.[6] BN nanotubes were synthesized by a chemical vapor deposition (CVD) method using melamine diborate as precursor.[7] The method used in this work can be described as a combination of thermal decomposition and chemical vapor deposition (TD−CVD). B−N−O precursors were heated at 1750 °C and give out vapor products which can be used to form BN nanotubes.[7] When the B−N−O precursors were decomposed in the atmosphere of the vapors at 1100 °C, BN whiskers with special structures were obtained, as shown in Figure 1. The as-prepared BN whiskers have an average diameter of ca. 500 nm (Figure 1a). The whiskers have a length up to tens of micrometers. The high-resolution transmission electron microscopy (HRTEM) image shows that these whiskers are composed of interweaved nanofibers with an average diameter of ca. 2

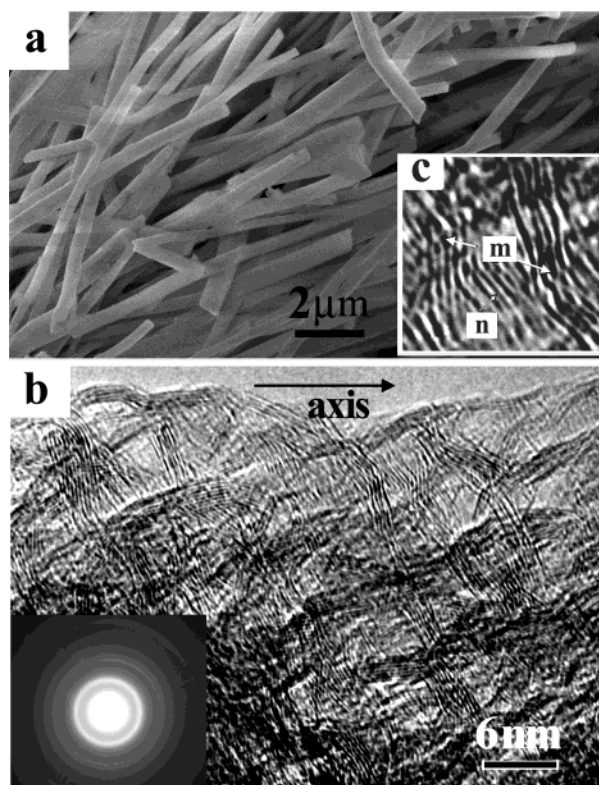* To whom correspondence should be addressed. Fax: +81-298-51-6280. E-mail: Yingchunzhu@yahoo.com.

Figure 1. Morphologies of the as-prepared BN whiskers. (a) SEM image of BN whiskers. (b) HRTEM image of the as-prepared BN whiskers. The inset is the ED pattern of the whiskers. (c) Magnified HRTEM images of the BN nanowire. The parallel structures indicated by "n" may be sp²-hybridized graphite-like BN structures; the cross-linked structures indicated by "m" may be sp³-hybridized BN structures.

nm (Figure 1b). The magnified image reveals that BN nanofibers mainly have a layered graphite-like structure with sp²-hybridized chemical bonding. Cross-linked sp³-hybridized structures were also found as shown in Figure 1c. The electron diffraction pattern is diffraction rings, indicating a polycrystalline characteristic (the inset of Figure 1b). The XRD pattern shows two broad peaks similar to those of HBN. The as-prepared BN seems to be analogous to TBN; however, the structure and properties of the as-prepared BN are quite different from those of TBN as confirmed by electron energy loss spectroscopy (EELS), IR, UV−vis absorption, PL, and CL analyses.

The electron energy loss spectrum of the whiskers shows the B and N K edges at 188 and 401 eV, respectively (Figure 2a). The sharp π^* and σ^* peaks are typical for the sp²-hybridized layered BN structure.[8] The well-defined peaks on the right-hand side of the σ^* bands indicate the presence of the sp³-hybridized BN structure.[9] The BN nanofibers are curved drastically in the nanowire as shown in Figure 1b. The curvature of the graphite-like network induces some sp³ bonding.[10] The coexistence of sp²- and sp³-hybridized bonding in BN has been reported.[11−14] Quantitative analysis reveals that the ratio of boron to nitrogen is ca. 1:1, as confirmed by a series of EELS measurements. The composition of the whiskers is also analyzed by energy-dispersive X-ray (EDX) spectroscopy. The EDX spectrum reveals that the whiskers are composed of B and N as shown in Figure 2b. The inset in Figure 2b shows the enlargement of Figure 2b, revealing the B and N peaks.

The infrared spectrum of the as-prepared BN whiskers is presented in Figure 3, which shows strong vibrations at 800, 812, 890, 909, 1270, and 1386 cm⁻¹. HBN shows two transverse optical (TO) phonon modes at 767 (783) and 1367 (1510) cm⁻¹
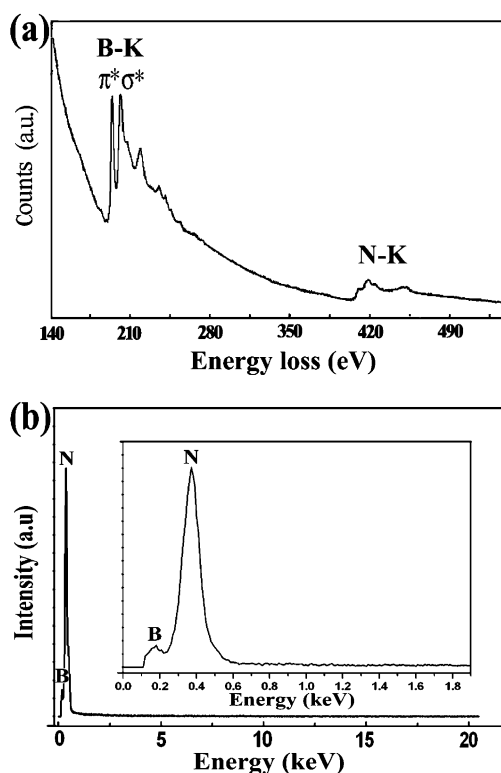

Figure 2. (a) EELS spectrum of the BN whiskers, which shows both sp²- and sp³-hybridized BN structures. (b) EDX spectrum of the BN whiskers. Inset: enlargement of (b).
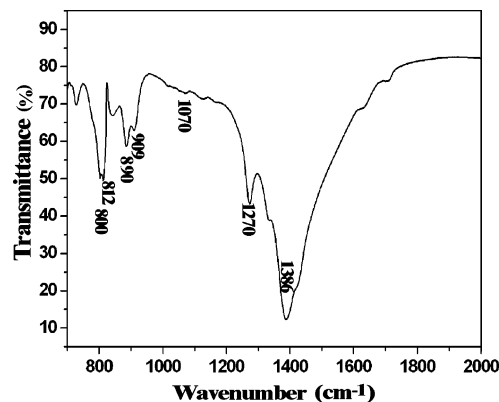

Figure 3. IR absorption spectrum of the BN whiskers.

and two longitudinal optical (LO) phonon modes at 778 (828) and 1610 (1595) cm⁻¹.[2] These phonon modes shifted to 800 and 1372 cm⁻¹ for multiwalled HBN tubes, and 811 and 1377 cm⁻¹ for polycrystalline HBN.[15] Buckled HBN shows BN vibrations at 790 and 1395 cm⁻¹.[12] Turbostratic HBN shows phonon modes at 792 and 1384 cm⁻¹. As for the as-prepared BN, the BN vibrations are shifted to 800 and 812 cm⁻¹ (LO−TO splitting) and 1386 cm⁻¹. The vibrations at 890, 909, and 1270 cm⁻¹ may correspond to the sp³-bonded BN vibrations, which are induced by the curvature of BN nanofibers.[10] These vibrations indicate the remnant of EBN which shows vibration modes around 900 and 1250 cm⁻¹.[14,16] The weak vibrations between 1000 and 1100 cm⁻¹ show the remnant of the sp³-bonded diamond-like BN.[17, 18]

The foregoing results show that the as-prepared sample is different from the boron nitrides reported previously, which may be described as a BN-nanofiber-interweaved network. The network has a distorted HBN skeleton, in which the σ-sp²-bonded skeleton is dotted with σ-sp³ chemical bonds.

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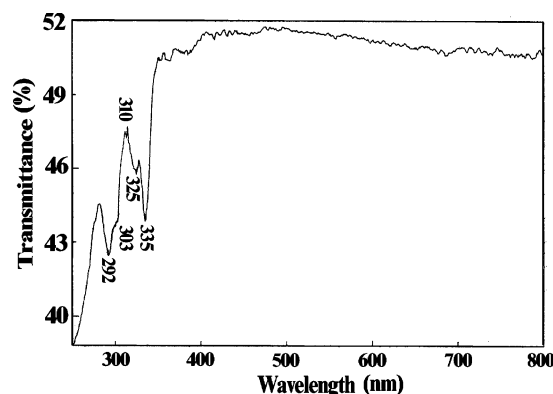*J. Phys. Chem. B, Vol. 108, No. 20, 2004* **6195**

Figure 4. UV−vis absorption spectrum of the BN whiskers. The band gap absorption is masked by the sub-bandgap absorption.
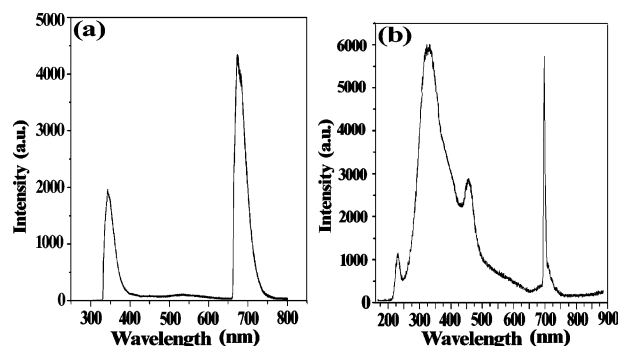

Figure 5. Luminescence spectra of the BN whiskers. (a) PL spectrum with excitation at 325 nm at room temperature. (b) CL spectrum with excitation at 5 kV recorded at 20 K.

The UV−vis absorption spectrum of the BN whiskers is presented in Figure 4. It can be seen that the absorption band edge is around 330 nm, corresponding to a band gap energy (E_g) of ca. 3.8 eV. The absorption properties reflect the electronic state of the materials, and are widely used to determine the band gap of semiconductors. The absorption properties of BN were studied by numerous researchers.[19−22] The analysis of the available literature data shows that the measured values of the BN band gap energy are widely dispersed in the range between 3.6 and 7.1 eV.[4,19−26] The dispersed values should be related to the variation of their microstructures. BN has numerous structures such as HBN, CBN, TBN, WBN, RBN, and EBN,[1] which are composed of various contents of sp³- and/or sp²-bonded structures depending on the preparation conditions. The difference between these BN structures is reflected by changes of their vibration modes, as observed by many researchers.[2,12,14−18] The structural changes certainly lead to changes in the electronic state, and resultantly lead to changes of the band gap energy. This is the reason the band gap energy of BN is reported to be widely dispersed. The as-prepared BN whiskers have a band gap energy of ca. 3.8 eV, which is close to the value reported in ref 19. Both the present BN whiskers and the BN film in ref 19 are essentially amorphous to electron diffraction, as shown in the inset in Figure 1b. The absorption band edge (330 nm) of the whiskers coincides with the strong emission bands centered at 340 and 330 nm in the PL and CL spectra, respectively, as shown in Figure 5. They may originate from absorption and emission centers associated with sp³-bonded structures, as discussed in detail as follows.

The UV absorption spectrum of the BN whiskers in Figure 4 shows multiple absorption peaks at 335, 325, 310, 303, and 292 nm. The energy differences between absorption peaks are

ca. 900, 1500, 730, and 1290 cm⁻¹, which coincide with the vibration modes shown in the infrared spectrum in Figure 3. Therefore, the multiple peaks of the UV−vis absorption band may be the reflection of the phonon−electron coupling associated with the infrared vibration modes.[27,28] Compared with the vibration spectrum, it can be seen that these energy differences are of the vibrations characteristic of both the sp³ bonding (900 and 1290 cm⁻¹) and sp² bonding (1500 cm⁻¹). This evidence indicates that these peaks may arise from absorption centers which are associated with both sp³- and sp²-bonded structures. This further indicates that the absorption center is associated with both sp³- and sp²- bonded structures. The observation also supports the assumption that the BN whiskers have a σ-sp²-bonded HBN skeleton which is dotted with σ-sp³ chemical bonds.

Figure 5a shows the photoluminescence of the BN whiskers excited with a 325 nm laser source at room temperature. The emission spectrum shows two strong narrow bands centered at ca. 340 and 700 nm. The two emission bands have an asymmetric shape, which sharply grow in intensity at the shorter wavelength side and extend to the longer wavelength. It is worth mentioning that the emission spectrum is taken from several BN whiskers under a microscope. Figure 5b shows the cathodoluminescence of BN whiskers recorded at 20 K. The CL spectrum exhibits more emission bands centered at ca. 230, 330, 450, and 700 nm due to the deep excitation energy. The luminescence spectra of the as-prepared BN whiskers are different from those of HBN, CBN, and TBN owing to their different structures.[4,29−32] We have prepared TBN by rf magnetron sputtering, which shows three broad PL emission bands at 360, 550 (main peak), and 686 nm. The difference in luminescence reversely indicates that the as-prepared BN is different from these boron nitrides reported previously.

The PL emission band at 340 nm in the as-prepared BN is different from that of HBN since this emission is excited by 325 nm, while HBN has no emission at 340 nm when it is excited above 310 nm.[4] Moreover, the BN whiskers show a narrow emission, while HBN shows a broad emission.[4,19] The PL band at 340 nm may correspond to the absorption band at 330 nm, which originates from the emission centers associated with sp³-bonded structures.[4,29] The emission band at 700 nm may also be associated with the sp³-bonded structures. There is no report on the PL emission band at 700 nm for HBN. The CL band at 700 nm has been observed in CBN, which is marked as a GC-1 center and suggested to originate from a vacancy-type defect.[33] It is also proposed that the emission originates from the dislocation band on the basis of the influence of high pressure on the CL spectrum.[34] The emission at 700 nm is also interpreted with the shorter charge-collection lengths or poorer electronic properties in terms of lifetime and mobility of carriers.[32] Despite the disagreement in explaining the emission mechanism, one general conclusion can be made that the 700 nm emission may originate from sp³-bonded structures, and size confinement of carriers favors the emission at 700 nm. The as-prepared BN microrods interweaved with nanofiber-like structures contain sp³-bonded structures and have a size confinement effect, and thus show strong PL and CL emission at 700 nm. The emission at 700 nm may be tentatively assigned to the defect-trapped states (vacancy-type defect).[33] The quantum confinement effect of the BN nanofibers favors the formation of defect-trapped states and results in strong luminescence emission.[35,36] The PL band at 700 nm is broader than the CL band due to the temperature difference and the different excitation depths.[34] The CL emission at 230 nm (5.4 eV) should

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be the near band gap emission of the BN whiskers,[30,31] which may originate from the HBN skeleton of the BN nanofibers. The emission at 330 nm may originate from the same emission center as the emission at 340 nm in PL. The emission at 450 nm may be a deep-level emission. The origin of some emissions cannot be confirmed at this stage of the experiments. However, more importantly, the BN whiskers composed of nanofiber-like structures are fabricated at present via the developed process, and they show strong PL and CL emission at ca. 330 and 700 nm.

Conclusions

In summary, BN whiskers interweaved with nanofibers have been synthesized by a TD−CVD method. The as-prepared BN whiskers can be described as a nanofiber-interweaved network, which has an σ-sp^2-bonded HBN skeleton dotted with σ-sp^3 chemical bonds. The σ-sp^3-bonded structure may act as the emission centers that emit strong UV and visible luminescences enhanced by the quantum confinement effect of the nanofibers.

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