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Hydrothermal synthesis of two photoluminescent nitrogen-doped graphene quantum dots emitted green and khaki luminescence

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HIGHLIGHTS

- Nitrogen-doped graphene quantum dots (N-GQDs) are prepared by hydrothermal routine.
- Two N-GQDs with different size distribution emit green/khaki photoluminescence.
- Two N-GQDs exhibit excitation-dependent/independent photoluminescence behaviors.

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ABSTRACT

A simple and effective chemical synthesis of the photoluminescent nitrogen-doped graphene quantum dots (N-GQDs) biomaterial is reported. Using the hydrothermal treatment of graphene oxide (GO) in the presence of hydrogen peroxide (H_2O_2) and ammonia, the N-GQDs are synthesized through H_2O_2 exfoliating the GO into nanocrystals with lateral dimensions and ammonia passivating the generated active surface. Then, after a dialytic separation, two water-soluble N-GQDs with average size of about 2.1 nm/6.2 nm, which emit green/khaki luminescence and exhibit excitation dependent/independent photoluminescence (PL) behaviors, are obtained. In addition, it is also demonstrated that these two N-GQDs are stable over a broad pH range and have the upconversion PL property, showing this approach provides a simple and effective method to synthesize the functional N-GQDs.

1. Introduction

Fluorescent semiconductor quantum dots (QDs) have generated much excitement for a wide variety of promising applications, especially those in biology and medicine [1]. However, most of the high-performance QDs require the use of heavy metal elements, which may represent serious limitations for their applications due to the known toxicity and potential environmental risk [2]. Therefore, the search for more benign substitutes of semiconductor QDs is worthwhile and urgent. Compared with heavy-metal-based QDs, the carbon nanomaterials emitted different photoluminescence (PL) have attracted tremendous attention because of their unique properties in the photostability, biocompatibility, toxicity, water solubility, and numerous possible applications [3,4]. Thereinto, the graphene quantum dots (GQDs), which possess one or few-layered graphene sheets with lateral dimensions smaller than 100 nm [5], are expected the excellent properties of graphene materials as well as new functions resulting from their quantum confinement and edge effects [6,7]. As a consequence, the GQDs have been actively pursued in bioimaging [8] and biosensing [9]. But the synthesis and insight of the GQDs with strong and tunable PL still remains a challenge [10].

Besides the synthetic strategy by using different carbon sources and preparing processes, the doping of the heteroatoms has also been demonstrated to be an effective way to tune the intrinsic properties of carbon nanomaterials. Up to now, several groups have reported the synthesis of nitrogen-doped GQDs (N-GQDs). Qu et al. [6] reported the synthesis of N-GQDs from graphene oxide (GO) using cyclic voltammetry within the potential window ±3 V with N-containing tetrabutylammonium perchlorate in acetontrile as the electrolyte to introduce N atoms into the resultant GQDs. The N-GQDs with N/C atomic ratio of ca. 4.3% emitted blue luminescence and possessed an electrocatalytic activity for the oxygen reduction reaction. Gong et al.

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[11] developed a solvothermal approach for doping nitrogen to GQDs using *N-N*-dimethylformamide as both solvent and nitrogen sources. The obtained N-GQDs showed a bright green emission centered at 520 nm, and were used as efficient two-photon fluorescent probes for cellular and deep-tissue imaging. Shu et al. [12] reported the preparation of the amine-functionalized GQDs with anti-mycoplasma properties, which exhibited the diameters of about 7.5 nm originating by the interaction of graphene oxide sheets, hydrogen peroxide (H_2O_2) and ammonia. Hu et al. [13] reported a hydrothermal route to prepare the N-GQDs by treating the GO in the presence of ammonia. In addition, Li and coauthors [14] developed the hydrothermal synthesis of N-GQDs by cutting N-doped graphene, and found that the N-GQDs possess bright blue PL and excellent upconversion PL properties. Recently, using a fresh GO suspension as starting material, we observed that the GO could be exfoliated into small pieces when H_2O_2 was added in the hydrothermal precursors [15]. In addition, considering the excellent properties of N-GQDs, ammonia was used as nitrogen source in the precursor solution to introduce doping nitrogen in the GQDs, and two water-soluble N-GQD products with the size distributions of about 2.1 nm/6.2 nm and the green/khaki luminescence were obtioned. In this paper, the hydrothermal synthesis of two N-GQDs is presented, and their PL behaviors are investigated.

2. Experimental section

The graphite powders were chemically oxidized by the modified Hummers' method to prepare the fresh GO water dispersion as the starting material. In a typical synthesis of the N-GQDs, 15 ml GO (about 0.5 mg mL^{-1}) was mixed with 0.3 mL of ammonia solution (28 wt% in water) and 1 mL of H_2O_2 (30 wt% in water), and then the mixture was transferred to a Teflon lined autoclave and heated at 180 °C for 3 h. After cooling to room temperature, the obtained colloidal light brownish was concentrated to tenth of the origin volume using a heating mantle, and then dialyzed in a dialysis bag (retained molecular weight: 3500 Da) for 48 h, two N-GQD water dispersions with the green (outside, labeled as N-GQDs1) and khaki (inside, labeled as N-GQDs2) PL properties could be obtained.

The morphology of the N-GQDs was characterized by transmission electron microscope (TEM, JEM-2100, Japan). Fourier transform infrared (FT-IR) spectra were recorded on a flourier transform spectrometer (Tensor 27, Bruker, Germany) using the KBr pellet technique. Ultraviolet–Visible (UV–Vis) spectra were recorded by a UV–Vis spectrophotometer (UV-1800, Shimadzu, Japan). X-ray photoelectron spectroscopy (XPS) was performed on an Escalab 250 (Thermo-VG Scientific, U.S.) with Al Kα (1486.6 eV) as the X-ray source. Photoluminescence (PL) spectra were recorded by a Spectro fluorometer (F-2500, Hitachi, Japan).

3. Results and discussion

Fig. 1 shows the TEM images of the N-GQDs obtained outside and inside the dialysis bag. The N-GQDs1 particles exhibit a relatively narrow size distribution between 1.6 and 2.9 nm with an average diameter of 2.1 nm (Fig. 1A). Correspondingly, most of the N-GQDs2 particles show spherical shape with size distribution in the range of 4–9 nm and an average diameter of 6.2 nm (Fig. 1B). The size distributions of two N-GQD particles are in accordance with the pore size of the dialysis bag, and also indicating the particles with broad size distribution could be synthesized under the hydrothermal conditions. The high resolution TEM images indicate that both N-GQDs1 and N-GQDs2 have discernible lattice structures, and their lattice spacing is about 0.22 nm and 0.21 nm, respectively, which is accordant with that of the graphite carbon source.

Introducing hydrophilic groups is a general protocol to improve the solubility of the GQDs. Fig. 2A shows the FT-IR spectra of the as-synthesized N-GQDs. The peak of the –OH group at about 3450 cm^{-1}, C=O group at about 1730 cm^{-1}, and the peak of the C–O group conjugated with condensed aromatic carbons at 1090 cm^{-1} appear, and the peak at 1400 cm^{-1} can be ascribed to the symmetric stretching vibration of COO^- [16], revealing that the obtained N-GQDs are rich in carboxylic groups and/or hydroxide groups. Interestingly, the peak at 1640 cm^{-1} corresponds well to the C=C/C–C vibrations in the graphite. These results indicate that the surfaces of the N-GQDs are partially oxidized, and the surface hydrophilic groups can stabilize the N-GQDs in aqueous media. Another interesting phenomenon here is the N-GQDs has the $-NH_2$ group vibration bands at 3166 cm^{-1}, which can be expressed as $-NH_3^+$ structure [17]. The result can be considered as the types of nitrogen presented on the surface of N-GQDs. Compared to the N-GQDs2, the N-GQDs1 exhibits higher transmittance corresponding to the stretching vibration N–H at 3166 cm^{-1} and the stretching vibration of COO^- at 1400 cm^{-1}, suggesting that the GQDs1 has more hydrophilic groups.

The surface composition and element analysis for the N-GQDs were characterized by the XPS technique. The XPS survey spectra of the N-GQD resultants (Fig. 2B) show the predominant C1s, N1s, and O1s peaks at ca. 284 eV, 400 eV, and 532 eV, respectively. A pronounced N1s peak was observed in the N-GQDs, while no N signal was detected in the GO (Fig. S1), indicating the successful incorporation of N atoms into the GQDs. The N/C atomic ratios of the N-GQDs1 and the N-GQDs2 were calculated to be 29.7% and 11.9%, respectively, which is much higher than that of the reported previously [6]. The high resolution N1s spectra of the N-GQDs1 and N-GQDs2 (Fig. 2C and D) reveal the presence of both pyrrolic-like (399.5 eV) and amino (401 eV) N atoms [13]. In addition to the C–N bond (285.2 eV), the high resolution C1s spectra of the N-GQDs1 and N-GQDs2 (Fig. 2E and F) further confirm the presence of

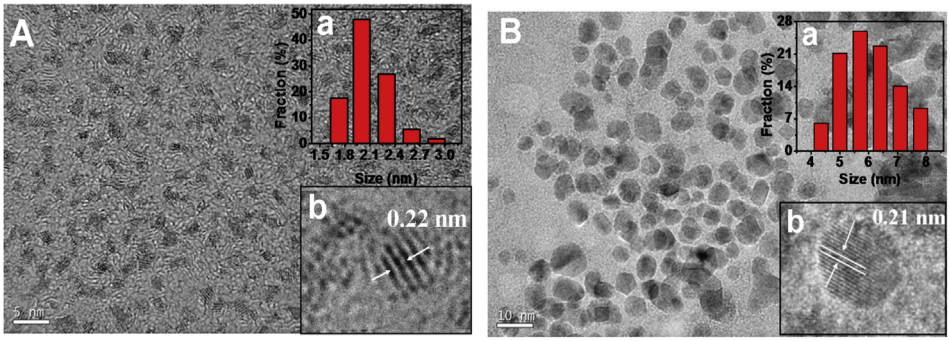

Fig. 1. Representative TEM images of the N-GQDs1 (A) and the N-GQDs2 (B). The insets show the size distributions (a) and the high resolution TEM images (b) of the N-GQDs.