Amorphous B-doped graphitic carbon nitride quantum dots with high photoluminescence quantum yield of near 90% and their sensitive detection of Fe²⁺/Cd²⁺

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ABSTRACT Graphitic carbon nitride quantum dots (CNQDs) are emerging as attractive photoluminescent (PL) materials with excellent application potential in fluorescence imaging and heavy-metal ion detection. However, three limitations, namely, low quantum yields (QYs), self-quenching, and excitation-dependent PL emission behaviors, severely impede the commercial applications of crystalline CNQDs. Here we address these three challenges by synthesizing boron-doped amorphous CNQDs *via* a hydrothermal process followed by the top-down cutting approach. Structural disorder endows the amorphous boron-doped CNQDs (B-CNQDs) with superior elastic strain performance over a wide range of pH values, thus effectively promoting mass transport and reducing exciton quenching. Boron as a dopant could fine-tune the electronic structure and emission properties of the PL material to achieve excitation-independent emission *via* the formation of uniform boron states. As a result, the amorphous B-CNQDs show unprecedented fluorescent stability (*i.e.*, no obvious fading after two years) and a high QY of 87.4%; these values indicate that the quantum dots obtained are very promising fluorescent materials. Moreover, the B-CNQDs show bright-blue fluorescence under ultraviolet excitation when applied as ink on commercially available paper and are capable of the selective and sensitive detection of Fe²⁺ and Cd²⁺ in the parts-per-billion range. This work presents a novel avenue and scientific insights on amorphous carbon-based fluorescent materials for photoelectrical devices and sensors.

Keywords: amorphous, boron doping, carbon nitride quantum dots, fluorescence imaging and sensors

INTRODUCTION

Fluorescence detection (FDT) is considered one of the most promising technologies for water quality evaluation, imaging, and biolabeling on account of its excellent sensitivity and operability [1–5]. As a key material for FDT, quantum dots (QDs) with a lateral scale of several nanometers have attracted great research attention [6–8]. The quantum confinement, surface state, and size effects of QDs give rise to intriguing properties in the resultant optical and electronic structures and conferring them with much broader applicability and higher fluorescence quantum yields (QYs) compared with traditional FDT materials [9–12]. Several QD-based FDT materials, such as CdS/CdTe [13–15], graphene [16–18], and carbon QDs, have recently been developed [19,20]. Unfortunately, the presence of heavy metals and potentially carcinogenic organic molecules in the majority of the available QDs could give rise to environmental problems and biological toxicity.

Graphitic carbon nitride QDs (CNQDs) are generally considered excellent candidates for fluorescence applications because of their low cost, high biocompatibility, low toxicity, and good water solubility [21–24]. Moreover, CNQDs consist of ordered tris-triazine moieties covalently connected by trigonal nitrogen and stacked in a graphitic fashion, which endows them with high QYs (*e.g.*, 30%–90%) and tunable fluorescent properties [25,26]. This intrinsic characteristic of CNQDs distinguishes them from traditional fluorescent materials and indicates their prospective applications in metal ion detection [27], security ink [3], and optoelectronic devices

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[28–30]. Nevertheless, major efforts in the FDT field are so far emphasized on the crystalline CNQDs-based materials. Similar to other metal-free-based QDs, crystalline CNQD-based FDT materials also present three primary drawbacks (i.e., low QYs, self-quenching and excitation-dependent properties), because of the formation of an intramolecular ground-state dimer complex or energy transfer between the adjacent QDs [31–33]. Fortunately, a growing class of amorphous QDs has been demonstrated to have more efficient FDT performance than their crystalline counterparts [4,32,34]. The isotropic characteristics of amorphous QDs induced by their short-range structural ordering endow these dots with long-term operating stability over a wide range of pH values, provide open active diffusion channels that could facilitate ion transport, and contribute to the formation of excitons, resulting in improvements in photoluminescent (PL) QY. The rational design and synthesis of amorphous CNQDs to maximize their stability and PL QY may be expected to produce materials with broad applicability in FDT.

In this work, we first developed amorphous boron-doped CNQDs (B-CNQDs) measuring approximately 5.0 nm in size *via* a hydrothermal process followed by the top-down cutting approach. Unlike conventional QDs and crystalline CNQDs, amorphous B-CNQDs demonstrate strong bright-blue PL emission intensity of millions scale under ultraviolet (UV) radiation, a high QY of 87.4%, distinct excitation-independent emission behaviors, and unprecedented fluorescence stability (i.e., no obvious fading after two years). When the B-CNQDs are used in ink, the information of specific graphics rubbed onto commercially available paper could clearly be read under UV excitation but is invisible in ambient light. The amorphous B-CNQDs also display outstanding selectivity and sensitivity in the detection of Fe^{2+} and Cd^{2+} in aqueous solution at concentrations as low as $10^{-9} \text{ mol L}^{-1}$. This work provides a new route for the rational design of high-performance FDT materials by using water-soluble amorphous carbon-based QDs.

EXPERIMENTAL SECTION

Materials

All of the reagents used in this work were of analytical grade and applied as received without further purification.

Preparation of amorphous B-CNQDs

Amorphous B-CNQDs were prepared by mixing citric

acid, boric acid, and urea (molar ratio: 1:6:6) with 10 mL of deionized water under uniform grinding for 5 min. Next, the mixture was placed in a 50-mL Teflon-lined autoclave and heated at 180°C for 2 h. After cooling to room temperature (25°C) in air, the product was dissolved in water, sonicated for approximately 6 h, passed through a 0.22- μm filter membrane to discard large particles with a flake-like structure, and then re-purified. Finally, the filtrate was collected and diluted to prepare B-CNQD suspensions (0.5 mg mL^{-1}). The contrast samples were synthesized by maintaining all of the above conditions while changing the molar ratio of boric acid.

Preparation of CNQDs

The CNQDs were prepared by following the procedure applied to the preparation of the B-CNQDs but without boric acid; all other parameters were held constant. The obtained samples were denoted CNQDs.

Preparation of bulk boron-doped graphitic carbon nitride

Bulk boron-doped graphitic carbon nitride (B-CN) was prepared by following the procedure applied to the preparation of the B-CNQDs but without ultrasound and filtration; all other parameters were held constant. The obtained samples were denoted B-CN.

Characterization

X-ray diffraction (XRD, Siemens D-5000) with Cu K α radiation ($\lambda = 0.154 \text{ nm}$) was used to assess the structural and textural properties of the B-CNQDs. Fourier transform infrared (FTIR) spectra in the wavelength range of 400–4000 cm^{-1} were recorded on an IRAffinity-1 FTIR spectrometer by using conventional KBr pellets. The chemical states of C, N, O, and doped B elements were tested by X-ray photoelectron spectroscopy (XPS, PHI Quantera X-ray photoelectron spectrometer with Al K α radiation, 300 W). Scanning electron microscopy (SEM) images of the precursor before filtration were obtained using a Hitachi S-4800 microscope. Transmission electron microscopy (TEM, FEI Tecai F20) was used to observe the nanostructures of the B-CNQDs. Atomic force microscopy (AFM) was performed on a Park Systems Corp. scanning probe microscopy system (Lui-Dong 906-10, Suwon, South Korea). Room-temperature ultraviolet-visible (UV-vis) absorption spectra were recorded on a UV-2450 Shimadzu system. The PL spectra were recorded on an F-2500 fluorescence spectrometer at room temperature. Time-resolved fluorescence (TRF) decay spectra were collected using a streak camera (C10910, Hamamatsu); here, the emission signal was reflected onto

the streak camera by a mirror.

Determination of fluorescence QYs

The fluorescence QY was determined by a typical slope method with quinine sulfate as the reference [26]: comparing the integrated photoluminescence intensity (360 nm excitation) and the absorbance value (its maximal absorption intensity was controlled in the range of 0–0.1) of the amorphous B-CNQDs with that of the references. Equation (1) was then applied:

$$\Phi_B = \Phi_{qs}(K_B/K_{qs})(\eta_B/\eta_{qs})^2, \quad (1)$$

where Φ is the QY, K is the slope determined by the curves, and η is the refractive index. The subscripts “qs” and “B” refer to quinine sulfate and the B-CNQDs, respectively. For these aqueous solutions, $\eta_{B(1.33)}/\eta_{qs(1.33)} = 1$. Thus, Equation (1) could be simplified to Equation (2):

$$\Phi_B = \Phi_{qs}(K_B/K_{qs}). \quad (2)$$

Fluorescence selectivity and interference measurements

Exactly 1 mL of the B-CNQD suspension (0.5 mg mL^{-1}) was mixed with deionized water. Chlorate solutions of Na^+ , K^+ , Ca^{2+} , Cu^{2+} , Fe^{2+} , Ni^{2+} , Sn^{2+} , La^{2+} , Ce^{4+} , and Cd^{2+} were then individually added to the suspension at a concentration of $20.0 \mu\text{mol L}^{-1}$ (final volume, 4 mL). After reacting for 30 min under static conditions, fluorescence emission spectra were recorded at room temperature under an excitation wavelength of 360 nm. The fluorescence intensity of B-CNQD solutions of different

pH (i.e., 1–14) was also recorded at room temperature under an excitation wavelength of 360 nm.

Fluorescence sensitivity detection of Fe^{2+} and Cd^{2+}

Fluorescence sensitivity was evaluated using the same procedures adopted for selectivity assessment, but the Fe^{2+} and Cd^{2+} concentrations were varied from 0 to $20.0 \mu\text{mol L}^{-1}$.

RESULTS AND DISCUSSION

The amorphous B-CNQDs were prepared by the hydrothermal method followed by the top-down cutting approach *via* ultrasound and filtration, the details of which are described in the EXPERIMENTAL SECTION. As shown in Scheme 1, after the hydrothermal reaction, B atoms are successfully doped into the carbon nitride (CN) framework. The SEM image in Fig. S1a confirms that the as-synthesized B-CN has a bulk structure with a diameter of $\sim 5 \mu\text{m}$, which agrees well with literature reports on this material [35,36]. The obtained bulk B-CN was then subjected to ultrasound treatment for 6 h. During ultrasonication, the ordered in-plane packing and interfacial stacking of the CN structures were destroyed or decreased, thereby cutting the bulk material first into nanosheets and then into amorphous nanodots (Fig. S1a, d). As shown in the SEM images in Fig. S1c, d, the B-CNQDs mainly range from 20 to 30 nm in size, which is insufficient to achieve high quantum confinement effects.

Scheme 1 Schematic of the synthesis process of the amorphous B-CNQDs. Urea, boric acid, and citric acid were used as precursor materials to prepare amorphous B-CNQDs by hydrothermal polymerization, ultrasound, and filtration. Amorphous B-CNQDs in an aqueous medium are faint yellow in color under ambient light and give a blue glow under a 360 nm ultraviolet lamp.

Therefore, large-sized B-CNQDs should be removed from the aqueous solution, and the nanoparticles should be purified to obtain particle sizes of below 10 nm. The TEM image in Fig. 1a shows uniformly distributed nanodots measuring only a few nanometers in size after filtration. The high-resolution TEM image in the inset in Fig. 1a reveals that the obtained B-CNQDs are amorphous in structure without detectable lattices. The particle size indicated by the Gaussian distribution histogram in Fig. 1b reveals that the B-CNQDs have diameters ranging from 1 to 9 nm, with an average size of 5 nm. The AFM confirms the good dispersion of the B-CNQDs (Fig. 1c), which is well consistent with the TEM observations. Interestingly, the thickness of the nanodots varies from 0.612 to 3.307 nm (Fig. 1d and Fig. S2), thereby indicating that the amorphous B-CNQDs comprise 3–10 CN layers (the CNQD interlayer spacing, 0.32 nm).

The XRD patterns of the bulk B-CN and the amorphous B-CNQDs reveal their structural and textural properties. As shown in Fig. 1e, two characteristic peaks at 27.4° and 13.1° , which respectively correspond to the typical graphitic interlayer stacking of the (002) plane and the periodic in-plane structural packing feature of the (100) lattice plane of CN [37,38], could clearly be observed in the XRD pattern of bulk B-CN. In the XRD pattern of the B-CNQDs, the peak corresponding to (100) phase disappears completely and only a weak and broad peak at 27.1° is observed, thus suggesting the destruction of the long-range in-plane ordering, decreased interplanar stacking, and increased stacking distance of the remaining layers [4,39]. The weak hump-like diffraction peak further confirms the amorphous nature of the B-CNQDs, which is consistent with the TEM results.

The FTIR spectra were used to verify the surface groups and chemical structures of the amorphous B-CNQDs. As shown in Fig. 1f, the spectrum of the amorphous B-CNQDs shows a peak at 790 cm^{-1} , which could be associated with the characteristic breathing mode of tri-s-triazine rings and reveals the similarity of their structure to that of CN [3]. More importantly, compared with that of bulk B-CN (810 cm^{-1}), the weak and left-shift peak corresponding to the tri-s-triazine rings implies the disruption of the in-plane structural packing motif of the B-CNQDs, consistent with the XRD results. The peaks at 1398 and 1660 cm^{-1} are respectively attributed to the C–N and C=N bonds of the C–N heterocycle [40,41]. The bands at 1112 and 1624 cm^{-1} are ascribed to the stretching vibrations of C–O and C=O [27], while the broad and intensified peak in the range of $3000\text{--}3500\text{ cm}^{-1}$ is assigned to the stretching vibrations of

N–H or O–H in uncondensed amino and hydroxyl groups [42]. This result suggests that the surface of the obtained amorphous B-CNQDs is rich in multiple hydrophilic groups. The weak band at 1260 cm^{-1} is attributed to the stretching mode of C–N–B, thereby indicating the successful incorporation of B atoms into the CNQD framework [43–46].

The chemical composition of the amorphous B-CNQDs was analyzed by XPS. The XPS full-survey scan spectrum of the dots is shown in Fig. 2a and reveals the coexistence of B, C, N, and O elements in the dots. The weak O 1s peak located at approximately 532 eV may be ascribed to the surface hydroxylation of the B-CNQDs [35,42,47]. The B, C, N, and O atomic percentages obtained from XPS are 1.24%, 39.76%, 54.47% and 4.53%, respectively, and the C/N ratio is 0.73 (Table S1), which is consistent with the typical theoretical value for CN. The high-resolution B 1s spectrum in Fig. 2b demonstrates the presence of C–N–B (191.6 eV; B is surrounded by three N atoms) [48,49], which is in accordance with the FTIR observations and indicates the successful substitution of B atoms into the carbon sites of the CNQD framework.

The high-resolution XPS spectra of C 1s, N 1s, and O 1s were analyzed to investigate the effect of B doping on the structure of the CN framework. As illustrated in Fig. 2c, the two main peaks observed at 284.6 and 288.0 eV could be ascribed to the pure graphitic species of C–C/C=C bonds in carbon impurities and sp^2 -hybridized carbon atoms bonded to the aliphatic amine in the aromatic rings (N–C=N) [50–52], respectively. The weak peaks located at 286.1 and 289.1 eV are respectively attributed to the C– NH_x ($x = 1, 2$) groups on the edges of heptazine units and C–O bonds at the edges of the B-CNQDs [27,40]. The peak ratios of C– NH_x and C–O calculated through C 1s are 7.06% and 2.43% (Table S2), respectively, thus reaffirming the enrichment of amino and hydroxyl groups in the amorphous B-CNQDs. The N 1s XPS spectrum of the B-CNQDs could be divided into four major peaks located at approximately 398.4, 399.6, 400.8, and 403.9 eV (Table S3). As shown in Fig. 2d, the intense peak located at 398.4 eV corresponds to the sp^2 -hybridized aromatic groups in tri-s-triazine rings (N–(C)₂), while the weak peak at 399.6 eV is attributed to the tertiary bridging N atoms in N–(C)₃ (where the N atom is surrounded by three C atoms) groups [28]. The peak with a binding energy of 400.8 eV suggests the presence of amino groups carrying hydrogen (N–H), thus implying the enrichment of amino groups in the B-CNQDs. The weak peak centered at 403.9 eV corresponds to charging effects or positive charge localization in heterocycles [53,54].

Figure 1 Structural characterization of the amorphous B-CNQDs. (a) TEM image of the amorphous B-CNQDs. Inset: corresponding high-resolution TEM image. (b) Particle size distribution obtained from the TEM results. (c) AFM image and (d) the corresponding height image of the amorphous B-CNQDs. (e) XRD patterns and (f) FTIR spectrum of the amorphous B-CNQDs.

Deconvolution of the O 1s core-level spectrum (Fig. 2e) suggests the presence of two chemically distinct species: O–H (533.0 eV) resulting from the surface dissociation of water, and C–O (531.5 eV), which originates from the C atom-bonded surface hydroxyl groups (C–O–H) [42,47]. These findings agree well with the FTIR results and affirm the presence of surface hydroxyl groups on the B-CNQDs (Table S4). Taken together, the TEM, XRD, FTIR, and XPS characterizations confirm that the as-prepared B-CNQDs consist of the main framework of amorphous CNQDs and doped B atoms with surface enrichment of amino and hydroxyl groups (Fig. 2f).

The optical properties of the amorphous B-CNQDs in

their aqueous solutions were detected by UV–vis diffuse reflectance and PL spectroscopy. Fig. 3a shows a strong absorption edge and characteristic peak located at 250 and 335 nm, respectively. The first edge, which corresponds to the π – π^* electronic transitions of aromatic sp^2 domains, produces nearly no fluorescence signal, and the second peak could be attributed to the n – π^* electronic transitions of C–O–H, C=N, and C–N–B in the B-CNQDs [25,27,55]. Upon UV light excitation, a strong blue fluorescence emission peak centered at 440 nm is observed in B-CNQDs because of the trapping of excited-state energy by the surface states [20].

The B-CNQDs demonstrate a Stokes shift of approxi-

Figure 2 Surface chemical compositions and states of B, C, N and O elements in the amorphous B-CNQDs. (a) XPS survey scan of the amorphous B-CNQDs. (b–e) High-resolution XPS spectra of B 1s, C 1s, N 1s, and O 1s of the amorphous B-CNQDs. Each spectrum was deconvoluted by fitting with Gaussian functions. (f) Proposed structure of the amorphous B-CNQDs (B, C, N, O and H atoms are respectively indicated as orange, gray, blue, red, and white spheres in the atomic model).

mately 105 nm, which could effectively improve the fluorescence efficiency of the dots owing to the drop in reabsorption events leading to nonradiative recombination [26]. The anti-Stokes excitation peak of the dots appears at 343 nm and could be ascribed to up-conversion emission mechanisms. The as-synthesized B-CNQDs emit a faint yellow glow under visible light and bright-blue luminescence under UV (360 nm) excitation (inset, Fig. 3a and Fig. S3). Interestingly, the optimized B-CNQDs show extremely strong PL signals (citric acid:boric acid:urea ratio, 1:6:6), accompanied by excitation-

independent wavelength behaviors different from those of most other reported CNQDs. As shown in Fig. 3b, the as-synthesized B-CNQDs exhibit a strong emission peak centered at approximately 440 nm, and no peak shift is observed in the PL spectra obtained upon excitation at $\lambda = 300\text{--}420$ nm. The strongest emission is achieved under 360 nm excitation. Pure CNQDs show fluorescence emission spectra and excitation-dependent behavior at different excitation wavelengths (Fig. S4), along with a sharp decrease in PL intensity. The excitation-dependent wavelength behavior of QDs is generally caused by the

Figure 3 Optical characterization of the amorphous B-CNQDs. (a) Normalized UV-vis absorption (black) and PL excitation (violet) and emission (blue) fluorescence spectra of the amorphous B-CNQDs. (b) The PL fluorescence spectra of the amorphous B-CNQDs at different excitation wavelengths ranging from 300 to 420 nm. (c) Representation of the fluorescence mechanism of the non-doped CNQDs and amorphous B-CNQDs: 1) electrons are excited from the ground-state and trapped by the surface states, 2) excited electrons return to the ground-state *via* a nonradiative route, and 3) excited electrons return to the ground-state *via* a radiative route. (d) Fluorescence images obtained under ultraviolet excitation (360 nm) when the amorphous B-CNQDs were used as ink. (e) TRF lifetime of the B-CNQDs and (f) TRF spectra of the pristine CNQDs and the amorphous B-CNQDs. The spectra are recorded under the excitation (wavelength, 400 nm) of a picosecond pulsed light-emitting diode at room temperature. (g) Comparison of the fluorescence QYs of the amorphous B-CNQDs and other reported QDs (specific parameters are given in Table S5).

size effect resulting from quantum dimensions and the inhomogeneous distribution of the surface states, re-

spectively [9,20]. In our work, however, the TEM and size statistics images in Fig. 1a, b indicate that the size of the

B-CNQDs is not uniform. Hence, the excitation-independent behavior of B-CNQDs may be ascribed to the uniform surface states introduced by B doping (labeled as the B-state; Fig. 3c); in this case, electrons trapped by the newly formed surface states are able to facilitate a high level of radiative recombination.

Interestingly, the bright-blue fluorescence of specific graphics on commercially available paper (the paper showed no background UV fluorescence) could easily be observed under UV excitation (360 nm) but is invisible in ambient light when the amorphous B-CNQDs were used as ink (Fig. 3d and Fig. S5). This finding demonstrates the promising applications of the dots in imaging ink and biolabeling. Moreover, the observed blue fluorescence shows no significant fading after two years (Fig. S6), thereby indicating the hyperstability of the B-CNQDs, which could be attributed to their amorphous structure. The effective separation and lifetime of photoexcited electrons over the amorphous B-CNQDs could be confirmed by TRF decay spectroscopy (Fig. 3e, f and Fig. S7). The average TRF lifetime (τ) calculated by the equation: $\tau = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$ is 1397.63 ps for the amorphous B-CNQDs and 746.13 ps for the pristine CNQDs. The fluorescence QY of the B-CNQDs excited by 360 nm UV light was calculated to be 87.4% when quinine sulfate was used as a standard (54%); this QY is much higher than that of pure CNQDs (49.5%) and exceeds those of most other QDs reported thus far (Fig. 3g and Table S5). These results confirm that B doping into the amorphous structures of the CNQDs can synergistically optimize the optical properties of the resultant materials and prevent fluorescence quenching to achieve high fluorescence QY.

The complex fluorescence mechanism of QDs renders identification of the relevant microprocess difficult but two hypotheses, namely, electronic conjugate structures and emissive traps [20,56,57], have been proposed. In general, the π - π^* electronic transitions of aromatic sp^2 domains in the B-CNQDs are unable to produce a fluorescent signal (Fig. 3a), thereby indicating the fluorescence mechanism of the B-CNQDs is not directly related to their electronic structures. In the hypothesis of emissive traps, the uniform surface states brought about by the appropriate amount of B doping should have a prominent impact on the fluorescence emission of the dots, resulting in the radiative recombination of electrons and holes trapped on the B-CNQD surface [20,58]. We tested the fluorescence spectra of B-CNQDs with different B doping contents in the excitation wavelength range from 300 to 420 nm to confirm the feasibility of this

explanation. As shown in Fig. S8, distinct excitation-dependent fluorescence behaviors are observed when the B contents in the CNQDs are regulated. The fluorescence intensity sharply decreases to tens of thousands units compared with the amorphous B-CNQDs with the appropriate amount of doped B atoms (Fig. 3b). The absorption spectra of these QDs depicted in Fig. S8d prove that the fluorescence mechanism depends on surface states, rather than electronic conjugate structures. The surface states of the B-CNQDs should be rather inconsistent because of their excitation-dependent behaviors. Thus, we propose that the strong and independent-excitation wavelength fluorescence emission of the B-CNQDs is mainly attributed to the appropriate surface-doping of B atoms.

The QDs, such as those obtained from carbon and graphene, generally show pH-sensitive fluorescence behaviors [4,18,59]. As shown in Fig. 4a, the normalized fluorescence intensity of the amorphous B-CNQDs is highly sensitive to the solution pH and increases sharply with an increase in pH from 2 to 5, remains stable at pH 5–11, and then decreases at pH 12–14. The effect of pH can be understood in terms of the change in surface charge owing to protonation–deprotonation. In this scenario, the dependence of fluorescence on the pH values suggests that fluorescent species in the amorphous B-CNQDs probably have alkalescence sites since the fluorescence is quenched in acidic and strong alkali media, consistent with earlier findings (FTIR, XPS) that the B-CNQDs contain large numbers of amino and hydroxyl groups.

The prospective use of the obtained amorphous B-CNQDs as sensors for metal ion detection was assessed. As shown in Fig. 4b, the fluorescence signals of the B-CNQDs were detected before and after the addition of perchlorate salts containing various metal ions (such as Na^+ , K^+ , Ca^{2+} , Cu^{2+} , Fe^{2+} , Ni^{2+} , Sn^{2+} , La^{2+} , Ce^{4+} , and Cd^{2+}) at a single concentration of $20 \mu mol L^{-1}$. The sensitivity of the fluorescence intensity of the B-CNQDs strongly relies on the metal ions in the same solution. The undetectable fluorescence quenching of B-CNQDs in the presence of Na^+ , K^+ , Ni^{2+} , and Ce^{4+} and the weak fluorescence quenching observed after the addition of Ca^{2+} , Cu^{2+} , Sn^{2+} , and La^{2+} could be attributed to nonspecific interactions between the amino and hydroxyl groups of the dots and the metal ions. In particular, the fluorescence intensity of the B-CNQDs is remarkably quenched in the presence of Fe^{2+} and Cd^{2+} . Fig. 4c shows a photograph of the B-CNQD solution after the addition of different metal ions under ambient light and UV irradiation (360 nm). The B-

Figure 4 Selectivity characterization of the amorphous B-CNQDs. (a) pH-sensitive fluorescence behaviors of the amorphous B-CNQDs. (b) Fluorescence responses of the amorphous B-CNQDs in the presence of different metal ions ($\lambda_{\text{ex}} = 360 \text{ nm}$, $[\text{M}^{n+}] = 20 \mu\text{mol L}^{-1}$). (c) Photographs of the B-CNQD solutions after the addition of different metal ions under ambient light (top row) and 360 nm ultraviolet irradiation (bottom row). (d, e) TRF lifetimes and the comparison of the TRF spectra of amorphous B-CNQDs in the presence of Fe^{2+} and Cd^{2+} . The spectra are recorded under the excitation (wavelength, 400 nm) of a picosecond pulsed light-emitting diode at room temperature.

CNQD solutions exhibit different colors because of the intrinsic properties of the different metal ions, and the fluorescence intensity of these samples varies greatly under UV irradiation. The fluorescence of the solutions was nearly completely quenched after the addition of Fe^{2+} and Cd^{2+} , consistent with the fluorescence intensity histogram (Fig. 4b) measured by fluorescence spectrometry. The TRF lifetimes in Fig. 4d, e also strongly demonstrate fluorescence quenching; specifically, the lifetimes of the B-CNQDs are sharply attenuated from 1397.63 ps (Fig. 3e) to 379.41 and 410.97 ps in the presence of Fe^{2+}

and Cd^{2+} , respectively. Fe^{2+} , an important component of hemoglobin, is essential for oxygen delivery in the human body. An imbalance between the supply and demand for Fe^{2+} could result in various diseases, such as anemia, cardiovascular disease and Alzheimer's disease. The wide use of Cd^{2+} in the mining, smelting, dye, battery and chemical industries may present great harm to the human body on account of the strong toxicity and bioaccumulation of the metal even at very low concentrations [60–62]. Thus, the amorphous B-CNQDs show great potential use for the selective detection of Fe^{2+} and Cd^{2+} .

Figure 5 Sensitivity analysis of the amorphous B-CNQDs. Change in fluorescence intensity of the amorphous B-CNQDs in water upon the addition of (a) Fe^{2+} and (c) Cd^{2+} (excitation wavelength, 360 nm). Stern–Volmer plots for the fluorescence quenching of the amorphous B-CNQDs with (b) Fe^{2+} and (d) Cd^{2+} in water, showing the variance of F_0/F with Fe^{2+} and Cd^{2+} . (e) Proposed fluorescence quenching mechanisms of the B-CNQDs in the presence of Fe^{2+} and Cd^{2+} ions.

We tested the fluorescence responses of the amorphous B-CNQDs in the absence and presence of Fe^{2+} and Cd^{2+} at the concentrations of 0–20 $\mu\text{mol L}^{-1}$ to highlight the detection sensitivity of the sensor for the target ions. As shown in Fig. 5a, c, the fluorescence signals of the B-CNQDs significantly decrease with an increase in Fe^{2+} and Cd^{2+} concentration, thus indicating the high sensi-

tivity of the dots toward Fe^{2+} and Cd^{2+} . Photographs of the color of the above solutions under ambient light and UV irradiation (360 nm) are shown in Figs S9 and S10. The fluorescence quenching of the B-CNQDs by Fe^{2+} and Cd^{2+} ions could be interpreted by Stern–Volmer analysis. The quenching efficiency of the dots may be well fitted by the following Stern–Volmer equation: $F_0/F = 1 + K_{\text{sv}}Q$,

where F_0 and F are the PL intensities of the B-CNQDs in the absence and presence of Fe^{2+} and Cd^{2+} , respectively, Q is the concentration of Fe^{2+} or Cd^{2+} , and K_{sv} is the Stern–Volmer constant. The linear dependence of the fluorescence quenching intensity on the concentration of Fe^{2+} or Cd^{2+} ions is clearly observed in the Stern–Volmer plots shown in Fig. 5b, d. The fluorescence of the pristine B-CNQDs could be completely quenched by the addition of $20 \mu\text{mol L}^{-1}$ Fe^{2+} and $20 \mu\text{mol L}^{-1}$ Cd^{2+} . Moreover, the B-CNQDs show wide linearity ranging from 0 to $20 \mu\text{mol L}^{-1}$ and good sensitivity with low detection limits of 2.3 and 1.1 nmol L^{-1} (calculated by the 3σ rule [63]) for Fe^{2+} and Cd^{2+} , respectively, at a signal-to-noise ratio of 3. These values indicate that the sensor is sufficiently sensitive to meet the limits of Fe and Cd in drinking water established by the U.S. Environmental Protection Agency (5.537 and $1.8 \mu\text{mol L}^{-1}$, respectively). The outstanding selectivity and fluorescence quenching of the synthesized dots may be ascribed to their formation of a stable non-fluorescent complex *via* the strong thermodynamic affinity and rapid chelation of Fe^{2+} and Cd^{2+} with the hydroxyl groups on the surface of the B-CNQDs (Fig. 5e, mechanism 1) and/or nonradiative electron-transfer involving the partial transfer of an electron in the excited-state to the d orbital of $\text{Fe}^{2+}/\text{Cd}^{2+}$ (Fig. 5e, mechanism 2) [2,4,64–66]. The excellent performance of the B-CNQDs reflects their suitable application as a fluorescent sensor for the quantitative analysis of Fe^{2+} and Cd^{2+} in an aqueous solution.

CONCLUSIONS

In summary, we successfully fabricated novel amorphous B-CNQDs *via* the hydrothermal method followed by the top–down cutting approach. The synergistic effects of the uniform surface B states and amorphous structures of the B-CNQDs significantly contributed to the latter's outstanding excitation-independent emission behavior and high blue PL QY of near 90%, which is much higher than that of pure CNQDs (49.5%) and most other QDs reported thus far. Systematic investigations indicate that the high structural disorder of the amorphous structures of the B-CNQDs not only endows them with superior elastic strain performance over a wide range of pH, but also effectively reduces exciton quenching, thereby improving their fluorescent stability and PL QY. Interestingly, tailoring of the B doping content results in the B-CNQDs exhibiting excitation-independent emission behaviors *via* the formation of uniform B states, as well as ultra-strong fluorescent emission signals; these observations indicate that the amorphous B-CNQDs are very promising

fluorescent materials for FDT. For example, when used as ink, the amorphous B-CNQDs emitted a blue glow on commercial paper; the dots could also be used as a sensitive fluorescence sensor for detecting Fe^{2+} and Cd^{2+} in aqueous solutions with a detection limit of as low as $10^{-9} \text{ mol L}^{-1}$. Our study provides a new route and scientific insights into the design of high-fluorescence-QY amorphous carbon-based materials, with potential applications in optical imaging, sensing and biolabeling.

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Conflict of interest The authors declare no conflict of interest.

Supplementary information Supporting data are available in the online version of this paper.

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非晶态硼掺杂石墨相氮化碳量子点: 近90%高荧光量子产率及高灵敏检测 $\text{Fe}^{2+}/\text{Cd}^{2+}$

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摘要 石墨相氮化碳量子点(CNQDs)作为一种具有吸引力的光致发光(PL)材料, 在荧光成像和重金属离子检测方面具有巨大的潜力。然而, 晶态CNQDs的商业化应用仍被其低荧光量子产率、自猝灭和激发波长依赖行为所限制。我们提出利用硼掺杂和CNQDs非晶化的协同策略——通过水热和自上而下的超声剥离方法制备非晶态硼掺杂CNQDs (B-CNQDs)——以解决以上三个问题。结构无序赋予了非晶态B-CNQDs大范围pH下优越的弹性应变性能, 从而可以有效促进电荷传输, 减少激子猝灭。同时, 通过形成均匀的硼掺杂表面态, 可以巧妙地调节CNQDs的电子结构和荧光发射特性, 实现无激发波长依赖行为。结果表明, 非晶态B-CNQDs具有优异的荧光稳定性(2年后无明显衰减), 且具有87.4%的高量子产率, 是非常有前途的荧光材料。在紫外光激发下, B-CNQDs在商业用纸上可以显示出特定图形的亮蓝色荧光。此外, B-CNQDs对 Fe^{2+} 和 Cd^{2+} 在ppb检测范围内具有高度的选择性和灵敏度。本工作可为开发具有高稳定性和高量子产率的非晶态碳基荧光材料用于光电器件和传感器提供实验基础和有益启示。