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Original article

The synthesis of B, N-carbon dots by a combustion method and the application of fluorescence detection for Cu^{2+}

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ABSTRACT

Heteroatom doping is an efficient approach to regulate the fluorescence properties of carbon dots. Using aminophenylboronic acid as the raw material, a combustion method was developed for the synthesis of boron, nitrogen-doped carbon dots (B, N-carbon dots). The B, N-carbon dots emitted green fluorescence and displayed high resistance to both photo bleaching and ionic strength. A facile fluorescence sensing approach for Cu^{2+} was fabricated *via* static fluorescence quenching. Under optimal conditions, a rapid detection of Cu^{2+} could be completed in 2 min with a linearity ranging from 1 μmol/L to 25 μmol/L and a detection limit of 0.3 μmol/L. Furthermore, the proposed method showed potential applications for the detection of Cu^{2+} in natural water samples.

1. Introduction

Carbon dots, generally small carbon nanoparticles less than 10 nm in size, have received extensively attention due to their excellent properties, such as low toxicity, favorable biocompatibility, stable photoluminescence and good solubility [1–4]. These fascinating merits make them widely used in the areas of physical/chemical sensors, fuel cells, photocatalytic devices and bioimaging aspect [5–12]. Most of the carbon dots emit blue fluorescence, which is unfavorable in bioimaging and insensitive to visual observation. Functionalization, mainly post-surface-modification and intrinsic heteroatom doping, are efficient ways to tune the chemical and physical properties of carbon dots [13]. Post-surface-modification is tedious and the stability of carbon dots is a major problem in the following applications. Intrinsic heteroatom doping is more popular. Incorporating metal ions and transition metal ions into the core of the carbon dots provides more conjugated intrinsic defects, resulting in the red shift of their fluorescence. However, metal and transition metal atoms are too much larger than carbon atom. This produces the ineffective and heterogeneous doping. In addition, the toxicity of metal ions is also a big issue. Inversely, both boron and nitrogen atoms are comparable with carbon atom in size, they can form into uniform doping and homogeneous intrinsic defects. The synthesis process is simpler, more effective and convenient. Recently, co-doped multiple heteroatom has begun to gain extensive attention because it can create a unique electronic structure owing to the synergistic effect between the doped heteroatom [14]. Nevertheless, to date, N, S-co doped and N, P-co doped carbon dots [15–17] have synthesized highly fluorescent carbon dots with high quantum yield (QY). However, most of them emit blue fluorescence. Though there was a serious of good results with reported B, N co-doped for chemical sensing using hydrothermal method [18,19], most of the B, N doped carbon nanomaterials were used for catalysis [20]. Therefore, the aim of this work is to tune the fluorescence properties of B, N-carbon dots and extend their application in chemical sensing.

Copper is a widely used industrial metal, with the rapid industrial development, environmental pollution has become a serious problem, the detection of Cu^{2+} is a significant issue in environmental monitoring [21,22]. Currently, various fluorescent materials have been developed for the determination of Cu^{2+}, including small organic molecules [23,24], noble metal nanoclusters [25] and semiconductor quantum dots [26]. However, most of the traditional fluorescent materials suffer the drawbacks such as high toxicity, vulnerable to photo bleaching, low stability and tedious post-treatment. Thus, it is still essential to develop carbon dots based fluorescence materials toward the detection

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of Cu^{2+} with lower toxicity, better photostability and simper post-treatment.

Herein, fluorescent B, N-carbon dots were obtained *via* a combustion method with aminophenylboronic acid (APBA) as the raw material. The as-prepared B, N-carbon dots emitted green fluorescence with a QY of 1.6%. They revealed high resistance to photobleaching and ionic strength. Using the B, N-carbon dots as the fluorescence probe, a facile fluorescence sensing approach for Cu^{2+} detection was developed *via* static fluorescence quenching. Finally, the proposed method showed its applicability to natural water samples spiked with Cu^{2+}.

2. Results and discussion

2.1. Characterization of the B, N-carbon dots

Aminophenylboronic acid was chosen as the precursor because it contains abundant boron, nitrogen elements and has a stable aromatic structure. The as-prepared B, N-carbon dots remains transparent without any aggregation for 12 months at room temperature, indicating their excellent stability. The morphology of the B, N-carbon dots was characterized by TEM. As shown in Fig. 1A, the B, N-carbon dots were homodispersed in a narrow diameter ranging 1.5–4.0 nm, with a mean size around 2.5 nm. To further explore the composition and structure of the B, N-carbon dots, FT-IR and XPS investigation were conducted (Fig. 1B–F), the B, N-carbon dots exhibited the characteristic peaks of the raw material (APBA). There were B—C bond (the absorption band at 1100 cm^{-1}), B—N bond (1390 cm^{-1}), C—O, C=O bonds (1643 cm^{-1}) and B—NH, B—OH bonds (3420–3500 cm^{-1}) within the B, N-carbon dots [27,28], which implied that both the boron and the nitrogen elements have been doped into the B, N-carbon dots. The XPS spectra showed C, N, B, O four elements with a C/N/O/B concentration ratio of 0.612/0.059/0.273/0.056, the boron and nitrogen contents are rather higher than the relative reported literatures [29,30]. The C 1s spectrum showed five peaks, centered at 283.9, 284.6, 285.2, 286.2 and 288.0 eV, attributed to C—B bond, C—C, C=C bonds, C—N bond, C—O bond and C=N bond, respectively. The N 1s spectrum showed two peaks, centered at 399.5 and 401.5 eV, corresponded to C—N bond and C—NH bond. The B 1s spectrum showed two peaks, centered at 190.8 and 191.7 eV, ascribed to B—C bond and B—O bond [5,21,31–34]. All the above results confirmed that the boron and the nitrogen elements were doped into the B, N-carbon dots.

2.2. Optical properties of the B, N-carbon dots

The optical properties of the B, N-carbon dots were characterized by UV–vis absorption and fluorescence emission spectra. As displayed in Fig. 2A, the B, N-carbon dots showed two unconspicuous absorption bands at 230 and 267 nm. The former might be ascribed to the π–π^* absorption of the C=C core, the latter might originate from C=N, C=O functional groups [35]. The maximum fluorescence excitation and emission wavelengths were 310 and 520 nm. The large stokes shift and intensive green fluorescence of the B, N-carbon dots (inset photo in Fig. 2A) indicated their potential application in bioimaging. The fluorescence of the B, N-carbon dots was excitation independent, the fluorescence emission wavelength kept constant at 520 nm under excitation from 300 to 390 nm (Fig. 2B), which confirmed the homogenous structure of the B, N-carbon dots. Using quinine sulfate as the reference, the QY of the B, N-carbon dots was estimated to be 1.6% (Table S1 in Supporting information). The pH value had an obvious effect on the fluorescence intensity of the B, N-carbon dots. The fluorescence intensity of the B, N-carbon dots firstly gradually increased at pH from 2 to 7, and then drops gradually from 7 to 12 (Fig. 2C), which might be ascribed to the considerable quantity of carboxyl and amino groups on their surface. The optimal pH is 7, so the neutral

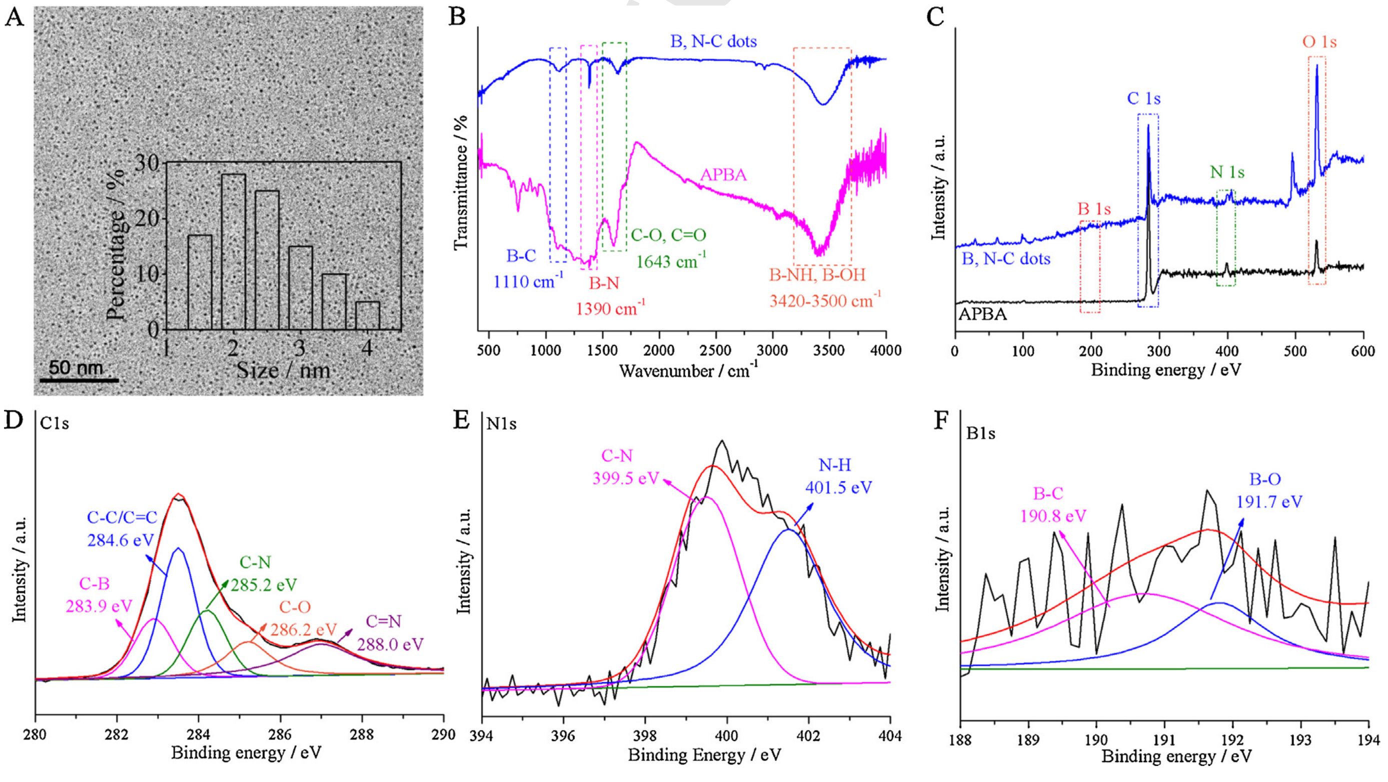

Fig. 1. (A) TEM image of the B, N-carbon dots. Inset: the corresponding size distribution of the B, N-carbon dots. (B) FI-IR spectra and (C) XPS spectra of APBA and the B, N-carbon dots. (D) C 1s spectrum, (E) N 1s spectrum and (F) B 1s spectrum of the B, N-carbon dots.

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