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Graphic entry for the Table of Contents (TOC)

We report the optimal conversion of graphene oxide (GO) into white-lighting BCNO hybrid nanostructures by one-step air oxidation with the aid of boric acid and urea.

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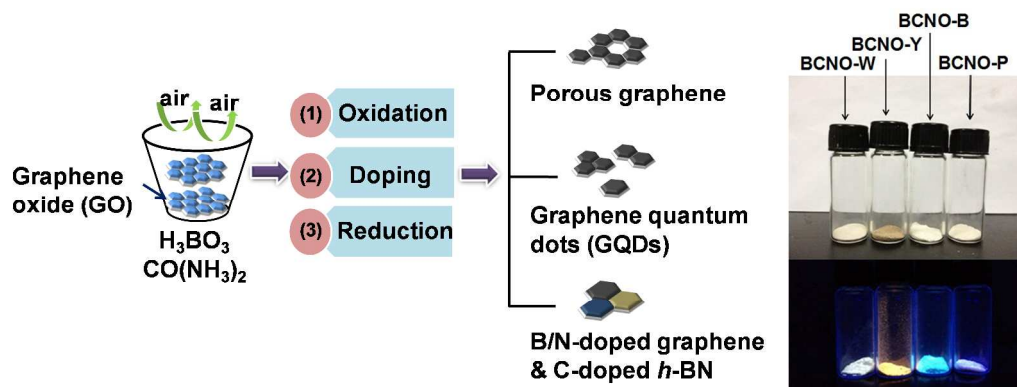
ARTICLE TYPE

Graphene oxide based BCNO hybrid nanostructures: tunable band gaps for full colour white emission

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The emission of BCNO phosphors has been easily tuned from the violet to the near red regions by varying the carbon content. Here we report the optimal conversion of graphene oxide (GO) into BCNO hybrid nanostructures by one-step air oxidation with boric acid and urea. White lighting phosphor was 10 obtained in which the doped porous graphene acts as interconnecting framework generating and transferring electrons under excitation light. Various carbon-related levels in the BN band structures play the essential role in emitting full colour white light. The quantum confinement in the various kinds of GQDs and GO are also beneficial to widen the emission spectrum.

Introduction

15 Oxynitride and nitride materials exhibit a variety of interesting optical properties widely used as host lattices for phosphors in light emitting diode (LED).[1] Recently, boron carbon oxynitride (BCNO) attracts much attention.[2] In 2008, Ogi *et al.* prepared the BCNO phosphors by reacting polyethylene glycol (PEG), boron 20 acid and urea through a one-step oxidation process,[2a] afterwards a large number of experiments explored their luminous properties in detail.[2b-f] Compared to the conversional oxynitride phosphors, these BCNO phosphors are merit of the following characteristics: rare-earth-ion free, low cost and high quantum efficiency; wide 25 excitation and wide emission in the photoluminescence (PL) spectra with adjustable peak locations. The emission of these BCNO phosphors has been easily tuned from the violet to the near red regions by varying the carbon content.[2] Based on these properties, Wang *et al.* prepared a white LED (WLED) using one 30 yellow-lighting BCNO phosphor coated on a commercial blue-lighting LED chip.[2b] However, up to now, there is no report on the direct synthesis of white-lighting BCNO phosphors. It seems much difficult for the rear-earth-ion-free candidates to generate white light.[1-2] More recently, Guo *et al.* discovered that carbon 35 quantum dots (CQDs) containing different sizes could emit white light,[3] but they found that there is a red shift from solution-state lighting to solid-state lighting. This triggers us to think that, it might be possible to obtain high efficient solid-state white-lighting BCNO phosphors by incorporating carbon components 40 of various shapes.

Graphene oxide (GO) is a marvelous candidate suitable for this target, because it can be either reduced to graphene, or further oxidized to defective smaller ones.[4] It is covalently decorated with oxygen-containing functional groups, and contains a mixture 45 of sp^2- and sp^3-hybridized carbon atoms. Manipulation of the size, shape and relative fraction of the sp^2-hybridized domains of

GO by reduction chemistry provides opportunities for tailoring its optoelectronic properties[4d-f]. The tunable PL spectra of GO during reduction are thus attributed to the variation of the relative 50 intensity ratios of PL emission from two different types of electronically excited states[4d]. It has also been reported that graphene quantum dots (GQDs) have both up-conversion and down-conversion PL properties, which widens their emission spectrum.[5] Furthermore, the bandgap of GO can also be easily 55 tuned by incorporating non-carbon elements.[4b] For example, B/N doped graphene, or BCN compounds, are expected to behave as semiconductors with tunable band gap energies, because these materials are thought to be the intermediates between graphene (0 eV) and hexagonal BN (*h*-BN, ~6.0eV). [6]

60 Based on the above results on the tunable PL spectra of BCNO and GO, we used GO as the only carbon source to make BCNO phosphors. In the present study, not only GO itself plays the role in emitting light, but what's more important is that the hybrid nanostructures which may have unexpected synergy effects, 65 opening much possibilities for white-lighting purpose.

Experimental Procedures

Materials

Boric acid (99.5%) was purchased from Taishan Shiji Co. Ltd. (Taishan, China). Urea (99.0%) was obtained from Xiangke 70 Chemical Work (Changsha, China). Graphite particles (10–15μm) were purchased from Xinghe Graphite Co. Ltd. (Qingdao, China). All these chemicals were used without further purification. Deionized water used in all the experiments was produced from a Millipore-ELIX water purification system.

75 Synthesis of BCNO phosphors

Large and single-layer GO nanosheets were prepared by a modified Hummer's method as reported[7]. As shown in electronic

supporting information, Figure S1, the obtained GO was thoroughly mixed with a various weight of boric acid and urea solution in demonized water. The mixture was warmed to 80℃ to form a thick slippery liquid, which was then dried at the same
5 temperature for 36h in vacuum. The dried mixture was then heated in air at 700-800℃ for 5 min. The samples were cooled to the room temperature and the BCNO powders were obtained.

We could obtain different lighting phosphors by varying the raw material ratios and the highest heat treatment temperatures in
10 air, which are listed in Table 1. The phosphors emitting yellow, blue, purple white light are named as BCNO-Y, BCNO-B, BCNO-P and BCNO-W respectively.

Table 1. Four typical different lighting BCNO phosphors and their preparation parameters

Phosphors	Weight ratio (GO/Boron acid/Urea)	Highest temperature in air (℃)	Powder color under solar light	Emission color excited at 365nm
BCNO-Y	20/30/600	800	Light gray	Yellow Green
BCNO-B	10/30/600	800	White	Greenish Blue
BCNO-P	20/30/600	750	White	Purperlish Blue
BCNO-W	10/30/600	750	White	White

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Characterization of BCNO phosphors

The surface morphologies of the GO and BCNO hybrid nanostructures were characterized by SEM using JSM-6700F microscope. The crystalline structure was investigated by XRD
20 on a D8ADVANCE type, using Cu Kα radiation with 2θ from 10° to 90°. UV-Vis spectra were recorded with a UV-1800 spectrophotometer and quartzcells with 1 cm path length. TEM was conducted using a JEM-2100F electron microscope at an acceleration voltage of 200 kV. XPS was investigated using K-
25 Alpha 1063 type with focused monochromatized Al Kα radiation (1486.6 eV), to determine changes in the atomic ratios and the existence of functional groups. Electron energy loss spectroscopy (EELS) and energy dispersive X-ray spectroscopy (EDS) analysis were performed using the associated equipments of SEM and
30 TEM.

The PL spectra of the BCNO phosphors were recorded using a spectrofluorophotometer (FL3, France) equipped with a xenon laser source. The EQE of the prepared particles was determined at an excitation wavelength of 365nm produced by a 150W Xe lamp
35 using an absolute PL quantum yield measurement system (Quantaurus-QY, Japan) with an A-10095-01 powder sample holder. The PL decay profiles and the time-resolved emission spectra (TRES) were collected with an FL3 spectrophotometer.

Results and Discussions

40 #### Chemical and Microstructural Analysis

As the white lighting phosphor, the BCNO-W phosphor was prepared from a mixture of GO, boric acid and urea with a weight ratio of 10/30/600. GO contains C and O with an atomic ratio of 16/9 (Figure S2). Urea is much excessive to boric acid and GO,
45 which could generate local ammonia atmosphere at high

temperatures enabling the reduction and nitrogen doping process.[8] No doubt that, air makes contribution to the oxidation. So the overall reaction is much complicated.[2] But one thing is sure, GO has much higher thermal and oxidation resistance than
50 PEG polymers.[4]

We focused on the BCNO-W phosphor to perform compositional characterizations, which are shown in Figure 1 and Figures S3 and S4. XPS full spectrum of BCNO-W (Figure S3) indicates the atomic contents of B, C, N and O are 30 at%, 18
55 at%, 21 at% and 32 at% respectively. XRD patterns (Figure 1a) indicate the existence of B_2O_3, BN and graphene (or doped graphene). The typical signal of GO at 11.2º is lost after the reaction, transferring to the typical signal of graphene at 17.5º.[4] Graphene-facilitated formation of h-BN has been observed in our
60 previous study,[6d] so the overlapped signals of BN and graphene at 26.2º and 43.4º may indicate h-BN. FT-IR analysis (Figure 1b) shows a strong and wide B-O (~1200cm^{-1}) band in BCNO-W, which covers the vibrations of C-N (1080 cm^{-1}) and B-C (1100 cm^{-1}). The strong carboxyl C-O (~1400cm^{-1}) band of GO
65 becomes nearly disappeared in BCNO-W and a new signal assigned to B-N appears at the same position.[6] The above analysis means that graphene nanosheets are present in the hybrid particles, which are isolable and surrounded by boron oxide (nitride) phases.
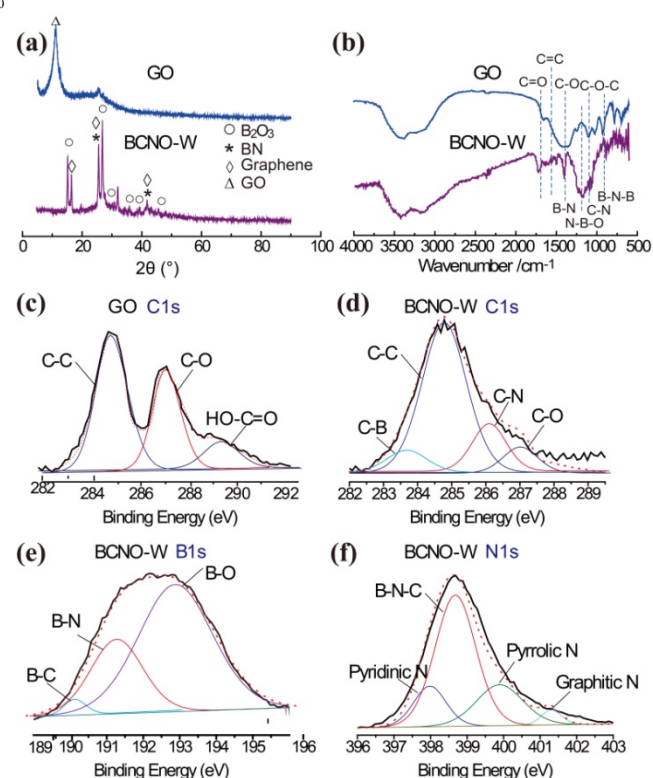
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Figure 1. Compositional analysis of the BCNO-W phosphor, compared to that of GO. (a) XRD patterns, (b) FT-IR, and XPS profiles of (c-d) C1s, (e) B1s and (f) N1s. The curves are
75 deconvolved by Gaussian fitting, thereby indicating possible bonding structures.

A deep study on the bonding structure of the BCNO-W hybrid was made using XPS C1s, B1s and N1s profiles, as shown in Figure 1d-f. According to B1s analysis (Figure 1e), the main

configuration is B-O bonding, and the rest corresponds to B-N and B-C bonding.[6c-e] It strongly indicates a large fraction of boron oxide phase. The N1s signal (Figure 1f) can be deconvoluted into four peaks, among which the main one is B-N-C bonding.[6-7] The

5 C1s analysis reveals four kinds of carbon,[7b] with two new peaks emerging as C-B and C-N bonding, compared to C1s signal of GO (Figure 1c). In addition, the intensity of C-O bonding is much lower than that of GO. This indicates that GO was almost completely reduced to graphene and doped with B and N at the

10 same time.[4,6] Since nitrogen has an atomic fraction of 21 at%, the predominant B-N-C structures (more specifically, B/N doped graphene) may have a weight percent up to 50wt%. We washed the BCNO-W powder with warm deionized water and recovered reddish residue. A much reduced B-O signal is observed in the

15 B1s signal (Figure S4), indicating the removal of most boron oxide. The residue consists mainly of large layers of B-N-C type doped graphene, as indicated from N1s analysis.

Microstructural analysis is shown in the typical SEM and TEM images in Figure 2 and Figures S5-S6. Honeycomb-like

20 morphologies at the micrometer scale could also be observed (Figure 2a-b). It seems that the ultrathin graphene atomic layers are etched into micro-holes and combined by glue-like boron oxide. TEM characterizations (Figure 2c-h) demonstrate the presence of nanosheets similar to few-layered graphene.

25 Numerous nanosized holes (Figure 2e,g) and nanosized inclusions (Figure 2d, f) could be observed. These inclusions were studied in high resolution and are shown in Figure 2d and 2h. They have clear lattice structures with lattice parameters of 0.34nm or 0.21 nm, corresponding to h-BN or the (1100) lattice

30 fringes of sp^2-type graphene.[8c] Since the diameters are down to 10 nm, they are typical GQDs.[5]

Electron energy loss spectroscopy (EELS) and energy dispersive X-ray spectroscopy (EDS) analysis for the BCNO-W phosphor are shown in Figure 3 and Figure S6 respectively. Four

35 ionization edges at about 188, 284, 400, and 530 eV are clearly apparent, corresponding to the characteristic K-edges of B, C, N, and O, respectively[2]. The results in EDS also confirmed that the particles are composed of B, C, N, and O atoms, with an atomic ratio to be 31:10:30:29. The phosphor was covalently bonded to

40 B, N, and O atoms with a soft (sp^2 hybridization) carbon framework via π^* and σ^* bands, indicating the B-C-N-O quaternary compound.

The incorporation of B and N into graphene (B/N doped graphene) has been studied in detail in our previous report[6d],

45 which uses a similar process derived from the same raw materials. So during the heat treatment in air, GO is changing in three different and combined ways: oxidation, doping, and reduction, as shown in Figure 4. GO is oxidized becoming porous both at the micro- and nano- scales. They are even splitting into much

50 smaller ones down to the quantum dots level. The removal of epoxy, carbonyl and carboxyl groups facilitates this etching and cutting process.[9] Both the high temperature and the local ammonia reductive atmosphere make contributions to the O-removal, leading to fully reduced GO, namely, graphene.[4,8-9] At

55 the same time, boron oxide and urea or ammonia react with GO to make B and N co-doping, leading to a large fraction of B-N-C type doped graphene.[7c-e] As expected, a variety of graphene-like carbon of different sizes can be formed in the process.
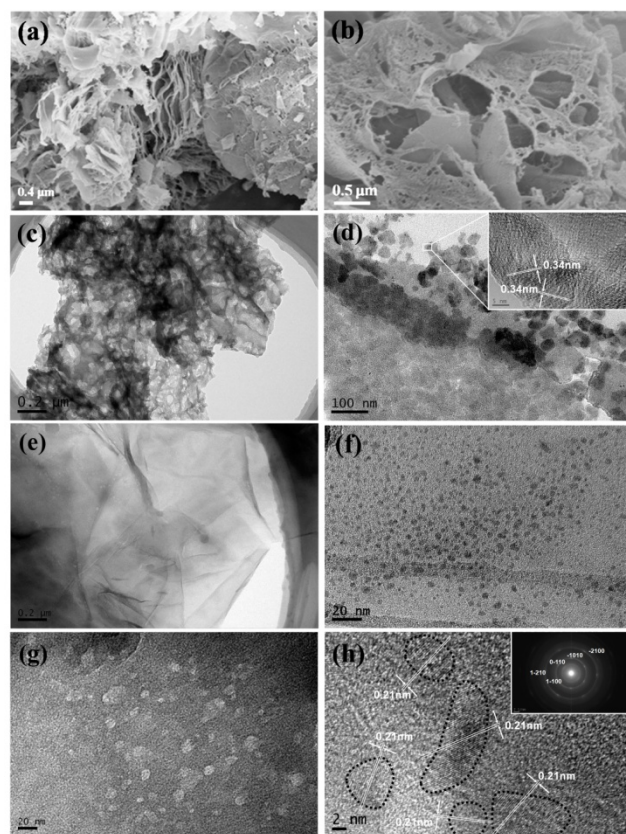

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Figure 2. Microstructural analysis of the BCNO-W phosphor. (a-b) Typical SEM images and (c-h) typical TEM images.
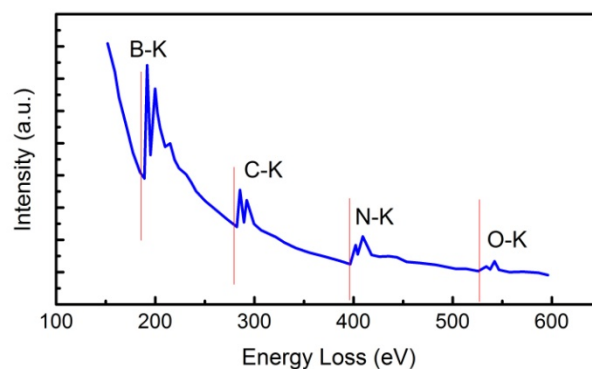

Figure 3. EELS analysis of the BCNO-W phosphor, indicating
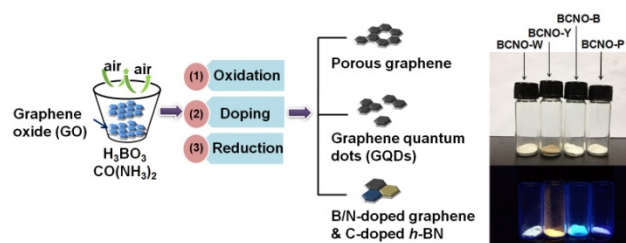65 the B-C-N-O quaternary compound.

Figure 4. Schematic illustration of the evolution of GO in the one-step air oxidation process. Associated are the images for typical phosphors under solar light (right up) and 365nm UV light
70 (right down).

Optical Property Analysis

The optical properties of the four typical phosphors are shown in Figure 5 and Figures S7-S8, including the PL spectra, PL decay curve, UV-Vis absorption spectra and Commission Internationale de l'Eclairage (CIE) diagram. The PL spectra (Figure S7) measured at room temperature exhibit an excitation dependent behavior. When excited at 365nm, as shown comparatively in Figure 5a, we could observe the very broad emission of BCNO-W phosphor, covering the full color range. On the contrary, the yellow, blue and purple lighting phosphors have much narrower emissions. The insets in Figure 5a are the optical images of the phosphors excited at 365 nm, emitting visible light very bright to naked eyes. The emission of the white lighting phosphors is located in the white region in the CIE diagram (x=0.292, y=0.324), as shown in Figure S8, Table 2 and Table S1. The measured external quantum efficiency (EQE) of the BCNO-W phosphor is as high as 28.2%, comparable to some rare-earth white lighting phosphors.[1] The PL decay curve in Figure 5b of BCNO-W suggests the contributions of three decay processes. The characteristic lifetime of τ_1, τ_2 and τ_3 are 2.41ns, 0.26ns and 6.34ns respectively, which can be assign to the various defects related to graphenes (GQDs, doped and porous graphene).[2e-f, 6]

The band gap of B-N-C is tunable between that of graphene and h-BN.[4,6] As shown in Figure 5c, the first absorption edge of the BCNO-W phosphor is the largest, corresponds to a band gap of 5.9 eV, belonging to h-BN phases. The second absorption edge of BCNO-W suggests a band gap of 3.4 eV, related to the B-N-C type doped graphene nanosheets.[4,6] Interestingly, we found that these two band gaps were tunble (increased) from yellow, blue and purple to white lighting phosphors. It indicates that lowering the annealing temperature or decreasing the GO loading are all beneficial to the doping and nitridation process, thus increasing the band gap of doped graphene and BN to a proper value for excitation.[6c-e]

Based on the above results, a modified PL white lighting mechanism is proposed and shown in Figure 6[2f]. The doped porous graphene acts as interconnecting framework generating and transferring electrons under excitation light. The 365nm (3.4 eV) absorption is due to the transition from the valance band to the conduction band. This means that the doping and oxidation open the band gap of graphene to 3.4 eV[6c]. BN is responsible for the light emission and the 210nm (5.9 eV) absorption is induced by the transition from the valence band to the conduction band in h-BN.[2d-f] The nitrogen vacancy level is 0.7-1.0 eV lower than the conduction band,[10] which is supposed to trap electrons forming paramagnetic luminescence centers.[2d] Carbon components form a series of new levels under the nitrogen vacancy level, including the levels of interstitial carbon, substitutional C_B and C_N and carbon impurity. These levels are ~1.7 eV, ~2.2 eV and ~3.4 eV lower respectively than the nitrogen vacancy level.[10,2] As reported,[10b] the interstitial carbon with different sized GQDs can generate deep levels (2-4 eV) below the conduction band. So, the transition from the conduction band or nitrogen vacancy level to the various carbon related levels will emit full visible colors, and thus forming white light. GQDs and GO can emit light under irradiation by themselves.[5] The size variation of GQDs, as well as the reported tunable PL properties of GO, both related to the quantum confinement effect, have great influences on the variation of their peak emissions.[4-5] It can be thought of another beneficial mechanism widening the emission spectrum. It is also regarded that the closed-shell BO^- and BO_2^- anions act as high-efficient luminescence centers,[2a] in this case, graphene can act as the electron fast transferring agent, increasing the luminescence intensity and the quantum efficiency.[4]
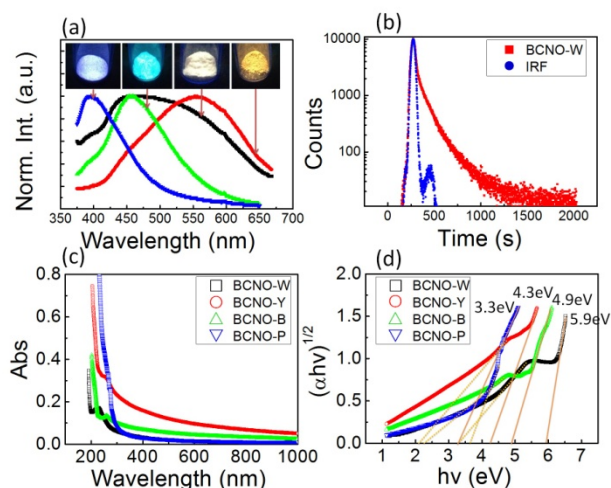

Figure 5. Optical properties of the phosphors. (a) PL spectra and the emission images under 365nm excitation, (b) PL decay curve of the BCNO-W phosphor, (c) UV-Vis absorption spectra of the phosphors, and (d) Tauc plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$, indicating the first band gaps and the second band gaps.

Table 2. Optical parameters of the four typical phosphors.

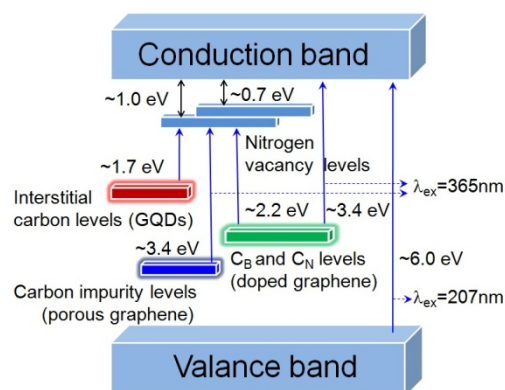| Phosphors	Peak emission excited at 365nm (nm)	CIE coordinate excited at 365nm, (x,y)	Extenal quantum efficiency (EQE) (%)	First band gap (eV)	Second band gap (eV)
BCNO-Y	550	(0.348,0.408)	16.7	3.3	2.1
BCNO-B	438	(0.186,0.219)	27.1	4.3	2.3
BCNO-P	388	(0.190,0.236)	45.9	4.9	3.7
BCNO-W	445	(0.292,0.342)	28.2	5.9	3.4

Figure 6. The proposed band structures of BCNO-W phosphor, explaining the PL white lighting mechanism.

Conclusions

One GO-based high efficient white lighting BCNO phosphor has been prepared for the first time. The doped porous graphene generates electrons under excitation and transfers them to BN
with various carbon related levels emitting full colour white light. The quantum confinement in the various kinds of GQDs and GO are also beneficial to widen the emission spectrum. The strategy proposed in this study may also widen the road to other novel white-lighting phosphors.

Acknowledgment

Notes and references

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† Electronic Supplementary Information (ESI) available: XPS profiles, SEM and optical properties of the phosphors. See DOI: 10.1039/b000000x/

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