

Red photoluminescence BCNO synthesized from graphene oxide nanosheets*

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In this paper, we demonstrate the conversion of graphene oxide (GO) into boron carbon oxynitride (BCNO) hybrid nanosheets via a reaction with boric acid and urea, during which the boron and nitrogen atoms are incorporated into graphene nanosheets. The experimental results reveal that GO is important for the photoluminescence (PL) BCNO phosphor particles. More importantly, in this system, the prepared BCNO phosphors can be used to prepare the materials needed for red light emitting diodes (LEDs).

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Graphene is one of the most promising materials for future nano-electronics, because of its two-dimensional characteristics, which can yield perfect electron confinement in one spatial dimension. Now, the doping in graphene, especially with light elements, such as boron and nitrogen, is believed to have peculiar electrical properties^[1,2]. Through previous researches^[3,4], we found that the content of the boron nitride (BN) in boron carbon nitride (BCN) nanostructures changes the resistance of sample. Theoretical studies based on ab initio calculations indicate that ternary B-C-N materials are appealing semiconductors with a tunable band gap energy, which is primarily controlled by the material's structure and chemical composition. For example, the band gaps are about 5.5 eV for BN^[5], 2.0 eV for BC₂N^[6] and 0.5 eV for BC₃N^[7]. These properties provide great possibilities for applying BCN in electronic and optoelectronic devices.

Since 1991, the study of photoluminescence (PL) from the BCN compounds has been followed with interest. The visible light PL from the layered BC₂N compounds at 4.2 K was characterized in 1996^[8]. In addition, theoretical calculations have predicted that visible light emission with tunable wavelength can be achieved in boron carbon oxynitride (BCNO) compound^[9-13], which is metal-free and non-toxic^[14]. Ref.[15] presented the graphene oxide (GO) based BCNO hybrid nanostructure for full-color white emission.

In this paper, GO-based BCNO phosphors with successful red PL are prepared via annealing GO with boric

acid and urea.

Large and single-layer GO nanosheets were prepared using a modified hummers method with natural graphite powder. The obtained GO (1 g) was added into demonized water along with boric acid (1.5 g) and urea (18 g), followed by a period of sonication for more than 1 h. The mixture was warmed to 80 °C to form a thick, slippery liquid, which was then dried at the same temperature for 36 h in vacuum. The dried mixture was heated in atmosphere at 700 °C for 5 min to obtain the BCNO particles.

The surface morphologies of BCNO nanosheets were characterized using a scanning electron microscope (SEM, JSM-6700F) and transmission electron microscopy (TEM, JEM-2100F). The crystalline structure and chemical composition of the sample were investigated by X-ray diffraction (XRD, D8ADVANCE) and X-ray photoelectron spectroscopy (XPS, K-Alpha 1063). Ultraviolet-visible (UV-Vis) spectra were recorded with a UV-1800 spectrophotometer. The photoluminescence (PL) performance was recorded using a spectrofluorophotometer (FL3, France). The time-resolved emission spectra (TRES) were collected with an FL3 spectrophotometer.

It is speculated that the obtained powder contains GO, boron oxide and BN. This hypothesis was later proved by XRD and XPS as shown in Fig.1. In the XRD spectra, an indication of GO is found at $2\theta=11.16^\circ$. However, for the BCNO phosphors, few-layered graphene (with boron oxide) shows a broader diffraction peak at approximately 14° , which is substantially higher than that of the GO

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films. The reduced interlayer spacing in BCNO can be attributed to the effective π - π stacking of tiny graphene that contains few structural defects. We can also see the hexagonal phase of BN in Fig.1(a) and the characteristic peaks centered at 26.2° , which belong to the (002) interlayer reflection of *h*-BN. We performed XPS for BCNO in order to verify the nanostructure of the obtained powder, which are shown in Fig.1(b)—(d). The curves are deconvoluted by Gaussian fitting, thereby indicating possible bonding structures. As shown in Fig.1(b), the C1s analysis reveals two kinds of carbon, which are graphitic carbon and C-R. Compared with the C1s spectrum of pristine GO nanosheets, the C-O bonding in the BCNO disappears, which suggests the removal of oxygen functionalities from the pristine GO after the boron (B) and nitrogen (N) incorporation reaction. According to the intensity and energy of the major peak in the B1s spectra shown in Fig.1(c), the main configuration for the B atom is the B-O bond, the residual of which corresponds to B that is bonded to N, which verifies the XRD results. Furthermore, the N1s signal shown in Fig.1(d) can be deconvoluted into five peaks, of which the main one is B-N. It can be concluded that B and N primarily bond as B-N, which strongly implies the existence of BN domains in the BCNO nanosheets.

The typical SEM images of the sample are shown in Fig.2(a)—(c). BCNO has a layer-by-layer structure at the micrometer scale. It seems that the ultrathin graphene nanosheets are combined with BN (or boron oxide) powder. Morphology characterization indicates the presence of BCNO layers which are similar to few-layered graphene shown in Fig.2(d). The TEM images shown in Fig.2(e)—(f) further suggest that numerous holes exist in the GO nanosheets and lattices are also found above it (Fig.2(e) and (g)). These lattices may be sp^2 clusters in graphene quantum dots (GQDs) that are obtained during the reaction process. The high resolution-transmission electronic microscope (HR-TEM) image in the inset of Fig.2(e) indicates that the lattice's diameter is about 5—9 nm. The crystallinity of a lattice with parameter of 0.21 nm corresponds to the (1100) lattice fringes of graphene, which proves that our GQDs were fabricated from GO^[15].

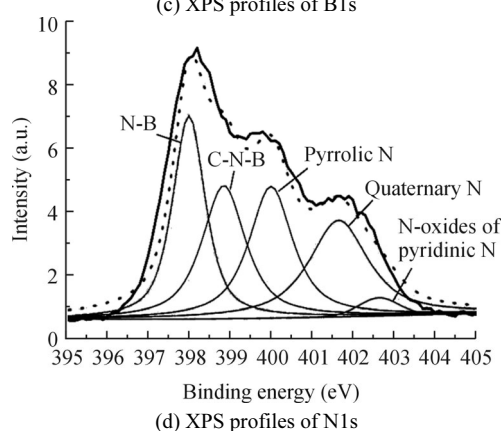
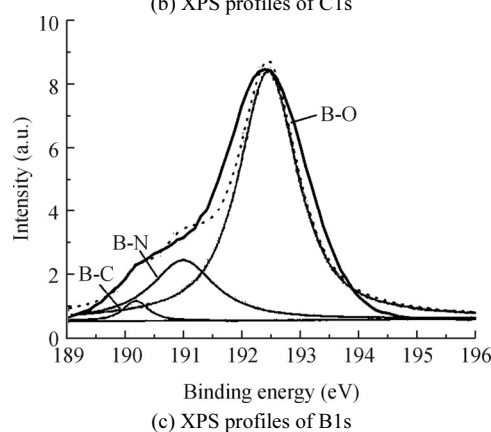
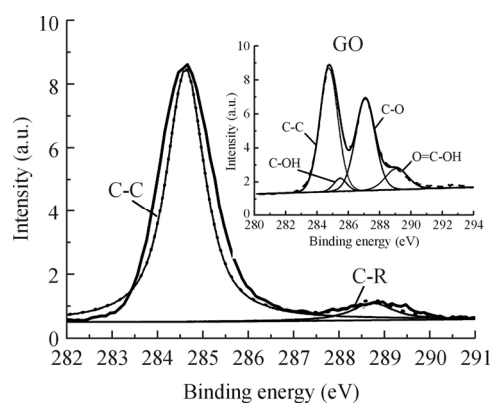
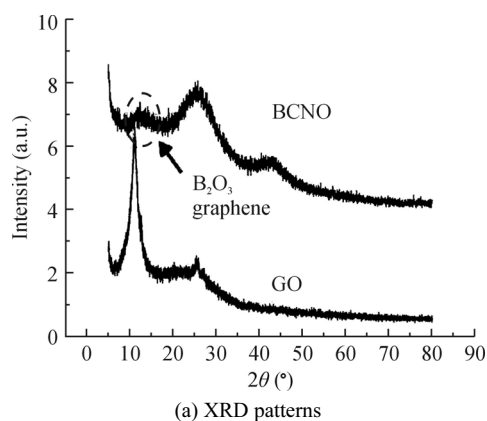


Fig.1 Compositional analysis of the BCNO phosphor compared with those of GO

The UV-Vis absorption spectra of BCNO phosphors are shown in the inset of Fig.3(a), which shows a typical absorption band assigned to the π - π^* transition of graphene sp^2 domains. Previous research has shown that the electronic properties of BCNO nanosheets are located between those of the graphene and the monolayer BN (B_2O_3). As shown in Fig.3(a), one absorption edge corresponds to a band gap of 2.6 eV, which is related to B_2O_3 (or BN). The presence of graphene domains in the BCNO nanosheets indicates the successful incorporation of B, N and O atoms. Fig.3(b) shows the PL decay curve of the BCNO phosphors after excitation at 365 nm. Research results indicate that there are three kinds of luminescence substance with lifetimes of τ_1 , τ_2 and τ_3 at 0.54 ns, 2.24 ns and 5.73 ns, respectively, which can be

assigned to various defects related to graphene (GQDs, doped and porous graphene).

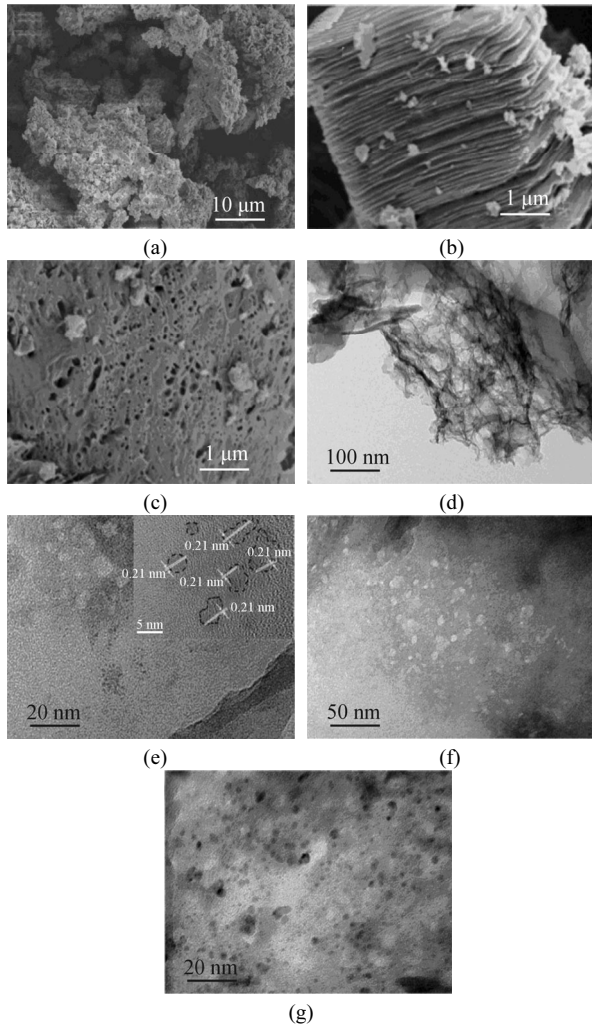


Fig.2 Microstructural analyses of (a)—(c) typical SEM images and (d)—(g) typical TEM images of the BCNO phosphor (The inset in (e) is the HR-TEM of the GQDs.)

In order to further research the optical property of the BCNO, a detailed PL absorption spectrum was carried out at room temperature, as shown in Fig.4(a). We observe a very broad emission of BCNO phosphors and the PL peak shifts to longer wavelengths, with the strongest peaks at 400 nm when excited at 365 nm. Along with the excitation wavelength changing from 360 nm to 420 nm, the BCNO phosphors exhibit an excitation-dependent PL behavior, which shows a red-shift, and the peak intensity decreases rapidly. This result may be attributed to the presence of particles with different sizes in the BCNO samples. The inset in Fig.4(a) are the optical image of the BCNO excited at 365 nm, which emits bright visible to the naked eyes. Fig.4(b) shows the Commission Internationale de l'Éclairage (CIE) diagram of the BCNO excited at 365 nm. The emission of the red lighting phosphors is located in the red region in the CIE diagram

($x=0.3214, y=0.3225$).

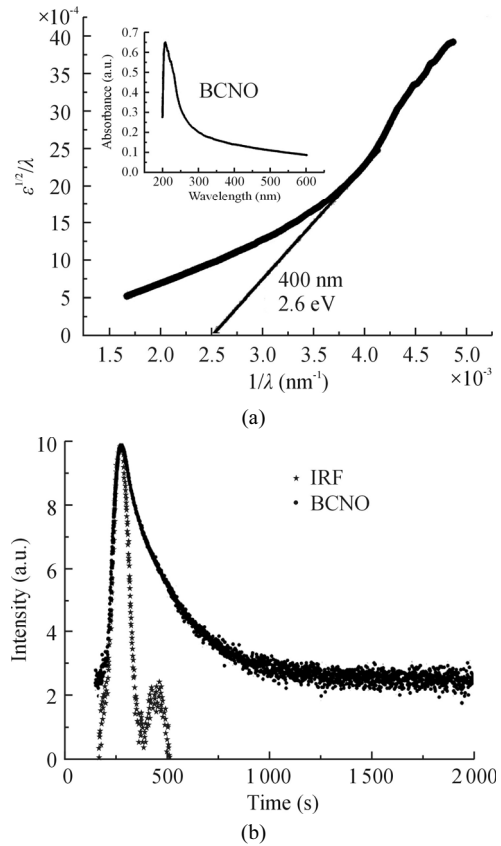
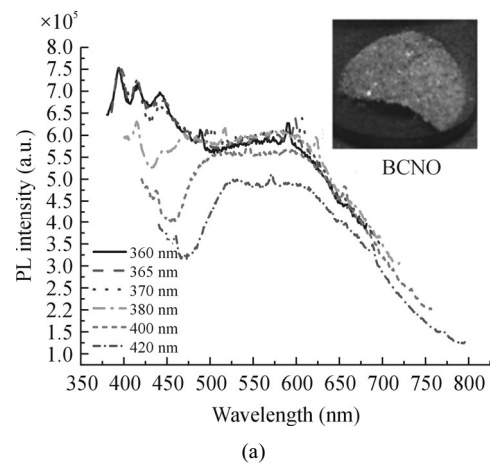


Fig.3 (a) Plot of $(\epsilon^{1/2}/\lambda)$ versus $1/\lambda$, indicating the only one band gap (The inset is UV-Vis absorption spectra of the phosphors.) (b) PL decay curve of the BCNO phosphor

Previous research has suggested the causes of the PL mechanism in BCNO powder occurs. Wang Wei-Ning *et al.*^[16] thought that the emission of the BCNO phosphors is due to the closed-shell BO^- and BO_2^- anions which act as high-efficiency luminescence centers. Liu Xiao-Feng^[17] researched the defect-related emission mechanism systematically, and thought that these emissions were assigned to different forms of carbon defects, rather than to inter-band transition or exciton emission. Based on the



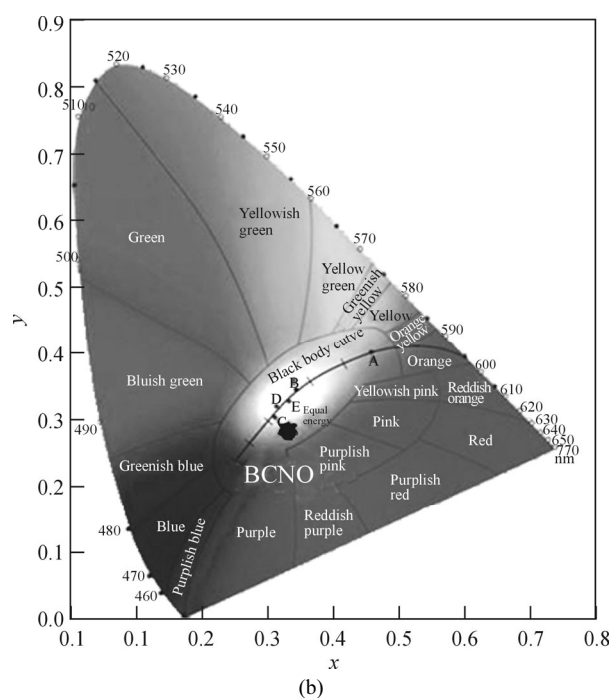


Fig.4 (a) PL spectra with excitation wavelength changing from 360 nm to 420 nm (The inset shows the optical image of the BCNO excited at 365 nm.); (b) CIE diagram under 365 nm excitation

TEM analysis, we find that GQDs and numerous holes exist in the graphene nanosheets in various dimensions, which indicates that the fluorescence mechanism is linked to the chemical structure of the graphene in BCNO phosphors. The luminescence mechanism is derived from intrinsic state emission (electron-hole recombination, quantum size effect/zig-zag sites) and defect state emission (surface energy traps). It may be the main influencing factor of the luminescence mechanism in BCNO phosphors.

We demonstrate an efficient method to simultaneously synthesize BCNO on a large scale by reacting GO with urea and boric acid. The mixture is composed of graphene, *h*-BN and boron oxide. The doped porous graphene generates electrons under excitation and transfers them to various defect carbons, which expands emission spectrum. This result suggests that the BCNO phosphors prepared here are appealing candidate for use in LEDs.

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