

Commercially activated carbon as the source for producing multicolor photoluminescent carbon dots by chemical oxidation†

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Using commercially activated carbon, we developed a simple and effective direct chemical oxidation route to prepare good biocompatible multicolor photoluminescent carbon dots.

Fluorescent semiconductor quantum dots (QDs) have generated much excitement for a wide variety of promising applications, especially in optoelectronic devices, biological labelling, and biomedicine.¹ However, using heavy metals as the essential elements in available high-performance semiconductor QDs has raised serious health and environmental concerns.² Therefore, the search for benign fluorescent nanomaterials with similar optical properties has become an urgent challenge.³ Recently, a new class of carbon-based fluorescent materials, including carbon nanoparticles (CNPs) and carbon quantum dots (CDs) as an alternative to QDs, has received particular attention. Compared with conventional QDs, carbon-based fluorescent materials are superior in chemical stability and biocompatibility.⁴ Some of these carbon nanostructured materials have been reported to emit efficiently in the visible range, which shows promise in the development of efficient carbon emitters.⁵ These environmentally friendly carbon nanomaterials have been prepared by laser ablation of graphite,^{5,6} electrochemical oxidation of graphite,⁷ electrochemical treatment of multiwalled carbon nanotubes (MWCNTs),⁸ chemical oxidation of a suitable precursor,^{9–17} proton-beam irradiation of nanodiamonds,¹⁸ microwave pyrolysis of saccharide,¹⁹ and thermal oxidation of suitable precursors.²⁰

Among these methods, chemical oxidation is an effective and convenient approach for large scale production and requires no elaborate equipment. This method is widely used by many research groups for the preparation of carbon nanoparticles. However, up to now, significant efforts have been devoted to the synthesis of various carbon precursors for the chemical oxidation method. For instance, Mustelin *et al.*⁹ and Scrivens *et al.*¹⁰ isolated CNPs from chemical oxidized arc-discharge single-walled carbon nanotubes (SWCNTs). Mao *et al.*¹¹ and Chen *et al.*¹² collected the combustion soots of candles and natural gas respectively, which served as the

source of carbon to prepare fluorescent CNPs. Travas-Sejdic *et al.*¹³ synthesized the carbon source by dehydration of carbohydrates with concentrated sulfuric acid. Liu *et al.*¹⁴ prepared photoluminescent CDs by employing surfactant-modified silica spheres as the carriers and resols as the carbon precursor with subsequent high temperature treatment and removal of silica carriers.

In this paper, by employing commercially activated carbon as the carbon source, we developed a simple and effective route to easily prepare photoluminescent CDs. The carbon precursor preparation step is omitted. In essence, the long range disordered structures of the carbon precursors for the chemical oxidation method lead us to use activated carbon, a more general and low-cost carbon source with amorphous structure, to prepare photoluminescent CDs. Our CD products are water-soluble, nanosized (~4.5 nm), and multicolor photoluminescent. The CDs have good biocompatibility and high quantum yield in a wide pH range (1 to 13). The obtained quantum yield of up to 0.126 is comparable to those for CDs prepared in the previous reports. Our preparation method presents a general and facile approach to produce photoluminescent CDs and can be carried out on a large scale.

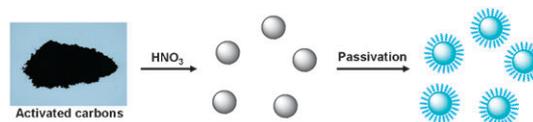
The overall synthetic procedure is illustrated in Scheme 1. We used three typical activated carbon sources including coal activated carbon (CAC), wood activated carbon (WAC) and coconut activated carbon (CNAC) as carbon sources. The activated carbon with amorphous structure was easily etched into individual CDs by treatment with nitric acid, and then the CDs were passivated using amine-terminated compounds. Many organic molecules could serve the purpose of surface passivation. For example, 4,7,10-trioxa-1,13-tridecanediamine (TTDDA) or diamine-terminated oligomeric poly (ethylene glycol) H₂NCH₂(CH₂CH₂O)_nCH₂CH₂CH₂NH₂ (*n*_{av} = 35, PEG_{1500N}) were reacted with the CDs, and two types of CDs had similar quantum yields. Finally, the colored homogeneous supernatant containing the carbon dots with amine-terminated compounds attached to the surface was obtained.

As shown in Fig. 1, the as-prepared CDs derived from three different activated carbon sources are well dispersed and have a similar size. These three types of CDs have a narrow size

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Scheme 1 Preparation procedure of multicolor photoluminescent CDs.

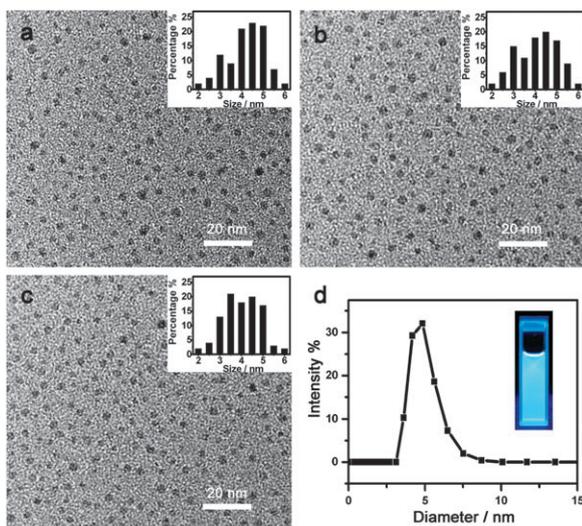


Fig. 1 TEM images of TTDDA-passivated CDs derived from CAC (a), WAC (b), and CNAC (c). The inset histograms are the size distributions of the CDs measured by TEM, where 100 CDs were measured and the average diameters were 4.5 ± 0.6 nm, 4.2 ± 0.8 nm and 4.2 ± 0.6 nm, respectively. (d) Size distribution of TTDDA-passivated CDs from CAC measured by a Malvern NanoZS zetasizer. Inset in (d): CDs under UV light (365 nm).

distribution in the range of 2–6 nm as estimated from the TEM images. Statistical results are shown in the insets. The absence of discernible lattice structures of CDs on the TEM image indicates that the resultant CDs are amorphous. Additionally, Dynamic light scattering (DLS) results (Fig. 1d) suggest that the average hydrodynamic diameter of passivated CDs from CAC in water is approximately 5 nm, which is in agreement with the TEM characterization.

The three types of CDs derived from different activated carbon sources have similar characterization results and photoluminescence properties. We take CAC as the representative in the following discussion. X-Ray photoelectron spectroscopy (XPS) results indicate that the crude CDs contained mainly carbon, oxygen and nitrogen (Fig. S1, ESI[†]). From the elemental analysis, the crude CDs are composed of C 68.16 wt%, H 5.42 wt%, N 1.01 wt%, and O (calculated) 25.41 wt%. The Raman spectrum (Fig. S2, ESI[†]) reveals that the resultant crude CDs possess both sp^2 and sp^3 hybrids, indicating an amorphous nature. This finding is consistent with the TEM analysis (Fig. 1). Furthermore, Fourier transform infrared (FTIR) spectra and zeta potential measurements are acquired to determine surface state of CDs (Fig. S3, ESI[†]). The results clearly show that TTDDA successfully passivated around the CDs (See ESI[†]).

The passivated CDs with organic moieties attached to the surface are strongly photoluminescent both in the suspension and in the solid state. The effect of surface passivation on the UV/Vis absorption and emission spectra of CDs is shown in Fig. S4, ESI[†]. The passivation greatly enhanced the photoluminescence intensity, with the quantum yield improving dramatically from 0.015 to 0.126. The CDs suspension exhibits strong blue luminescence under excitation at 365 nm after surface passivation (Fig. 1d).

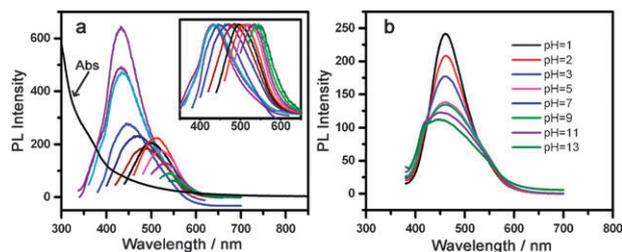


Fig. 2 (a) The absorption (Abs) and photoluminescence emission spectra (with progressively longer excitation wavelengths from 300 nm to 520 nm in 20 nm increment) of carbon dots surface-passivated with TTDDA in an aqueous solution. In the inset, the emission spectral intensities are normalized. (b) Effect of the solution pH value on CDs fluorescence ($\lambda_{\text{ex}} = 360$ nm).

As shown in Fig. 2a, the emission spectra of the CDs derived from CAC are broad, ranging from violet (~ 430 nm) to yellowish-green (~ 550 nm), with a dependence on the excitation wavelengths. As the excitation wavelength increases, the emission peak position shifts to longer wavelengths and the intensity decreases. The full width at a half maximum (FWHM) at 320 nm is only 85 nm, which is smaller than those previously reported by the chemical oxidation method (Table 1). This result further confirms the narrow size distribution of as-prepared CDs. The quantum yields of the TTDDA-passivated CDs also express excitation-dependent properties varying from 0.126 to 0.04, which are either comparable or superior to previous reports (Table 1).

The pH value of the CDs solution affects the photoluminescence of the CDs (Fig. 2b). The fluorescence intensity of the nanoparticles decreases significantly upon changing from an acidic to a basic solution, and the fluorescence emission peak shifts to shorter values with increasing pH. If the pH is switched repeatedly between 13 and 1, the photoluminescence intensity varies reversibly. This is an interesting phenomenon, and even though the mechanism is not clear, this environment-sensitive character could be exploited for molecular sensing. Additionally, the CDs showed excellent photostability with respect to photoirradiation and exhibited

Table 1 Comparison of the characterization of CDs obtained in our experiment with CDs prepared with different start materials by chemical oxidation method in the literatures

Start materials	Diameter	Emission wavelengths	QY ^a	FWHM ^b
C1 ¹⁰	1 × 18 nm	515–540 nm	0.016	100 nm
C2 ¹¹	~1 nm	415–615 nm	0.02	130 nm
C2 ¹⁵	2–6 nm	510 nm	0.03	135 nm
C3 ¹²	4.8 ± 0.6 nm	420 nm	0.0043	140 nm
C4 ¹³	2–6 nm	430–510 nm	0.13	100 nm
C4 ¹⁶	1–2 nm	490–550 nm		125 nm
C4 ¹⁶	4–5 nm	400–520 nm		120 nm
C5 ¹⁴	1.5–2.5 nm	430–580 nm	0.147	125 nm
C6 ^c	4.5 ± 0.6 nm	430–550 nm	0.126 ± 0.011	85 nm
C7 ^c	4.2 ± 0.8 nm	430–550 nm	0.117 ± 0.017	90 nm
C8 ^c	4.2 ± 0.6 nm	430–550 nm	0.122 ± 0.014	85 nm

^a QY = quantum yield; ^b FWHM = the full width at a half maximum; ^c This study. C1 = arc soot of SWCNTs, C2 = candle soot, C3 = natural gas soot, C4 = carbohydrates, C5 = resols, C6 = CAC, C7 = WAC, and C8 = CNAC.

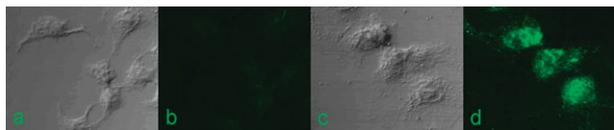


Fig. 3 Bright field (a, c) and confocal fluorescence microphotographs (b, d) of live COS-7 cells. (a, b) Control cells without CDs; (c, d) the cells treated with the CDs.

no meaningful reduction in the observed intensities in the experiment of continuously repeating excitations for 10 h with a UV-lamp at a wavelength of 365 nm (Fig. S5, ESI†).

Table 1 lists the characterization of CDs obtained in our experiment and CDs prepared by the chemical oxidation method in the literature for comparison. In combination with the reports in the literature, we can conclude that most of the carbon species with amorphous structures can be used as precursors for preparation of CDs. We can also conclude that the carbon materials with an amorphous structure are easier to break down into small fractions, by treatment with nitric acid, than bulk carbon allotropes with periodic structures, graphite and diamond. Furthermore, all of the materials that are easily dehydrated and carbonized can be used as the starting material to prepare CDs, such as carbohydrates,^{13,16} resols¹⁴ and biomass materials.

Mechanistically, the radiative recombination of excitations has been proposed as a possible mechanism.⁵ The photoluminescence from carbon dots may arise from the results of the surface passivation. In our experiment, the results suggest that there must be a quantum confinement of emissive energy traps to the CDs. A large surface to volume ratio in a dot is necessary in order for the dot, upon surface passivation, to exhibit strong photoluminescence. Larger carbon particles (30–50 nm in average diameter prepared by 5 M HNO₃, Fig. S6, ESI†) with the same surface morphology and surface passivation were found to be much less luminescent than the smaller CDs (~4.5 nm). Different sizes and a distribution of different emissive trap sites in the sample are responsible for the multicolor photoluminescence of CDs.

To assess the prospects of CDs as a bioimaging material, we tested their photostability and cell permeability. COS-7 cells were cultured according to a reported protocol.²¹ After an incubation of 24 h with the CDs, as shown in Fig. 3d, the COS-7 cells became bright, which indicated that the CDs had penetrated into the cells, and the CDs were able to label both the cell membrane and the cytoplasm of COS-7 cells. Moreover, photoluminescence intensity of the labelled cells exhibited no obvious reduction in the experiment of continuous excitation for 10 min, which indicated that the CDs have a remarkably high photostability with low photobleaching.

In summary, we have developed a general and facile method to prepare multicolor photoluminescent CDs by chemical oxidation of commercially activated carbon. Furthermore, these CDs showed excellent properties for bioimaging applications, such as high luminescence, easy penetration into live cells, remarkable photostability, and nontoxicity to cells. This novel nanomaterial is an excellent candidate for a live-cell

imaging agent. The use of commercially activated carbon leads to the low cost production of CDs for practical applications.

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