Facile synthesis of BCNO quantum dots with applications for ion detection, chemosensor and fingerprint identification

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ABSTRACT

Boron carbon oxynitride quantum dots (BCNO QDs) with blue emission were prepared via the template of SBA–15 (a typical mesoporous silica). A modulated photoluminescence sensor was developed based on the different quenching effects of Cu^{2+} or Hg^{2+} ions on the luminescence intensity of BCNO QDs. The Cu^{2+} or Hg^{2+} ions have an interaction with BCNO QDs due to the electrons transfer between the BCNO and Cu^{2+} or Hg^{2+} ions, and the detection limit of Cu^{2+} or Hg^{2+} ion concentration can be as less as 10 nM. The BCNO–Cr^{6+} mixture can be served as a turn–on fluorescent sensor for detecting the ascorbic acid based on the inner filter effect since overlapping of excitation and emission spectra between Cr^{6+} ions and BCNO QDs. Moreover, the BCNO QDs can also be applied to fingerprint identification and organic fluorescent films under ultraviolet excitation.

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1. Introduction

Luminescence materials have been widely used in white light emitting diodes (LEDs), displays, fluorescence labeling, and biomedical areas [1–3]. Various luminescence materials have been developed such as rare earth doped phosphors [4–6], quantum dots [7–10], carbon based [11–13], and boron nitride based (BN, BCN, BCNO) luminescence materials [14–16]. Quantum dots have been recognized as excellent candidates for the next–generation lighting and display. Different series of QDs, including CdSe, CdS, CuInS, $CsPbX_3$, carbon and graphene dots, have been explored for QD–based LEDs (QLEDs) [7–9,11,12]. In addition, QDs have great potential applications in ion detection, chemical sensors and biosensor. Water soluble QDs with their surfaces coated with ample carboxyl or amine groups are easier to conjugate biomolecules or special functional groups, which is in favor of application for QDs as fluorescent probes [17]. Water soluble CdS QDs capped by polyphosphate, L-cysteine or thioglycerol were applied to selective ion detection and the detection limit was about 0.1 μM for Cu^{2+} ion [18]. Wu and Yan [19] applied Ni^{2+}–modulated homocysteine–capped CdTe QDs as a turn-on photoluminescence sensor for detecting histidine in biological fluids with the detection limit of 0.3 μM. D. Pan et al. [20] developed a novel eco-friendly approach to prepared grapheme quantum dots from coffee grounds with poly(ethylene imine) functionalization for Fe^{3+} and Cu^{2+} ions detection. N. Zarghami et al.

[21] reported a simple strategy for sensitive detection of telomerase activity using liposome-encapsulated cadmium telluride QDs. O. Akinloye et al. [22] developed a novel peptide-based fluorescence-based biosensor for detection and measurement of negatively charged engineered nanoparticles (ZnO, Fe_3O_4, CeO_2). In order to achieve ion detection in aqueous phase, the semiconductor QDs were usually needed to cap organic functional groups to realize aqueous dispersion. Carbon dots were also applied to ion detection [23] and fingerprint identification [24], which have good performance in chemical sensors. However, the ion detection mechanism especially the electron transition process between the quantum dots and ions are still needed to deeply investigate. As an important category of layer materials analogous to graphene, hexagonal boron nitride (BN) has attracted increasing attention due to its fascinating physical properties such as unique optical features, promising dielectric performance, high thermal conductivity and chemical stability [25–27]. Hexagonal BN QDs have been successfully prepared and show very good performance in cells imaging and biomedical areas [28–30]. Up to now, to the best of our knowledge, there is no report about BN QDs for further investigation besides cells imaging and biomedical applications. In addition, the applications of BN based QDs in ion detection, chemosensor, and organic luminescence films are imperative to develop, compared with other luminescence QDs [31–33].

BCNO phosphor is a typical non–rare earth doped BN based luminescence material, which was first prepared by T. Ogi with combustion method in 2008 [16]. BCNO phosphors have been attracted much attention due to its excellent characteristics: free rare–earth ions, no toxicity and pollution, wide range of excitation (ultraviolet to blue light) and

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emission spectra (blue to red light), and high quantum efficiency [16,34,35]. BCNO phosphors have great potential applications in white LEDs, display, phosphorus pigment, DNA labeling, and biological imaging [36]. At present, BCNO phosphors have been synthesized with various methods, such as solid state reaction method, microwave method, the molten salt growth method, electrospinning and liquid phase method [34,37–41]. Different sizes and shapes of BCNO phosphors have been obtained with above methods. Micron sized BCNO particles were synthesized by combustion, microwave or liquid phase method, and BCNO nanofibers with a diameter of 200 nm were obtained via eletrospinning [40]. BCN nanosheets and BCNO nanoparticles were prepared by Lei using salt melt method [35]. In addition, the emission spectra of BCNO phosphors can be modulated by carbon sources, polymer decomposition temperature and doping elements [42–44]. Up to now, BCNO QDs have remained much less explored and it still remains challenges for their facile preparations and further investigation. Very recently, C. Zhi et al. [45] prepared blue fluorescent monolayer BN and BCNO QDs for bio–imaging probes, which was significant for the development of BN based QDs. According to the reports, there are abundant chemical bonds in BCNO phosphors including B—N, B—O, C—N, C—C, C—O, C—H, N—H, and O—H bonds, which have important influences on absorption and emission properties [46–48]. In addition, there are more chemical bonds in surface states and large specific surface of nanoparticles for BCNO QDs which are more sensitive to some specific ions. Therefore, BCNO QDs may have excellent sensitivity and selectivity for chemical or biological sensors due to its special structure and surface chemical bonds.

In this paper, we have successfully synthesized blue emitting BCNO QDs with 4.5 ± 0.9 nm via the template of SBA–15. BCNO QDs have very good dispersion in water without further surface functionalization. In addition, we investigated the fluorescent properties between the BCNO QDs and metal ions via theoretical and experimental study, and found that Cu^{2+} or Hg^{2+} ions had the fluorescence quenching effects on BCNO QDs, which was induced by electrons transfer process between Cu^{2+} or Hg^{2+} ions with BCNO QDs. Moreover, we fabricated BCNO–Cr^{6+} based fluorescent chemosensor for the detection of ascorbic acid, and the photoluminescence of BCNO QDs can be turned–off by the Cr^{6+} and turned on by adding the ascorbic acid. Furthermore, the fingerprint identification and luminescence polymer films were also realized using BCNO QDs under ultraviolet light.

2. Experiment

2.1. Computational Details

All the calculations were carried out using the spin–polarized DFT method implemented in the DMol3 code [49,50]. Full geometry optimizations without symmetry constraints were performed employing the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional [51] with Grimme's dispersion correction [52]. A double numerical plus polarization (DNP) basis set [49] with a global orbital cutoff of 4.6 Å was adopted. For the core treatment, we used the most accurate all electron relativistic method [53], which considered all core electrons explicitly and introduced relativistic effects into the core. The self–consistent field (SCF) procedure was used with a convergence threshold of 10^{-6} au on the energy and electron density. For geometry optimization, the convergence thresholds of the energy, the maximum force, and the maximum displacement were set to 10^{-6} Ha, 0.001 Ha/Å and 0.005 Å, respectively.

2.2. Calculation Models

We used a finite BN nanoflake with the edges passivated by hydrogen atoms to represent a BN sheet. The PBE–D/DNP optimized B—N bond length within central region of BN nanoflake region is 1.45 Å, in line with the literature value for the bulk hexagonal BN (1.45 Å) [54].

BCNO nanoflake was then created by the substitution of single N with C and O atom from BN nanoflake as shown in Fig. 5, and the geometries were subsequently optimized with all the relaxed atom coordinates. The interaction between BCNO central region and metal ions was investigated. The metal ions were initially located above C atom and the geometry was fully relaxed. The partial density of states (PDOS) and total density of states (TDOS) of BCNO with metal ions were obtained to investigate the electrons transfer process between BCNO and metal ions.

2.3. Synthesis of SBA–15/BCNO Composites

SBA–15 was used as template and reaction vessel with pore size of 7 nm, and the morphology of SBA–15 was shown in Fig. S1. Boric acid (H_3BO_3), urea (CH_4NO_2) and citric acid ($C_6H_8O_7$) were used as boron, nitrogen and carbon sources, respectively. Initially, 0.01 mol boric acid, 0.05 mol urea and 0.002 mol citric acid were added into 20 mL ethyl alcohol, and it was heated to 60 °C to form a clear transparent solution. Then, 0.25 g SBA–15 was added into the above solution and stirred vigorously until the ethyl alcohol was evaporated to obtain precursor, and the precursor was sintered at 650 °C for 2 h under an air condition to obtain SBA–15/BCNO composites. The purity of all the raw materials is analytical pure.

2.4. Posttreatment of SBA–15/BCNO Composites

Firstly, SBA–15/BCNO composites were washed twice with hot water to remove the redundant B_2O_3. The SBA–15 template was removed by 4% HF solution, and the residual HF was neutralized by $CaCO_3$ and CaF_2 precipitation was formed. The BCNO solution was centrifuged at 10000 rpm (revolutions per minute) to remove the CaF_2 precipitation and supernatant was lyophilized by a freeze dryer, and BCNO QDs were obtained.

2.5. Metal Ion Detection

Different concentrations of metal ion solution with same BCNO QDs contents (1.6 mg/mL) were prepared by controlling volume of $CuCl_2$, $FeCl_3$, $AlCl_3$, $MgCl_2$, $Zn(CH_3COO)_2$, $CaCl_2$, KCl, $CrCl_3$, $NiCl_2$, NH_4Cl, $BaCl_2$, $AgNO_3$, $MnCl_2$, $PbCl_2$, $CoCl_2$ or $HgCl_2$ solutions (1 mM). Simultaneously, different volumes of deionized water were added so that the mixed solution of BCNO QDs and metal ions kept the same volume. The metal ion concentration in the mixed solution was fixed at 100 μM (μmol/L). A series of $CuCl_2$, $HgCl_2$ and $K_2Cr_2O_7$ solutions with different Cu^{2+} and Hg^{2+} ion concentrations (0, 0.01, 0.1, 1, 2, 5, 10, 20, 50, 100, 500 μM) and various Cr^{6+} concentrations (0–500 μM) with same BCNO QDs contents were also prepared.

2.6. Fingerprint Identification

0.01 g BCNO QDs were dispersed in 1 mL distilled water, and 0.1 g PVA (polyvinyl alcohol) was added into the solution and it was heated to 80 °C to dissolve the PVA. The above solution was smeared on the finger, and pressed on the banknote, and a flexible film was obtained after volatilizing the water, which was used for fingerprint identification under ultraviolet irradiation.

2.7. Characterization

The microstructure of BCNO QDs was measured by a transmission electron microscope (TEM, JEOL 2100). The thickness and morphology of BCNO QDs on quartz substrate were measured by an atomic force microscope (AFM, Bruker, Nanoscope V). X–ray photoelectron spectroscopy (XPS, PHI1600EXCA) was used to characterize the chemical states of BCNO QDs. The chemical binding status was measured via fourier transform infrared (FTIR) spectrometer (Bruker, WQF–410). The