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Highly luminescent carbon nanodots by microwave-assisted pyrolysis†

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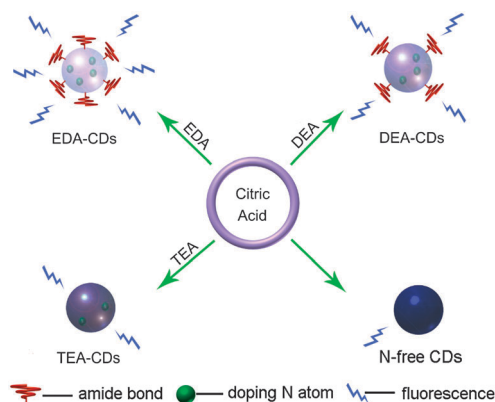
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Carbon nanodots (CDs) with a low cytotoxicity have been synthesized by one-step microwave-assisted pyrolysis of citric acid in the presence of various amine molecules. The primary amine molecules have been confirmed to serve dual roles as N-doping precursors and surface passivation agents, both of which considerably enhanced the fluorescence of the CDs.

Photoluminescent carbon nanodots (CDs) have attracted growing interest very recently.^{1–4} In comparison to fluorescent semiconductor quantum dots (QDs), which are usually composed of heavy metals as the essential elements to achieve high performance fluorescence, the carbon nanodots are advantageous both in their green synthesis and good biocompatibility for biomedical applications. So far, various methods have been explored to prepare the CDs, including laser ablation,⁵ electrochemical oxidation,^{4,6} chemical oxidation,^{7,8} thermolysis^{9,10} and microwave assisted methods.^{2,11–18} Among them, the microwave assisted pyrolysis of proper carbon source(s) is a low-cost, efficient and facile technique for large quantity production of CDs. Compared to other methods in conjunction with or without a sorting process,^{5,19} however, the microwave pyrolysis method still suffers from a main drawback as the resultant CDs often show a relatively low quantum yield (typically, QY < 10%).^{2,11,16,17} In our previous work,^{14,15} we have demonstrated that the introduction of amine-group enriched molecules, such as 4,7,10-trioxo-1,13-tridecanediamine (TTDDA) and poly-ethylenimine (PEI), as the passivation agents during the microwave pyrolysis process can enhance the fluorescent performance of the resultant CDs with QY values up to 12.02% and 15.3%, respectively. However, the mechanism of fluorescent enhancement by the amine passivation agent is still unknown. If revealed, further fluorescent enhancement reaching to the levels of practical significance could be possible.

Using citric acid (CA), containing carboxyl groups to facilitate the dehydration and carbonization, as the carbon source and 1,2-ethylenediamine (EDA) as the surface passivation agent in the present study, we produced, by microwave pyrolysis, CDs with an unprecedented photoluminescent (PL) QY value of 30.2% (Fig. S1†), which is beyond our expectation and comparable to that of common fluorescent semiconductor quantum dots.^{20–22} To gain a better understanding of the role of amine groups in the fabrication of these highly luminescent carbon nanodots by the microwave pyrolysis method, we also used various other amine molecules, including diethylamine (DEA), triethylamine (TEA) and 1,4-butanediamine (BDA), as the passivation agents and correlated their structures to the PL properties of the resultant CDs (Scheme 1). Herein, we report the use of this newly-developed microwave pyrolysis method for preparing the first CDs with drastically improved photoluminescent performance comparable to common fluorescent semiconductor quantum dots. Furthermore, the mechanism of fluorescent enhancement by the amine passivation agent is discussed while the potential use of the resultant CDs for biomedical imaging is demonstrated by laser scanning confocal microscopy imaging of L929 cells with and without the CD labeling.

The UV-Vis spectrum of the as-prepared EDA-CDs given in Fig. 1a shows a peak at around 360 nm and another absorption band at 240 nm attributable to the π - π^* transition.¹² A bright blue color PL emission with a peak at around 460 nm was observed upon excitation of the aqueous solution of EDA-CDs at 360 nm (Fig. 1a). Fig. 1b shows a high-resolution transmission



Scheme 1 Synthesis of CDs in the presence of various amines.

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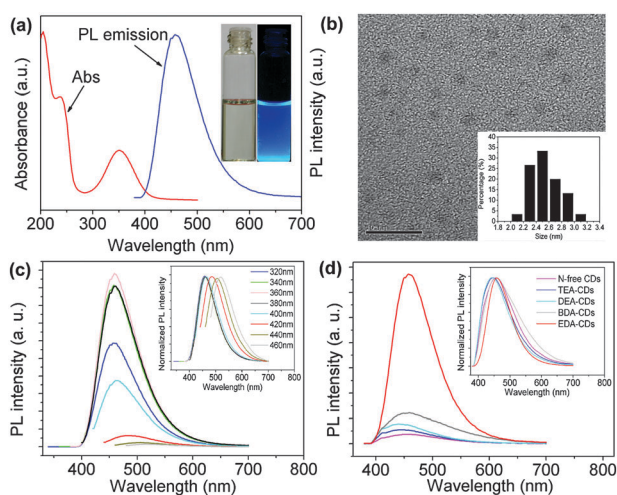


Fig. 1 (a) UV-Vis spectra and the PL emission spectra ($\lambda_{\text{ex}} = 360$ nm) of the CDs aqueous solution. (b) HRTEM image of CDs, scale bar: 10 nm. (c) PL emission spectra of CDs (the inset is the normalized PL emission spectra). (d) PL spectra (excited at 360 nm) of CDs prepared with different amine molecules (the inset is the normalized PL spectra).

electron microscopy (HRTEM) image of the EDA-CDs, which clearly reveals that the pristine CDs can be well-dispersed with a narrow size distribution of 2.2–3.0 nm in diameter. The absence of any discernible lattice structures from Fig. 1b suggests an amorphous nature for the as-prepared CDs. This is further supported by the X-ray diffraction profile of CDs (Fig. S4[†]). Using quinine sulfate as a standard, we measured the quantum yield of the EDA-CDs, at 360 nm excitation, to be 30.2% (Fig. S1[†]), a value which is much higher than those of most CDs previously reported.^{9–18,23} To further explore the optical properties of the as-prepared EDA-CDs, we carried out a detailed PL study with different excitation wavelengths ranging from 320 to 460 nm (Fig. 1c). Unlike most other luminescent CDs, the as-prepared EDA-CDs exhibit an excitation-dependent PL behavior only when the excitation wavelength is larger than 400 nm. More specifically, the PL peak shifted from 460 to 530 nm by changing the excitation wavelength from 400 to 460 nm. In contrast, the PL peak remained almost unchanged (at 460 nm) for the excitation wavelength over 320–400 nm. As different energy levels associated with different “surface states” formed by different functional groups are responsible for the excitation-dependent-emission phenomenon,¹⁸ the observed excitation-independent emission over 320–400 nm indicates a relatively uniform and well-passivated CD surface.

To further optimize the performance of CDs, we have also investigated the influence of different pyrolysis conditions (e.g., the molar ratios of amine/carboxyl groups and the microwave irradiation time) on PL properties of the resultant CDs. As shown in Fig. S5[†] it seems that the optimum microwave time is 2 min for this particular reaction system as either a longer or shorter treatment time reduced the optical adsorption and PL emission. We believe that a short microwave irradiation time (<2 min) was not enough to complete carbonization for the best optical performance. However, an irradiation time longer than 2 min led to significant water evaporation, which over-heated the CD particles and destroyed their surface

structure, and hence decreased the PL emission. For different amine/carboxyl group ratios, Fig. S6[†] shows 2:3 as the optimum ratio. To understand the role of amine groups used in the microwave assisted method, we tested secondary, tertiary and primary amines, including DEA, TEA and BDA. Fig. 1d and Fig. S8[†] show the PL spectra for the EDA-CDs, DEA-CDs, TEA-CDs and BDA-CDs; their quantum yields are listed in Table S1.[†] These results clearly reveal that all of the amine molecules used in this study enhanced the CD fluorescence to a certain extent. A careful examination of the QY values and the elemental analysis data in Table S1[†] reveals that the PL quantum yield and lifetime increase with increasing N content. For TEA-CDs, a 0.58% N atomic content was detected while both the X-ray photoelectron spectroscopy (XPS, Fig. 2c) and Fourier transform infrared spectroscopy (FTIR, Fig. S2[†]) show no signal for an amide bond. Apparently, these N elements mainly exist as doping N in the core of the dot, contributing up to a 50% increase in their QY value. For EDA-CDs, the QY value greatly increased with the N content. The FTIR spectrum (Fig. S2[†]) shows the ν (C=O) and ν (C–N) peaks, which indicate the formation of amide bonds on the carbon dot surface. The high-resolution N 1s spectrum of the EDA-CDs (Fig. 2d) shows strong signals from both amide-N and doping N atoms, indicating the presence of both type N elements. Thus, the primary amine molecules (i.e., EDA) play dual roles in the microwave-assisted pyrolysis process: as the precursor for N-doping and the passivation agent, which both greatly contribute to the PL enhancement of CDs. As for another primary amine, BDA, its longer hydrophobic alkyl chain may hinder the formation of carbon dots during pyrolysis, thus decreasing the N content and PL intensity. The corresponding data for DEA-CDs further demonstrated that different amine molecules can lead to different doping N and amide-N contents, and hence the formation of carbon dots with different PL performances. In the literature,^{5,19,24,25} N-containing molecules were used as passivation agents or carbon sources to obtain highly luminescent carbon dots. Passivation agents containing primary amine groups, including TTDDA and diamine-terminated oligomeric poly(ethylene glycol), were

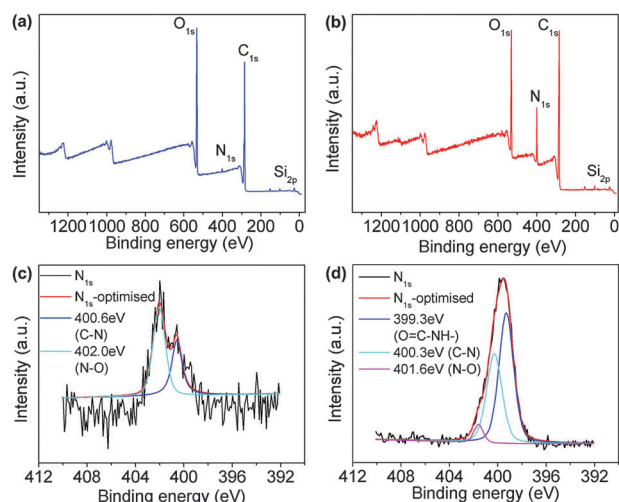


Fig. 2 XPS spectrum of TEA-CDs (a) and EDA-CDs (b), XPS N 1s spectrum of TEA-CDs (c) and EDA-CDs (d).

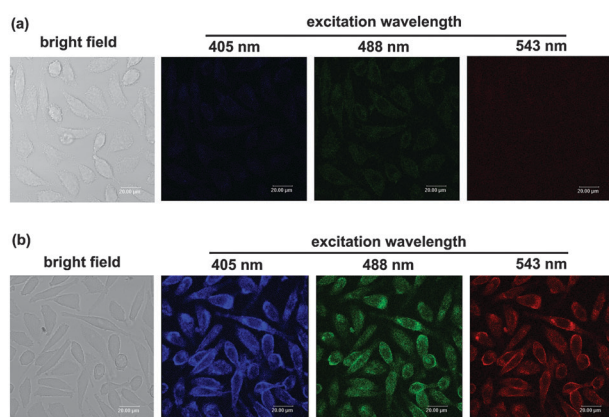


Fig. 3 Laser scanning confocal microscopy images of L929 cells without labeling as a negative control (a) and EDA-CDs labeled L929 cells (b).

used to form amide bonds on the surface of pre-formed CDs for the fluorescence enhancement.^{5,19,24} On the other hand, certain N-containing carbon sources (*e.g.*, ethylenediamine-tetraacetic acid²⁵) have also been used for intrinsically doping N atoms into the carbon core to change the PL properties of the resultant CDs.⁴ Because the formation of carbon dots and the surface passivation processes are accomplished simultaneously during the microwave-assisted pyrolysis, the N-doping and the formation of surface amide groups can co-exist and both contribute to the fluorescence enhancement.

To assess the resultant CDs for potential biomedical imaging applications, L929 cells were used to first evaluate the cytotoxicity of the EDA-CDs by the MTT assay. Fig. S10† shows that the EDA-CDs exhibited extremely low cytotoxicity with cells retaining viability of about 100% even at a concentration of 3 mg ml⁻¹ and 84% at 6 mg ml⁻¹. Having established the biocompatibility, we introduced the EDA-CDs into L929 cells for *in vitro* bioimaging using a confocal microscopy. As seen in Fig. 3b, L929 cells incubated with CDs in the medium became bright, showing blue, green and red colors upon excitation at 405 nm, 488 nm and 543 nm, respectively, whereas no visible fluorescence was detected in control cells (Fig. 3a, without incubation with CDs) under the same condition. CDs were observed mainly in the cell membrane and the cytoplasmic area, especially around the cell nucleus, while the photoluminescence of CDs was very weak in the cell nucleus. With no blinking and low photobleaching, the above laser scanning confocal microscopy study indicated that these CDs are of a remarkably high photostability and biocompatibility and are ideal for bioimaging.

In summary, we have developed a facile microwave mediated pyrolysis method to synthesize highly luminescent carbon nanodots from citric acid and various amine molecules. It was found that the amine molecules play dual functions as N-doping precursors and surface passivation agents for the carbon dots as both enhanced the PL performance. Of particular interest, the as-prepared CDs fabricated from citric acid and

1,2-ethylenediamine show quantum yields up to 30.2%, a value which is much higher than that of other carbon dots. Moreover, our preliminary results indicate that the resultant CDs are highly biocompatible compared with common semiconductor quantum dots, holding a great potential for biomedical applications.

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