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High photoluminescent nitrogen-doped carbon dots with unique double wavelength fluorescence emission for cell imaging

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ABSTRACT

High photoluminescent (PL) nitrogen-doped carbon dots (N-CDs) have been synthesized using ferric ammonium citrate (FAC) and urea as raw materials by simple one-pot hydrothermal process. The N-CDs possess bright blue fluorescence (centred at 450 nm; 36.2% quantum yield) and green fluorescence (centred at 530 nm; 47.6% quantum yield) only by adjusting the excitation wavelength from 310 nm to 510 nm. The N-CDs exhibited high N content of 32.81 wt%, low cytotoxicity, and good PL stability at different pH values, ion strengths and temperature, respectively. As-prepared N-CDs were explored for cell imaging with great biocompatibility. The remarkable properties of N-CDs indicated their potential toward sensing and biological applications.

1. Introduction

The carbon dots (CDs) have attracted tremendous attentions because of their tunable emission, small size, low toxicity and good water solubility. The excellent properties of CDs make them have great potential applications in biolabeling, sensing, biomedicine, photocatalysis and optoelectronic devices [1–3]. Most of the CDs show emission in the blue range under the ultraviolet excitation. The prepared CDs only emit a color of strong fluorescence with excitation-dependent emissions have been reported. However, it will be more meaningful for extending the application of CDs in sensing, biology, and illumination if the CDs can show different bright colors only by adjusting the excitation wavelength [4–7]. Furthermore, N doping of CDs not only can adjust the emission of CDs, but also can effectively regulate their intrinsic properties and improve the optical features of CDs [4,8–10].

Herein, we synthesized high PL N-CDs via one-pot hydrothermal carbonization of FAC and urea in dimethylformamide. The N-CDs exhibit high N content, good PL stability, and very bright blue and green fluorescence (correspondingly emission centers at 450 nm and 530 nm). Furthermore, the synthesized N-CDs possess excellent biocompatibility, which were used for fluorescence imaging in PC12 cells.

2. Experimental

The N-CDs were synthesized by facile one-pot hydrothermal treatment of FAC and urea with the mass ratio of 1: 1 (0.5 g: 0.5 g), 1:3 (0.5 g: 1.5 g), 1:4 (0.25 g: 1.5 g), 1:9 (0.165 g: 1.5 g) and 1:12 (0.125 g: 1.5 g), and they were named as N-CDs1, N-CDs2, N-CDs3, N-CDs4 and N-CDs5, respectively. Typically, 0.165 g FAC and 1.5 g urea were dissolved in 5 mL DMF, mixed and then transferred into a Teflon-lined autoclave and heated at 160 °C for 6 h. After naturally cooling to room temperature, obtained solution was centrifuged to remove non-fluorescent deposits. Finally, the suspension was diluted to 50 mL with distilled water for further use.

3. Results and discussion

The TEM image (Fig. 1a and Fig. S1) revealed that the average size of N-CDs (1:9) is in the range of 3.4 ± 1.5 nm. The result of AFM

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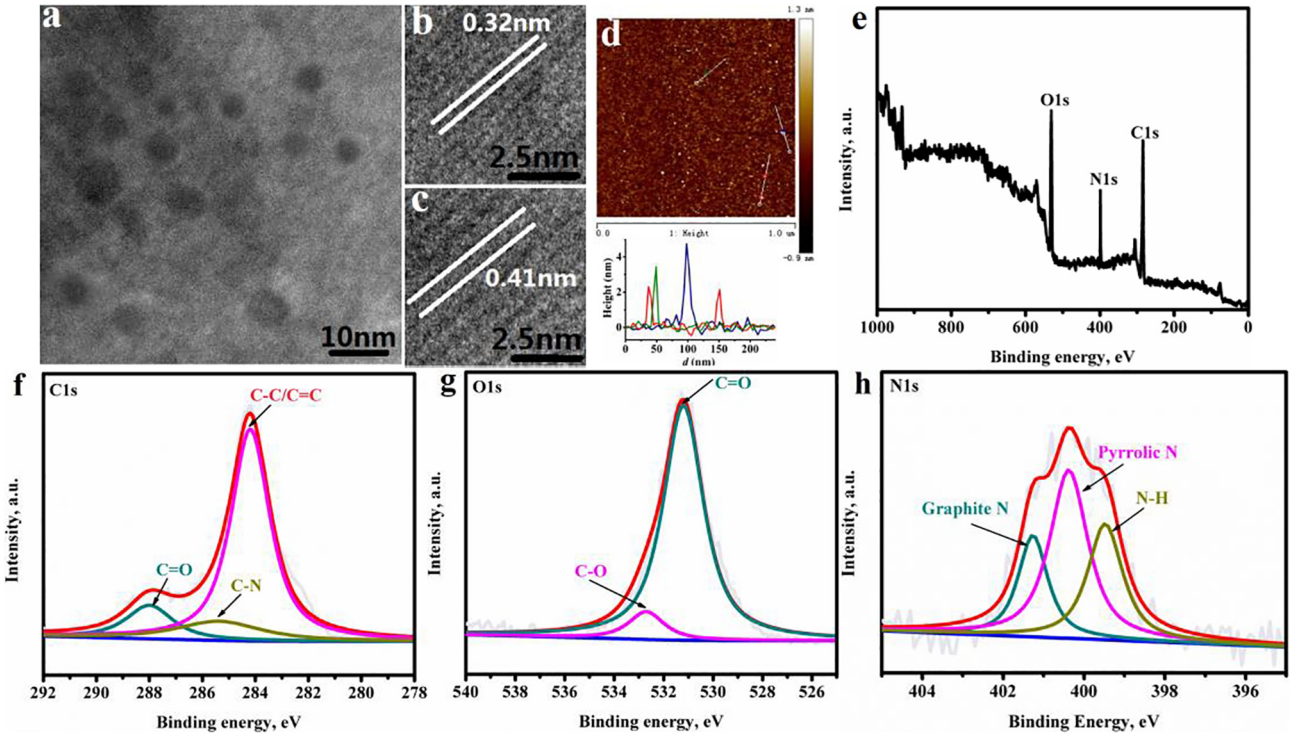

Fig. 1. (a) TEM image of the prepared N-CDs. (b-c) HRTEM images and lattice structures of different N-CDs. (d) AFM image of N-CDs and its height profiles for the selected lines. (e) Survey XPS data of N-CDs. High resolution XPS spectra of (f) C1s, (g) O1s and (h) N1s binding peaks.

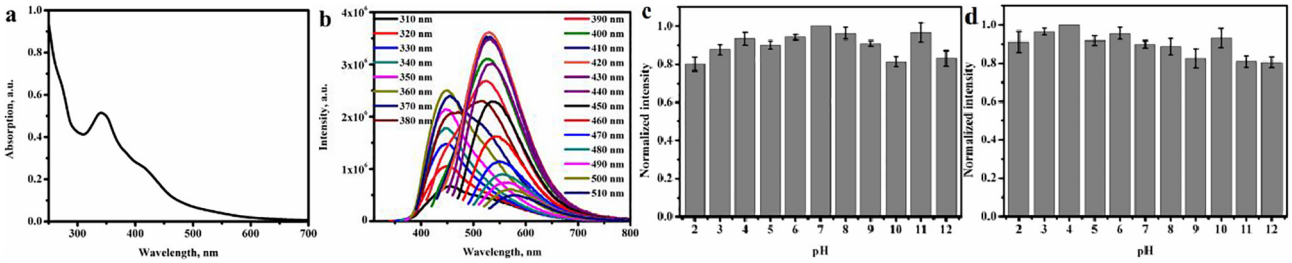

Fig. 2. (a) UV-vis absorption and of the N-CDs. (b) Emission spectra of the N-CDs at different excitation wavelengths from 310 to 510 nm. Normalized intensity (c) at 450 nm (λ_{ex} = 360 nm) and (d) at 530 nm (λ_{ex} = 420 nm) of the N-CDs in the pH range indicated.

image showed that the heights of the N-CDs are about 1.9–4.5 nm (Fig. 1d), which were coincided well with the TEM, demonstrating that the prepared N-CDs are mostly spherical in shape. The HRTEM images (Fig. 1b–c) indicated that N-CDs may have multiple types of particles and could also contained domains of different structures. The XRD pattern (Fig. S2) showed several sharp diffraction peaks at 22.1° and 28.7°, which were attributed to (2 2 2) plane of carbon and (0 0 2) plane of graphite, respectively [11,12].

The composition of N-CDs was revealed by the XPS full survey spectra (Fig. 1e), which illustrated that there were three peaks at 284 eV, 400.1 eV and 531 eV, which corresponded to C1s, N1s and O1s, respectively. The high-resolution XPS spectrum of C1s can be mainly fitted into three peaks (Fig. 1f), the peaks at 284.6 eV, 285.9 eV and 287.9 eV are corresponded to C-C/C=C, C-N and C=O, respectively [11]. The O1s XPS spectrum (Fig. 1g) showed two peaks at 531.3 eV and 532.7 eV, which could be attributed to C=O and C-O bonds [13]. The XPS spectrum of N1s peak (Fig. 1h) revealed the presence of N-H bond of amine groups (399.5 eV), pyrrolic N (400.4 eV), graphite N (401.3 eV), respectively [12]. The relative amount of graphite N, pyrrolic N and amino N are 21.1%, 48.8% and 30.1%, respectively.

The FT-IR analysis was used to characterize the surface groups of N-CDs. As shown in Fig. S3a, as-prepared N-CDs by different mass ratios of FAC and urea showed similar transmittance peaks, which are at 3200–3450 cm^{-1} corresponding to the O-H and N-H stretching vibrations [14]. While the absorption peaks at 1662 cm^{-1} and 1625 cm^{-1} are attributed to C=N and C=O stretching vibrations [4]. The band at 1410 cm^{-1} is assigned to deformation vibration of O-H [15]. The band at 1065 cm^{-1} reveals the existence of C-O [16]. The FT-IR results are coincident well with the result of the XPS spectrum, illustrating that the surface of N-CDs is functionalized with hydroxy, amine and carboxyl groups, and also predicting that the rich hydrophilic groups on N-CDs surface potentially enabling them to interact with other types of materials to extend application of N-CDs. The Raman spectra of produced all five N-CDs in Fig. S3b show two superimposed broad peaks: the D-band at 1335 cm^{-1} (sp^3 hybrid carbon) and the G-band at 1580 cm^{-1} (sp^2 hybrid carbon), which attributed to a hybridized vibrational pattern (A_{1g}) related with graphene edges and the in-plane vibration pattern E_{2g} of the graphite, respectively [17].

The UV-vis absorption spectrum of N-CDs (Fig. 2a) showed a n-π* transition at 340 nm typical for N-CDs. The broad peak at