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Exploring the blue luminescence origin of nitrogen-doped carbon dots by controlling the water amount in synthesis[†]

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Introduction

Fluorescent carbon dots (CDs), as a new type of carbon materials, have aroused scientific attention quickly due to their unique physical properties, facile functionalization and low toxicity in recent years.1-3 These advantages impart CDs with immense potential applications including bioimaging, drug delivery, phototherapy and biosensing.4-7 Synthetic strategies for CDs can be generally classified into "top-down" and "bottom-up" methods,8-11 and the latter are preferred by chemists. Early chemical syntheses only produced CDs with low QY which greatly limits their practical application.¹²⁻¹⁴ But recently, researchers found that doping heteroatoms,¹⁵⁻¹⁸ especially the nitrogen elements, into CDs was able to improve the QY significantly. For example, Zhu et al. produced luminescent N-doped carbon dots with a QY of up to 80% at 200 °C for 5 h.18 Dong and co-workers prepared N and S co-doped CDs with a high QY of 73% at 200 °C for 3 h.16 In most reports, hydrothermal reactions at high temperature were indispensable, which is adverse for industrial production. By far, the formation mechanisms and the photoluminescence (PL) origins of CDs are still controversial.^{1,19} The former is difficult to achieve agreement with because numerous precursors and plenty of routes have been reported. As for the latter, two kinds of fluorescence mechanisms are popular at present. One is the bandgap transition of electrons within the conjugated π domains,20 while the other is associated with the intricate defects in CDs.²¹⁻²³ When the heteroatoms are doped into CDs,

A series of nitrogen-doped carbon dots (N-CDs) with high quantum yield (QY) and product yield were prepared by hydrothermally treating the same carbon sources with different amounts of water at 110 °C for 4 hours. Along with the increasing water amount in synthesis, the graphitization degree of the N-CDs decreased but the corresponding QY increased firstly and then decreased. When the water amount in synthesis was 0.5 mL, the obtained N-CDs had the highest QY of 73% and a product yield of 63% respectively. The optimal N-CDs were applied as bioimaging probes successfully due to their excellent PL properties and low cytotoxicity. Detailed characterization results on these N-CDs proved that the blue luminescence mainly originated from the functional group C=O in the COOH on the N-CD surfaces.

the situation becomes even more complicated.^{16,24} Therefore, it is a great challenge to develop a facile, eco-friendly, low cost, low temperature and high yield method for producing N-CDs with high QY, and in the meantime, to find the PL origin of the N-CDs by simple methods.

In the present work, a series of N-CDs with similar size but different QY were obtained using the same starting materials citric acid (CA), ethylenediamine (EDA) and Milli-Q water under the same hydrothermal conditions. The only factor adjusted in the parallel reactions was the volume of the water (defined as W) added in the reaction that rendered the dramatic QY changes of the products. By optimizing the reaction conditions, the QY of our N-CDs reached up to 73% at 110 °C and the corresponding yield was 63%. After careful characterizations, luminescence origins of such N-CDs were suggested, which were closely related with the water in the reaction systems.

Experimental

2.0 g of CA and 700 μ L of EDA were added into poly(*para*phenol)-lined stainless steel autoclaves, followed by the addition of different amounts of water respectively (W = 0.0, 0.2, 0.5, 1.0, 2.0 and 5.0 mL). The sealed autoclaves were heated at 110 °C for 4 h. After cooling down to room temperature, 5 mL of water was added into the reactants to form a clear solution. The N-CDs were purified by adding methanol into the solution and collecting the precipitates after centrifugation. The obtained sample could be easily redispersed into water. When *W* was 0, 0.5 and 5.0 mL, the corresponding product was designated as N-CDs-1, N-CDs-2 and N-CDs-3 respectively.

A JEM-2010 transmission electron microscope operating at 200 kV was employed to obtain high resolution transmission electron microscopy (HRTEM) images. The dynamic light

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scattering (DLS) spectra were measured on a Malvern ZS-90 Zetasizer. Fluorescence spectra were recorded by a Horiba Jobin Yvon fluoroMax-4 spectrofluorometer. The UV-Vis absorption spectra were measured on a Unico UV-2802 PC spectrometer. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Nexus 470 FTIR spectrometer. The Raman spectra were recorded by an XploRA Raman spectrometer with an excitation wavelength of 785 nm. The crystal structure of the two CDs were characterized by a Bruker D8 Advance X-ray diffractometer. X-ray Photoelectron Spectroscopy (XPS) was recorded by an AXIS Ultra DLD spectrometer. The time-resolved fluorospectroscopy of the sample was measured by an FLS 920 spectrometer.

The quantum yield (QY) was measured using an F-3018 quantum yield accessory including an integrating sphere attached to the spectrofluorometer. Firstly, the aqueous solution of N-CDs was diluted to keep the absorption intensity below 0.1 at the best excitation wavelength of 352 nm. Subsequently, the aqueous solution was added into a 10 mm fluorescence cuvette, placed in the integrating sphere and excited with monochromatic light of 352 nm. The fluorescence spectra were recorded in the ranges of 342–362 nm and 370–600 nm respectively. Meanwhile, the fluorescence spectra of ultrapure water were also recorded under the same conditions. Finally, a software was used to calculate the QY on the basis of both the sample spectra and the water signals. Each experiment was conducted three times in parallel to obtain the average value of the QY.

Results and discussion

The transmission electron microscopy (TEM) images of the N-CDs (Fig. 1a-c) verify their homogeneous dispersion and uniformity, with average diameters of 2.5 nm (Fig. S1[†]). Hydrodynamic diameters of these samples measured by DLS are about 3.3 nm, due to water cladding around the N-CDs (Fig. S2[†]).²⁵ Both TEM and DLS results demonstrate that W does not affect the final particle sizes of the N-CDs. The high resolution TEM (HRTEM) images, as shown in the insets in Fig. 1a-c, exhibit a clear fringe distance of 0.24 nm for each sample, close to the (1120) crystal lattice distance of graphite.²⁶ X-ray diffraction patterns (Fig. 1d and S3[†]) show that all the N-CD samples have the same diffraction peak at around 23°, corresponding to an interlayer spacing of 0.38 nm. This value is slightly larger than that of the bulk graphite (0.335 nm), owing to the presence of the functional groups on the CD surfaces.²⁷ Interestingly, the XRD peak intensity of the N-CDs decreases as W increases, which means that water could hinder graphitization during the reaction. The Raman spectra in Fig. 1e have two typical peaks at 1325 and 1590 cm⁻¹, representing D and G bands of the carbon materials, respectively.28 The intensity ratio $(I_{\rm D}/I_{\rm G})$ values of the N-CDs, *i.e.*, the ratio between the disordered structure and the graphitic structure of carbon materials, are listed in Table S1.[†] It is observed that this ratio increases from 1.07 to 1.35 when W increases from 0 to 5 mL, suggesting that the water reduced the graphitization degree of the N-CDs, in accord with the XRD results.²⁹ Notably, our products possess

much higher I_D/I_G values than many other reported N-CDs,³⁰ which results from the lower reaction temperature.

The FTIR spectra in Fig. 2 illustrate that all N-CD samples have similar IR bands around 3430, 1385, 1180 and 1048 cm⁻¹, corresponding to the vibrations of O–H/N–H, C–H, C–N and C–O respectively.^{31–33} They also have characteristic peaks at 1710, 1648 and 1550 cm⁻¹, representing the typical stretching vibrations of C=O in carboxyl, C=N and C=C in aromatic rings, respectively.^{27,34} These results indicate that N-CDs consist of graphite structures in the cores and amorphous carbon on the surface, similar with those previously reported CDs.^{8,27} Although the spectra of these samples look almost the same, the C=O vibration intensity at 1710 cm⁻¹ increases firstly but then decreases as *W* increases. It is known that carboxyl groups and carbonyl groups are parts of the edge states for luminescent centers,^{35–37} and thus such IR spectra changes will influence the samples' fluorescence finally.

The X-ray photoelectron (XPS) spectra are employed to analyze the surface states of the N-CDs. In the wide spectrum of N-CDs (Fig. 1f), three typical peaks of C_{1s} (286 eV), N_{1s} (401 eV) and O_{1s} (531 eV) are similar for different N-CD samples, implying that the as-prepared N-CDs consist of the same elements.³⁸ This situation is the same with the high resolution C_{1s} spectra which are fitted into three Gaussian peaks at 284.6, 286.2 and 288.4 eV (Fig. 3a), corresponding to the sp² carbon (C=C) in graphite, the sp³ carbon (C-C, C-O and C-N) and the oxidized carbon (C=O), respectively.26 However, the N1s and O1s spectra of these three samples are quite different. The N_{1s} curve displays two peaks at 400.6 and 401.5 eV, which can be ascribed to the pyrrolic N (C=N) and the graphite N (N-H) respectively.^{26,39} The O_{1s} spectrum shows two typical peaks at 531.7 and 533.1 eV, which are assigned to the C=O and C-O respectively.²⁶ It is clear that the composition of both the N_{1s} and O_{1s} spectra changed relatively when W changed (Fig. 3b and c). Such changes are summarized in Table 2. The C=N bond content increased gradually as W reduced, suggesting more and more N atoms were doped into the CDs, in accord with the element analyses of the N-CDs (Table 1).27 However, the C=O



Fig. 1 The upper figures are TEM and HRTEM images of (a) N-CDs-1, (b) N-CDs-2 and (c) N-CDs-3. The scale bar in the insets represents 1 nm. The lower figures are (d) XRD patterns, (e) Raman spectra and (f) XPS wide spectra of these N-CDs.



Fig. 2 (a) FT-IR spectra of the N-CDs prepared with addition of different *W*. (b) Enlarged view from 1600 to 1900 cm⁻¹. Curve 1 to curve 6 represent the samples with W = 0.0, 0.2, 0.5, 1.0, 2.0 and 5.0 mL respectively.

bond content in the products exhibited a different trend, as it rose firstly but then dropped (Table 2), which is consistent with the FT-IR results. According to the above TEM, XRD, Raman, FT-IR and XPS analyses, it is clear that *W* plays a key role in both the surface functionalization and the core graphitization of the N-CDs.

It is very hard to investigate the formation mechanism of the N-CDs because various precursors were used successfully and the synthetic conditions differed from one another.^{22,40} In a similar system employing CA and amines, Sun et al. reported that the formation of the N-CDs involved two steps.²⁶ Firstly, with the help of amines, the CA molecules self-assembled into a sheet structure and dehydrolyzed to form a graphene framework under hydrothermal conditions. Meanwhile, amidation took place between the CA and the amine molecules. Secondly, amides reacted with the neighbouring carboxylic groups to form a pyrrolic N species through intramolecular dehydrolysis.⁴⁰ Based on the above mechanism and our experimental results, we believe that W plays an important role in the dehydrolysis, especially in the step of amidation. When W is less than the optimal 0.5 mL, amidation takes place easily and thus plenty of pyrrolic N species are obtained. When W is more than 0.5 mL, the high concentration of water in the autoclaves



Fig. 3 High resolution XPS spectra of the different N-CDs, including (a) $C_{1s'}$ (b) N_{1s} and (c) O_{1s} respectively.

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Table 1 The C, O and N content of the N-CDs produced with different $\ensuremath{\mathcal{W}}$

W(mL)	C (%)	O (%)	N (%)	Yield (%)	QY (%)
0.0	48.49	35.54	15.97	62.21	37.50
0.2	50.02	35.16	14.82	60.34	60.91
0.5	51.34	34.72	13.94	63.40	73.23
1.0	52.66	34.27	13.07	62.16	58.74
2.0	54.13	33.45	12.42	63.05	36.19
5.0	55.51	33.26	11.23	62.32	24.68

suppresses the amidation. However, W also controls the formation of the C=O and COOH groups on the N-CD surfaces as the FTIR and XPS measurements revealed. Hence, the optimal W implies a balance between the amidation and the carboxylation.

The UV-visible absorption spectra of all the samples shown in Fig. 4a contain three typical absorption bands at 242, 282 and 352 nm, corresponding to the electron transitions from the π (or n) orbital to the π^* orbital of the C=C, C=N and C=O bonds respectively.⁴¹ The absorption at 282 nm becomes strong gradually but the absorption at 352 nm increases firstly and then decreases when *W* reduces. Just like the above FT-IR and XPS analyses, such UV-visible absorption evolutions also confirm that reducing *W* improves the C=N bond content in the final products, but the C=O bond content is highest when *W* is 0.5 mL.

All N-CD samples exhibit blue fluorescence under UV light (Fig. 5) and their PL emission spectra are red shifted upon the varied excitation wavelengths typically (Fig. 4b and S6[†]), which is ascribed to varied fluorescence characteristics of the N-CDs particles with different sizes and the distribution of different emissive sites on the nanoparticle surfaces.^{1,42} Their PL emission intensities are highest at 452 nm when the excitation wavelength is 352 nm, implying that they share the same emitting centers and luminescence mechanisms.16 The QY of these samples varies along with W (Fig. 6), and the highest QY of 73% is realized when W is 0.5 mL, which is in agreement with the fluorescence brightness of the N-CDs (Fig. 5). The PL excitation spectra of all the N-CD samples are compared in Fig. S5,† and each curve has two peaks at 242 and 352 nm respectively, which are in accord with the UV-Vis absorption bands in Fig. 4a. The former originates from the aromatic sp² domains which always emit no fluorescence, while the latter is due to the

Table 2 $\,$ XPS data analysis of N1s and O1s in the N-CDs obtained with different W

<i>W</i> (mL)	Pyrrolic N (%)	Graphite N (%)	C=O (%)	С-О (%)
0.0	79.16	20.84	36.51	63.49
0.2	68.34	31.64	49.67	50.37
0.5	54.62	45.38	65.05	34.95
1.0	50.17	49.83	51.38	48.62
2.0	46.93	53.07	40.26	59.74
5.0	39.26	60.74	27.37	72.63

(a) c=N

Counts

sp³C

(b)

Counts

(c)

Counts

o-c

C=O

V-CDs

C=N



Fig. 4 (a) The UV-visible absorption spectra of all the N-CD samples. (b) The excitation curve and the emission spectra of N-CDs-2. The excitation curve is obtained by detection of fluorescence at 452 nm, while the emission spectra are obtained by different excitation wavelengths varying from 310 to 470 nm.

absorption of the C=O bonds on the CD surfaces.^{8,43} Since the surface defects composed of functional groups serve as luminescent centers for capturing excitons,^{21,44} the more C=O bonds on the CD surface, the higher the QY of the N-CDs. Therefore, both QY data and the PL analyses confirm that the blue fluorescence of the N-CDs mainly derives from the C=O groups on the N-CD surfaces. To get deep insight into the fluorescence origin, the fluorescence lifetime of all samples



Fig. 5 Photograph of the N-CDs under UV light (365 nm). Samples 1 to 6 represent the products with W = 0.0, 0.2, 0.5, 1.0, 2.0 and 5.0 mL, respectively.



Fig. 6 The product yield and QY of the N-CDs prepared with different W. The product yield is calculated by dividing the weight of the obtained CDs by that of the raw materials (CA and EDA).



Fig. 7 PL decay curve of N-CDs-2 measured by monitoring the emission at 450 nm when excited at 352 nm.

were measured and compared in Fig. 7, S7 and Table S2,† respectively. The fluorescence decay curves of all N-CD samples can be fitted by a single-exponential formula with a long life-time of 15 ns, further demonstrating that all the samples have the same luminescence process.⁴³

It has been revealed that the complex fluorescence mechanisms of the CDs can be ascribed to quantum confinement, carbogenic cores and surface states.1,21,45 In the present research, since all N-CD samples have similar particle sizes, the quantum confinement effect can be excluded firstly. Secondly, it is well known that doping N atoms into carbon cores in the form of pyrrolic $N^{26,27}$ can dramatically improve the OY of the CDs. And thus N doping should improve the QY of our N-CDs to some extent. However, the QY evolutions of the N-CDs didn't obey the changes of the C=N content when W was less than 0.5 mL, suggesting that there is no direct relationship between the QY and the N content. Therefore, surface states are responsible for the changes of the PL features of the N-CDs, which are composed of sp² and sp³ hybridised carbons and other functionalized surface defects.²¹ These surface states behave as energy traps like aromatic molecules and serve as luminescent centers for capturing the photo-generated excitons.⁴⁴ The more



Fig. 8 A model for illustrating the water-controlled QY of the different N-CDs.

functional groups on the surfaces, the more luminescent centers the CDs will have, thus achieving brighter fluorescence emissions.¹⁶ Based on the above analyses on experimental data, we propose a model to illustrate how the water content controls the QY of the N-CDs. Fig. 8 illustrates that the N-CDs prepared in a modest amount of water have the greatest number of COOH groups as luminescent centers on the surface.³⁵ Both more and less water leads to a QY drop, corresponding to the number changes of the COOH functional groups. In a word, the functional groups on the particle surfaces are the main factor in controlling the PL features of our N-CDs.

Conclusions

In comparison with many other reports concerning N-CDs, our present research has shown three advantages at least. Firstly, a facile method is developed to synthesize N-CDs with high QY at relatively low temperature, which is favorable for massive production. Secondly, the functional group C=O in COOH on the CD surface is proved to be the main origin of the blue fluorescence by detailed characterizations and analyses. Finally, water is found to be a key factor in controlling the carbon dot synthesis under hydrothermal conditions, which was neglected by those previous researches. In addition, the optimal N-CDs were applied in cell imaging successfully due to their high QY and low cytotoxicity (Fig. S8 and S9†), confirming that such N-CDs have a promising future as both luminescent sensors and biomedical probes.

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