New BCN Fibres for Strong Ultraviolet and Visible Light Luminescence

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Novel B_3CN_3 fibres with a special structure have been synthesized by a pyrolysis process. High-resolution TEM analysis shows that the as-prepared B_3CN_3 fibres can be described as a nanofibre-interweaved network. Strong photoluminescence at 370 nm and 700 nm from the as-prepared B_3CN_3 fibres are observed at room temperature, which suggests that B_3CN_3 is a promising ultraviolet- and visible-light-emitting material.

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The ternary BCN compounds have attracted considerable attention because of the structural similarity and the quite different physical properties of graphite and hexagonal boron nitride (h-BN). As is well known, graphite a semimetal and an excellent host material, while h-BN is an insulator that limits the intercalation properties.[1] It is believed that the hybrid ternary BCN compounds, depending on the structure and composition, can manifest the intermediate tunable properties between the extremes for carbon and BN. This suggests potential applications as semiconductors, photoelectric devices, electrode materials, etc.[2] BCN compounds (powders, films, nanotube and nanofibres) with various composition and structures have been synthesized by many methods such as nitridation of solid-phase precursor,[3] pyrolysis of solid-phase,[4] CVD,[5] PVD,[6] high temperature and high pressure techniques[7] and shock synthesis (mechanical milling).[8] So far, mainly carbon-rich BCN ternary phases have been reported in the literature. However, there is a lack of reports on the synthesis of nitrogen-rich BCN compounds.

Light-emitting materials have significant applications in light-emitting diodes (LEDs), semiconductor laser diodes (LDs) and digital versatile discs (DVDs).[9] As semiconductors, the study of photoluminescence (PL) from the BCN compounds has been followed with interest since 1991, the luminescence was firstly observed in a wide range (300–500 nm) with a peak at 375 nm (3.3 eV), which was effectively excited by light near 310 nm (4.0 eV).[10] Then Watanabe *et al.*[11] reported PL from the BC_2N thin films with peak intensity at 580–600 nm at both 4.2 K and room temperature, which is a particularly reliable composition of the BCN compounds. Strong PL peaked at 430 nm was also detected on the $B_{42}C_{33}N_{25}$ thin films using the 380 nm irradiation, which implies a band gap of about 3.0 eV.[12] Bai *et al.*[13] synthesized large-scale highly aligned BCN nanofibres with various composition and found that the photoluminescence peak wavelength shifts in the range of 470–390 nm by changing the compositions of the BCN nanofibres, which shows an interesting blue and violet-light-emitting material with adjustable optical properties.

In this Letter, we prepare new nitrogen-rich BCN fibres with an empirical formula B_3CN_3 by pyrolysis of a precursor, which emit strong ultraviolet and visible luminescence at room temperature. The strong light emission property of the BCN fibres suggests a new candidate for future optoelectronic applications such as DVDs for higher storage capacity and LDs for undersea optical communications.

The precursor was synthesized by stirring a hot solution of melamine and boric acid at 95°C for 15 min, which was followed by natural cooling to room temperature. Then white fibre-like crystals precipitated gradually. The solution was kept under room temperature for 12 h to fulfill the precipitation process. The white precipitates were filtered and dried at 70°C for 24 h to obtain the precursor. Pyrolysis of the precursor was performed in a graphite furnace with graphite crucible under flowing N_2 at 1900°C for 3 h. Further annealing at 550°C in air for 2 h was applied to eliminate the free carbon.

The morphology and structure of the pyrolysis product were determined by scanning electron microscopy (JSM-5900) and high-resolution transmission electron microscopy (JEM-2010, operated at 200 kV). The composition of the pyrolysis product was determined by x-ray photoelectron spectrometer (VG ESCAlab MK-2, Mg K_α radiation). Perkin-Elmer LS50-B fluorescence spectrometry was used for the room-temperature PL experiments of the pyrolysis product.

The BCN fibres have the same crystal shape as the precursor (Fig. 1(a)), with an exception that the crystal size is obviously decreased as compared with that of the precursor. By controlling the cooling rule in synthesizing the precursor precisely, it is possible to further increase the crystal size of the precursor and resultantly the BCN fibres. The high-resolution transmission electron microscopy image shows that these fibres are composed of interwoven nanofibres

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with an average diameter of about 2 nm (Fig. 1(b)). The electron diffraction pattern is diffraction rings, indicating a polycrystalline characteristic (inset in Fig. 1(b)). The XRD pattern of the BCN fibres shows turbostratic graphite-like structure with broad (002) and (100) reflections, which is consistent with those of BCN reported in the literature.[3,14]

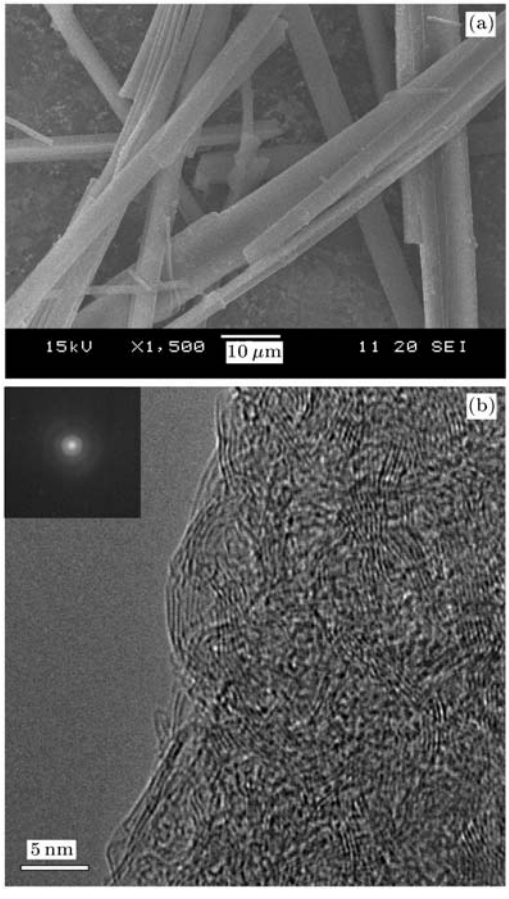


Fig. 1. Morphologies of the as-prepared B_3CN_3 fibres. (a) SEM image of the B_3CN_3 fibres. (b) HRTEM image of the B_3CN_3 fibres. Inset: the ED pattern of the fibres.

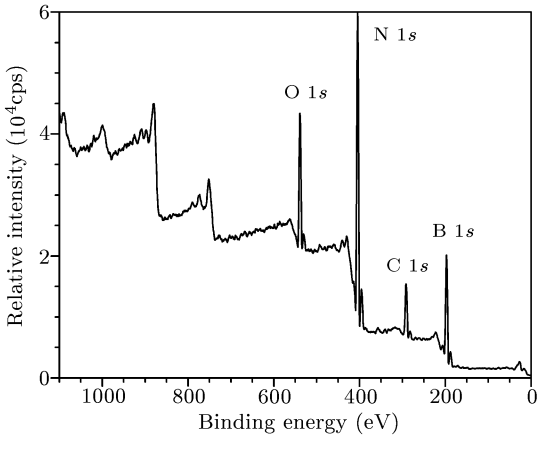


Fig. 2. XPS spectrum of the B_3CN_3 fibres.

The XPS analysis indicates that the product predominately consists of B, C, N elements and a small amount of O, which may be due to surface adsorption (Fig. 2). Quantitative analysis reveals that the atomic percentages of B, C, and N are 39.5, 11.63, and 37.35%, respectively, and the atomic ratio of them is believed to be 3.397:1.000:3.246. Thus an approximate composition of the BCN fibres can be described as B_3CN_3.

Light emission of the wide band gap materials may significantly extend the range of prospective applications. The PL spectra for the BCN fibres were stimulated using the 310 nm (4.0 eV) irradiation corresponding to the resonant absorption, as shown in Fig. 3. Two strong PL emissions peaked at about 370 nm (3.35 eV) and 700 nm (1.77 eV) were detected at room temperature. The PL spectrum clearly indicates that the BCN fibres are semiconductors. Simultaneously, it reversely indicates that the as-prepared BCN is different from those BCN compounds reported previously since there is no report on the PL emission band at 700 nm for the BCN compound.

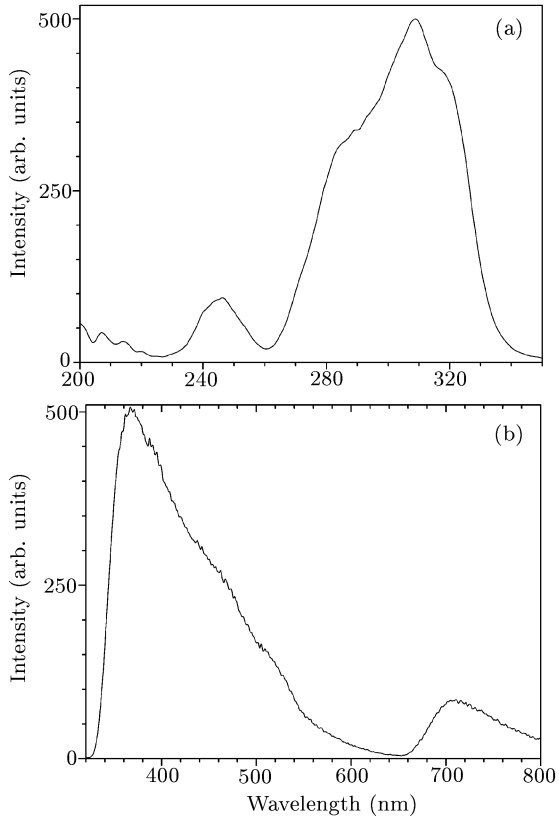


Fig. 3. Room-temperature excitation (a) and photoluminescence (b) spectra of the B_3CN_3 fibres.

As shown in Fig. 3(b), the two emission bands have an asymmetric shape, which sharply grows in intensity at the shorter wavelength side and extends to the longer wavelength, and the FWHM of the two PL

peaks is nearly 1.0 eV and 0.25 eV, respectively. These two characteristics indicate that there may be multiple channels for the spectral feature of PL on the BCN fibres. During the nonequilibrium pyrolysis process, the graphite-like layers can be randomly wedged by B and N atoms and the constituent atoms B, C, and N have different diffusion rates to the proper lattice positions. Thus, unavoidably, there are some defects that exist in the fibre structure. These defect levels distribute widely in the electronic band structure of BCN fibres, which is considered to be the main reason for the broadened PL spectra.[13] Simultaneously, such wide band gaps suggest a cubic phase for the fibres, since the hexagonal BCN structures are unlikely to have a band gap over 1.6 eV.[15] The B_3CN_3 fibres are curved drastically in the nanowire as shown in Fig. 1(b). The curvature of the graphite-like network induces some sp^3 bonding.[16] The 700 nm emission may originate from sp^3-bonded structures, and the quantum confinement effect of the BCN fibres will favour the formation of defect-trapped states and result in strong luminescence emission.[17]

In summary, a novel B_3CN_3 fibre interweaved with nanofibres has been synthesized by pyrolysis of a precursor. Strong photoluminescence emissions at 370 nm and 700 nm from the as-prepared B_3CN_3 fibres are observed at room temperature. Based on HRTEM studies, it is found that the broadened PL spectra result from defects in the B_3CN_3 fibres. Our results suggest that the B_3CN_3 fibres are interesting ultraviolet- and visible-light-emitting materials for future optoelectronic applications.

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